RARE-EARTH OXIDES IN ALUMINOBOROSILICATE GLASSES AND THEIR IMPACT ON MOLYBDENUM OXIDE SOLUBILITY IN NUCLEAR WASTE GLASSES

By

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ABSTRACT OF THE DISSERTATION

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Dissertation Director:
Ashutosh Goel

The United States department of energy (DOE) has proposed an alkali alkaline-earth aluminoborosilicate-based glass-ceramic to immobilize the projected high-level waste (HLW) generated from reprocessing of its spent civilian nuclear fuel. The glass-ceramic is expected to improve molybdenum oxide (MoO$_3$) retention, which otherwise suffers from poor solubility in borosilicate-based glasses typically used for HLW immobilization in several countries. Irrespective of the waste form chosen, a fundamental understanding of the compositional and structural drivers governing MoO$_3$ solubility in borosilicate/aluminoborosilicate glasses is desired to design advanced waste forms with higher loading capacities. The literature in this regard reports several studies, yet several open questions need to be addressed. This work addresses two open questions regarding MoO$_3$ solubility: (i) What are the solubility and retention limits of MoO$_3$ in aluminoborosilicate glasses as a function of glass chemistry? (ii) Why does MoO$_3$ exhibit
significantly higher solubility with the incorporation of rare-earth oxides (RE$_2$O$_3$) in aluminoborosilicate glasses?

A systematic study conducted on a series of model HLW glasses reveals that MoO$_3$ solubility improves by 2x from 1.5 mol% to 3 mol% when RE$_2$O$_3$ (RE = Nd) is added to a Na$_2$O-CaO-Al$_2$O$_3$-B$_2$O$_3$-SiO$_2$ glass. The results, when analyzed in the context of past literature, reveal that (i) RE$_2$O$_3$ phase separates a homogenous aluminoborosilicate-based glass into borate-rich, and aluminosilicate-rich regions and preferentially enters the borate-rich region; (ii) the excess RE$^{3+}$ clusters in the aluminosilicate-rich region and (iii) molybdenum enters the RE-borate-rich region as the molybdate oxyanion (MoO$_4^{2-}$) forming a stable Mo-RE-B-O glass phase which suppresses crystallization of alkali/alkaline-earth molybdates and improves MoO$_3$ solubility. The above hypothesis is further explored by investigating the partitioning and clustering behavior of RE$^{3+}$ (RE = Nd/La) in a peralkaline aluminoborosilicate glass doped with varying concentrations of RE$_2$O$_3$ (0.001 to 5 mol%). In these glasses, free induction decay (FID)-detected electron paramagnetic resonance (EPR) reveals that RE$^{3+}$ co-exists as EPR-detectable – isolated RE$^{3+}$ centers & dipole-coupled RE clusters, and EPR-undetectable exchange-coupled RE clusters, with higher RE$_2$O$_3$ concentrations further promoting RE$^{3+}$ clustering. The environment of the EPR-detectable RE as investigated by electron spin echo envelope modulation (ESEEM) spectroscopy reveals an alkali/silica-rich environment for the isolated RE$^{3+}$ centers and an alkali/boron/silica-rich environment for the dipole-coupled RE clusters. The EPR-undetectable RE clusters are predicted to exist in alkali/boron-rich nano-scale regions, depleting the leftover glass of the same elements. Based on these findings, a study is eventually performed to investigate further the role of RE$^{3+}$ in
improving the solubility of MoO$_3$ in alkali alkaline-earth aluminoborosilicate-based model high-level waste glasses. It is thus hypothesized that MoO$_3$ preferentially enters the alkali/boron-rich environment of the exchanged-coupled RE clusters where the molybdate oxyanion (MoO$_4^{2-}$) achieves its charge neutrality primarily from RE$^{3+}$ than alkali ions, thereby suppressing the crystallization of the alkali molybdate phase and improving MoO$_3$ solubility.

A subsidiary study investigating the impact of ruthenium oxide (RuO$_2$) – one of the components of HLW, on the crystallization behavior and electrical conductivity of MoO$_3$-containing nuclear waste glasses is also presented. RuO$_2$ in these glasses is found to exhibit very low solubility (460 parts per million by weight), and above the solubility limit is observed to precipitate into polyhedral/needle-shaped RuO$_2$ crystals, which impart metal-like conductivity in the investigated glasses.
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List of Abbreviations

ESEEM – Electron Spin Echo Envelope Modulation

FID – Free Induction Decay

HLW – High-Level Waste

ICP-OES – Inductively Coupled Plasm Optical Emission Spectroscopy

MAS – Magic Angle Spinning

MQMAS – Multiple Quantum Magic Angle Spinning

NMR – Nuclear Magnetic Resonance

PPM – Parts Per Million

SEM-EDS – Scanning Electron Microscopy - Energy Dispersive Spectroscopy

SNF – Spent Nuclear Fuel

XRD – X-ray Diffraction

NN – Nearest Neighbors

NNN – Next Nearest Neighbors
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Chapter 1. Introduction

1.1 Commercial high-level waste (HLW) in the United States

According to the United States Nuclear Regulatory Commission (NRC), there are currently 94 licensed to operate nuclear power plants in the US, contributing to 20% of the country’s total electricity demand. These power plants operate on a “once-through” nuclear fuel cycle, in which the fuel experiences a single pass through the reactor, and the resultant spent nuclear fuel (SNF),\(^1\) is stored in temporary on-site facilities awaiting long-term disposal in a geological repository (which is yet to be commissioned).\(^1\) The current inventory of SNF stands at an estimated 79,825 MTU\(^2\) (as of December 2017) and is expected to increase to \(~145,825\) MTU by 2050, as per the US Energy Information Administration (EIA).\(^2\) The SNF is categorized as high-level waste (HLW) and can be recycled to produce new fuel bundles, thereby improving the energy conversion efficiency and potentially reducing the cost of electricity generation. Therefore, the US Department of Energy (DOE), through the Fuel Cycle Research and Development (FCRD) program, is considering reprocessing of SNF by Transuranic Extraction (TRUEX\(^{\text{plus}}\)) process.\(^1,^3\) Figure 1.1 shows a flowchart of a typical nuclear fuel cycle, including the reprocessing of SNF, which is currently not practiced in the United States.

The reprocessing of SNF by the TRUEX\(^{\text{plus}}\) process will reduce a significant volume of HLW generated from the “once-through” nuclear fuel cycle. However, it is also expected to generate three non-fissionable secondary HLW streams of (i) alkali A)/alkaline-earth (AE) (e.g., \(^{137}\)Cs, \(^{90}\)Sr), (ii) rare-earths (RE) (e.g., La, Nd), and (iii)

\(^1\) Spent nuclear fuel is also referred to as “used nuclear fuel” as per the U.S. NRC
\(^2\) Metric tons of uranium
undissolved solids (UDS) (e.g., Mo, Zr, platinum group metals (PGM)), which will have to be disposed of safely, to avoid risks of environmental contamination due to spillage.\textsuperscript{1,3} Table 1.1 reports the composition of the combined (A/AE + RE + UDS) non-fissionable waste streams expected from the TRUEX\textsuperscript{plus} process.

**Figure 1.1**: Flowchart of the nuclear fuel cycle. *Reprocessing is currently not practiced in the US (Courtesy US NRC).*

**Table 1.1**: Composition of fission products expected from HLW streams in the US.\textsuperscript{1}

<table>
<thead>
<tr>
<th>Component</th>
<th>Mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td>A\textsubscript{2}O</td>
<td>11.7</td>
</tr>
<tr>
<td>AEO</td>
<td>11.3</td>
</tr>
<tr>
<td>RE\textsubscript{2}O\textsubscript{3}</td>
<td>47.6</td>
</tr>
<tr>
<td>MoO\textsubscript{3}</td>
<td>13.9</td>
</tr>
<tr>
<td>ZrO\textsubscript{2}</td>
<td>10.6</td>
</tr>
<tr>
<td>PGM oxides</td>
<td>1.4</td>
</tr>
<tr>
<td>Others</td>
<td>3.4</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
</tr>
</tbody>
</table>
1.2 Immobilization of HLW generated from SNF

Borosilicate glass is currently a benchmark material for the immobilization of HLW generated from SNF reprocessing. It is commonly used (or will be used) in several countries, including France, Japan, the UK, and the US (for legacy defense waste) for nuclear waste immobilization. The popularity of the borosilicate-based glass matrix for waste immobilization arises from its ability to incorporate a wide array of ionic species in its structure, ease of large-scale processing, radiation heat tolerance, and long-term chemical durability. However, molybdenum oxide (MoO$_3$), an integral component of HLW, exhibits very solubility in borosilicate glass (~1 mol%). Increasing the concentration of MoO$_3$ beyond its solubility limit in the glass results in liquid-liquid phase separation of a yellow phase enriched in alkali molybdates during the glass melt stage, followed by crystallization of alkali/alkaline-earth molybdate phases (e.g., Na$_2$MoO$_4$, CaMoO$_4$) in the resultant glass. The phase separation and crystallization of the Mo-containing phases can severely impact the long-term stability and compromise the safety of the final waste form. For instance, alkali molybdates are highly soluble in aqueous environments, thus tend to lower the chemical durability of the borosilicate glass matrix. Alkali molybdates can also incorporate certain radioactive alkalis such as short-lived $^{137}$Cs or long-lived $^{135}$Cs (present in the HLW) in their structure, which can leach out of the glass matrix when exposed to aqueous conditions, thereby contaminating the environment. Given, the problems mentioned above associated with low MoO$_3$ solubility limit, borosilicate glass-based waste forms allow limited waste loading (~18 mass%), thereby increasing the cost of vitrification. Hence these glasses are economically a less attractive
option for the HLW immobilization of commercial HLW waste generated in the United States.

To overcome the limitation of low waste loading posed by a borosilicate glass matrix, scientists at the US DOE are exploring alternative waste forms with higher loading capacities and comparable or better long-term performance than a borosilicate glass to immobilize the projected commercial HLW expected from the TRUEX\textsuperscript{plus} process. An innovative aluminoborosilicate-based glass-ceramic waste form has been proposed with an expected waste loading of 42-50 mass\%, higher than the reported 15-20 mass\% for borosilicate-based glasses.\textsuperscript{1, 3} The proposed glass-ceramic waste form will allow higher waste loading by incorporating MoO$_3$ in the base aluminoborosilicate glass up to its solubility limit and retaining the insoluble fraction in alkali/alkaline-earth molybdate (e.g., Na$_2$MoO$_4$, CaMoO$_3$) crystals.\textsuperscript{1, 3} Furthermore, the proposed glass-ceramic will also improve the retention ability of RE$_2$O$_3$ in the waste form by undergoing a controlled crystallization process into target phases of rare-earth oxyapatite ($\text{AEO}_x\text{RE}_{(10-x)}\text{Si}_6\text{O}_{26}$), rare-earth borosilicate (RE$_5$BSiO$_{13}$) as well as alkaline-earth molybdates (AEMoO$_4$).\textsuperscript{3}

In the pursuit of developing the advanced waste form with enhanced waste loading, it is of paramount importance to understand the compositional and structural drivers governing the solubility/retention limits of MoO$_3$ in aluminoborosilicate glasses whose compositions mimic the glass-ceramic waste form proposed for immobilization of HLW expected from the TRUEX\textsuperscript{plus} process. Apart from MoO$_3$, the proposed glass-ceramic waste form contains more than 25 oxide components with varying concentrations. Some of these components are known to affect the solubility of MoO$_3$ and the crystallization tendency of the aluminoborosilicate glass. Significant amongst these are rare-earth oxides (RE$_2$O$_3$)
which account for the highest fraction of oxides in the expected HLW streams (~48 mass%).\textsuperscript{1, 3} It has been previously reported that solubility of MoO\textsubscript{3} improves significantly in RE\textsubscript{2}O\textsubscript{3} (e.g., Nd\textsubscript{2}O\textsubscript{3}) containing aluminoborosilicate glasses.\textsuperscript{15, 18, 19} To design the advanced waste forms, it is essential to understand the underlying mechanism governing the improved solubility of MoO\textsubscript{3} in RE\textsubscript{2}O\textsubscript{3}-containing aluminoborosilicate-based glasses.

Platinum group metals (PGMs), including ruthenium oxide (RuO\textsubscript{2}) are some of the minor oxides expected from the TRUEX\textsuperscript{plus} process, which are expected to influence the melt chemistry of the aluminoborosilicate glasses and impact the performance of the melters used in HLW vitrification. Although their expected concentration in the waste is less than 1.5 mass\% (Table 1.1),\textsuperscript{1} they are known to exhibit very low solubility in borosilicate-based melts and glasses (tens to few thousand parts per million (ppm)).\textsuperscript{20-22} Above their solubility limit, these PGMs are known to precipitate in the melt as insoluble crystals, which can alter the rheology and electrical conductivity of the melt, thereby disrupting the regular operation of the melters used for glass/glass-ceramic processing.\textsuperscript{20, 21, 23-27} PGMs are also known to act as nucleating agents, increasing the crystallization rate of other crystalline phases in the glass.\textsuperscript{19, 28} Hence, their precipitation into the melt (above their solubility limit), during the processing of the aluminoborosilicate-based glass-ceramic waste form, can potentially lead to uncontrolled crystallization of certain undesirable phases, which could severely impact the retention ability of Mo in glass-ceramic and could also severely impact the long-term stability of the glass-ceramic waste form.

Given the problems mentioned above associated with MoO\textsubscript{3} incorporation in aluminoborosilicate-based glasses, systematic studies are required to independently evaluate the impact of various oxide components present in the HLW on the solubility of
MoO₃ and its crystalline phase evolution in the proposed HLW glasses/glass-ceramics. This work mainly focuses on investigating the impact of RE₂O₃ on the solubility of MoO₃ in aluminoborosilicate glasses due to their overwhelming concentration in the HLW streams. It also presents a subsidiary study investigating the solubility limit of RuO₂ and its impact on the crystallization tendency of MoO₃ containing aluminoborosilicate-based glasses. Below is a concise overview of the relevant literature consulted during this work.

1.3 Literature review

1.3.1 Structural role of RE₂O₃ in aluminoborosilicate glasses

In the context of HLW immobilization, the structure of RE₂O₃ containing aluminoborosilicate glasses has been studied in detail primarily by researchers from two countries, the United States²⁹-³⁴ and France.¹⁸, ³⁵-³⁹ Based on these investigations, two viewpoints have been proposed regarding the mechanism of RE³⁺ incorporation and its coordination environment in aluminoborosilicate glasses. According to the scientists in the United States (henceforth referred to as Li et al.),³⁰, ³² the role of RE³⁺ in peralkaline (Na/Al > 1) Na₂O–Al₂O₃–B₂O₃–SiO₂ glasses depends on the homogenous versus heterogeneous nature of the parent (RE₂O₃ free) glass, as governed by the ratio of [Na₂O]ex/[Al₂O₃] where [Na₂O]ex = [Na₂O] - [Al₂O₃]. Li et al. suggest that in a homogeneous sodium aluminoborosilicate glass ([Na₂O]ex/[Al₂O₃] > 0.5) RE₂O₃ addition leads to incipient (nano-scale) phase separation into borate-rich and silicate-rich phases wherein the RE³⁺ preferentially dissolves in the borate-rich phases of the glass forming RE-metaborate-like structures (1BO₄:RE:2BO₃).³⁰, ³², ³³ The dissolution of RE³⁺ in the borate-rich phases continues until its saturation limit is reached (i.e., [RE₂O₃] = 1/3[B₂O₃], according to ³⁰). Further increasing
the RE$_2$O$_3$ concentration beyond the saturation limit causes the excess RE$^{3+}$ to enter the silicate-rich phases, forming “some kind” of clusters.$^{30,32,33}$

The second viewpoint proposed by the French scientist (henceforth referred to as Caurant et al.) is based on studies conducted on RE$_2$O$_3$ containing peralkaline Na$_2$O–CaO–Al$_2$O$_3$–B$_2$O$_3$–SiO$_2$ glasses.$^{38,40}$ Caurant et al. tend to disagree with RE$^{3+}$ inducing nano-scale phase separation or their tendency to form clusters in the peralkaline aluminoborosilicate glass. They propose that RE$^{3+}$ are accommodated in the depolymerized region of the homogenous peralkaline aluminoborosilicate glass (mixed borosilicate network) where their electroneutrality is maintained by charge compensation from Na$^+$ or Ca$^{2+}$.$^{38,40}$ Further they argue, that clustering of RE$^{3+}$ or the formation of RE-O-B linkages (when RE$^{3+}$ charge compensate the tetrahedral BO$_4^-$ units) might only occur when the Na$^+$ and Ca$^{2+}$ are entirely consumed in charge balancing the tetrahedral AlO$_4^-$ followed by BO$_4^-$ units in the glass, i.e., there are no leftover Na$^+$ or Ca$^{2+}$ for charge compensating the RE polyhedra.$^{40}$ Thus, according to Caurant et al., the preference for Na$^+$ or Ca$^{2+}$ charge compensation follows the order Al$^{3+} > $ B$^{3+} > $ RE$^{3+}$. $^{38,40}$ Having discussed the proposed structural models for RE$^{3+}$ incorporation in aluminoborosilicate-based glasses, we proceed to discuss the structural role of MoO$_3$ in these glasses and the mechanisms governing its improved solubility upon RE$_2$O$_3$ addition.

1.3.2 Structural role of MoO$_3$ in aluminoborosilicate glasses

Molybdenum is known to predominantly exist in +6 valence state in borosilicate/aluminoborosilicate glasses synthesized under oxidizing conditions.$^4, 41$ Literature reveals that Mo$^{6+}$ exists in the structure of an aluminoborosilicate glass in a
tetrahedral coordination environment (surrounded by four oxygens) forming the molybdate oxyanion $\text{MoO}_4^{2-}$.\textsuperscript{4, 10, 18, 19, 42-44} In aluminoborosilicate glasses, based on extended X-ray absorption fine structures (EXAFS) spectroscopy, bond valence modeling, and molecular dynamics simulations it has been shown that $\text{MoO}_4^{2-}$ does not form direct linkages with the network formers ($\text{B}^{3+}$, $\text{Al}^{3+}$ or $\text{Si}^{4+}$) present in the glass.\textsuperscript{4} It is reported to exist in the depolymerized region of the glass where it satisfies its formal charge (achieves charge neutrality) being compensated by the alkali (e.g., Na\textsuperscript{+}) or alkaline-earth (e.g., Ca\textsuperscript{2+}) cations present in the glass.\textsuperscript{4, 9, 42} Increasing the concentration of MoO$_3$ above the solubility limit results in the phase separation of alkali molybdates (e.g., Na$_2$MoO$_4$) in the melt followed by the crystallization of alkaline-earth molybdates (e.g., CaMoO$_4$) during the cooling of melt to room temperature.\textsuperscript{4, 19, 42} The low solubility of MoO$_3$ in aluminoborosilicate glasses and its phase separation/crystallization into alkali/alkaline earth molybdates beyond the solubility limit has been explained based on the proximity of MoO$_4^{2-}$ to these cations (e.g., Na\textsuperscript{+} or Ca\textsuperscript{2+}).\textsuperscript{4, 19, 42}

MoO$_3$ exhibits higher solubility in a RE$_2$O$_3$-containing aluminoborosilicate glass than their RE$_2$O$_3$-free counterparts.\textsuperscript{15, 18, 19} It has also been reported that RE$_2$O$_3$ addition inhibits nucleation of alkali and alkaline earth molybdate crystals during thermal aging.\textsuperscript{15, 19} Chouard et al.\textsuperscript{18} have discussed two potential mechanisms governing the improved MoO$_3$ solubility in Na$_2$O–CaO–Al$_2$O$_3$–B$_2$O$_3$–SiO$_2$–Nd$_2$O$_3$ glasses. The first mechanism argues that Nd$^{3+}$ suppresses the crystallization tendency of Na$_2$MoO$_4$ and CaMoO$_4$ by replacing some of the Na$^+$ and Ca$^{2+}$ acting as charge compensators for the MoO$_4^{2-}$ units, thereby
improving MoO\textsubscript{3} solubility.\textsuperscript{18} However, this mechanism has been disregarded by Chouard et al.\textsuperscript{18} due to the absence of neodymium molybdate crystalline phases in the glass-ceramic obtained upon slow cooling of the MoO\textsubscript{3} and Nd\textsubscript{2}O\textsubscript{3}-containing melt. The other mechanism argues that although Nd\textsuperscript{3+} does not charge compensate the MoO\textsubscript{4}\textsuperscript{2−} units in the glass, it is located in the depolymerized region within a close distance of the MoO\textsubscript{4}\textsuperscript{2−} units. The proximity of Nd\textsuperscript{3+} has a “dispersing effect” on the MoO\textsubscript{4}\textsuperscript{2−} uni, preventing their clustering and crystallization into molybdate phases, thereby improving the MoO\textsubscript{3} solubility in the glass.\textsuperscript{18}

1.3.3 RuO\textsubscript{2} in borosilicate-based glasses

Ruthenium, one of the PGMs, exhibits complex chemistry in borosilicate glasses, as reported by the several possible oxidation states (0, +3, +4, +5, +7, and +8) it can assume depending on the host glass composition and melting environment (oxygen partial pressure of the melt).\textsuperscript{20, 22} However, in HLW glasses, which are processed under ambient conditions (oxidizing environment), Ru exists primarily in the +4 state (RuO\textsubscript{2}) along with low fractions of 0 state (metallic Ru).\textsuperscript{20, 21, 23, 26, 27, 45} The problem associated with RuO\textsubscript{2} during HLW immobilization arises from its sparingly low solubility in the borosilicate melt with the reported limit ranging from tens to a few thousand ppm by weight.\textsuperscript{20-22} As the concentration of RuO\textsubscript{2} in the melt exceeds the solubility limit, Ru precipitates and forms needle-like or polyhedral RuO\textsubscript{2} crystals, which are distinguished by their high density ($\rho_{\text{RuO}_2} = 6.97$ g/cm$^3$) and metal-like conductivity ($\sigma = 2.5 \times 10^4$ $\Omega^{-1}$ cm$^{-1}$).\textsuperscript{24, 25} Once formed, the RuO\textsubscript{2} crystals are stable up to 1200 °C and decompose at 1580 °C\textsuperscript{23} which is above the highest operating temperature of the melters used in HLW vitrification (~1150 °C Joule heated ceramic-lined melters (JHCM); 1300–1400 °C Cold crucible induction
melters (CCIM). Owing to their high density, the precipitated RuO$_2$ crystals settle to the floor of the melter, and as sedimentation continuous, they form a highly conducting layer between the electrodes used for heating the melt (in the case of JHCM melters), potentially resulting in their short-circuiting.\textsuperscript{23} Although, short-circuiting of electrodes during the proposed vitrification of the HLW glass-ceramic could be avoided by using CCIM melters (as they employ inducting coils to heat melt as opposed to electrodes submerged in the melt in case of JHCM), the presence of the RuO$_2$ crystals, could alter the crystalline phase assemblage of the glass-ceramic waste form. RuO$_2$ crystals can act as nucleating agents, increasing the crystallization rate of other phases, as has been previously reported for spinel and acmite crystallization in defense based HLW in the U.S.\textsuperscript{28} Therefore, the behavior of RuO$_2$ in these proposed glass-ceramic waste forms needs to be investigated in the context of its solubility in the corresponding aluminoborosilicate glass and its impact on the crystallization phase evolution upon exceeding the solubility limit.

1.4 Outline of the thesis

This doctoral thesis systematically investigates the solubility and retention limits of MoO$_3$ in aluminoborosilicate-based model HLW glasses. The emphasis is on understanding: Why does MoO$_3$ exhibit considerably higher solubility in rare-earth-containing aluminoborosilicate glasses?

Accordingly, Chapter 2 presents a study to evaluate the solubility and retention limits of MoO$_3$ in Nd$_2$O$_3$-free and Nd$_2$O$_3$-containing Na$_2$O–CaO–Al$_2$O$_3$–B$_2$O$_3$–SiO$_2$ glass system. The compositions investigated in this study are derived from an alkali alkaline earth aluminoborosilicate-based glass-ceramic waste form proposed by the US DOE for HLW immobilization. Three series of aluminoborosilicate glasses have been synthesized
by adopting a tiered approach to increase the compositional complexity and systematically varying MoO$_3$ and Nd$_2$O$_3$ concentrations. These glasses have been characterized using X-ray diffraction (XRD), scanning electron microscopy – energy dispersive spectroscopy (SEM-EDS), magic angle spinning nuclear magnetic resonance spectroscopy (MAS NMR; $^{11}$B, $^{23}$Na, and $^{27}$Al nuclei were probed), inductively coupled plasma – optical emission spectroscopy (ICP-OES), and liquidus temperature measurements. It is observed that the solubility of MoO$_3$ increases by up to two folds with Nd$_2$O$_3$ addition in these glasses. Exceeding the concentration of MoO$_3$ beyond its solubility limit leads to the crystallization of sodium molybdate (Na$_2$MoO$_4$) and calcium molybdate (CaMoO$_4$), their fractional concentrations varying based on glass chemistry. By reviewing the previously reported viewpoints on the impact of rare-earth cations (RE$^{3+}$) on the structure of aluminoborosilicate glasses and their implications on the solubility of MoO$_3$ in the glasses investigated in this study, a novel hypothesis is proposed explaining the mechanism governing the solubility of MoO$_3$ in rare-earth containing aluminoborosilicate glasses. The work has been published in Journal of Physical Chemistry B (Brehault et al., J. Phys. Chem. B 2018, 122, 1714-1729; DOI: https://doi.org/10.1021/acs.jpcb.7b09158).

Chapter 3 focuses on understanding the partitioning and clustering mechanism of RE$^{3+}$ in alkali aluminoborosilicate glasses. This study is undertaken to understand the mechanism governing the incorporation of RE$^{3+}$ in these glasses. A homogenous peralkaline (Na/Al > 1) aluminoborosilicate glasses with the batched composition of 25 Na$_2$O– 10 Al$_2$O$_3$– 10 B$_2$O$_3$– 55 SiO$_2$ (mol%) has been chosen for RE$_2$O$_3$ addition. The concentration of RE$_2$O$_3$ is systematically varied by doping Nd$_2$O$_3$ (0.001–0.1 mol%) and 5 mol% La$_2$O$_3$. Combining free induction decay (FID)-detected electron paramagnetic
resonance (EPR), electron spin echo envelope modulation (ESEEM), and $^{11}$B/$^{27}$Al MAS NMR spectroscopies, the clustering and coordination environment of Nd$^{3+}$ is probed. Quantitative FID-detected EPR analysis reveals three different Nd$^{3+}$ forms co-existing in the glasses: isolated Nd$^{3+}$ centers, dipole-coupled Nd clusters (Nd–O–X–O–Nd, where X = B/Al/Si) where the Nd–Nd distance is 4–5.5 Å, and spin-exchange-coupled Nd clusters, further sub-divided into two types, close-ranged (Nd–O–Nd) where the Nd–Nd distance is 3–4 Å, and more distance more distant clusters (Nd–O–La–O–Nd) where Nd–Nd distance is 4–5.5 Å. The fractional populations of these three RE forms as extracted from the spectral decomposition of the FID-detected EPR spectra reveals that high Nd$_2$O$_3$ concentration and La$_2$O$_3$ co-doping promote extensive RE clustering with more than 90% REs existing as dipole-coupled and exchange-coupled clusters even at Nd$_2$O$_3$ concentrations as low as 0.01 mol%. The ESEEM analysis of the EPR-detectable Nd$^{3+}$ forms – isolated Nd$^{3+}$ centers and dipole-coupled Nd clusters reveals that the isolated Nd$^{3+}$ centers preferentially exist in a Na/Si-rich environment and the dipole-coupled Nd clusters form in the Na/B/Si-rich environment. Combining the ESEEM and MAS NMR results, structural models are proposed for all three RE forms, with the exchange-coupled RE clusters predicted to exist in a Na/B-rich environment. Based on these observations, a mechanistic model is developed that explains the high tendency of RE$^{3+}$ to form clusters in the Na/B-rich environment of the glass. The manuscript based on this work was submitted to the journal, Chemistry of Materials and has been accepted for publication.

Chapter 4 presents results discussing the impact of RE$_2$O$_3$ (Nd$_2$O$_3$/La$_2$O$_3$), MoO$_3$, and ZrO$_2$ on the structure of aluminoborosilicate-based model nuclear waste glasses. The compositions of these glasses have been derived from the actual glass-ceramic waste form
proposed by the US DOE for immobilization of its commercial HLW. Based on our improved understanding of the structural role of RE$^{3+}$ in alkali aluminoborosilicate glasses (discussed in Chapter 3), we explore the role of RE$^{3+}$ in the structure of soda-lime aluminoborosilicate glasses and the impact of their addition on glass properties (density, molar volume, and glass transition temperature). We have characterized these glasses using multiple spectroscopies, including Raman, MAS NMR, FID-detected EPR, and ESEEM. By systematically adding MoO$_3$ and ZrO$_2$ to these rare-earth-containing aluminoborosilicate glasses, we discuss the changes observed in the speciation of boron and aluminum as obtained from the $^{11}$B and $^{27}$Al MAS NMR analysis. The manuscript for this work is currently being drafted.

Chapter 5 presents a study undertaken to investigate the solubility of RuO$_2$ and its impact on the crystallization tendency and electrical conductivity of MoO$_3$-containing model HLW glasses. The baseline glass chosen for this work is a nine oxide (Na$_2$O-CaO-Al$_2$O$_3$-B$_2$O$_3$-SiO$_2$-MoO$_3$-Nd$_2$O$_3$-ZrO$_2$-RuO$_2$) system to which RuO$_2$ in concentration varying from 0.05 to 0.3 mol% is added. The glasses are characterized for their crystallinity using XRD and SEM-EDS and their electrical conductivity in the range 50-600 °C using combined AC impedance spectroscopy and two-probe DC technique. The crystalline phase evolution has been studied by XRD and SEM-EDS. The solubility limit of RuO$_2$ in these glasses, as determined by ICP-OES experiments, is 460 ppm by weight. It is revealed that increasing the RuO$_2$ concentration above the solubility limit results in sub-micron-sized Ru-rich inclusions in the glass matrix, which agglomerate to form needle-shaped RuO$_2$ crystals. These needle-shaped RuO$_2$ crystals result in an apparent metal-like conductivity observed for the 0.3 mol% RuO$_2$ containing glass. The work has been published in the

Chapter 6 summarizes the key conclusions of this doctoral research, and Chapter 7 discusses the recommendations for future work.
References


43. Magnin, M.; Schuller, S.; Mercier, C.; Trebosc, J.; Caurant, D.; Majerus, O.; Angeli, F.; Charpentier, T., Modification of molybdenum structural environment in borosilicate glasses with increasing content of boron and calcium oxide by $^{95}$Mo MAS NMR. *Journal of the American Ceramic Society* 2011, 94 (12), 4274-4282.


Chapter 2. Compositional Dependence of Solubility/Retention of Molybdenum Oxides in Aluminoborosilicate based Model Nuclear Waste Glasses

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Abstract

Molybdenum oxides are an integral component of the high-level waste streams being generated from the nuclear reactors in several countries. Although borosilicate glass has been chosen as the baseline waste form by most of the countries to immobilize these waste streams, molybdate oxyanions (MoO$_4^{2-}$) exhibit very low solubility (~1 mol.%) in these glass matrices. In the past three to four decades, several studies describing the compositional and structural dependence of molybdate anions in borosilicate and aluminoborosilicate glasses have been reported in the literature, providing a basis for our understanding of fundamental science that governs the solubility and retention of these species in the nuclear waste glasses. However, there are still several open questions that need to be answered to gain an in-depth understanding of the mechanisms that control the solubility and retention of these oxyanions in glassy waste forms. This article is focused on finding answers to two such questions: (1) What are the solubility and retention limits of MoO$_3$ in aluminoborosilicate glasses as a function of chemical composition? (2) Why is there a considerable increase in the solubility of MoO$_3$ with incorporation of rare-earth oxides (for example, Nd$_2$O$_3$) in aluminoborosilicate glasses? Accordingly, three different series of aluminoborosilicate glasses (compositional complexity being added in a tiered approach) with varying MoO$_3$ concentration have been synthesized and characterized for their ability to accommodate molybdate ions in their structure (solubility) and as a glass-ceramic (retention). The contradictory viewpoints (between different research groups) pertaining to the impact of rare-earth cations on the structure of aluminoborosilicate glasses are discussed and their implications on the solubility of MoO$_3$ in these glasses are
evaluated. A novel hypothesis explaining the mechanism governing the solubility of MoO$_3$ in rare-earth containing aluminoborosilicate glasses has been proposed.
2.1 Introduction

Owing to its ability to accommodate a plethora of ionic species in its molecular structure, glass is widely considered to be the benchmark material for long-term immobilization of complex mixed radioactive wastes. The cost of vitrifying radioactive waste is directly proportional to the volume of glass to be produced. It is therefore desirable to maximize the waste loading in glass to decrease the overall volume, without posing unacceptable risk for melter operation or long-term performance of the waste form in terms of radiation and chemical stability. One major challenge in designing advanced glass formulations with enhanced waste loadings is the low solubility of some complex ionic species, for example, MoO$_4^{2-}$, SO$_4^{2-}$, CrO$_4^{2-}$, and TcO$_4^{-}$, in borosilicate based nuclear waste glasses. This problem impacts the design and performance of nuclear waste glasses worldwide, while the relative importance of its impact is country-specific and depends on the chemistry of each nuclear waste.$^{1-8}$

Molybdenum oxides are an integral component of the high level waste streams being generated from the nuclear reactors in several countries including USA (TRUEX$^{\text{plus}}$ process),$^{9,10}$ France (reprocessing of UMo fuel from gas graphite reactors),$^{11-13}$ UK,$^{14,15}$ and Japan.$^{16,17}$ However, distinction needs to be made as molybdenum is not one of the more important components of legacy defense waste, as the burn-ups used for production of plutonium do not produce as much Mo fission product as those burn-ups used for nuclear power.$^{18}$ Although borosilicate glass has been chosen as the baseline waste form by all the above-mentioned countries to immobilize their high level wastes, molybdenum oxides present in their waste streams exhibit very low solubility (~1 mol.%) in these glass matrices.$^{19}$ Further increase of MoO$_3$ concentration in these glasses usually on cooling
results in liquid-liquid phase separation and subsequent crystallization of alkali molybdate phases (for example, Na₂MoO₄) which are highly soluble in aqueous environments.⁵ Therefore, considerable effort is being made to design novel glass/glass-ceramic compositions which can retain higher concentration of molybdate ions in their structure without affecting the long-term performance of the final waste form. In this regard, most of the research in UK and France is focused on designing glass compositions dissolving the maximum concentration of MoO₃ in their structure without crystallization of alkali molybdates (or preferring the crystallization of chemically durable, CaMoO₄, based phases).⁴, 5, 11, 14, 15, 20, 21 On the other hand, research in the USA is directed towards designing a glass-ceramic that can retain the highest possible concentration of molybdenum in glass and crystal matrices, while preventing crystallization of any poorly durable phases such as alkali molybdates.⁹, 10, 22 While the solubility of MoO₃ in most of the borosilicate glass compositions is limited to ~1.5–1.6 mol%, the glass-ceramic being developed in USA is expected to retain ≥4 mol% MoO₃ in the final waste work with a crystalline phase assemblage including AeMoO₄, oxyapatite, (A,Ae)ₓLnₙ₋ₓSi₆O₂₆, and lanthanide borosilicate (e.g., Ln₃BSi₂O₁₃), where A denotes alkali, Ae alkaline-earth, and Ln lanthanide (rare earth) metals.

In the pursuit of developing an advanced waste form with enhanced waste loading, considerable effort has been made in the past 3-4 decades to understand the fundamental science and mechanisms controlling the solubility of MoO₃ in borosilicate/aluminoborosilicate glasses, resulting in significant advancements in our understanding about the structure and chemistry of these glasses. However, there are still some open questions which need to be answered to gain an in-depth understanding about
the compositional dependence of MoO$_3$ solubility in the aluminoborosilicate glassy waste forms. This article is focused on finding answers to two such questions described below.

i. How do the solubility and retention limits of MoO$_3$ in aluminoborosilicate glasses vary with glass chemistry? What happens if these limits are exceeded?

ii. Why does MoO$_3$ exhibit considerably higher solubility in rare-earth (Nd$_2$O$_3$) containing aluminoborosilicate glasses?

While the first question has been addressed in the literature, current understanding is qualitative in nature.\textsuperscript{4, 21, 23} In this paper, we aim to present quantitative data pertaining to the solubility and retention of MoO$_3$ in aluminoborosilicate glasses as a function of glass chemistry. Regarding the second question about increase in MoO$_3$ solubility, the recent literature on this topic points to the network modifying role of Nd$_2$O$_3$ in aluminoborosilicate glasses.\textsuperscript{20, 21} However, its impact on the solubility of MoO$_3$ is still unclear.\textsuperscript{21} In this paper, a new hypothesis is presented describing the impact of Nd$_2$O$_3$ on the solubility of MoO$_3$ in aluminoborosilicate glasses.

The problem of solubility/retention of molybdenum in aluminoborosilicate glasses is also an important topic beyond its use in nuclear waste immobilization. Molybdenum electrodes are often used in commercial glass manufacturing as a lower cost alternative to SnO$_2$.\textsuperscript{24} During the glass melting process, some concentration of molybdenum from the electrodes is dissolved into the molten glass. In order to avoid the formation of Mo-containing crystalline defects, it is important not to exceed the solubility limit of molybdenum during glass melting. Hence, the dependence of Mo solubility on glass chemistry is of critical importance for ensuring high quality, defect-free industrial glass production.
In preface to the technical details, it is helpful to differentiate between two terms – “solubility” and “retention”. The true “solubility” is defined as the concentration of MoO$_3$ in glass at an established equilibrium between dissolved and atmospheric MoO$_3$. However, the glass-making process does not necessarily allow the glass melt to reach a homogeneous equilibrium. While a component may be dissolved in the non-crystalline liquid phase up to its solubility limit, any additional concentration could exist in the form of undissolved crystalline inclusions. We therefore define “retention” as the total concentration of molybdenum oxide that is present in both the glassy matrix and any crystalline inclusions, i.e., $\text{Mo}_{\text{solubility}} + \text{Mo}_{\text{crystal}}$. Note that some authors further distinguish between water soluble and water insoluble crystalline inclusions, given the importance of aqueous chemical durability and potential cracks in waste forms.$^{25,26}$ Although for the sake of simplicity, we discuss the solubility and retention of molybdenum oxides in glasses, Mo is known to exist as a tetrahedral molybdate ion $[\text{Mo(VI)O}_4^{2-}]$ in silicate and borosilicate glass chemistries.$^{12}$ Therefore, any discussion pertaining to solubility or retention of molybdenum in this paper refers to molybdate ions. Furthermore, while Mo$^{6+}$ is the prevailing oxidation state in most of the borosilicate based nuclear waste glass chemistries (due to the highly oxidizing conditions of the waste feed), other oxidation states, such as Mo$^{3+}$, Mo$^{4+}$, and Mo$^{5+}$, may be present under more reducing conditions or appear transiently as a result of the concentration fluctuations under the processing conditions.$^{27}$ These species would inevitably create other structural elements, which may have different types of bonding to the glass network. However, most of the molybdenum in the studied glasses is expected to exist in hexavalent oxidation state, especially considering the
colorless nature of the as-formed glasses. Therefore, the influence of redox states on the solubility or retention of molybdenum in borosilicate glasses will not be considered in this current study.

2.2 Experimental

2.2.1 Design of glass compositions

A simplified nuclear waste glass-ceramic composition comprising 11.87 Na$_2$O–14.15 CaO–5.35 Al$_2$O$_3$–9.74 B$_2$O$_3$–5.38 Nd$_2$O$_3$–46.09 SiO$_2$–3.29 ZrO$_2$–4.13 MoO$_3$ (mol%) was chosen as the baseline for this work. The baseline composition above has been derived from the more complex GC-Mo-Li 6.25 glass-ceramic composition being considered for immobilization of a waste stream derived from aqueous reprocessing of spent nuclear fuel, wherein simplification has been made to the composition. In the simplified baseline glass for this study, Na$_2$O represents the total fraction of alkali oxides (Na$_2$O+Li$_2$O+Cs$_2$O), CaO represents the alkaline-earth oxides (CaO+BaO+SrO), and Nd$_2$O$_3$ represents RE$_2$O$_3$ (Y$_2$O$_3$+La$_2$O$_3$+Ce$_2$O$_3$+Pr$_2$O$_3$+Nd$_2$O$_3$+Sm$_2$O$_3$+Eu$_2$O$_3$+Gd$_2$O$_3$).

For this work, the baseline composition was further simplified into three different series of glass compositions. The first series labeled as Na-Mo-$x$ comprises glasses in the system 25 Na$_2$O–5 Al$_2$O$_3$–10 B$_2$O$_3$–(60-$x$) SiO$_2$–$x$ MoO$_3$ ($x$ = 0–4 mol%). The glasses in this series were intentionally kept devoid of CaO to avoid competition between two network modifying cations (Na$^+$ and Ca$^{2+}$) for charge balancing any AlO$_4$ and BO$_4$ units, as this would add complexity to the glass structure. In the second series labeled as Ca-Mo-$y$, CaO was introduced in the glass system at the expense of Na$_2$O on an equimolar basis, resulting in a series of glasses with compositions 12.5 Na$_2$O–12.5 CaO–5 Al$_2$O$_3$–10 B$_2$O$_3$–(60–$y$) SiO$_2$–$y$ MoO$_3$ ($y$ = 0–4 mol%). The aim was to understand the influence of
calcium on the solubility and retention of molybdate ions. The third series labeled as RE-Mo-z was designed with an aim of investigating the influence of rare-earth oxides on the solubility of molybdenum in these glasses, given the simultaneous presence of both Ca and Na. Therefore, 5 mol% Nd$_2$O$_3$ was introduced in the glass system at the expense of SiO$_2$, resulting in compositions 12.5 Na$_2$O– 12.5 CaO– 5 Al$_2$O$_3$– 5 Nd$_2$O$_3$– 10 B$_2$O$_3$– (55–z) SiO$_2$– z MoO$_3$ (z = 0–4 mol%). Table S1 presents the batched compositions investigated in the present study.

2.2.2 Synthesis by melt-quench technique

High-purity powders of SiO$_2$ (Alfa Aesar; > 99.5%), Na$_2$SiO$_3$ (Alfa Aesar; > 99%), Al$_2$O$_3$ (Sigma Aldrich; ≥ 98%), H$_3$BO$_3$ (Alfa Aesar; ≥ 98%), CaCO$_3$ (Alfa Aesar; ≥ 98%), Nd$_2$O$_3$ (Alfa Aesar, 99%), and MoO$_3$ (Alfa Aesar, 99.5%) were used as glass precursors. Na$_2$SiO$_3$ was preferred over Na$_2$CO$_3$ as the precursor for Na$_2$O to avoid any detrimental effect of alkali carbonate on the platinum crucible. Homogeneous mixtures of batches (corresponding to ~70 g glass) were melted in Pt-Rh crucibles in the temperature range of 1400–1500 °C for 1–2 h in air, followed by quenching of melts on a steel plate. The batch temperature was lowered with increasing MoO$_3$ content based on the decrease in apparent viscosity of glass melts.

2.2.3 Characterization of melt-quenched samples

2.2.3.1 Crystallinity in melt-quenched samples – qualitative and quantitative analysis

The melt-quenched samples were crushed to fine powders with particle size <45 μm. Some melt-quenched samples had a layer of salt on their surfaces. All samples were analyzed qualitatively by X-ray diffraction (XRD; PANalytical – X’Pert Pro; Cu K$_a$ target at 40 kV and 40 mA). The acquisitions were performed in the 2θ range of 10–90° with step
size of 0.013° and dwell of 0.10 s at each step. The quantitative crystalline phase analysis of samples was performed by PANalytical X’Pert Pro XRD with a Cu-Kα source at 45 kV and 40 mA in the 2θ range of 10–90° with 0.002° 2θ step size and dwell time of 5.7 s, with 5 or 10 wt.% ZnO (NIST SRM-674b) included as an internal standard. The quantitative phase analysis was performed by Rietveld – Reference Intensity Ratio (RIR) method using PANalytical HighScore software.

Microstructural observations were conducted on fractured crystalline samples using a field emission – scanning electron microscope (FE-SEM; ZEISS Sigma). Energy dispersive spectroscopy (EDS; X-Max Oxford Instruments; Aztec software) was employed to perform the elemental distribution mapping in the crystalline microstructure.

The liquidus temperature of rare-earth containing glasses (RE-Mo-z) was measured using gradient furnace method following the ASTM C829-81. Briefly, glass patties were crushed into powder with particle size ≤ 841 μm. The resultant glass powder was laid in a Pt/Rh boat placed on a refractory brick and then loaded into an electric gradient furnace for measurement. The compositional and phase analysis of the crystalline phase formed at the liquidus temperature was performed by EDS and XRD, respectively.

2.2.3.2 Chemical analysis of melt-quenched samples

The concentration of Na₂O in the melt-quenched samples was measured by flame emission spectroscopy (PerkinElmer Flame Emission Analyst 200), while the concentration of all the remaining oxides was determined by inductively coupled plasma-optical emission spectroscopy (ICP – OES; PerkinElmer ICP-OES Optima 2000DV; PerkinElmer ICP-OES Optima 7300V). The samples with white salt phase deposited on
their surfaces were washed and ultra-sonicated in acetone before the chemical analysis. Table S2 presents the experimentally analyzed compositions.

2.2.4 Structural analysis of glasses

The structure of rare-earth free glasses was studied using multi-nuclear magic angle spinning-nuclear magnetic resonance (MAS NMR) spectroscopy. MAS NMR analysis could not be performed on Nd$_2$O$_3$-containing glasses due to the strong paramagnetic effect of Nd$^{3+}$, leading to substantially broadened NMR spectra and the inability to resolve different resonances.

The MAS NMR spectra of $^{11}$B and $^{23}$Na were acquired using commercial spectrometers (VNMRs, Agilent) and MAS NMR probes (Agilent). The samples were powdered in an agate mortar, packed into 3.2 mm zirconia rotors, and spun at 20 kHz for $^{11}$B MAS NMR and 22 kHz for $^{23}$Na MAS NMR. $^{23}$Na MAS NMR data was collected at 16.4 T (185.10 MHz resonance frequency), using a 0.6 µs (~π/12 tip angle) pulse width for uniform excitation of the resonances. A range of 400 to 1000 acquisitions were co-added and the recycle delay between scans was 2 s. $^{11}$B MAS NMR experiments were conducted at 11.7 T (160.34 MHz resonance frequency), incorporating a 4 s recycle delay, short radio frequency (RF) pulses (0.6 µs) corresponding to a π/12 tip angle, and signal averaging of 400 to 1000 scans. The acquired spectra were processed with minimal apodization and referenced to aqueous boric acid (19.6 ppm) and aqueous NaCl (0 ppm), respectively. Fitting of the MAS NMR spectra was performed using DMFit$^{28}$ and the CzSimple model, accounting for distributions in the quadrupolar coupling constant, was utilized for $^{23}$Na MAS NMR spectra. The “Q MAS ½” and Gaus/Lor functions were used to fit 3- and 4-fold coordinated boron resonances in the $^{11}$B MAS NMR data, respectively, and $N_4$ was
calculated from the relative areas of these peaks, with a small correction due to the overlapping satellite transition of the 4-fold coordinated boron peak. 29

27Al MAS NMR experiments on glasses were conducted at 16.4 T using a commercial spectrometer (VNMRs, Agilent) and a 1.6-mm MAS NMR probe (Agilent) with spinning speeds of 25 kHz. MAS NMR data were acquired using RF pulses of 0.6 µs (equivalent to a π/12 tip angle), recycle delays of 2 s, and signal averaging of 1000 acquisitions. MAS NMR data were processed using commercial software, without additional apodization and referenced to aqueous aluminum nitrate at 0.0 ppm. A weak background signal from the zirconia MAS rotors was detected by 27Al MAS NMR of an empty rotor and subsequently subtracted from the MAS NMR data of the glass samples. This signal, at approximately 16 ppm, is clearly distinct from the Al peaks in the glasses, but nonetheless has been removed to ensure higher quantitative accuracy in the 27Al MAS NMR experiments.

29Si MAS NMR data were collected at 4.7 T (39.69 MHz resonance frequency) using a 5 mm MAS NMR probe. Powdered samples were packed into 5 mm zirconia rotors and all measurements were conducted using 5 kHz sample spinning. Measurements were made with signal averaging of 320 to 2200 acquisitions, using π/6 pulse widths of 1.4 µs and recycle delays of 90 s. 29Si spectra were processed without additional line broadening and referenced to tetramethyl silane at 0.0 ppm.

X-ray photoelectron (XPS; Thermo K-alpha; Thermo Fisher Scientific) spectroscopy was used to study the structural coordination of molybdenum (Mo 3d) and neodymium (Nd 3d and Nd 4d) in glasses. The glasses were fractured prior their analysis by XPS. All the spectra were deconvoluted in CASA XPS software using Gaussian-
Lorentzian peak fitting after Shirley background subtraction. The deconvolutions were carried out subject to the constraint of a constant full width half maxima (FWHM) for the same element. All photoelectron binding energies were referenced to adventitious C 1s contamination peaks at a binding energy of 285.0 eV.

2.3 Results

2.3.1 Crystallinity in glasses

Figure 2.1 presents the images of melt-quenched samples in the system 25 Na$_2$O–5 Al$_2$O$_3$–10 B$_2$O$_3$–(60–$x$) SiO$_2$–$x$ MoO$_3$ ($x = 0$–4 mol%), while Figure 2.2a presents their XRD data. Homogeneous, transparent, and completely amorphous samples were obtained for compositions with $x = 0$ and 0.5 mol%. An increase in MoO$_3$ content to 1 mol% resulted in a white translucent sample, while further increase in MoO$_3$ content to 1.5 mol% yielded a completely white and opaque sample. These physical characteristics can be attributed to either of the following scenarios: (i) liquid-liquid phase separation, or (ii) volume crystallization in the studied glasses. The XRD data of sample $x = 1$ reveals the presence of slight crystallization of SiO$_2$ and $\gamma$-Na$_2$MoO$_4$ (orthorhombic) phases in the glassy matrix, while Na$_2$MoO$_4$ (cubic) joined the crystalline phase assemblage with increasing MoO$_3$ content to 1.5 mol%. Increasing MoO$_3$ content to 2 mol% resulted in a white-colored opaque glass-ceramic with a thin layer of white-colored salt deposited on its surface. The concentration and thickness of this salt layer increased with further increase in MoO$_3$ content from 2–4 mol% as is evident from Figure 2.1. The quantitative phase analysis by Rietveld – RIR analysis on XRD data (Table 2.1) reveals that the resulting glass-ceramics with $x = 2$–4 mol% were mostly amorphous (97–99 wt. %), with crystalline phase assemblage comprising Na$_2$MoO$_4$ and $\gamma$-Na$_2$MoO$_4$. The XRD data of the salt layer
presented in Figure 2.2b depicts their highly crystalline nature (high intensity phase reflections) with their phase assemblage being dominated by cubic Na$_2$MoO$_4$ followed by Na$_2$(MoO$_4$)(H$_2$O)$_2$. Figure 2.3 shows the SEM image along with EDS elemental mapping of an interface between glass-ceramic and salt layer for sample Na-Mo-4. The salt layer showed a dendritic microstructure, rich in Na$_2$O and MoO$_3$, confirming the crystallization of sodium molybdate phases, while most of the SiO$_2$ and Al$_2$O$_3$ were confined to the glassy matrix.

An equimolar substitution of Na$_2$O by CaO in 12.5 Na$_2$O– 12.5 CaO– 5 Al$_2$O$_3$– 10 B$_2$O$_3$– (60–y) SiO$_2$– y MoO$_3$ (y = 0–4 mol%), system resulted in homogeneous, transparent, and amorphous samples for compositions with x varying between 0–1.5 mol%, as is evident from XRD data presented in Figure 2.4a. An increase in MoO$_3$ content to 2 mol% yielded a white, translucent sample, while the sample turned completely opaque for y = 2.5 mol% (like the trend observed in Na-Mo-x series, Figure 2.1). Further increase in MoO$_3$ content to 3 and 4 mol% led to formation of a white-colored salt layer on the surface glass-ceramic samples. The resulting glass-ceramics were mostly amorphous (~96 wt. %) (Table 2.1) with small fractions of CaMoO$_4$ as the only crystalline phase, as shown in Figure 2.4a. The XRD analysis of the salt layer formed on the surface of these samples (Figure 2.4b) shows the crystallization of CaMoO$_4$ as the dominant phase, followed by cubic Na$_2$MoO$_4$, Na$_2$MoO$_4$•2H$_2$O and Na$_2$Mo$_2$O$_7$ as secondary phases. Figure 2.5 shows the SEM image along with EDS elemental mapping of an interface between glass-ceramic and salt layer for sample Ca-Mo-4. The salt layer shows two distinct types of microstructures. One is rich in Na and Mo, suggesting sodium molybdate phases, while the other contains Ca and Mo, suggesting calcium molybdate phases. The glass-ceramic part of the sample comprises
calcium- and molybdenum-rich crystalline inclusions embedded in aluminoborosilicate glass matrix.

Figure 2.1: Images of melt-quenched glass/glass-ceramics from the series Na-Mo-x. The layer of white salt can be seen on the surface of glass/glass-ceramic samples in images of Na-Mo-3 and Na-Mo-4.
Table 2.1: Rietveld refinement of the three glass series (wt.%)

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Figure 2.2: (a) XRD patterns of melt-quenched glasses/glass-ceramics from series Na-Mo-x, and (b) XRD pattern of the white salt obtained on the surface of the sample Na-Mo-3.
Figure 2.3: SEM image and EDS elemental maps (for Mo, Si, Al and Na) of the interface between white salt and bulk glass-ceramic obtained after quenching of melt for sample Na-Mo-4.
Figure 2.4: XRD patterns of melt-quenched glasses/glass-ceramics from series Ca-Mo-y, and (b) XRD pattern of white salt obtained on the surface of the sample Ca-Mo-4.
Figure 2.5: SEM image and EDS elemental maps (for Mo, Si, Al, Ca, and Na) of the interface between white salt and bulk glass-ceramic obtained after quenching of melt for sample Ca-Mo-4.

Incorporating 5 mol% Nd$_2$O$_3$ at the expense of SiO$_2$ in 12.5 Na$_2$O–12.5 CaO–5 Al$_2$O$_3$–5 Nd$_2$O$_3$–10 B$_2$O$_3$–(55–z) SiO$_2$–z MoO$_3$ (z = 0–8 mol%) had a significant impact on solubility of molybdate ions in the glass structure, as completely transparent and amorphous samples were obtained from compositions with z varying between 0–3 mol% (Figure 2.6 and Figure 2.7a). An increase in MoO$_3$ content to 3.5 mol% resulted in a purple, translucent sample. However, its physical appearance was different from that observed for samples Na-Mo-1.5 or Ca-Mo-2 (Figure 2.1), as shown in Figure 2.6. The XRD data shows the presence of low intensity phase reflections corresponding to crystallization of CaMoO$_4$ (Figure 2.7a). Increasing MoO$_3$ to 4 and 5 mol% yielded opaque, volume crystallized glass-ceramics (Figure 2.6) with CaMoO$_4$ as the only crystalline phase. Further increase in MoO$_3$ to 6 mol% resulted in formation of a thin white colored salt layer on the surface of glass-ceramic as shown in Figure 2.6. The XRD analysis of this salt layer revealed the formation of CaMoO$_4$ as the dominant phase, followed by sodium molybdate based secondary phases – cubic Na$_2$MoO$_4$, and Na$_2$MoO$_4$•2H$_2$O (Figure 2.7b). Upon cleaning the salt layer from the surface of glass-ceramic (by ultra-sonicating in acetone), a faint dendritic pattern on was observed on the surface of glass-ceramic with 6 mol.% MoO$_3$ which became
prominent with increasing MoO$_3$ content to 8 mol%. The amount of residual glassy phase in the glass-ceramics varied between 86–97 wt. % and decreased with increasing MoO$_3$ content in these samples, resulting in ~86 wt. % for the highest MoO$_3$ level tested (Table 2.1). While the XRD data of the glass-ceramic samples demonstrated the presence of CaMoO$_4$ as the only crystalline phase in these materials, the SEM imaging followed by EDS elemental mapping of these glass-ceramics (Figure 2.8) reveal the presence of three different microstructures – (1) a dendritic microstructure, rich in calcium, neodymium and molybdenum, spread across the surface of glass-ceramic in long chains; (2) a microstructure rich in sodium and molybdenum, and (3) a phase rich in silica, alumina, and neodymium with small concentrations of sodium and calcium (being used to charge compensate AlO$_4$ (and possibly some BO$_4$) units. The dendritic microstructure rich in Ca, Mo, and Nd (region 1) in Figure 2.8 corresponds to CaMoO$_4$ crystals as neodymium is known to incorporate in CaMoO$_4$ crystal structure as has been shown by Wang et al.$^{31}$ using micro laser induced breakdown spectroscopy. The microstructural organization of these materials suggest that the crystalline phase assemblage of resultant glass-ceramic (upon heat treatment) is expected to contain some volumetric CaMoO$_4$, with Na$_2$MoO$_4$ and a calcium-neodymium-rich phase on the surface. The EPMA results on RE-Mo-6 and RE-Mo-8 results (presented in Figure S1-S9) are in good agreement with the SEM-EDS results where the small white colored crystalline inclusions found in the bulk of the polished sample are rich in calcium, molybdenum and neodymium, while the glassy phase is rich in calcium, neodymium, aluminum and silicon. We could not confirm the presence or absence of phase separation in these samples due to difficulty with detection of boron in the presence of molybdenum and limited spatial resolution of ~1 μm for microanalysis. The
quantification of boron in molybdenum containing samples by EPMA is a known challenge, and has also been highlighted by Chouard et al., as $B K\alpha$ X-ray has an energy of 183.3 eV, but might shift slightly due to its bonding with Mo. This X-ray line energy is very close to the Mo $M_\zeta$ line that is at 192.6 eV. In addition, the K-shell absorption edge of boron is at 188 eV, just below the Mo $M_\zeta$ line.

Table 2.2 presents the liquidus temperature ($T_L$) values of glasses from series RE-Mo-$z$ (where, $z$ varies between 0–3 mol.%) along with the first crystalline phase that forms in the melt at that temperature. The liquidus temperature of all the studied glasses varies between 1305–1330 °C and decreases from 1330 °C to 1305 °C with increasing MoO$_3$ concentration in glasses from 0 to 2 mol.%. However, with increase in MoO$_3$ concentration to 3 mol.%, the $T_L$ again increases to 1331.7 ± 2.9 °C. According to the XRD analysis (not shown), the composition of crystal formed at liquidus in all the rare-earth containing glasses Ca$_2$Nd$_8$(SiO$_4$)$_6$O$_2$.

**Table 2.2: Liquidus temperature ($T_L$) of Nd$_2$O$_3$ containing glasses**

<table>
<thead>
<tr>
<th>Glass</th>
<th>$T_L$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RE-Mo-0</td>
<td>1330 ± 0</td>
</tr>
<tr>
<td>RE-Mo-1</td>
<td>1325 ± 0</td>
</tr>
<tr>
<td>RE-Mo-2</td>
<td>1306.7 ± 2.9</td>
</tr>
<tr>
<td>RE-Mo-3</td>
<td>1331.7 ± 2.9</td>
</tr>
</tbody>
</table>
Figure 2.6: Images of melt-quenched glass/glass-ceramics from the series RE-Mo-z. The layer of salt can be seen on the surface of glass/glass-ceramic samples in images of RE-Mo-6 and RE-Mo-7 and RE-Mo-8.
Figure 2.7: a) XRD patterns of melt-quenched glasses/glass-ceramics from series Re-Mo-z, and (b) XRD pattern of white salt obtained on the surface of the sample RE-Mo-8.
Figure 2.8: SEM microstructure and EDS elemental maps of the surface of RE-Mo-8 glass-ceramic. The Region 1 marked in these images is rich in Ca, Nd, and Mo; Region 2 is rich in Na and Mo; Region 3 is rich is Si, Al, and Nd. The Region 1 and 2 are also expected to contain majority of boron. However, due to its lower atomic mass and significant overlap of its characteristic X-ray energies with molybdenum, it is difficult to detect boron using EDS.

2.3.2 Solubility and retention of MoO$_3$ in glasses

Figure 2.9 presents the quantitative ICP-OES results demonstrating the target versus experimentally measured incorporation of MoO$_3$ in the studied glass systems. The data presented in Figure 2.9 for all the investigated glass systems can be divided into two
parts: (i) a *linear curve* indicating all targeted MoO$_3$ is either dissolved in the glass or in crystals within the analyzed glass/glass-ceramic sample, which is denoted “apparent solubility,” (ii) a *plateau (parallel to x – axis)* representing the retention limit of MoO$_3$ in the samples, the excess of which partitioned to a salt phase that was washed off prior to chemical analysis, which is denoted “retention limit.” To distinguish between “true” and apparent solubility of Mo, the presence of crystals must be assessed (see below). For samples in Na-Mo-x series, the “true” solubility limit of MoO$_3$ may be defined as ~0.5 mol% (1.12 wt.%), as further increase in molybdenum concentration resulted in the formation of crystalline inclusions of Na$_2$MoO$_4$ in the glassy matrix. On the other hand, the retention limit of MoO$_3$ in this system may be defined as 2 mol% (4.41 wt.%), as higher concentrations of MoO$_3$ could not be incorporated in the glass/glass-ceramic system, instead resulting in the formation of alkali molybdate rich crystalline salt on the surface of glass-ceramic which was removed prior to chemical analysis by ICP-OES.

An equimolar substitution of Na$_2$O by CaO (series Ca-Mo-y) led to an increase in MoO$_3$ “true” solubility and retention limits to ~1.5 mol% (3.37 wt. %) and 2.82 mol% (6.22 wt. %), respectively. As has been discussed in *Section 2.3.1*, white colored crystalline salt rich in alkali and alkaline-earth molybdates was found on the surface of glass-ceramic Ca-Mo-3, thus, demonstrating that the retention limit of MoO$_3$ in this glass/glass-ceramic system has been achieved or exceeded.

The partial substitution of 5 mol% Nd$_2$O$_3$ for SiO$_2$ in the glass system had substantial impact on MoO$_3$ solubility and retention limits. The MoO$_3$ “true” solubility limit in the system RE-Mo-z increased to ~3 mol% (5.45 wt. %) in comparison to ~1.5 mol% for Ca-Mo-y glass system. Further increase in MoO$_3$ concentration resulted in
formation of CaMoO$_4$ crystalline inclusions in the RE-Mo-z samples. The retention limit of Nd$_2$O$_3$-containing system increased to 6.7 mol% (11.71 wt. %), as analyzed by ICP-OES data. This is interesting, because although salt formation was observed on the surface of samples with MoO$_3 \geq 6$ mol%, suggesting that retention limit for this composition has been achieved or exceeded, 6.7 mol% MoO$_3$ was still incorporated (retained) in these samples. The plausible explanation for this behavior has been presented in the discussion section.

\textbf{Figure 2.9:} ICP-OES data depicting the targeted vs. measured concentration of MoO$_3$ in the studied glass systems. The letters C (for crystal) and S (for salt) have been placed over the data points to highlight the concentration of MoO$_3$ where crystal formation or salt precipitation is initiated.
2.2.3 Structure of glasses

2.3.3.1 $^{11}$B, $^{23}$Na and $^{27}$Al MAS NMR

Figure 2.10 presents the $^{11}$B MAS NMR spectra of glasses from Na-Mo-x series (Figure 2.10a) where x varies between 0 – 1 mol%, and Ca-Mo-y, where y varies between 0–2 mol% (Figure 2.10b). The $^{11}$B MAS NMR spectra of all the glasses shows two main features, a broad peak associated with BO$_3$ (B$^{\text{III}}$) units centered at ~13 ppm and a peak at ~ -1.6 ppm attributed to BO$_4$ (B$^{\text{IV}}$) units.$^{37-39}$ The deconvolution of MAS NMR spectra of these glasses reveal that Na$_2$O/CaO ratio had a significant impact on their borate speciation as the fraction of N$_4$ units in Ca-Mo-y glasses (N$_4 = 48$–49%) was considerably lower than Na-Mo-x glasses (N$_4 = 70$–71% N$_4$ units). The decrease of B$^{\text{IV}}$ units with substitution of sodium by calcium demonstrates that the charge compensation of tetrahedral boron units is favored by sodium ions. The analysis of $^{23}$Na MAS NMR spectra from these glasses corroborated the $^{11}$B MAS NMR results, as the isotropic chemical shift for $^{23}$Na moves to high shielding, and the quadrupolar coupling constant (C$_Q$) gets smaller with the partial substitution of Na$_2$O by CaO, as shown in Figure 2.11. These observations suggest the change in the structural role of sodium from modifier to charge compensator when CaO is added. Similar results on alkali/alkaline-earth aluminoborosilicate glasses have been published by Quintas et al.$^{40}$ In accordance with the literature on this subject, there is only modest impact of molybdenum incorporation on sodium or borate speciation in the studied glasses,$^{4,12}$ with a continuous change in $^{23}$Na NMR parameters with increasing MoO$_3$ (Figure 2.11).
Figure 2.10: $^{11}$B MAS NMR of glasses in series (a) Na-Mo-x, and (b) Ca-Mo-y.
Figure 2.11: A plot showing the variation in isotropic chemical shift (δ_{CS}), and quadrupolar coupling coefficient (C_Q) for sodium (as a function of MoO_3 concentration) as calculated from ^{23}Na MAS NMR spectroscopy of glasses from Na-Mo-x and Ca-Mo-y series.

Figure 2.12 shows a comparison of ^{27}Al MAS NMR spectra recorded for the Na-Mo-x (Figure 2.12a) and Ca-Mo-y (Figure 2.12b) glass series. The spectra show nearly symmetric peaks located around 60 ppm in both series, which reflects the tetrahedral coordination (Al^{IV}) of aluminum atoms in aluminosilicates. This confirms adequate charge-balancing of Al tetrahedra, as expected for these highly peralkaline glass compositions.
2.3.3.2 XPS analysis

XPS was used to study the structural coordination of molybdenum and neodymium in the rare-earth containing glasses (RE-Mo-z). Figure 2.13 presents the Mo 3d (Figure 2.13a) and Nd 3d (Figure 2.13b) XPS spectra of glass RE-Mo-3. The observed features in

Figure 2.12: $^{27}$Al MAS NMR of glasses in series (a) Na-Mo-x, and (b) Ca-Mo-y.
the XPS spectra for the RE-Mo-3 glass are representative of all the Nd\textsubscript{2}O\textsubscript{3}-containing glass samples discussed in this study. Table 2.3 presents the binding energies (peak positions from XPS data) for Mo 3d\textsubscript{3/2}, Mo 3d\textsubscript{5/2}, Nd 3d\textsubscript{3/2}, Nd 3d\textsubscript{5/2} and Nd 4d spin states as observed in the present study, along with a comparison with their values reported in literature.\textsuperscript{15, 45, 46} The Mo 3d XPS spectra shows two main peaks at 232 eV and 235 eV corresponding to Mo\textsuperscript{6+} 3d\textsubscript{5/2} and 3d\textsubscript{3/2} spin states, respectively. This confirms the assertion of Mo being mainly in a hexavalent oxidation state in the studied glasses. According to Farges et al.,\textsuperscript{47} Mo is present primarily as [Mo(VI)O\textsubscript{4}\textsuperscript{2−}] species in most of the silicate and aluminosilicate glass compositions synthesized at f(O\textsubscript{2}) values ranging from 1 atm to 10\textsuperscript{−12} atm. Regarding the structural coordination of neodymium, the Nd 3d spectra exhibit two main peaks at 983 eV and 1005 eV, corresponding to Nd 3d\textsubscript{5/2} and Nd 3d\textsubscript{3/2}, respectively, while the Nd 4d spectra exhibits a single broad peak at 121 eV. According to the literature,\textsuperscript{45, 46} these binding energies are typically found for neodymium environments in Nd\textsubscript{2}O\textsubscript{3} and Nd(OH)\textsubscript{3}, i.e. Nd\textsuperscript{3+}. 
Figure 2.13: The deconvoluted XPS spectra of (a) molybdenum and (b) neodymium from glass RE-Mo-3.

Table 2.3: Mo 3d, Nd 3d and Nd 4d peak position (eV), derived from X-ray Photoelectron Spectroscopy data.

<table>
<thead>
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<th>Peak position (eV)</th>
<th>Literature Nd oxides</th>
<th>RE-Mo-0</th>
<th>RE-Mo-1</th>
<th>RE-Mo-2</th>
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<td>-</td>
<td>235.78</td>
<td>235.68</td>
<td>235.62</td>
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</table>
2.4 Discussion

2.4.1 Solubility of molybdate ions in rare-earth free aluminoborosilicate glasses

The coordination of MoO$_4^{2-}$ ions in a borosilicate or aluminoborosilicate glass is highly dependent on its homogeneous vs. heterogeneous nature. According to available literature on this topic, in a homogeneous borosilicate glass, molybdate ions are located in the depolymerized regions of the glass structure (i.e., non-bridging oxygen (NBO)–rich regions) containing alkali and alkaline-earth cations to compensate their negative charge.$^{48}$ On the other hand, in a phase separated borosilicate glass, incorporation of even small concentration (~1 mol% MoO$_3$) of molybdate ions are known to further promote phase separation, resulting in segregation of alkali-borate-rich amorphous domains from a silica-rich matrix.$^{19}$ An increase in MoO$_3$ concentration in this case leads to a decrease in SiO$_2$ content in alkali-borate-rich regions and an increased volume fraction of a SiO$_2$-rich phase, and most of the molybdate ions coordinate into the alkali-borate-rich region.$^{19}$ Similar structural behavior of molybdate ions can be expected in aluminoborosilicate glasses based on their homogeneous or heterogeneous nature. However, most of the literature pertaining to molybdenum incorporation in aluminoborosilicate glasses relates to homogeneous parent glasses, where molybdate ions are not directly linked to the aluminoborosilicate glass network but rather located within alkali and alkaline-earth domains in the glass.$^{12}$ This explanation is in good agreement with the results obtained in the present study for glasses in Na-Mo-x and Ca-Mo-y series. The structural position of molybdate ions in the depolymerized regions of glass (rich in NBOs), and being charge compensated by Na$^+$ in Na-Mo-x and both Na$^+$ and Ca$^{2+}$ in Ca-Mo-y glasses, explains the crystallization of Na$_2$MoO$_4$ and CaMoO$_4$ phases in the respective series of glasses. Since MoO$_3$
incorporation in the studied glasses did not affect their boron and aluminum speciation, it is highly likely that sodium and calcium are being pulled from the silica matrix to form Na$_2$MoO$_4$ or CaMoO$_4$ phases, thus leading to repolymerization of the silicate network. Interestingly, $^{29}$Si MAS NMR of glasses in Na-Mo-x series (Figure S10) does not exhibit any significant shift as a function of MoO$_3$ content. However, this does not imply absence of re-polymerization in the silicate network, as insignificant shifts in $^{29}$Si MAS NMR spectra can be due to small or undetectable change in the silicate network owing to the low concentration of MoO$_3$, and additional complications due to Si/Al mixing in the glass network.

The drastic change in boron speciation, i.e., the substantial reduction in the fraction of boron in four-fold coordination due to introduction of CaO (at the expense of Na$_2$O), may be explained based on the higher ionic field strength of Ca$^{2+}$ compared to Na$^+$. Higher field strength cations significantly favor the formation of NBO, lowering the degree of preference in formation of B$^{IV}$ over NBO.$^{49}$ For detailed explanations, readers are referred the following literature.$^{40, 49, 50}$ The consequences of this difference in modifier behavior (e.g., $N_d$) is such that the Ca$^{2+}$ is then more associated with silicon, forming a much higher proportion of Si-NBO than the analogous Na-bearing glasses. As discussed above, incorporation of MoO$_3$ in Na$_2$O–CaO–Al$_2$O$_3$–B$_2$O$_3$–SiO$_2$ glass will result in formation of alkali and alkaline-earth molybdate species, first as associated moieties in the glass and ultimately as precipitated crystals. However, the formation of CaMoO$_4$ (over Na$_2$MoO$_4$) as the preferential crystalline phase in these glass-ceramics may be attributed to the unavailability of Na$^+$ to associate with MoO$_4^{2-}$, because the majority of sodium is being used to charge compensate for B$^{IV}$ and Al$^{IV}$ units, as reflected in the B and Al coordination
numbers and the $^{23}\text{Na}$ NMR data. Further, the higher solubility of molybdate ions in Na$_2$O–CaO–Al$_2$O$_3$–B$_2$O$_3$–SiO$_2$ glass system, in comparison to Na$_2$O–Al$_2$O$_3$–B$_2$O$_3$–SiO$_2$ system, may be attributed to the slower tendency of the former towards devitrification due to the higher activation energy of crystallization of CaMoO$_4$ (~50–60 kcal/mole) versus Na$_2$MoO$_4$ (~28 kcal/mole).

2.4.2 Impact of Nd$_2$O$_3$ on MoO$_3$ solubility in aluminoborosilicate glasses

Before we discuss the impact of Nd$_2$O$_3$ on the solubility of MoO$_3$ in the aluminoborosilicate glasses under investigation, it is important to understand the structural role of Nd$_2$O$_3$ in these glasses, as it has direct implications on the solubility of MoO$_3$. The structural coordination of rare-earth cations in alkali/alkaline-earth aluminoborosilicate glasses has been studied in detail primarily by researchers from two countries – USA$^{33, 34}$ and France$^{40, 60-65}$ owing to their high relevance in the field of nuclear waste immobilization. Based on the investigated compositional chemistries, there exist two different opinions about the coordination of rare-earth cations in these glasses. According to the U.S. scientists (hereafter referred as Li et al.), who studied a wide array of glass compositions in Na$_2$O-Al$_2$O$_3$-B$_2$O$_3$-SiO$_2$ based peralkaline and peraluminous systems, the role of rare-earth cation in a peralkaline (Na/Al > 1) glass (most nuclear waste glasses are peralkaline) is decided by the ratio of Na$_2$O$_{ex}$/B$_2$O$_3$, where Na$_2$O$_{ex} = [\text{Na}_2\text{O}] - [\text{Al}_2\text{O}_3]$.$^{33}$ It has been suggested that if Na$_2$O$_{ex}$/B$_2$O$_3$ < 0.5, the baseline aluminoborosilicate glass is heterogeneous (phase separated), while glasses with Na$_2$O$_{ex}$/B$_2$O$_3$ > 0.5 are homogeneous in nature. In case of phase separated glass (Na$_2$O$_{ex}$/B$_2$O$_3$ < 0.5), the rare-earth cation is mostly incorporated in the borate portion of the structural phase.$^{33}$
The rare-earth free peralkaline glasses with $\text{Na}_2\text{O}_{\text{ex}}/\text{B}_2\text{O}_3 > 0.5$, for example, $60\text{SiO}_2$–$15\text{B}_2\text{O}_3$–$20\text{Na}_2\text{O}$–$5\text{Al}_2\text{O}_3$ (mol.%),\textsuperscript{52, 58} have been shown to be homogeneous. The incorporation of rare-earth cations in these glasses phase separates the homogeneous aluminoborosilicate glass into borate- and aluminosilicate-rich zones where the rare-earth cations preferentially enter the borate-rich phase forming a double chain structure similar to rare-earth metaborate. Once the concentration of rare-earth cations in the glass exceeds its solubility limit in the borate phase, the rare-earth cations are incorporated in the aluminosilicate phase as some kind of “cluster”. This mechanism has been proven for Gd$_2$O$_3$ and Nd$_2$O$_3$ containing aluminoborosilicate glasses by transmission electron microscopy (TEM) and multi-spectroscopic techniques, including electron energy loss spectroscopy (EELS) and optical spectroscopy.\textsuperscript{33, 34, 53, 54, 56}

In case of studies performed by the French scientists (hereafter referred as Caurant et al.) on this subject, majority of the experimental research has employed the following two baseline compositions (mol.%): $16.56\text{Na}_2\text{O}$–$8.28\text{CaO}$–$5.32\text{Al}_2\text{O}_3$–$10.65\text{B}_2\text{O}_3$–$59.17\text{SiO}_2$\textsuperscript{21, 62} and $14.41\text{Na}_2\text{O}$–$6.33\text{CaO}$–$3.05\text{Al}_2\text{O}_3$–$8.94\text{B}_2\text{O}_3$–$1.90\text{ZrO}_2$–$3.56\text{RE}_2\text{O}_3$–$61.81\text{SiO}_2$ (RE: Rare-earth).\textsuperscript{40, 63, 65, 66} Considering the $\text{Na}_2\text{O}_{\text{ex}}/\text{B}_2\text{O}_3$ criteria as proposed by Li et al.,\textsuperscript{33} both the baseline compositions (when rare-earth free) should be homogeneous in nature. While similar results have been published by Caurant et al.,\textsuperscript{40, 60, 62, 63} they tend to disagree with Li et al.\textsuperscript{33, 52, 58} with regard to the induction of phase separation by rare-earth cations in a homogeneous aluminoborosilicate glass. According to Caurant et al.,\textsuperscript{21, 62} Nd$^{3+}$ cations act as network modifiers in aluminoborosilicate glasses where they remain located in the depolymerized silicate regions of the glassy network and thanks to their high ionic field strength, they impose their local environment composed of

\textcolor{white}{.}
6–8 NBOs. Nevertheless, in order to ensure local electroneutrality of the configuration, a fraction of the lower field strength modifier cations present in the glass composition such as alkali and alkaline-earth cations are located in the second coordination sphere of the Nd$^{3+}$ cations. Further it has been reported that glass–in–glass phase separation in rare-earth containing glasses is detected when CaO/Na$_2$O > 1, while the glasses with CaO/Na$_2$O < 1 are homogeneous in nature.$^{40}$

In order to clarify the contradiction between the results from two research groups, Caurant et al.$^{67}$ conducted an extensive study investigating two different series of per-alkaline glass compositions (first with Na$_2$O$_{ex}$/B$_2$O$_3$ < 0.5 and second with Na$_2$O$_{ex}$/B$_2$O$_3$ > 0.5) derived from 14.41 Na$_2$O– 6.33 CaO– 3.05 Al$_2$O$_3$– 8.94 B$_2$O$_3$– 1.90 ZrO$_2$– 3.56 Nd$_2$O$_3$– 61.81 SiO$_2$ as the base composition. In accordance with Li et al.$^{33}$ they reported that the key chemical parameter governing the overall structural organization in these glasses is the Na$_2$O$_{ex}$/B$_2$O$_3$ ratio, where Na$_2$O$_{ex}$ = [Na$_2$O] − [Al$_2$O$_3$] −[ZrO$_2$], and the high field strength cations, for example, Ca$^{2+}$ and Nd$^{3+}$, only interfere on the second order of their structural organization, inducing more disorder in it. Based on Nd$^{3+}$ optical absorption spectroscopy and Nd$^{3+}$ L3-edge X-ray absorption spectroscopy, Caurant et al.$^{67}$ indicated towards the possible formation of Nd$^{3+}$, Ca$^{2+}$, NBOs and BO$_4^-$ rich areas in the glasses with Na$_2$O$_{ex}$/B$_2$O$_3$ > 0.5. They attributed the presence of borate units around Nd$^{3+}$ ions in the glass structure as a reason for slower tendency towards apatite crystallization (upon slow cooling of glass melt) with increasing B$_2$O$_3$ concentration. However, they still reported the glasses to be “sufficiently homogeneous in terms of Si/B mixing” to undergo crystallization of the Nd-rich silicate apatite phase by slow cooling the melt. In case of B$_2$O$_3$ rich glasses,
i.e., Na$_2$O$_{ex}$/B$_2$O$_3$ < 0.5, they reported the presence of glass–in–glass phase separation where formation of Na-rich or Nd-metaborate phase was confirmed.

In the present study, Na$_2$O$_{ex}$/B$_2$O$_3$ > 0.5 for the rare-earth free glass Ca-Mo-0. Therefore, in accordance with the existing literature on this topic, this glass should be homogeneous in nature where sodium is mainly acting as a charge compensator for AlO$_4^-$ and BO$_4^-$ units. This assertion is supported by the $^{23}$Na, $^{27}$Al and $^{11}$B MAS-NMR results of Ca-Mo-$\gamma$ glass series as discussed in the results section. Further, when Nd$_2$O$_3$ is added to the glass Ca-Mo-0 (resulting in RE-Mo-0), each Nd$^{3+}$ brings 3 NBOs, while it needs 6–8 NBOs to fulfill its coordination in order to be homogeneously incorporated in the glass structure.$^{67}$ Therefore, for each mole of Nd$_2$O$_3$, 3 to 5 moles of (Na$_2$O + CaO) will be required to homogeneously incorporate Nd$^{3+}$ ions within the fully charge-compensated polyhedral. Since the majority of the sodium is acting as a charge compensator for four coordinated aluminum and boron, Nd$^{3+}$ will tend to coordinate with NBOs being generated by Ca$^{2+}$ in order to fulfill its coordination shell. However, there is not enough concentration of network modifiers to meet this requirement. In this scenario, Nd$^{3+}$ can be incorporated in the glass through the following two possible mechanisms: (i) they can form clusters where they can share their own NBOs, or (ii) they can contribute to the charge compensation of BO$_4$ units (since AlO$_4^-$ units are completely charge balanced by Na$^+$).

According to Caurant et al.$^{67}$ both mechanisms are possible, where a part of Nd$^{3+}$ charge compensates boron to form BO$_4$ units, while the remaining form clusters, thus distributing itself in borosilicate phase of the glass. Although they do not agree with the hypothesis of phase separation in rare-earth containing glasses as proposed by Li et al.$^{53}$ their results from reference$^{67}$ point in the same direction where Nd$^{3+}$ are distributed in the borosilicate
matrix, preferentially being associated with tetrahedral borate moieties followed by clustering in silicate part.

Regarding the impact of Nd$_2$O$_3$ on the solubility of MoO$_3$ in aluminoborosilicate glasses, it has been proposed that it is the close relationship between Nd$^{3+}$ and MoO$_4^{2-}$ tetrahedral entities in the depolymerized region of the glassy network that is at the origin of the increase of molybdenum solubility and of the disappearance of phase separation and crystallization of molybdate phases.$^{20,21,68}$ According to the proposed hypothesis, the presence of neodymium has a “dispersing effect” on the MoO$_4^{2-}$ units in the glass which avoids their clustering and crystallization of molybdate phases.$^{21}$ While the proposed hypothesis tends to explain the suppression in crystallization of molybdate phases, it contradicts the results from the same research group presented in reference$^{67}$ regarding structural coordination of Nd$^{3+}$ in aluminoborosilicate glasses as discussed above.

In our opinion, when incorporated in aluminoborosilicate glass, MoO$_4^{2-}$ associates itself with Nd$^{3+}$, Ca$^{2+}$, NBOs and BO$_4^{-}$ rich regions. This is in agreement with the TEM studies on molybdenum containing borosilicate glasses reported by Kawamoto et al.,$^{19}$ where it has been shown that molybdate ions prefer to enter the borate-rich phase of a phase separated borosilicate glass (discussed above). While we could not ascertain the possibility of phase separation in rare-earth aluminoborosilicate glass due to poor detection of boron in both SEM-EDS and EPMA and limited spatial resolution, this does not negate the possibility of phase separation in glasses upon addition of molybdenum oxide. This argument is based on the fact that both Li et al.$^{33}$ and Caurant et al.$^{67}$ have discussed the formation of rare-earth rich borate regions in aluminoborosilicate glasses, although the latter describes their glasses to be “sufficiently homogeneous” when Na$_2$O$_{eq}$/B$_2$O$_3$ > 0.5.
Therefore, it is highly likely that once incorporated into the borate phase, MoO$_4^{2-}$ ions coordinate with the rare-earth-borate phase to form a rare-earth-molybdate-borate glassy phase. The formation of this Nd$_2$O$_3$–MoO$_3$–B$_2$O$_3$ glassy phase resulted in higher solubility of molybdate ions in the studied glasses. This assertion is supported by the fact that stable glass-forming regions in the La$_2$O$_3$–MoO$_3$–B$_2$O$_3$ and Nd$_2$O$_3$–MoO$_3$–B$_2$O$_3$ systems have been reported by Aleksandrov et al.$^{35,36}$ According to the literature, molybdenum exists as MoO$_4^{2-}$ species in the Nd$_2$O$_3$–MoO$_3$–B$_2$O$_3$ glassy system. Neutron diffraction and reverse Monte Carlo (RMC) simulations show an existence of pronounced intermediate – range ordering through MoO$_4$–BO$_4$ and MoO$_4$–BO$_3$ linkages.$^{69}$

Our hypothesis is also supported by the crystallization of Nd-rich CaMoO$_4$ phase in RE-Mo-$_z$ glasses with MoO$_3$ ≥ 3.5 mol% (Figure 2.8). An increase in MoO$_3$ ≥ 3.5 mol.% likely exceeded the concentration of molybdate ions that could be accommodated in the Nd$_2$O$_3$–MoO$_3$–B$_2$O$_3$ glassy structure, thus leading to crystallization of CaMoO$_4$. The proposed hypothesis also gains support from the crystallization of Ca$_{2.2}$Nd$_{7.8}$(SiO$_4$)$_6$O$_{1.9}$ based apatite phase at the liquidus temperature in rare-earth containing glasses. This may be attributed to the structural re-arrangement between the silicate component of glass and neodymium clusters at high temperatures resulting in crystallization of apatite.

2.4.3 Salt formation in molybdenum-rich glass melts

While the glass-ceramics from the Ca-Mo-$y$ and RE-Mo-$z$ systems exhibited the crystallization of CaMoO$_4$ phase in their glassy matrix, the white salt phase formed in MoO$_3$-rich melts contained both CaMoO$_4$ and polymorphs of Na$_2$MoO$_4$. The chemical difference between the nature of crystalline molybdates, which may form in the high temperature melt versus the cooled glass-ceramic, may be explained based on temperature-
induced coordination changes of boron, leading to the modifications in the activity of alkali/alkaline-earth cations, which act as either charge compensators or network modifiers. According to previous studies, boron partially changes from tetrahedral to triangular coordination with increasing temperature in borosilicate glasses. Therefore, an increase in the activity (i.e., concentration) of network modifying alkali cations can be expected at an increased temperature, according to the reaction:

\[ \text{Na}_{\text{CC}} + \text{BO}_4^- = \text{BO}_3^- + \text{NBO} + \text{Na}_{\text{NM}} \]

where, Na_{CC} and Na_{NM} refer to charge compensating and network modifier roles of Na, respectively. Thus, under oxidizing conditions, alkali molybdates will form in the molten stage due to higher availability of alkali cations in the presence of 3-coordinated boron. On the other hand, the partial transformation of boron from 3- to 4- coordination during cooling of the glass will increase the proportion of Na cations involved in charge compensation of boron. Consequentially, there will be no more Na\(^+\) to charge compensate molybdate groups, and Ca\(^{2+}\) ions will be required to fulfill this role.

2.5 Conclusions

An attempt has been made to understand the compositional and structural dependence of molybdate ions in aluminoborosilicate based model nuclear waste glasses. The higher solubility of MoO\(_3\) in Na-Ca-Al-B-Si-O glass in comparison to Na-Al-B-Si-O has been explained on the basis of unavailability of sodium ions to charge compensate MoO\(_4^{2-}\), thus resulting in the charge compensation of latter by Ca\(^{2+}\). This leads to the crystallization of CaMoO\(_4\) (over Na\(_2\)MoO\(_4\)) in calcium-containing aluminoborosilicate glasses. Since the activation energy of crystallization for CaMoO\(_4\) is about double that of Na\(_2\)MoO\(_4\), this results in higher solubility of MoO\(_3\) in Na-Ca-Al-B-Si-O glass system.
Further, the introduction of Nd$_2$O$_3$ in the Na-Ca-Al-B-Si-O glass system increases the solubility of MoO$_3$ from 1.5 mol% to 3 mol%. This increase in MoO$_3$ solubility as a function of Nd$_2$O$_3$ has been explained on the basis of three-step mechanism where in Step 1, a fraction of rare-earth cations distributes themselves in the borate rich areas of glass while the remaining rare-earth cations cluster in the silicate/borosilicate region. In Step 2, the MoO$_4^{2-}$ ions are incorporated into the rare-earth borate phase, thus forming a stable Nd-Mo-B-O glassy region. In Step 3, any further increase in MoO$_3$ concentration (in this case MoO$_3$ ≥ 3.5 mol%) is likely to exceed the concentration of molybdate ions that could be accommodated in the Nd$_2$O$_3$–MoO$_3$–B$_2$O$_3$ glassy structure, thus leading to crystallization of Nd-rich CaMoO$_4$.

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**Supplementary Information**

The online version of this article contains supplementary information including batched glass composition; experimental glass compositions; EDS point spectra of samples; backscattered secondary electron images of glass; WDS maps of glasses, $^{29}$Si MAS NMR of glasses.
References


Chapter 3. Insight into the Partitioning and Clustering Mechanism of Rare-Earth Cations in Alkali Aluminoborosilicate Glasses

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Abstract

Rare-earth (RE) containing alkali aluminoborosilicate glasses find increasingly broad technological applications, with their further development only impeded by yet-poor understanding of coordination environment and structural role of RE ions in glasses. In this work we combine free induction decay (FID)-detected electron paramagnetic resonance (EPR), electron spin echo envelope modulation (ESEEM), and MAS NMR spectroscopies, to examine the coordination environment and the clustering tendencies of RE$^{3+}$ in a series of peralkaline aluminoborosilicate glasses co-doped with Nd$_2$O$_3$ (0.001–0.1 mol%) and 5 mol% La$_2$O$_3$. Quantitative EPR spectral analysis reveals three different Nd$^{3+}$ forms coexisting in the glasses: isolated Nd$^{3+}$ centers, dipole-coupled Nd clusters (Nd–O–X–O–Nd, where X = Si/B/Al), and spin-exchange-coupled Nd clusters, (Nd–O–Nd) and (Nd–O–La–O–Nd). Extensive RE clustering is observed at high RE$_2$O$_3$ concentrations, with more than 90% REs converting to dipole- and exchange-coupled Nd clusters already at [RE$_2$O$_3$] = 0.01 mol%. ESEEM analysis of the EPR-detectable Nd centers indicates a Na/Si-rich environment (four Na$^+$ per Nd$^{3+}$) for the isolated Nd$^{3+}$ centers and the Na/Si/B-rich environment (2–3 Na$^+$ and 1–2 boron per each Nd$^{3+}$) for the dipole-coupled Nd clusters, while the EPR-undetectable exchanged-coupled RE clusters are predicted to exist in a Na/B-rich environment. The RE clustering induces nano-scale glass phase separation, while the Na/B-rich environment of the RE clusters implies a depletion of the same elements from the remaining host glass. Based on our results, we develop a mechanistic model that explains the high tendency of RE$^{3+}$ to form clusters in alkali aluminoborosilicate glasses.
3.1 Introduction

Our understanding of the mechanism of rare-earth (RE) clustering in SiO₂ glass and its suppression by Al₂O₃ and P₂O₅¹⁵ has resulted in the development of RE-doped fiber amplifiers and lasers, thus, bringing a paradigm shift in the field of telecommunication. However, this has not been the case with multicomponent silicate glasses, where the technological development in the field of RE-containing glasses has been primarily confined to the academic realms. A major reason for the slow transition from academia to real-world applications is our poor understanding of the structural role of RE cations in these glasses (as discussed in more detail in the following paragraphs), thus, resulting in an ambiguity in their structure-property relationships. For example, RE³⁺ are usually considered to play the role of network modifiers in the structure of alkali aluminoborosilicate glasses.⁶, ⁷ Based on our conventional wisdom, network modifying cations are expected to depolymerize the silicate/aluminoborosilicate glass network by creating non-bridging oxygens (NBOs), and some evidence of it has indeed been reported.⁶, ⁷ Such RE-induced glass depolymerization is expected to decrease the glass transition temperature (T_g) of the glasses. Nevertheless, RE₂O₃ additions to silicates, aluminosilicates, and aluminoborosilicate glasses have been shown to have the opposite effect of shifting their T_g towards the higher side.⁷⁻¹³ While the literature attributes the increase in T_g to the stronger RE–O⁻ bonds being formed in the glass,⁷, ⁸, ¹¹ this is simply a hypothesis as no structural evidence has ever been reported to this effect.

The lack of understanding about the fundamental science governing the role of RE³⁺ in the structure of multicomponent silicate glasses becomes a bottleneck in explaining
the trends observed in functional glasses. For example, MoO$_3$-loading in an alkali aluminoborosilicate-based nuclear waste glass has been shown to be highly dependent on the nature and concentration of RE present in the glass.\textsuperscript{14} However, the reason for this dependence is debatable as it is not explicit if RE$^{3+}$ simply act as network modifiers in these glasses or if they induce clustering and phase separation.\textsuperscript{15, 16} Other examples, where our lack of understanding about the role of rare-earth cations in the structure of multicomponent silicate glasses has slowed down their further technological development, can be quoted from the field of biomaterials\textsuperscript{17} and solid-state lasers or optical amplifiers.\textsuperscript{18} Thus, the present study is directed towards understanding the structural role of rare-earth cations in alkali aluminoborosilicate glasses. The overarching goal is to find answers to the following questions: Do RE$^{3+}$ distribute homogeneously or heterogeneously in the matrix of alkali aluminoborosilicate glasses? In either case, what is their chemical coordination environment in multicomponent glasses, and what mechanisms define their distribution in the glass network?

Accordingly, we have selected the Na$_2$O-Al$_2$O$_3$-B$_2$O$_3$-SiO$_2$ based quaternary glass system with Na/Al > 1. The choice of glass system has been made considering that it is the backbone of the specialty glass industry and a potential candidate for several upcoming technological innovations. As an example, cover glasses used as the outer contact surface of touch-screen electronic displays are designed primarily in the Na$_2$O-(K$_2$O)-Al$_2$O$_3$-B$_2$O$_3$-(P$_2$O$_5$)-SiO$_2$ systems where alkali/Al$_2$O$_3$ $\geq$ 1.\textsuperscript{19} Similarly, borosilicate-based nuclear waste glasses are generally designed in Na$_2$O-Al$_2$O$_3$-B$_2$O$_3$-SiO$_2$ systems with Na/Al $>$ 1.\textsuperscript{15, 20, 21} Further, RE$^{3+}$-doped alkali aluminoborosilicate glasses have been proposed as broad
emission bandwidth laser media suitable for use at powers higher than petawatt or exawatt levels. Therefore, insights into the structural role of rare-earth cations in the Na₂O-Al₂O₃-B₂O₃-SiO₂ systems are not only of scientific interest but also have a tangible impact on the design of functional glasses for a broad spectrum of technological applications.

3.2 Distribution/partitioning of rare-earth cations in alkali aluminoborosilicate glasses – Literature review

Two opposing viewpoints are prevailing in the glass science community. The first viewpoint suggests that RE³⁺ induce nano-scale phase separation in homogenous peralkaline (Na/Al > 1) aluminoborosilicate glasses leading to the segregation of borate-rich and silicate-rich phases. RE³⁺ are believed to preferentially dissolve in the borate-rich region forming RE-metaborate-like structures (1BO₄:RE:2BO₃). Once the RE³⁺ concentration in the glass exceeds the limit of saturation in the borate-rich region (i.e., [RE₂O₃] = 1/3[B₂O₃], according to reference²³), they enter the silicate-rich region forming RE-clusters. On the other hand, the second viewpoint argues against the clustering tendency of RE³⁺ or the RE³⁺ induced nano-scale phase separation in the glass network. This hypothesis suggests that RE³⁺ enter the depolymerized region of a homogenous peralkaline aluminoborosilicate glass and establish their local environment by directly coordinating with the alkali/alkaline earth ions for charge compensation.⁶,²⁷

Both viewpoints are based on thorough investigations involving a suite of spectroscopic and microscopic techniques like electron energy loss spectroscopy (EELS), extended X-ray absorption fine structures (EXAFS), fluorescence spectroscopy, nuclear magnetic resonance (NMR), Raman spectroscopy, and transmission electron microscopy (TEM).⁶,²³-²⁷ However, neither of these techniques provides an atomic-scale picture of RE
clustering and their coordination environment (beyond the first neighbor shell, typically oxygen) in alkali aluminoborosilicate glasses. Also, all these techniques lack in their ability to selectively probe the RE$^{3+}$ centers, quantify possible RE speciation (isolated centers versus RE clusters) and estimate the extent of RE clustering in glasses. Therefore, to gain deeper insight into the local environment and distribution of RE$^{3+}$ over a length scale longer than few Å (beyond next neighbor distances), we need a spectroscopic technique that is selective in its ability to probe selective RE ions, has an improved concentration sensitivity, and a higher spatial resolution.

3.3 **Electron paramagnetic resonance (EPR) is a method of choice to study RE$^{3+}$ environment in glasses**

EPR spectroscopy is a technique capable of probing paramagnetic ions in solids. It offers several important advantages over other techniques (e.g., EXAFS, fluorescence spectroscopy, NMR, Raman spectroscopy) conventionally used for characterization of RE$^{3+}$ speciation and clustering in glasses.1, 2, 24, 28-30

(1) EPR has a superior concentration sensitivity, benefiting from its ability to selectively probe the paramagnetic RE$^{3+}$ centers only, without an overwhelming background contribution from other (often more abundant) centers and defects in glasses. The EPR sensitivity is better than 1 ppb (part per billion), or about 3–4 orders of magnitude higher than in other techniques, like UV-Vis, Raman, NMR, and EXAFS. EPR can be used to probe broad ranges of RE concentrations from 0.0001 to 1 mol%.

(2) Unlike other techniques, EPR allows an accurate evaluation of the number of spins contributing to the signal (known as spin counting) without any underlying assumptions.
Pulsed EPR techniques (as used in this work) offer superior spectral resolution which allows resolving multiple RE$^{3+}$ species (e.g., isolated RE$^{3+}$ centers versus RE clusters) if present in the glass.\(^3\)

Electron spin echo envelope modulation (ESEEM) is one of many pulsed EPR methods that can probe the coordination environment of RE$^{3+}$ ions by measuring electron-nuclear hyperfine interactions with magnetic nuclei in the glass matrix.\(^3\) ESEEM can often probe the second and third coordination shells around RE$^{3+}$, which is far beyond of what is accessible when using EXAFS and optical absorption spectroscopy.

Given these advantages, EPR has been previously employed for investigating RE$^{3+}$ speciation and coordination environment in silicate and phosphate-based glasses.\(^3\)-\(^5\), \(^33\)-\(^37\) Specifically, in silica-rich glasses, several articles published by Sen and co-workers,\(^3\), \(^5\), \(^37\) Saitoh et al.,\(^4\) and Arai et al.\(^33\) have reported on the spatial distribution (RE–RE distances) of the dopant RE$^{3+}$ and their next-nearest neighbor atoms in glasses. Here, we build up on these previous works to examine the RE$^{3+}$ speciation in alkali aluminoborosilicate glasses (Na/Al > 1).

In this study, we combine pulsed EPR spectroscopy (Free induction decay (FID)-detected EPR and ESEEM) and \(^{11}\)B/$^{27}$Al magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy to probe the speciation and local environment of rare-earth cations (Nd$^{3+}$) in peralkaline (Na/Al > 1) aluminoborosilicate glasses. From quantitative spectral EPR analysis we determine that Nd$^{3+}$ is present in three different forms in our glasses: isolated Nd$^{3+}$ centers, dipole-coupled Nd clusters, and spin-exchange-coupled Nd clusters. The fractional concentrations of each species are determined as a function of total Nd concentration in the glass and also after adding additional 5 mol\% of diamagnetic La$^{3+}$.\(^3\)
Extensive RE clustering (more than 90% of total RE) is observed at RE concentrations as low as 0.01 mol% in the glasses. From ESEEM spectroscopy and supported by $^{11}\text{B}$ and $^{27}\text{Al}$ MAS NMR, we find that isolated Nd$^{3+}$ centers are preferentially formed in the Na/Si-rich coordination, while the Nd clusters are formed in the Na/B-rich coordination. Based on these results, we propose the structural models for isolated and clustered RE species in the peralkaline aluminoborosilicate glasses and develop a charge compensation model to explain the high tendency of RE$^{3+}$ to form clusters.

3.4 Experimental details

3.4.1 Rationale for glass composition design

A peralkaline (Na/Al $> 1$) sodium aluminoborosilicate glass with a batched composition of 25 Na$_2$O$-$ 10 Al$_2$O$_3$$-$ 10 B$_2$O$_3$$-$ 55 SiO$_2$ (mol%) has been selected for RE$_2$O$_3$ addition. This glass composition is chosen based on the criterion proposed by Li et al.,$^{23}$ specifically [$\text{Na}_2\text{O}]_{ex}/[\text{B}_2\text{O}_3]$ $>$ 0.5, where [$\text{Na}_2\text{O}]_{ex} = [\text{Na}_2\text{O}] - [\text{Al}_2\text{O}_3]$, for designing homogenous peralkaline aluminoborosilicate glasses with no detectable (microscopic) phase separation. The spectroscopic examination by Wu and Stebbins$^{38}$ have confirmed the validity of this criterion, demonstrating that peralkaline sodium aluminoborosilicate glasses with [$\text{Na}_2\text{O}_{ex}]/[\text{B}_2\text{O}_3] = 1.7$ (similar to the one reported in the present study [$\text{Na}_2\text{O}_{ex}]/[\text{B}_2\text{O}_3] = 1.5$) are indeed homogeneous.

Nd$^{3+}$ are chosen as EPR spin probes for investigating the RE$^{3+}$ speciation and their local environments in alkali aluminoborosilicate glasses. Accordingly, the baseline glass (mol%, 25 Na$_2$O$-$ 10 Al$_2$O$_3$$-$ 10 B$_2$O$_3$$-$ 55 SiO$_2$) has been doped with varying concentrations of Nd$_2$O$_3$ in the range from 0.001 to 0.1 mol% to produce a series of glasses labeled as Ndx, where ‘x’ is the Nd$_2$O$_3$ concentration in mol% (Table 3.1).
Our preliminary experiments on Nd-containing glasses reveal that the Nd$_2$O$_3$ concentrations greater than 0.1 mol% are unsuitable for pulsed EPR experiments, resulting in: (1) significant EPR line broadening, due to excessive dipole-dipole interactions between paramagnetic Nd$^{3+}$ ions, making it impossible to resolve the individual contributions from different Nd species present in the glasses; and (2) too short T$_2$ spin relaxation times of Nd$^{3+}$ (e.g., T$_2$ < 100 ns, below the detection limit of our EPR experiment), owing again to strong Nd–Nd dipole-dipole interactions and also strong spin-exchange interactions, resulting in most of Nd centers to become EPR-invisible (undetectable). To overcome this experimental limitation and to examine RE speciation at concentrations higher than 0.1 mol%, a second series of glasses has been synthesized where Nd$_2$O$_3$ (x = 0.001–0.1 mol%) has been co-doped with La$_2$O$_3$ [(5 – x) mol%]. Accordingly, the second glass series has a composition: 23.75 Na$_2$O–9.50 Al$_2$O$_3$–9.50 B$_2$O$_3$–52.25 SiO$_2$–(5.00 – x) La$_2$O$_3$–x Nd$_2$O$_3$ (mol%) and labeled as LaNd$_x$. La$^{3+}$ is used as it is commonly viewed as a diamagnetic substitute of Nd$^{3+}$ in glass chemistry due to their similar coordination environments (6–8 oxygens surrounding the RE ions) and their similar cation field strengths. Table 3.1 presents the batched compositions of all glasses examined in this work.

3.4.2 Glass synthesis by melt-quenching

High purity powders of Na$_2$SiO$_3$ (Alfa Aesar > 99%), Al$_2$O$_3$ (Sigma-Aldrich ≥ 98%), H$_3$BO$_3$ (Alfa Aesar ≥ 98%), SiO$_2$ (Alfa Aesar ≥ 99.5%), La$_2$O$_3$ (Sigma-Aldrich, 99.9%), and Nd$_2$O$_3$ (Alfa Aesar, 99%) were used as precursors for glass synthesis. The batches corresponding to 50 g of glass were melted in 90% Pt – 10% Rh (wt.%) crucibles covered with a Pt lid (to reduce losses due to volatilization). The La$_2$O$_3$-free batches were melted at 1773 K while La$_2$O$_3$-containing at 1823 K for 1 hour. The melts were quenched
on a copper plate followed by annealing for 2 hours at temperatures set about 50 K lower than their respective glass transition temperatures ($T_g = 824$ K for La$_2$O$_3$-free and 840 K for La$_2$O$_3$-containing baseline glasses, as determined by differential scanning calorimetric curves at a heating rate of 20 K/min — STA449F5 Jupiter, NETZSCH, Figure 3S1 — Supplementary Information). The post-annealed glass samples were visibly transparent and amorphous when examined by X-ray diffraction (not shown).

**Table 3.1:** Batched composition (in mol%) of melt-quenched glasses examined in this work. Relative fractions of trigonal BO$_3$ ($N_3 = [BO_3]/([BO_3] + [BO_4])$) and tetrahedral BO$_4$ ($N_4 = [BO_4]/([BO_3] + [BO_4])$) boron units estimated from $^1$B MAS NMR spectra of Nd$_2$O$_3$-free base glasses, Nd0 and LaNd0 (Figure 3.5b).

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3.4.3 *Electron paramagnetic resonance (EPR) spectroscopy*

Pulsed EPR experiments were performed on the monolith glass samples diced to fit into standard 4 mm EPR tubes. A Bruker EPR spectrometer (Elexsys580E) operating at X-band frequency (9.7 GHz) was used with a dielectric resonator (EN-4118X-MD4) and a helium-flow cryostat (Oxford CF935). All pulsed EPR experiments were performed at 4.6 K.

Field-sweep EPR spectra were recorded using an FID-detected EPR experiment by applying one excitation \( \pi/2 \) pulse of duration 400 ns to 1 \( \mu \)s and integrating an FID signal over 400–800 ns window starting at a time point 64 ns after the excitation pulse (e.g., the dead-time in our EPR experiments). FID-detected EPR has many advantages against the often-used echo-detected EPR by providing improved spectral sensitivity and, more importantly, by eliminating any distortions to EPR spectral lineshape originating from interfering ESEEM effects.41-43 The echo-detected EPR spectra measured for two of our samples are compared with their FID-detected counterparts in Figure 3S2, illustrating the spectral lineshape distortions and the significant loss in signal intensity in the echo-detected EPR spectra as compared to the FID-detected EPR spectra. To allow a quantitative comparison of the EPR signal intensities and lineshapes measured for different samples, the as-recorded FID-detected EPR spectra were normalized per sample weight and further corrected for differences in their measured \( T_2 \) spin relaxation times while taking into account the initial dead-time (64 ns) and the FID detected window (400–800 ns) in each experiment.

ESEEM experiments were performed using a two-pulse (Hahn) echo pulse sequence \( (\pi/2-\tau-\pi-\tau\text{-echo}) \), with \( \pi/2 \) and \( \pi \) pulses set to 16 ns and 32 ns, respectively.
Before Fourier transformation (FT), the measured ESEEM time-domains were normalized by dividing the experimental data with the fit exponential curves and subtracting a unit baseline. After FT, the ESEEM spectra were phase-corrected to compensate for the missing dead time (the initial $\tau = 104$ ns in all ESEEM experiments) and finally plotted in the cosine FT mode. All FID-detected EPR and ESEEM spectral simulations were performed using the EasySpin toolbox developed for MATLAB. The same normalization procedure was applied to the simulated ESEEM time domains to allow their direct comparison with the experimental FT ESEEM spectra.

3.4.4 $^{11}$B and $^{27}$Al MAS NMR spectroscopy

$^{11}$B and $^{27}$Al MAS NMR spectra were acquired on the baseline La$_2$O$_3$-free (Nd0) and La$_2$O$_3$-containing glass (LaNd0) to examine the impact of adding La$_2$O$_3$ on boron and aluminum speciation in the glass structures. $^{11}$B MAS NMR spectra were collected at 14.1 T and 11.7 T using Bruker Avance-II+–600 and Avance-III-500 MHz spectrometers. Measurements were performed using a Varian 4 mm MAS NMR probe at a spinning frequency of 12 kHz. The data were acquired using a single pulse method, and both pulse time calibration and chemical shift referencing were achieved using solid NaBH$_4$. All $^{11}$B isotropic chemical shifts were referenced against the IUPAC standard BF$_3$Et$_2$O ($\delta_{\text{iso}} = 0.0$ ppm) using NaBH$_4$ as a secondary reference ($\delta_{\text{iso}} = -42.06$ ppm).

$^{27}$Al MAS NMR spectra were collected at 14.1 T and 9.4 T using Bruker Avance-II+–600 and Bruker HD-400 MHz spectrometers. The FID curves were measured via the single-pulse method using a Bruker 3.2 mm MAS NMR probe, enabling a sample spinning frequency of 20 kHz. Both pulse time calibration and $^{27}$Al isotropic chemical shift referencing were achieved using 1.1 M Al(NO$_3$)$_3$, the primary IUPAC standard ($\delta_{\text{iso}} = 0.0$ ppm).
ppm). The variable field $^{11}$B and $^{27}$Al MAS NMR data were simulated using the QuadFit simulation program, where the multi-field approach was used to further constrain the simulation parameters.

### 3.5 Results and Discussion

#### 3.5.1 FID-detected EPR

The FID-detected EPR spectra of all La$_2$O$_3$-free (Ndx) and La$_2$O$_3$-containing (LaNdx) glasses examined in the present study are shown in Figure 3.1a and Figure 3.1b, respectively. The spectra reveal complex transformations, with both EPR spectral intensities and spectral lineshapes changing while increasing the Nd$_2$O$_3$ concentrations from 0.001 to 0.1 mol% (Figure 3.1a), and also after the addition of 5 mol% La$_2$O$_3$ (Figure 3.1b). A detailed analysis of these spectral transformations, as presented next, reveals that Nd$^{3+}$ ions co-exist in several structural forms in these glasses, including isolated Nd$^{3+}$ centers and two types of Nd clusters. The isolated Nd$^{3+}$ centers are observed to be the dominant species only in the glasses with the lowest RE$_2$O$_3$ concentrations (0.001 mol%), and the Nd cluster population grows rapidly to become dominant at RE$_2$O$_3$ concentrations higher than 0.01 mol%. These concentration-dependent changes in Nd speciation are a cause of the striking transformations in the EPR spectral lineshapes observed in Figure 3.1.
Figure 3.1: FID-detected EPR spectra of peralkaline sodium aluminoborosilicate glasses doped with varied concentrations of [Nd_2O_3] and with (a) none, and (b) 5 mol% of [La_2O_3], as labeled in the figure legend. The spectral intensities in each sample were normalized per unit sample weight and also corrected for differences in spin relaxation times and other instrumental settings as described in Experimental section. All spectra were measured at 4.6 K.

3.5.1.1 Low Nd_2O_3 concentrations (0.001–0.01 mol%): Isolated Nd^{3+} centers

As seen in Figure 3.1, the EPR signals measured at low Nd_2O_3 concentrations (0.001–0.01 mol%), in both La_2O_3-free and La_2O_3-containing glasses, maintain the same spectral lineshape, and only the overall signal intensity changes between the samples. This EPR signal has been assigned to the isolated Nd^{3+} centers that are expected to be in abundance at low Nd_2O_3 doping levels. The signal assignment to isolated Nd^{3+} centers is further supported by the EPR simulation shown in Figure 3.2a (the dotted black line), performed assuming an effective spin S = 1/2 with a rhombic g-factor (3.5, 1.94, 1.0) and a significant g-factor strain, δ_g = (0.8, 0.3, 0.5). The derived g-factor values agree well with the values reported for isolated Nd^{3+} centers in Y_2SiO_5 and La-nicotinate crystals doped with 0.001 at% Nd_2O_3, where Nd^{3+} are known to occupy substitutional C_1-symmetry sites, being directly coordinated by six to eight oxygen atoms and with Si/C atoms in the next-nearest shell. The derived g-factor values are characteristic of Nd^{3+} ions with the ground-state Kramer doublet preferentially defined by spin projections ±1/2 in the ^4I_9/2
The broad g-factor strain distribution in our EPR simulation reflects a high disorder in coordination environment of isolated Nd$^{3+}$ ions in the glasses. Hereafter, this EPR signal from isolated Nd$^{3+}$ centers as observed in the glasses doped with low concentrations of Nd$_2$O$_3$ will be referred to as the signal S1.

**Figure 3.2:** Deconvolution of the measured EPR spectra as weighted sums of two contributing EPR signals: the S1 signal (dash red) from isolated Nd$^{3+}$ centers, and the S2 signal (dash yellow) from dipole-coupled Nd–Nd clusters. The experimental spectrum in Nd0.001 (a), with the lowest Nd$_2$O$_3$ concentration and no added La$_2$O$_3$, was taken to be purely from isolated Nd$^{3+}$ centers (the pure S1 signal). The S2 signal was determined from the EPR spectrum measured for LaNd0.1 (h), after subtracting a small contribution of the S1 signal. The simulated EPR signal for isolated Nd$^{3+}$ centers shown in (a) assumes a rhombic electron g-factor (3.5, 1.94, 1.0). The blue circles on the spectral curves in (a, d, e, and h) indicate the magnetic field positions where the ESEEM experiments were performed.

Notably, the intensity of signal S1 does not scale proportionally with total Nd$_2$O$_3$ concentration in glasses (Figure 3.1). The scaling discrepancy is most obvious when
comparing two La$_2$O$_3$-free glasses, Nd0.001 and Nd0.01, where a 10× increase in Nd$_2$O$_3$ concentration results in a 1.5× decrease in the S1 signal intensity (Figure 3.1a). Similarly, when comparing glasses, Nd0.001 and LaNd0.001, the addition of 5 mol% La$_2$O$_3$ is observed to cause a substantial (2.6×) decrease in the S1 signal intensity even though Nd$_2$O$_3$ concentration is kept constant (cp. Figures 3.1a and 3.1b). This non-linear dependence of the S1 signal intensity on Nd$_2$O$_3$ and La$_2$O$_3$ concentrations provides a strong evidence of Nd$^{3+}$ ions co-existing in multiple spectroscopically distinct forms in the investigated glasses. Some of these forms (e.g., isolated S1 centers) contribute fully to the EPR spectra, while other forms (see discussion below) remain EPR-invisible. The S1 signal shows up at its full strength only in the glass Nd0.001, i.e., with the smallest concentration of RE$_2$O$_3$. Here, all Nd$^{3+}$ centers are in the isolated S1 form and therefore, they fully contribute to the EPR signal intensity. The situation changes significantly when increasing the Nd$_2$O$_3$ concentration to 0.01 mol% (Nd0.01), or after adding 5 mol% La$_2$O$_3$ (LaNd0.001). In these two glasses only a small fraction of total Nd remains in the isolated S1 form which explains the disproportionally weak EPR signals, and a larger fraction of Nd$^{3+}$ is converted to EPR-invisible form(s), not contributing to the measured EPR spectra. More evidence of the complex speciation of Nd$^{3+}$ in the investigated glasses, involving several EPR-visible and EPR-invisible Nd$^{3+}$ forms, is found in the EPR spectra of glasses with [Nd$_2$O$_3$] ≥ 0.05 mol%, as discussed next. The nature of EPR-invisible Nd$^{3+}$ forms is discussed in the section 3.5.1.6.

3.5.1.2 High Nd$_2$O$_3$ concentrations (0.05–0.1 mol%)

As Nd$_2$O$_3$ concentration increases further, the integrated EPR signal intensity keeps increasing but at a much slower rate than expected if all added Nd$^{3+}$ ions were EPR-visible.
With Nd$_2$O$_3$ concentration changing by 100× from 0.001 mol% to 0.1 mol%, the integrated EPR signal intensity increases only by 2× in La$_2$O$_3$-free glasses and 5× in La$_2$O$_3$-containing glasses (Figure 3.1). The slower-than-expected growth of the EPR signal intensity in glasses doped with higher concentrations of Nd$_2$O$_3$ (0.01–0.1 mol%) further supports our conclusion about the complex speciation of Nd$^{3+}$, where only a small fraction of added Nd$^{3+}$ contributes to the observed EPR spectra, and a large fraction of Nd$^{3+}$ is converted into some EPR-invisible Nd form(s).

In addition to the changes in the signal intensity, the EPR spectral lineshape also changes at high Nd$_2$O$_3$ concentrations (Figure 3.1). In both La$_2$O$_3$-free and La$_2$O$_3$-containing glasses, the EPR lineshape gradually broadens out, and its center of gravity shifts to higher magnetic fields as Nd$_2$O$_3$ concentration increases above 0.01 mol%. Similar spectral transformations have been previously reported for Nd$^{3+}$ and other RE$^{3+}$ in silica- and non-silica-based glasses doped with elevated RE$_2$O$_3$ concentrations (0.01–1 mol%).

Two models have been proposed in the literature to explain these spectral transformations. One model emphasizes an intrinsic disorder of local RE environments in glasses and, thus, attributes the observed spectral transformations to a gradual change in the average atomic coordination environment of RE$^{3+}$ at high RE$_2$O$_3$ concentrations. The second model suggests the formation of RE$^{3+}$ clusters at high RE$_2$O$_3$ concentrations, e.g., through the formation of RE–O–RE like short-range linkages, where two or more RE$^{3+}$ are interconnected by bridging oxygens. Spin dipolar interactions between two or more RE$^{3+}$ ions within such short-range clusters (e.g., RE–O–RE, RE–O–X–O–RE) can then explain both the observed EPR lineshape broadening and the up-field center shift, as further confirmed in the detailed EPR spectral simulations. Each of these models, or a
combination of both, can as well be responsible for the EPR spectral transformations observed in our glasses at higher Nd$_2$O$_3$ concentrations (Figure 3.1). To help interpret these EPR spectral transformations, we performed the EPR spectral deconvolution analysis, as discussed in the next section.

3.5.1.3 Two-component decomposition of the FID-detected EPR spectra

In the previous EPR studies, the highly distorted EPR spectral lineshapes measured using echo-detected EPR had severely limited their quantitative spectral analysis. In the present study, the highly accurate lineshapes measured using FID-detected EPR allow us for a more in-depth spectral analysis, thus, providing further insight into Nd$^{3+}$ speciation in the investigated glasses.

A closer inspection of the spectral transformations in Figure 3.1 suggests that the EPR spectra in all eight glasses can be accurately described as simple weighted sums of two basic spectral components, hereafter referred to as the S1 and S2 signals, as demonstrated in Figure 3.2. The S1 signal originates from isolated Nd$^{3+}$ centers (see Section 3.5.1.1), and this signal is the only spectral component in the EPR spectrum of glass Nd0.001 (Figure 3.2a). The second signal, S2, is derived from the EPR spectrum of glass LaNd0.1 after subtracting a small contribution of the S1 signal (see the yellow trace for the derived S2 signal and the red trace for the subtracted S1 component in Figure 3.2h). The rationale behind this procedure for deriving the S2 component from the spectrum of LaNd0.1 is the observation that this spectrum demonstrates the most noticeable change from the S1 signal (e.g., the broadest EPR lineshape and the largest up-field shift) as compared to other samples. In other words, the spectrum of glass LaNd0.1 has the largest contribution from the signal S2 and a minimal contribution from the signal S1. The nature
of the thus-derived S2 signal and its assignment to a specific Nd-related species is discussed in section 3.5.1.5.

The decomposition of the EPR spectra as weighted sums of the two spectral components, S1 (red) and S2 (yellow), are shown for all La2O3-free and La2O3-containing glasses in Figure 3.2b–2h. The S1 component (isolated Nd³⁺ centers) is dominant only at low Nd₂O₃ concentrations (0.001–0.01 mol%), and the equilibrium shifts in favor of the S2 signal at Nd₂O₃ concentrations ≥ 0.05 mol%. The addition of 5 mol% La₂O₃ induces further changes into the equilibrium of the two spectral components, as the S1 signal becomes further suppressed at the expense of the S2 signal.

3.5.1.4 Three species model for Nd³⁺ ions in glasses

By integrating the signal intensities of the S1 and S2 components extracted from each EPR spectrum in Figure 3.2, we determine the absolute concentrations of S1 and S2 centers in each glass. The derived absolute S1 and S2 concentrations are plotted as a function of Nd₂O₃ and La₂O₃ concentrations in Figure 3.3a, and they are converted to the fractional Nd concentrations in Figure 3.3b. The absolute concentrations of S1 centers (isolated Nd³⁺ centers) show a weak dependence on [Nd₂O₃], staying consistently at the level 2–4×10¹⁷/cm³ even though the total Nd₂O₃ concentration changes by 100×, from 4×10¹⁷/cm³ (0.001 mol%) to 4×10¹⁹/cm³ (0.1 mol%). The fractional concentration of S1 drops sharply from ~100% in the glass Nd0.001 to 0.3% in Nd0.1. Concurrently, the absolute concentration of S2 centers (EPR-active Nd clusters) shows an almost linear increase with the total Nd₂O₃ concentration, from an undetectably low level in the glasses Nd0.001 and LaNd0.001 to about 6–8×10¹⁷/cm³ in Nd0.1 and LaNd0.1. The fractional concentration of S2 is remarkably constant at 1–4% through the entire Nd₂O₃ concentration.
range in both La$_2$O$_3$-free and La$_2$O$_3$-containing glasses. When comparing La$_2$O$_3$-free and La$_2$O$_3$-containing glasses, the addition of 5 mol% La$_2$O$_3$ consistently suppresses the fractional concentration of S1 centers by 2–3 times, while it has only a marginal effect on the fractional concentration of S2 centers.

**Figure 3.3:** Absolute (a) and fractional (b) concentrations of EPR-active Nd centers in La$_2$O$_3$-free (solid circles, solid lines) and La$_2$O$_3$-containing (open circles, dashed lines) glasses plotted as a function of the total [Nd$_2$O$_3$]: (blue) isolated Nd$^{3+}$ centers (the S1 signal), and (red) dipole-coupled Nd clusters (the S2 signal). The vertical, concentration axis in (a) was calibrated by recognizing that all Nd centers in Nd0.001 are isolated and therefore EPR-active, thus contributing 100% to the total EPR signal intensity. The dashed purple lines in (a) and (b) specify the expected total Nd$^{3+}$ concentrations, including both EPR-active and EPR-invisible Nd centers, nominally doped in the glasses.

Notably, in all glasses (except Nd0.001), the fractional concentrations of S1 and S2 centers, as derived from our EPR analysis, do not sum up to 100% to account for the total Nd concentration in glasses (Figure 3.3b). The latter suggests that a large fraction of Nd centers stay undetectable in the EPR experiments. Hereafter, these EPR-invisible (undetectable) Nd centers are referred to as the S3 centers. From the measured S1 and S2 fractions in Figure 3.3b, we infer that the fraction of EPR-invisible S3 centers varies significantly with La$_2$O$_3$ and Nd$_2$O$_3$ concentrations in glasses. In glasses with Nd$_2$O$_3$
concentrations higher than 0.01 mol%, a large fraction of Nd centers (more than 95%) belongs to the category of EPR-invisible S3 centers.

Based on the above EPR analysis, while quantitatively evaluating both EPR lineshapes and EPR intensities in a series of glasses with varied Nd$_2$O$_3$ and La$_2$O$_3$ concentrations (Figure 3.2 and 3.3), we, thus, are able to formulate a three-species model for Nd$^{3+}$ centers in peralkaline aluminoborosilicate glasses. The model identifies two EPR-detectable Nd$^{3+}$ centers (S1 and S2), each having a distinct EPR lineshape signature, and also one (or several) EPR-invisible Nd$^{3+}$ species (collectively labeled as S3). The fractional concentrations of all three species in the examined glasses have been determined from our EPR spectral decomposition analysis as a function of La$_2$O$_3$ and Nd$_2$O$_3$ concentrations.

### 3.5.1.5 Nature of S2 centers: EPR-visible Nd clusters

The S2 signal lineshape derived from our EPR decomposition analysis (a yellow trace in Figure 3.2) differ distinctly from the S1 signal of isolated Nd$^{3+}$ centers (a red trace in Figure 3.2). The S2 signal has substantially broader linewidth, and its center of gravity is shifted upfield from the S1 signal. As discussed above (in section 3.5.1.2), similar spectral transformations have been reported in silicate and other glasses for RE$^{3+}$ at elevated concentrations.$^3$, $^5$, $^{34-37}$, $^{51}$, $^{52}$ The transformed EPR signals have been usually assigned to either: (1) isolated RE$^{3+}$ centers with coordination environment different from that in glasses with low RE$_2$O$_3$ concentrations,$^{34-36}$, $^{52}$ or (2) short-range RE clusters, for example RE–O–RE, where RE$^{3+}$ ions are coupled through strong dipolar interactions.$^3$, $^5$, $^{37,51}$ Next, we evaluate these two models as a possible origin of the S2 signal in our glasses.

Examining a possible isolated Nd$^{3+}$ center nature of the S2 signal, we attempted to fit its EPR spectral lineshape assuming an effective spin S = 1/2. The best simulation fit
resulted in the anisotropic g-factor values (2.0, 1.0, 0.6). These g-values are unphysical in case of the isolated Nd$^{3+}$ centers and for any possible combinations of ground-state Kramer doublets derived from the $^4I_{9/2}$ multiplet.$^{49,50}$ Such unphysical g-factor values argue strongly against the assignment of the S2 signal to isolated Nd$^{3+}$ centers. Additional argument against the assignment of S2 to isolated Nd$^{3+}$ centers was observed when setting up our pulsed EPR experiments and optimizing the power of microwave pulses to achieve the desired $\pi/2$ spin rotations. Given the g-factor values $g = (2.0, 1.0, 0.6)$ for S2 were substantially smaller than $g = (3.5, 1.94, 1.0)$ for S1, the microwave pulses of larger amplitude were expected in case of S2 as compared to S1. Exactly the opposite was observed in our experiments with the optimized pulses being $\sim$1.6× weaker in case of S2, thus arguing against the isolated Nd$^{3+}$ center nature of the S2 signal. On the other hand, this observation of the lower amplitude pulses for S2 was perfectly consistent with the S2 assignment to Nd clusters, as discussed next.

Better EPR fits for the S2 signal lineshape have been obtained using the Nd cluster model. Similar to Sen et al.,$^{51}$ the spectral simulations were performed considering on average 4–6 Nd$^{3+}$ ions per cluster, with average distances of 4–5.5 Å between ions within the clusters, while allowing a broad distribution of random asymmetric shapes and topologies of the Nd clusters. Only dipole-dipole interactions between Nd$^{3+}$ spins were allowed within each cluster, and spin-exchange couplings were ignored.$^{51}$ These spectral simulations, in combination with the requirement of lower amplitude pulses, leads us to conclude that the S2 signal, as derived from our EPR analysis, should be associated with the dipole-coupled Nd clusters.
The tendency of RE\(^{3+}\) to form short-range clusters, with two or more RE\(^{3+}\) ions interconnected by oxygens atoms (e.g., RE–O–RE), has been previously reported in pure silica/silicate glasses and other host materials.\(^1\), \(^3\), \(^51\), \(^53\)–\(^56\) It has been argued that RE clustering in crystals/glasses is thermodynamically favored by the requirement to maintain a local charge balance.\(^4\), \(^53\)–\(^56\) In alkali aluminoborosilicate glasses, network modifying cations, like Na\(^+\), play a major role of charge compensators for trivalent Al\(^{3+}\) (AlO\(_4^–\)) and B\(^{3+}\) (BO\(_4^–\)), each requiring one Na\(^+\) for their complete integration into tetrahedral silica-rich network.\(^19\), \(^20\), \(^38\), \(^57\) When RE\(^{3+}\) are added to alkali aluminoborosilicate glasses, they also require local charge compensation by Na\(^+\) in order to integrate into the glass network.\(^6\), \(^7\) Unlike Al\(^{3+}\) and B\(^{3+}\), the isolated RE\(^{3+}\) ions take more than one Na\(^+\), typically 3–4 Na\(^+\), for their local charge compensation owing to their preferred octahedral or higher order coordination.\(^6\), \(^7\), \(^39\) In the glasses investigated in the present study, several trivalent cations (B\(^{3+}\), Al\(^{3+}\), La\(^{3+}\), and Nd\(^{3+}\)) compete for the same limited pool of Na\(^+\), and thus a global charge compensation for all cations at once may prove challenging. We, thus, hypothesize that the RE\(^{3+}\) clustering could be one of that structural mechanisms through which the global competition for Na\(^+\) charge compensation could at least be partially resolved in alkali aluminoborosilicate glasses. Indeed, our ESEEM results presented in section 3.5.2 (Table 3.2) show that the Nd-clusters (the S2 centers) require on average fewer numbers of Na\(^+\) in their coordination shells as compared to the isolated Nd\(^{3+}\) centers (the S1 centers), and thus a large fraction of Na\(^+\) is released through the Nd clustering and this Na\(^+\) becomes available for charge compensation of other network forming cations.

Three types of short-range Nd clusters can be considered as possible candidates for the S2 signal:\(^5\), \(^34\), \(^46\), \(^51\), \(^53\), \(^55\), \(^58\) (1) the next-neighbor (NN) clusters where two (or more)
Nd$^{3+}$ are directly linked to each other through bridging oxygen atoms, e.g., Nd–O–Nd; (2) the next-to-next-neighbor (NNN) clusters where Nd$^{3+}$ are interconnected through a mediator network-forming ion, e.g., Nd–O–X–O–Nd (with X = Si, B, or Al); and (3) the NNN clusters that are interlinked through diamagnetic La$^{3+}$ ions, e.g., Nd–O–La–O–Nd, in case of the La$_2$O$_3$-doped glasses. From a viewpoint of the EPR experiments, the crucial difference between these three types of Nd clusters is the strength of (anti)ferromagnetic spin-exchange interactions (J) between Nd$^{3+}$ within the clusters. Strong J couplings can have multiple effects on the EPR signal appearance, from slightly broadening the EPR signals to causing their complete disappearance.

The NN clusters as candidates for the S2 signal can be ruled out. Indeed, excessively strong spin-exchange couplings are expected in such short-range clusters, especially for light lanthanide ions like Nd$^{3+}$ and Ce$^{3+}$.

Exchange interactions of J = 3–150 GHz have been reported in the NN pairs (Nd–X–Nd, with X = O or F) in several oxide crystals. Interactions of such magnitude would completely broaden out the EPR signals to make them EPR-invisible (see discussion of the EPR-invisible S3 centers in section 3.5.1.6). The spectral linewidth of the S2 signal (Figure 3.2) is much narrower than that and is clearly inconsistent with such strong exchange couplings as would be expected in the NN pairs. Therefore, more distant NNN clusters, with substantially weaker spin-exchange interactions, must be considered as candidates for the S2 signal.

As a rule of thumb, the strength of spin-exchange interactions in RE$^{3+}$ pairs scales down by an order of magnitude for each extra bond between RE$^{3+}$.

Indeed, much weaker spin-exchange interactions (hundreds MHz) have been reported for Nd$^{3+}$ in distant NNN pairs (Nd–O–X–O–Nd, with X = C, V, or Y), with Nd$^{3+}$ separated by 4.2–7.1 Å.
The exchange interactions of this smaller magnitude would be fully consistent with the S2 signal lineshape (Figure 3.2). We therefore conclude that the long-range NNN clusters, with Nd$^{3+}$ ions interconnected by Nd–O–X–O–Nd linkages, where X is either network forming (Si$^{4+}$, Al$^{3+}$, and B$^{3+}$) or non-framework (Na$^{+}$) cations, should be considered as the prime candidates for the S2 signal.

The long-range NNN clusters bridged by La$^{3+}$ (Nd–O–La–O–Nd), as may occur in the La$_2$O$_3$-containing glasses, should be treated separately. They should in fact be assigned to the EPR-undetectable (invisible) S3 centers, and not to the EPR-detectable S2 centers. Although no reports are available on spin exchange couplings of RE$^{3+}$ in the La$^{3+}$-bridged NNN pairs in oxide glasses and crystals, several studies have reported strong (anti)ferromagnetic couplings ($J = 3$–204 GHz) between organic radicals and transition metal ions bridged via diamagnetic RE$^{3+}$ ions, such as Y$^{3+}$, La$^{3+}$, and Ho$^{3+}$, in organic chain materials.$^{60-63}$ These J couplings are comparable in magnitude to $J = 3$–150 GHz in the short-range NN pairs (Nd–O–Nd)$^{46,53}$ Additional argument in favor of this assignment of the (Nd–O–La–O–Nd) clusters to the EPR-invisible centers is the observation that the number of EPR-detectable S2 centers does not increase (in fact, decreases slightly) in the La$_2$O$_3$-containing glasses as compared to the La$_2$O$_3$-free glasses (Figure 3.3). In a simple picture, the 50× excess of diamagnetic La$^{3+}$ with respect to paramagnetic Nd$^{3+}$ in the La$_2$O$_3$-containing glasses should be expected to completely dilute a large majority of EPR-invisible NN pairs (Nd–O–Nd) and to convert them into the long-range NNN pairs (Nd–O–La–O–Nd). If these (Nd–O–La–O–Nd) pairs were EPR-detectable S2 clusters, a significant increase in the EPR signal should have been observed which is opposite to what we see in our experiments. This suggests that the 50× dilution of paramagnetic Nd$^{3+}$ with
diamagnetic La\(^{3+}\) in the La\(_2\)O\(_3\)-containing glasses results only in an interconversion of one kind of EPR-invisible S3 centers (Nd–O–Nd) to an another kind of EPR-invisible S3 centers (Nd–O–La–O–Nd), while the number of the EPR-visible S1 centers (isolated Nd\(^{3+}\) centers) and S2 centers (Nd–O–X–O–Nd, with X = Si, B, Al) remains low at all times in the glasses.

### 3.5.1.6 Nature of EPR-invisible S3 centers

The EPR analysis presented in section 3.5.1.4 reveals that a large fraction of Nd\(^{3+}\) in the investigated glasses remains EPR-invisible (referred to as the S3 centers). The fraction of EPR-invisible S3 centers exceeds 90% of total Nd content in the glasses with [Nd\(_2\)O\(_3\)] > 0.01 mol%. Here we consider two plausible mechanisms that can turn Nd\(^{3+}\) into EPR-invisible entities. The first mechanism is related to a strong spin-exchange interaction between Nd\(^{3+}\) within S3 clusters, and the second mechanism refers to the so-called microscopic glass basicity that may favor a partial reduction of trivalent Nd\(^{3+}\) into divalent Nd\(^{2+}\) in the glasses.\(^{64}\)

As discussed in section 3.5.1.5, we identify two types of Nd cluster configurations that can result in strong (anti)ferromagnetic interactions between Nd\(^{3+}\) within clusters, thus, making them the EPR-invisible S3 centers. These are: (1) the short-range NN clusters with Nd\(^{3+}\) interconnected by bridging oxygens (Nd–O–Nd) in both La\(_2\)O\(_3\)-free and La\(_2\)O\(_3\)-containing glasses, and (2) the NNN clusters with Nd\(^{3+}\) bridged by diamagnetic La\(^{3+}\), (Nd–O–La–O–Nd), in the La\(_2\)O\(_3\)-containing glasses. In disordered glassy systems, the clusters can arrange in various shapes and sizes (dimers, trimers, etc.), with a broad distribution of Nd–Nd distances and interconnected topologies, thus, forming a complex network of pairwise spin dipole and exchange interactions. Strong (anti)ferromagnetic exchange
interactions within such NN and NNN clusters can make Nd$^{3+}$ spins EPR-invisible in several ways: (1) by pairing up the Nd$^{3+}$ spins in each cluster into EPR-silent singlet states, or more complicated spin-frustrated states, with low lying excited states and therefore, fast longitudinal ($T_1$) spin relaxation; (2) by significantly broadening the EPR spectrum beyond a detectability limit; (3) by introducing additional spin relaxation mechanisms, thus, making longitudinal ($T_1$) or transverse ($T_2$) spin relaxation times of S3 clusters undetectably short. Next, we discuss these mechanisms in some more detail, thus, reaching the conclusion that in order for the S3 centers to be EPR-invisible they have to be the clusters with strong spin-exchange interactions.

Specific to our pulsed EPR experiments, the spin relaxation times of S3 centers would have to be shorter than 50 ns to make them EPR-undetectable. Such short $T_1$ relaxation times are too short to be expected if S3 centers were isolated Nd$^{3+}$ centers or dipole-coupled NNN clusters (Nd–O–X–O–Nd, with X = Si, B, Al). For example, the measured $T_1$ relaxation times for S1 (isolated Nd$^{3+}$ centers) and S2 (dipole-coupled Nd centers) signals resolved in our EPR experiments are both found to be around $T_1 \approx 200$ µs at 4.6 K, with only slight dependence on Nd$_2$O$_3$ and La$_2$O$_3$ concentrations in all examined glasses. These long $T_1$ times for S1 and S2 are in full agreement with $T_1 > 100$ µs reported for other Nd$^{3+}$ centers in various host matrices when measured below 5 K.$^{3,47,65,66}$ Such long $T_1$ are indeed expected for both isolated Nd$^{3+}$ centers and dipole-coupled Nd clusters since all excited Kramer doublets in Nd$^{3+}$ centers are separated by hundreds of cm$^{-1}$ from the ground state Kramer doublet,$^{67,68}$ and thus all known phonon-assisted $T_1$ spin relaxation processes should be frozen out at temperatures below 5 K.$^{49}$ There is only one plausible mechanism that may potentially shorten $T_1$ of S3 centers to below the EPR detectable limit
(e.g., $T_1 < 50$ ns, more than 1000× shorter than it is in S1 and S2), and this involves strong spin-exchange couplings between Nd$^{3+}$ spins in S3 clusters. We, therefore, hypothesize that the EPR-undetectable S3 centers in the investigated glasses are short-range NN clusters (Nd–O–Nd) or La$^{3+}$-bridged NNN clusters (Nd–O–La–O–Nd) with strong intra-spin-exchange couplings.

Similar arguments are also valid when examining potential reasons for too short transverse $T_2$ spin relaxation times in S3 centers. The reported values of $T_2$ for the isolated Nd$^{3+}$ centers in different host materials (measured below 5 K) fall in the range between 1 and 100 µs, with shorter $T_2$ observed at higher Nd$_2$O$_3$ concentrations.$^3, 47, 69$ Consistently, the $T_2$ measured for S1 (isolated Nd$^{3+}$) and S2 centers (dipole-coupled Nd–O–X–O–Nd clusters) in our glasses are also found to be in the same range, i.e., ~1 µs, with $T_2$ in S2 centers being only slightly shorter (by ~20%) than $T_2$ in S1 (Figure 3S3). Comparably long $T_2$ on the order of a few µs would also be expected for the S3 centers unless some other $T_2$ relaxation mechanisms are involved, thus shortening their $T_2$ times below the EPR detection limit (e.g., $T_2 < 50$ ns). Strong exchange couplings between Nd$^{3+}$ spins in the NN (Nd–O–Nd) or NNN (Nd–O–La–O–Nd) clusters is one of such mechanisms that can drastically shorten $T_2$, thus making the S3 centers EPR-undetectable.

The second possible mechanism that can lead to the EPR-invisible Nd centers (S3 centers) is the partial reduction of paramagnetic Nd$^{3+}$ to diamagnetic Nd$^{2+}$. In silicate-based glasses, the co-existence of several oxidation states has been demonstrated for a few RE$^{3+}$, such as Ce$^{4+/3+}$, Sm$^{3+/2+}$, Eu$^{3+/2+}$, and Yb$^{3+/2+}$ redox pairs.$^{70-73}$ The reduction of Nd$^{3+}$ to Nd$^{2+}$ has also been previously observed in phosphate glasses irradiated with $\gamma$ rays,$^{74}$ but not in silica-based glasses. Based on the literature$^6, 7, 27, 75$ on Nd$_2$O$_3$-doped silicate glasses and
our own experience, the majority of Nd in the investigated glasses are expected to be in the 3+ state, though the presence of a minor fraction of Nd$^{2+}$ in the glasses cannot be excluded. Therefore, this mechanism seems to be an unlikely cause of generation of S3 centers in the present study.

3.5.2 Electron Spin Echo Envelope Modulation (ESEEM)

The ESEEM experiments are performed to probe the nuclear coordination environment of the EPR-active Nd centers (S1 and S2) in La$_2$O$_3$-free and La$_2$O$_3$-containing glasses. Figures 3.4a and Figure 3.4b present the ESEEM spectra of four glasses (Nd0.001, Nd0.1, LaNd0.001, and LaNd0.1) acquired at two different magnetic fields, 350 and 550 mT. The spectra of glasses containing a low concentration of Nd$_2$O$_3$ (Nd0.001 and LaNd0.001) measured at both fields 350 and 550 mT represent the S1 centers with only a small admixture (5–10%) from the S2 centers. The situation is more complicated in glasses containing high concentrations of Nd$_2$O$_3$ (Nd0.1 and LaNd0.1), where the ESEEM spectra are mostly from the S2 centers but with a sizable contribution (15–35%) from the S1 centers, especially when measured at the low field of 350 mT. The extent of contribution from S1 centers can be seen by inspecting the FID-detected spectra and their decompositions into the S1 and S2 states, as presented for Nd0.1 and LaNd0.1 in Figures 3.2d and 3.2h, respectively.
Figure 3.4: Two-pulse FT-ESEEM spectra in La$_2$O$_3$-free and La$_2$O$_3$-containing glasses doped with [Nd$_2$O$_3$] = 0.001 and 0.1 mol%. The spectra were measured at two magnetic field positions: (a) 350 mT and (b) 550 mT, as identified with the blue circles in Figure 3.2. The positive (basic) and negative (combination) peaks from $^{10,11}$B, $^{23}$Na and $^{27}$Al nuclear spins are labeled with vertical sticks. All spectra were measured at 4.6 K.

The ESEEM spectra resolve several peaks from magnetic isotopes $^{10}$B (nuclear spin $I = 3$, natural abundance 20%), $^{11}$B ($I = 3/2, 80\%$), $^{23}$Na ($I = 3/2, 100\%$), and $^{27}$Al ($I = 5/2, 100\%$), as marked in Figure 3.4. The peaks from $^{23}$Na and $^{27}$Al spins are seen to overlap in all the spectra, making their independent analysis difficult. In order to resolve the individual contributions from $^{23}$Na and $^{27}$Al, we performed an additional ESEEM experiment on a glass with the similar composition as Nd0.01 except that all Na$_2$O was replaced with an equivalent concentration of K$_2$O (see Figure 3A1 and discussion in Appendix A). With $^{23}$Na completely removed from the K$_2$O-containing (KNd0.01) glass we were able to accurately determine the $^{27}$Al coordination in the Nd$^{3+}$ centers, and then these $^{27}$Al parameters were used as fixed while fitting the ESEEM spectra of the Na-containing glasses (like LaNd0.001 and LaNd0.1 in Figure 3A2).

Despite the high concentration of SiO$_2$ in our glasses (> 50 mol%), no peaks from $^{29}$Si could be resolved in the ESEEM spectra (Figure 3.4). The lack of detectable ESEEM signals from $^{29}$Si can be explained by the low natural abundance (4.7%) of $^{29}$Si isotopes,
and by its low nuclear spin \( I = \frac{1}{2} \) as compared to high spins \( I = 3/2, 5/2, \) or 3) for \(^{10,11}\text{B}, ^{23}\text{Na}, \) and \(^{27}\text{Al}. Since ESEEM amplitudes generally scale proportionally to \( I(I+1) \), much weaker modulation amplitudes are expected in case of \(^{29}\text{Si} \) with its \( I = \frac{1}{2}. \)

The ESEEM spectra are fitted using the two-shell model developed by Dikanov et al.\(^76\) for situations when hyperfine couplings are weak (see Appendix A for details). Our focus in these simulations is to determine the proximity distances \( (R_1) \) and the numbers \( (N_1) \) of magnetic nuclei in the first coordination shell (3–4.5 Å) around \( \text{Nd}^{3+} \) in the S1 and S2 centers. The ESEEM simulation results are shown in Figures 3A1-3A2 (Appendix), and all parameters derived from the ESEEM fits for the S1 and S2 centers in \( \text{La}_2\text{O}_3 \)-free and \( \text{La}_2\text{O}_3 \)-containing glasses are summarized in Table 3.2. The proximity distances \( (R_1) \) and the numbers of spins \( (N_1) \) for \(^{10,11}\text{B} \) and \(^{27}\text{Al} \) nuclei are shown as broad ranges, for example, \( R_1 = 3.2–3.6 \) Å and \( N_1 = 0.4–0.7 \) in case of \(^{27}\text{Al} \) nuclei around the S1 centers. These ranges should be understood as the indication that the combinations \( (R_1 = 3.2 \) Å with \( N_1 = 0.4) \) and \( (R_1 = 3.6 \) Å with \( N_1 = 0.7) \) produce equally good fits to the experimental data. Here, non-integer numbers of \(^{27}\text{Al} \) spins \( (N_1 = 0.4–0.7) \) should be understood as: (1) only 40–70\% of the S1 centers have one \(^{27}\text{Al} \) atom in their first coordination shells at a distance \( R_1 = 3.2–3.6 \) Å, thus forming one Nd–O–Al linkage, and (2) the remaining 30–60\% of the S1 centers do not have any \(^{27}\text{Al} \) atoms in their first coordination shells.
Table 3.2: Proximity distances (R₁) and numbers of nuclear spins (N₁), including \(^{10/11}\)B, \(^{23}\)Na, and \(^{27}\)Al, in the first (proximal) coordination shell of Nd\(^{3+}\) ions in the S1 and S2 centers, as derived from the ESEEM simulations (Figures 3A1-3A2).

<table>
<thead>
<tr>
<th></th>
<th>(^{10})B or (^{11})B</th>
<th>(^{23})Na</th>
<th>(^{27})Al</th>
</tr>
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<tbody>
<tr>
<td><strong>S1 centers</strong></td>
<td></td>
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<tr>
<td>(Isolated Nd(^{3+}) centers)</td>
<td>La(_2)O(_3)-free &amp; La(_2)O(_3)-containing</td>
<td>R(_1) = 3.2–3.6 Å, N(_1) = 0.2–0.4</td>
<td>R(_1) = 3.2 Å, N(_1) = 4</td>
</tr>
<tr>
<td><strong>S2 centers</strong></td>
<td></td>
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<td></td>
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<tr>
<td>(Nd clusters)</td>
<td>La(_2)O(_3)-free</td>
<td>R(_1) = 3.2–3.6 Å, N(_1) = 0.5–1</td>
<td>R(_1) = 3.2 Å, N(_1) = 3</td>
</tr>
<tr>
<td></td>
<td>La(_2)O(_3)-containing</td>
<td>R(_1) = 3.2–3.6 Å, N(_1) = 1–2</td>
<td>R(_1) = 3.2 Å, N(_1) = 2</td>
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</table>

The ESEEM data (Table 3.2) reveals that the S1 (isolated Nd\(^{3+}\) centers) and S2 centers (dipole-coupled Nd–O–X–O–Nd clusters) have noticeably different first coordination shells. The environment of isolated Nd\(^{3+}\) centers (S1 centers) is rich in Na and depleted of B and Al, with on average four Na atoms and fewer than one B/Al atoms in their first coordination shell. Addition of 5 mol% La\(_2\)O\(_3\) to the glass produces no effect on the environment of S1 centers. As compared to the S1 centers, the environment of the S2 centers (dipole-coupled Nd clusters) is found to be noticeably depleted of Na and enriched in B/Al, and the environment changes further after addition of 5 mol% La\(_2\)O\(_3\). In La\(_2\)O\(_3\)-free glasses, the S2 centers have on average three Na, one B and one Al, which changes to two Na, two B and one Al in the La\(_2\)O\(_3\)-containing glasses (Table 3.2).

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2 The two-shell model approximation\(^7\) was used in the ESEEM simulations. In addition to nuclear spins in the first coordination shell around Nd\(^{3+}\), the contribution to ESEEM from the second-shell nuclei (remote nuclei > 4.5 Å) was also considered using (R\(_2\) = 4.5 Å, N\(_2\) = 1.5) for \(^{10/11}\)B spins, (R\(_2\) = 4.5 Å, N\(_2\) = 3.7) for \(^{23}\)Na spins, and (R\(_2\) = 4.5 Å, N\(_2\) = 1.5) for \(^{27}\)Al spins. The respective N\(_2\) numbers for each isotope were calculated based on the glass composition (Table 3.1). The same second-shell coordination parameters (R\(_2\), N\(_2\)) were assumed for both S1 and S2 centers.
The distances \( (R_1 = 3.2–3.6 \, \text{Å}) \) and the numbers \( (N_1 = 0.4–0.9) \) derived from our ESEEM analysis for \( ^{27}\text{Al} \) coordination around \( \text{Nd}^{3+} \) centers compare closely with the values reported in the previous ESEEM studies on the \( \text{Nd}^{3+} \) and \( \text{Er}^{3+} \)-doped silica glasses that were additionally co-doped with small concentrations (1–2 mol\%) of \( \text{Al}_2\text{O}_3 \).\(^4,\)\(^33\) A direct comparison of our results with these previous reports is complicated because of significant differences in our and their glass compositions (e.g., smaller \( \text{Al}_2\text{O}_3 \) concentrations, with no \( \text{B}_2\text{O}_3/\text{Na}_2\text{O} \) added, in the previous reports). Furthermore, the \( \text{RE}^{3+} \) speciation and the fractional concentrations of isolated \( \text{RE}^{3+} \) centers (S1) versus dipole coupled \( \text{RE}–\text{RE} \) clusters (S2) have not been specified in the previous ESEEM studies. Therefore, their reported coordination numbers \( (R_1, N_1) \) should be viewed as a statistical average over unknown concentrations of isolated \( \text{RE}^{3+} \) centers and \( \text{RE}^{3+} \) clusters. As evident from our ESEEM analysis (Table 3.2), the \( \text{RE}^{3+} \) coordination environment (the numbers of \( \text{Al}, \text{B} \) and \( \text{Na} \) atoms in the first coordination shells) varies significantly depending on the \( \text{RE} \) speciation. Our EPR/ESEEM results call for a re-examination of the previous results on \( \text{RE} \)-doped silica glasses, including the reported effect of \( \text{Al}^{3+} \) and \( \text{La}^{3+} \) co-doping on \( \text{RE}^{3+} \) clustering,\(^33,\)\(^77\) to bring it on a more quantitative ground by accurately determining \( \text{RE}^{3+} \) speciation in those glasses, as demonstrated in the present work.

As noted above, no ESEEM peaks from \( ^{29}\text{Si} \) spins are resolved in our spectra (Figures 3.4 and 3A1-3A2), and as such no direct spectroscopic information could be obtained about numbers and proximity distances of \( \text{Si} \) atoms around \( \text{Nd}^{3+} \) centers. Nevertheless, by assuming a six-fold coordination for \( \text{RE}^{3+} \) (\( \text{Nd}^{3+}, \text{La}^{3+} \)) in the glasses, and using the ESEEM-derived coordination numbers of \( \text{B} \) and \( \text{Al} \) (Table 3.2), we anticipate at
least 4–5 Si atoms in the first coordination shells of each Nd$^{3+}$ ion in both isolated centers (S1) and dipole-coupled Nd-clusters (S2).

Lastly, we note that our ESEEM spectra in the La$_2$O$_3$-containing glasses (Figure 3.4) show no resolvable contribution from $^{139}$La spins, even though the natural abundance of this isotope (99.9%) and its spin (I = 7/2) are both high. The lack of detectable ESEEM signals from $^{139}$La spins in our glasses is consistent with the previous ESEEM reports in the Yb/La-codoped silica glasses where it has been speculated that La$^{3+}$ enters only into the remote 4$^{th}$ coordination shells around paramagnetic Yb$^{3+}$.$^{77, 78}$ Alternatively, the lack of detectable $^{139}$La signals may reflect excessively large nuclear quadrupolar (NQI) couplings of $^{139}$La spins. The large NQI would broaden out the ESEEM peaks to make them undetectable, possibly hidden beneath the stronger nearby peaks from $^{10}$B, $^{23}$Na, and $^{27}$Al.

3.5.3 $^{11}$B and $^{27}$Al Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR)

To help interpret the EPR and ESEEM data, we also perform the $^{27}$Al and $^{11}$B MAS NMR experiments on two baseline glasses, i.e., Nd0 (RE$_2$O$_3$-free) and LaNd0 (containing 5 mol% La$_2$O$_3$). La$^{3+}$ and Nd$^{3+}$ are often viewed as equivalent in terms of their effect on glass chemistry and network structure.$^{39, 40, 79}$ Indeed, both ions have a comparable field strength (FS), e.g., FS(Nd$^{3+}$) = 0.54 at d$_{Nd-O}$ = 2.35 Å, versus FS(La$^{3+}$) = 0.51 at d$_{La-O}$ = 2.43 Å, and both ions preferably coordinate with 6–8 oxygens in oxide glasses.$^{39, 40}$ We recognize that unlike EPR, $^{27}$Al and $^{11}$B NMR experiments probe only the average glass structure from prospects of bulk speciation of network-forming $^{27}$Al and $^{11}$B sites, and as such, these experiments do not provide any direct information about immediate coordination environment around RE$^{3+}$ in glasses. Therefore, our aim in conducting the
NMR experiments is to understand the impact of RE\(^{3+}\) (5 mol% La\(_2\)O\(_3\)) on the structural speciation of network-forming Al and B sites in the glasses and to correlate these NMR-derived structural changes with the RE\(^{3+}\) speciation and their coordination environment as determined from the EPR/ESEEM experiments.

3.5.3.1 \(^{27}\)Al MAS NMR

The \(^{27}\)Al MAS NMR spectra in both Nd0 (La-free) and LaNd0 (5 mol% of La\(_2\)O\(_3\)) glasses show a single broad peak centered at around 60 ppm (Figure 3.5a). Based on the previous NMR studies,\(^{15,38}\) the peak is assigned to Al\(^{3+}\) ions in a tetrahedral coordination environment (AlO\(_4\) sites). Notably, the addition of 5 mol% La\(_2\)O\(_3\) induces no change in the position and linewidth of the AlO\(_4\) peak. This observation agrees with other NMR studies on peralkaline aluminoborosilicate glasses with large concentrations of Na\(^+\) available to charge compensate all AlO\(_4^-\), \([\text{Na}_2\text{O}]/[\text{Al}_2\text{O}_3] > 1.6,7,40\) In such glasses, a single AlO\(_4\) peak has been always reported that was insensitive to changes in glass composition, including addition of sizeable concentrations (up to 10 mol%) of non-framework cations, like divalent (Ca\(^{2+}\)) or trivalent (RE\(^{3+}\)) ions. This single, composition-insensitive AlO\(_4\) peak was interpreted as an evidence of:\(^{6,7,38,40,80,81}\) (1) the negatively charged AlO\(_4^-\) sites having a strong preference for charge compensation by weak-field strength cations like Na\(^+\) (when available), and only as a second choice by other high-field strength cations, for example, Ca\(^{2+}\) or RE\(^{3+}\); and (2) the charge-compensated AlO\(_4^-\)-Na\(^+\) units being uniformly dispersed in SiO\(_2\) network preferentially linked to four SiO\(_4\) units. Taken together these two points explain the insensitivity of the AlO\(_4\) peak to changes in glass composition and to incorporation of high field strength cations (RE\(^{3+}\)) in peralkaline aluminoborosilicate glasses. Specific to our glasses with \([\text{Na}_2\text{O}]/[\text{Al}_2\text{O}_3] = 2.5\), this interpretation implies that
an absolute majority of AlO$_4$ in both Nd0 (La$_2$O$_3$-free) and LaNd0 (5 mol% La$_2$O$_3$) glasses maintain the uniform coordination environment being charge compensated by Na$^+$, and only a minor fraction of AlO$_4$ (potentially around 1–2%, if counting the fractions of EPR-detectable S1 and S2 centers as revealed from our EPR experiments) forms the direct Al–O–Nd linkages and thus find itself in a different environment. Such small quantities may be undetectable in $^{27}$Al NMR experiments.

On the other hand, the coordination environment of EPR-invisible S3 centers, that constitute the majority of Nd$^{3+}$ and La$^{3+}$ in our glasses, remains unknown. We hypothesize that the S3 centers might maintain preferentially Al-depleted (possibly Si/B-rich) first coordination shells, and thus the number of direct Al–O–RE linkages remains always low (around 1–2%) even at elevated RE$_2$O$_3$ concentrations, that would explain the insensitivity of the $^{27}$Al NMR signal to addition of 5 mol% La$_2$O$_3$ in LaNd0 (Figure 3.5a). More

**Figure 3.5:** $^{27}$Al MAS-NMR (a) and $^{11}$B MAS-NMR (b) spectra of Nd0 (La$_2$O$_3$-free) and LaNd0 (La$_2$O$_3$-containing) glasses measured at 14.1 T. The spectra were normalized to the maximum peak intensity and vertically shifted for clarity.
systematic and combined NMR/EPR studies would be required to understand the number and nature of direct Al–O–RE linkages in peralkaline alumino-borosilicate glasses.

3.5.3.2 $^{11}$B MAS NMR

The $^{11}$B MAS NMR spectra in glasses Nd0 and LaNd0 resolve two peaks (Figure 3.5b). The narrow peak at 0 ppm is from tetrahedral borate sites (BO$_4$), and the broad peak at 14 ppm is from several species of trigonal borate sites (BO$_3$)$_{15, 38, 39}$ Relative fractions of the BO$_3$ and BO$_4$ sites in the glasses, as determined from the NMR peak integration, are summarized in Table 3.1. The addition of 5 mol% La$_2$O$_3$ induces a decrease in the fraction of tetrahedral boron (N$_4$) from N$_4$ = 0.66 in Nd0 to 0.37 in LaNd0. Similar interconversion of BO$_4$ to BO$_3$ has been reported in borosilicate and alumino-borosilicate glasses in response to a reduced Na$^+$ concentration or when Na$^+$ was substituted with high-field strength cations like Ca$^{2+}$ or La$^{3+}$.$^{7, 38-40, 82}$ In our glasses (Nd0 and LaNd0), the molar ratio $\frac{[\text{Na}_2\text{O}]}{[\text{Al}_2\text{O}_3]+[\text{B}_2\text{O}_3]} = 1.25$ is kept constant and high, with more than enough Na$^+$ available to charge compensate all AlO$_4$$^-$ and BO$_4$$^-$ sites in both glasses. It is then counterintuitive as to why a simple addition of 5 mol% La$_2$O$_3$ (which potentially is an additional charge compensator for BO$_4$$^-$ sites) results in a 2× drop of N$_4$ in LaNd0 compared to Nd0?

The answer to this question is provided from our ESEEM experiments (Table 3.2), showing that Nd$^{3+}$ (and likewise La$^{3+}$) have a strong affinity towards Na$^+$ on their own. Depending on the speciation, each Nd$^{3+}$ ion can immobilize as many as four Na$^+$ if it stays in the isolated S1 form, or two–three Na$^+$ if clustered as the S2 species. Similar conclusions of 3–4 Na$^+$ per RE$^{3+}$ have been reached in the previous NMR studies when interpreting the speciation of network former ions ($^{29}$Si, $^{11}$B, and $^{17}$O) in RE-doped aluminoborosilicate and borosilicate glasses.$^{7, 27, 39}$ The NMR analysis was based on simple charge
compensation arguments, while additionally postulating that all RE$^{3+}$ ions were isolated (no RE clustering) in the glasses that were doped with high RE$_2$O$_3$ concentrations (2–7 mol%). Even though the assumption of no RE clustering was not well justified, the estimated number of 3–4 Na$^+$ per RE$^{3+}$ was remarkably similar to that directly measured for isolated S1 centers in our ESEEM experiments.

Recognizing the competition between BO$_4^-$, AlO$_4^-$, and LaO$_6^{3-}$ (assuming a six-coordinated La$^{3+}$) for Na$^+$, we can reformulate the concentration of Na$^+$ that remains available for charge compensation of BO$_4^-$ sites in La$_2$O$_3$-containing glasses as: $[\text{Na}_2\text{O}]_{\text{ex}} = [\text{Na}_2\text{O}] - [\text{Al}_2\text{O}_3] - n[\text{La}_2\text{O}_3]$. This new definition of $[\text{Na}_2\text{O}]_{\text{ex}}$ is a direct extension of an earlier definition of $[\text{Na}_2\text{O}]_{\text{ex}}$ originated from the NMR studies on sodium borosilicate glasses, now including an additional term that accounts for the effect of RE$^{3+}$ on an overall Na$^+$ availability for BO$_4^-$. The new definition $[\text{Na}_2\text{O}]_{\text{ex}}$ assumes that charge compensation by Na$^+$ follows the order AlO$_4^-$ > LaO$_6^{3-}$ > BO$_4^-$, with AlO$_4^-$ being the strongest competitor for Na$^+$ and BO$_4^-$ being the weakest. Thus, firstly each AlO$_4^-$ site consumes one Na$^+$, followed by each LaO$_6^{3-}$ consuming $n$·Na$^+$, and finally, the leftover Na$^+$ is used for charge compensation of BO$_4^-$ sites. According to our ESEEM results (Table 3.2) and past literature, the number ($n$) of Na$^+$ attracted by each RE$^{3+}$ ion can vary between 2–4 depending on the RE$^{3+}$ speciation in glasses (e.g., isolated RE$^{3+}$ centers vs. RE clusters). Next, we demonstrate the potential of this new definition of $[\text{Na}_2\text{O}]_{\text{ex}}$ in correctly predicting the N$_4$ fraction in our LaNd0 glass.

The ratio $R = [\text{Na}_2\text{O}]/[\text{B}_2\text{O}_3]$ has been long identified as one of the key parameters determining the structural organization in ternary borosilicate glasses and also extended to multicomponent glasses like alkali aluminoborosilicates. It has been demonstrated
that the correctly estimated value of $R$ allows an accurate prediction of fractional populations of $BO_3$ and $BO_4$ units in glasses. Using our definition for $[Na_2O]_{ex}$, we can estimate the ratio $R' = [Na_2O]_{ex}/[B_2O_3] = 1.5$ for Nd0, and $R' = [Na_2O]_{ex}/[B_2O_3] = 0.43$ for LaNd0, simply based on their glass compositions (Table 3.1). In the case of LaNd0, we assume similar coordination of $La^{3+}$ and $Nd^{3+}$ ions and use the value of $n = 2$, as derived from our ESEEM experiments for Nd clusters (the S2 centers) in $La_2O_3$-containing glasses (Table 3.2). Indeed, our EPR experiments (Figure 3.3b) show that the Nd/La clusters, including the S2 and S3 centers, are the predominant Nd/La species in all LaNdx glasses. Using these estimated $R'$ values and referring to the plot of $N_4$ versus $R$ in Figure 3S4 derived from the previous NMR studies of ternary alkali borosilicate glasses with high $SiO_2$ content, we can immediately predict the value of $N_4 = 0.62$ for Nd0, and $N_4 = 0.4$ for LaNd0. Both predicted values are in excellent agreement with the $N_4$ numbers measured in our NMR experiments (Table 3.1), thus demonstrating the predictive accuracy of the new expression for $[Na_2O]_{ex}$. It seems worthwhile examining the predictive utility of this new expression against a broader set of RE-doped aluminoborosilicate glasses.

As discussed in section 3.5.4.3, the main hurdle in universalizing this new criterion $[Na_2O]_{ex}$ to glasses with varied compositions is the EPR-undetectable S3 clusters with their yet-uncharacterized speciation and coordination environments. Further studies, combining EPR, NMR and other spectroscopic techniques, would be required to generalize and to improve on the accuracy and universality of the new $[Na_2O]_{ex}$ criterion governing the boron speciation in glasses.

As a final note, we would like to emphasize that according to the previous studies, the $R' = 0.43$ predicted for our LaNd0 glass falls below the critical limit ($R = 0.5$) where
the nano-scale phase separation to Si-rich and B-rich regions may start to develop in sodium borosilicate/aluminoborosilicate glasses depending on their thermal history.\textsuperscript{23, 24, 85-87} Indeed, the heat flow versus temperature curves obtained from a differential scanning calorimeter for our LaNd0 glass demonstrated a well-defined crystallization peak ($T_p = 1043$ K) when being heated above $T_g$ (840 K), while no such peak was observed in the Nd0 glass with $R' = 1.5$ (Figure 3S1). We emphasize that it is the simple addition of 5 mol\% La$_2$O$_3$ and the requirement of minimum two Na$^+$ ions per RE$^{3+}$ that brought the LaNd0 glass to this point of potential immiscibility.

3.5.4 Structural Models for Nd$^{3+}$ centers in sodium aluminoborosilicate glasses

By combining the EPR, ESEEM and NMR results, we propose the following structural models for isolated (S1) and clustered (S2, S3) Nd$^{3+}$ centers in the Ndx and LaNdx glasses.

3.5.4.1 Isolated Nd$^{3+}$ centers (S1 centers)

As shown by the ESEEM experiments (Table 3.2), the isolated Nd$^{3+}$ centers (the S1 centers) have similar coordination environments in the La$_2$O$_3$-free and La$_2$O$_3$-containing glasses. Thus, each isolated Nd$^{3+}$ center has on average either one Al$^{3+}$ or one B$^{3+}$ in its first coordination sphere along with four Na$^+$ ions. The conclusion of either one Al$^{3+}$ or one B$^{3+}$ is based on the observation that the coordination numbers, $N_1 = 0.7$ for Al$^{3+}$ and $N_1 = 0.4$ for B$^{3+}$, as determined from ESEEM experiments, add up to approximately one for the S1 centers. The potential structure is visualized in Figure 3.6a, where Nd$^{3+}$ is shown in octahedral coordination, forming six Nd–O–X linkages with the network forming cations X = (Si, Al, or B). As presented, the structure involves five Si linkages and one Al linkage. Alternatively, the Al linkage can be replaced by the B linkage with the relative
probability of 0.7:0.4, where the linked B$^{3+}$ or Al$^{3+}$ are in tetrahedral coordination, as is evidenced by our NMR experiments. Along with four Na$^{+}$ in the coordination sphere of each isolated Nd$^{3+}$ center, the overall net charge of the S1 center is zero. Traditionally, the role of RE$^{3+}$ in silicate glasses is viewed as a network modifier or charge compensator.\textsuperscript{6, 7, 12, 24, 39, 88, 89} Interestingly, the structure of the S1 center shown in Figure 3.6a can also be recognized as a network former where Nd$^{3+}$ is fully polymerized into a glass network as a loosely defined octahedron that is interconnected by oxygen bridges to other (conventional) network formers.

Considering the relative abundance of the network forming cations Al$^{3+}$/B$^{3+}$/Si$^{4+}$ = 20/20/55 in the investigated glasses, and under the assumption of their uniform spatial distribution and no preferential coordination at Nd$^{3+}$ sites, we expect on average $N_1 = 1.3$ of the Nd–O–Al linkages and the same number of Nd–O–B linkages around each Nd$^{3+}$. These statistical numbers are noticeably larger than $N_1 = 0.7$ for $^{27}$Al and $N_1 = 0.4$ for $^{10,11}$B derived from our ESEEM experiments. We can, thus, conclude that the isolated S1 centers are preferentially formed in a Na/Si-enriched and Al/B-depleted environment in both Nd$\textsubscript{x}$ and LaNd$\textsubscript{x}$ glasses. This conclusion seems in conflict with one of the popular viewpoints discussed in the literature,\textsuperscript{23-26} where isolated RE$^{3+}$ have been argued to preferentially enter into borate-rich regions, forming RE-metaborate-like structures (1BO$_4$:RE:2BO$_3$) that would imply near 8× higher B coordination numbers from what we measure in our ESEEM experiments.\textsuperscript{23, 24, 68}
Figure 3.6: Proposed coordination structures for: (a) isolated Nd$^{3+}$ centers (the S1 centers); (b, c) dipole-coupled NNN clusters (the S2 centers) in La$_2$O$_3$-free (b) and La$_2$O$_3$-containing (c) glasses, derived from the EPR/ESEEM analysis; (d, e) exchange-coupled, EPR-invisible Nd clusters (the S3 centers) of the NN type (Nd–O–Nd) in La$_2$O$_3$-free and La$_2$O$_3$-containing glasses (d), and the NNN type (Nd–O–La–O–Nd) in La$_2$O$_3$-containing glasses (e), based on discussion in sections 3.5.1.6 and 3.5.4.3. Six-fold coordination is assumed for isolated Nd$^{3+}$ centers as well as for each Nd$^{3+}$ ion in Nd clusters, via bridging oxygens (solid lines), or via tri-coordinated oxygens associated with aluminum and boron (dashed lines). For the EPR-active Nd centers (the S1 and S2 centers), the first coordination shell of each Nd$^{3+}$ ion is specified with the numbers of B, Na, and Al atoms as determined from the ESEEM experiments (Table 3.2). For the EPR-silent Nd clusters (the S3 centers), the first coordination shell environment is extrapolated from the S2 structures thus maintaining the same numbers of B, Na, and Al. The calculated local net charge is zero for the isolated Nd$^{3+}$ centers (a) and for the NNN clusters in La$_2$O$_3$-free glasses (b), the net charge is -0.5 (per Nd$^{3+}$ ion) in the NNN clusters in La$_2$O$_3$-containing glasses (c), and it is -1 per Nd$^{3+}$ in both NN and NNN types of the EPR-silent S3 clusters (d, e). Although the structures of the NN and NNN clusters (b-e) are shown as dimers and
trimers, they can be easily expanded to incorporate more coupled Nd$^{3+}$ ions within each cluster.

Our ESEEM results also seem to be in conflict with the earlier reports suggesting that co-doping with near stoichiometric concentrations of Al$^{3+}$ helps improving the RE$^{3+}$ solubility in silica glasses and in particular alleviate the undesired RE clustering.$^1$ Although the microscopic mechanism of Al$^{3+}$ co-doping on RE$^{3+}$ speciation is not well understood, it has been argued, primarily based on the ESEEM studies, that trivalent Al$^{3+}$ may form the RE–O–Al linkages, presumably substituting some RE$^{3+}$ with Al$^{3+}$ in the RE clusters and effectively decoupling the RE$^{3+}$ ions from each other through what can be thought of as a simple dilution effect.$^4$ We note however that the earlier studies were performed on the Na-free silicate glasses.$^3$–$^5$ With a large surplus of Na$^+$ like in glasses examined in our work, it might be thermodynamically advantageous to form isolated Nd$^{3+}$ centers of a kind shown in Figure 3.6a, with a minimum (or none) Al/B linkage and with four dedicated Na$^+$ ions for charge compensation.

3.5.4.2  EPR-active Nd clusters (S2 centers)

The proposed NNN structures of the EPR-active Nd clusters (the S2 centers) in La$_2$O$_3$-free and La$_2$O$_3$-containing glasses are presented in Figure 3.6b and Figure 3.6c, respectively. The structures are shown as Nd–Nd pairs, but they can easily be expanded to larger Nd clusters. The Nd$^{3+}$ within the clusters are separated by 4–5.5 Å, bridged by several Nd–O–X–O–Nd linkages (where X = Si, Al, or B, but not La$^{3+}$). These ions are coupled through a weak inter-spin-exchange interaction (therefore, they remain EPR visible) and through a strong spin dipolar interaction (therefore, their broad EPR lineshapes).
According to the ESEEM data (Table 3.2), the first coordination shell of Nd clusters (the S2 centers) changes noticeably after adding 5 mol% La$_2$O$_3$. While in La$_2$O$_3$-free glasses, each Nd$^{3+}$ in the S2 clusters is coordinated by one B, one Al, and three Na ions (Figure 3.6b), the coordination environment evolves to two B, one Al, and two Na atoms per Nd$^{3+}$ in La$_2$O$_3$-containing glasses, thus, becoming more enriched in boron and depleted of sodium (Figure 3.6c). In order to keep the overall net charge low, we assume that the side Nd–O–Al and Nd–O–B linkages involve tri-coordinated oxygens in both La$_2$O$_3$-free and La$_2$O$_3$-containing glasses. In a way, each Nd$^{3+}$ in the clusters can be viewed as a charge compensator for one linked AlO$_4^-$ and one BO$_4^-$ at the same time, boron in the bridging position (Nd–O–B–O–Nd) is shown to be in trigonal configuration (BO$_3$) in the La$_2$O$_3$-containing glasses (Figure 3.6c). For the structures shown in Figure 3.6b and 3.6c, the resulting net charge per Nd$^{3+}$ is 0 and -0.5, respectively. Similar NNN structures have been reported in the RE-containing crystals including Na$_8$Y$_3$(SiO$_3$)$_{12}$ (ID: mp-1202365), NdAl$_3$(BO$_3$)$_4$ (ID: mp-6535), and NaNdB$_6$O$_{13}$ (ID: mp-1198569).

By comparing the S1 structure in Figure 3.6a with the S2 structure in Figure 3.6b and then S2 in Figure 3.6c, we identify two clear tendencies: (1) the Na coordination number per Nd$^{3+}$ gradually goes down, and synchronously (2) the B coordination number grows up. The first tendency is explained by the limited surplus of Na$^+$ in the glasses and by the global competition between several network former cations (B$^{3+}$, Al$^{3+}$ and RE$^{3+}$) for charge compensation by Na$^+$, as discussed in section 3.5.1.5. Large numbers of Na$^+$ (four Na$^+$ per RE$^{3+}$) are required to charge compensate the isolated S1 centers and to completely integrate them into the glass network, as shown in Figure 3.6a. As RE$^{3+}$ concentration increases, the problem builds up of insufficient Na$^+$ surplus to fully charge compensate all
RE$^{3+}$ and to maintain them in the isolated S1 form. We hypothesize that this Na$^+$ deficiency problem is resolved through RE clustering. Within the RE clusters (Figures 3.6b, 3.6c), each RE$^{3+}$ immobilizes only 2–3 Na$^+$ (instead of 4), thus adapting to the Na$^+$ deficiency. We further hypothesize that, instead of Na$^+$, the net charge compensation within the RE clusters is achieved through the enrichment in B coordination numbers. Tri-coordinated oxygens shared with tetrahedral BO$_4^-$ sites and the bridging tri-coordinated boron (BO$_3$) linkages, as shown in Figures 3.6(b, c), help to maintain the net charge low within the RE clusters. This charge compensation mechanism, utilizing tri-coordinated oxygens, is similar to what is found in peraluminous alkali aluminosilicate glasses ([Na$_2$O] < [Al$_2$O$_3$]), where the deficiency in Na$^+$ for AlO$_4^-$ charge compensation is similarly resolved by sharing oxygens between three network forming sites.$^{91}$

As the last note, we emphasize that our ESEEM-derived structures in Figures 3.6(a-c) are in striking contrast with the popular viewpoint that isolated RE ions enter the B-rich environment, forming RE-metaborate-like structures (1BO$_4$:RE:2BO$_3$),$^{23-26}$ and that the RE clusters are preferentially formed in the B-depleted, Si-enriched environment.$^{23-25,68}$ Our ESEEM results show convincingly that the opposite arrangement is actually correct: (1) The isolated Nd$^{3+}$ centers form preferentially in B-depleted, Si-rich glass environment, and (2) the S2 (and possibly S3) clusters form in B-enriched, Si-depleted glass phase. The RE-metaborate-like structures (1BO$_4$:RE:2BO$_3$), as originally proposed for the isolated RE$^{3+}$ centers,$^{23-26}$ are in fact more consistent with the S2 clusters.

3.5.4.3 Hypothesis-driven structure of EPR-silent Nd clusters (S3 centers)

Our EPR results reveal that the EPR-silent Nd clusters (the S3 centers) constitute the majority of Nd$^{3+}$ species in both La$_2$O$_3$-free and La$_2$O$_3$-containing glasses. The
fractional weight of these clusters (S3) grows monotonously with Nd$_2$O$_3$ concentration, exceeding 95% of total Nd$^{3+}$ in glasses with [Nd$_2$O$_3$] > 0.05 mol%. Addition of 5 mol% La$_2$O$_3$ promotes further conversion of a significant fraction (~30–50%) of the isolated Nd$^{3+}$ (S1) centers to the EPR-silent Nd (S3) clusters (Figure 3.3b), while leaving the fraction of EPR-active clusters (S2) approximately unaffected.

Our EPR experiments provide limited information on the nature of these EPR-silent Nd clusters (S3 centers), only revealing them as EPR-invisible. In our discussion in sections 3.5.1.5 and 3.5.1.6, we have identified the main mechanism behind their EPR invisibility, which is the presence of strong (anti)ferromagnetic exchange interactions between Nd$^{3+}$ within the S3 clusters. Two types of exchange-coupled cluster configurations are thus formulated: (1) the short-range NN clusters with Nd$^{3+}$ ions bridged by oxygen, (Nd–O–Nd), in both La$_2$O$_3$-free and La$_2$O$_3$-containing glasses, and (2) the long-range NNN clusters with Nd$^{3+}$ ions bridged by diamagnetic La$^{3+}$, (Nd–O–La–O–Nd), in the La$_2$O$_3$-containing glasses. The respective structures are shown in Figures 3.6d and 3.6e. These structures are partially based on the published crystalline structures of Na$_x$RE$_{(10-x)}$Si$_6$O$_{26}$ and RE$_5$BSi$_2$O$_{13}$, whose phases are known to nucleate out in RE-doped alkali-borosilicate glasses when exceeding RE solubility limits or after prolonged heat treatments.$^{23, 24, 92, 93}$ Indeed, one of our highly doped glasses (LaNd0.1) was observed to develop a La$_5$BSiO$_{13}$ crystalline phase after 72 hours of heat-treatment at 865 K (Figure 3S5).

The proposed NN structure (Nd–O–Nd) in Figure 3.6d and the La-bridged NNN structure (Nd–O–La–O–Nd) in Figure 3.6e are both derived from the structures of EPR-active S2 clusters (Figure 3.6b, 3.6c) after replacing one of the bridging Nd–O–X–O–Nd linkages with the Nd–O–Nd–O–Nd and Nd–O–La–O–Nd linkages, respectively. In the
short-range (Nd–O–Nd) clusters in Figure 3.6d, the Nd³⁺ are separated by 3–4 Å and linked via direct oxygen bridges, thus, resulting in strong spin-exchange couplings. On the other hand, in the long-range (Nd–O–La–O–Nd) clusters, the strong super-exchange interactions between two remote Nd³⁺ ions propagate via diamagnetic La³⁺ bridges, as hypothesized in section 3.5.1.5. The La-bridged NNN structure in Figure 3.6d can also be viewed as part of a larger NN-type cluster where mixed RE³⁺ ions are interconnected through the short-range RE–O–RE linkages. This large cluster consists mostly of diamagnetic La³⁺ but with a small inclusion of paramagnetic Nd³⁺ (e.g., reflecting the 50:1 ratio of La:Nd in our La₂O₃-containing glasses). Therefore, direct linkages (Nd–O–Nd) are rare, and most of the linkages in such mixed NN clusters are between mixed RE pairs (Nd–O–La).

Although yet to be determined, the coordination shells of the S3 clusters in Figures 3.6(d, e) are shown to be enriched in B and partially depleted of Na, as projected from the structurally similar S2 clusters in Figures 3.6(b, c). The partial Na-depletion of the S3 clusters (with two Na⁺ per RE³⁺) is consistent with our ¹¹B NMR results demonstrating that the BO₄ vs BO₃ speciation is controlled by a global competition for charge compensation by Na⁺, through the newly derived expression for [Na₂O]ₓ with n = 2, as discussed in sections 3.5.3.2 and 3.5.4.2. The level of B-enrichment is yet to be confirmed, for example through systematic ¹¹B NMR studies.

Since the RE clusters (S2 and S3 in Figures 3.6) represent a vast majority of RE species (> 90%) in our glasses, their compositional chemistry may play a crucial role in tuning microscopical and mechanical properties of the host glass. The RE clusters formed in Na/B-enriched environment can be viewed as nano-scale-size glass phases, nucleating from the glass and that are enriched in RE, B and Na as compared to the rest of the host
glass. The RE/B/Na enrichment in these cluster phases also means the depletion of the same elements from the rest of the host glass. The depletion effect can be small at small RE concentrations ([Re$_2$O$_3$] < 0.1 mol%), but it can become substantial at higher RE concentrations (like 5 mol% in our La$_2$O$_3$-containing glasses). Each RE$^{3+}$ within the S2/S3 clusters immobilizes two B and two Na, acting like sponges pulling Na and B from the glass matrix leaving behind a B/Na-depleted glass phase. Therefore, the process of RE cluster formation can be thought as a mechanism inducing a nano-scale phase separation in the glass where RE-rich phase (S2 and S3 clusters) is B/Na-enriched, and the second (RE-free) phase is B/Na-depleted with respect to the nominal chemical composition of the glass. This phase separation as induced by RE clustering can be anticipated to alter mechanical, thermal, and chemical properties of the host glass.

3.6 Summary and Conclusion

Our combined EPR/NMR investigation of Nd$_2$O$_3$ and La$_2$O$_3$ containing peralkaline Na$_2$O-Al$_2$O$_3$-B$_2$O$_3$-SiO$_2$ glasses provides several new insights into the partitioning and structural speciation of RE$^{3+}$ in aluminoborosilicate glasses. Our quantitative FID-detected EPR analysis resolves three major Nd species in the glasses: (S1) the isolated Nd$^{3+}$ centers, (S2) the dipole-coupled NNN clusters (Nd–O–X–O–Nd), with Nd$^{3+}$ separated by 4–5.5 Å and interconnected by network-former bridges (X = Si, B, Al), and (S3) the exchange-coupled, EPR-invisible Nd clusters that are further subdivided into two categories of the NN clusters (Nd–O–Nd) separated by 3–4 Å and the La-bridged NNN clusters (Nd–O–La–O–Nd) separated by 4–5.5 Å. The fractional populations of these three RE species as extracted from the EPR spectral decompositions are found to depend strongly on total RE concentrations in the glass. The isolated centers (S1) are only abundant at low [RE$_2$O$_3$] <
0.01 mol%, and the NN and NNN clusters (S2 and S3) prevail at higher concentrations, exceeding 99% of total RE in glasses with [RE$_2$O$_3$] ≥ 0.1 mol%. For example, at [Nd$_2$O$_3$] = 0.1 mol% the average distance of 30 Å is expected between Nd ions assuming their uniform (no clustering) distribution in the glass. The Nd–Nd distances of 3–5.5 Å observed in the NN and NNN clusters are much shorter than that, thus emphasizing highly non-uniform distribution of RE ions in the glasses and their high tendency to form clusters with much shorter RE–RE distances.

The ESEEM experiments provide further insight into the near shell coordination environment of the EPR-detectable Nd$^{3+}$ species (S1 and S2) in the investigated glasses. Thus, on average four Na and one Al (or one B) are found in the 1$^{st}$ coordination shells of isolated Nd$^{3+}$ centers (S1), and the numbers change to fewer Na (two–three), more B (one–two) and more Al (one) in the coordination shells of each Nd$^{3+}$ in the NNN clusters (S2). The significant observation here is a substantial change in the preferred coordination environment from isolated Nd$^{3+}$ centers (S1) to the NNN clusters (S2), with fewer Na and more B involved in case of the clusters. This observation provides us an important clue on the possible mechanism behind the high tendency of RE$^{3+}$ to cluster in the glasses. Indeed, in order to form one isolated RE$^{3+}$ center (S1) requires a large number (four) of Na$^+$ ions for its charge compensation. Recognizing an additional (strong) competition for the same Na$^+$ pool from network-forming AlO$_4^-$ and BO$_4^-$, one may expect that four Na$^+$ are not easily available for each RE$^{3+}$ (especially at high RE$_2$O$_3$ concentrations, like 5 mol% in our La$_2$O$_3$-containing glasses), and therefore the isolated Nd$^{3+}$ centers (S1) cannot be formed. We hypothesize that the charge compensation problem for RE$^{3+}$ ions in glass matrix is resolved through their clustering. Indeed, our ESEEM data confirm that as little as two Na$^+$
per each RE$^{3+}$ are sufficient for their charge compensation. We further hypothesize that instead of Na$^+$ the charge compensation in RE clusters is achieved through the B enrichment of their 1st coordination shells (as evident from the ESEEM data) and by employing the tri-coordinated oxygen structures with AlO$_4$ and BO$_4$ (Figure 3.6b-e), similar to reported in per-aluminous silicate glasses with [Na$_2$O] < [Al$_2$O$_3$] $^{91}$, along with BO$_3$–bridged RE–RE linkages.

The tendency of RE$^{3+}$ to cluster in B/Na-enriched environment has an important consequence on the overall glass structure. In a way, the RE$^{3+}$ clusters can be viewed as initial seeds of a nano-scale glass phase separation, where one (cluster) phase is enriched in RE$^{3+}$, B$^{3+}$ and Na$^+$, and the second (leftover) phase is depleted of the same components. This RE-induced nano-scale phase separation can be anticipated to have a significant effect on physico-chemical and mechanical properties of host glasses.

3.7 Appendix A. Details of ESEEM simulations for LaNd0.001, LaNd0.1 and K-Nd0.01.

The ESEEM simulations are performed using the two-shell model developed by Dikanov et. al.$^{76}$ Accordingly, all nuclear spins around the S1 and S2 centers are subdivided into two subgroups. One group comprises of the proximal nuclear spins at distances of 3–4.5 Å, that define the first and second coordination shells around the Nd centers, and the second group accounts for more distant nuclear spins (> 4.5 Å). The numbers of spins (N$_2$) in the second group (the distant shell) are assumed to be fixed during the simulations, and they are calculated as N$_2 = (4\pi/3)\rho R^3$, using the average density ($\rho$) of the respective nuclei in the glass and by setting the proximity distance R$_2$ at 4.5 Å.$^{76}$ Of primary interest in our
two-shell model simulations are the nuclei in the first (proximal) shell. Thus, the proximity distance ($R_1$) and the numbers of spins ($N_1$) in the proximal shell are two fitting parameters during the ESEEM simulations. We note that these two parameters ($R_1$, $N_1$) may show some interdependence since the integrated ESEEM amplitude generally scales as a product of $N_1/R_1^6$.

All nuclear spins contributing to the ESEEM effects in our glasses, including $^{11}$B, $^{23}$Na, and $^{27}$Al, have their spins $I > \frac{1}{2}$. Therefore, their nuclear quadrupolar interactions (NQI) should be accounted during the simulation. The best fits to our experimental ESEEM data are obtained using the NQI parameters: ($C_Q \equiv e^2Qq/h = 4$ MHz, $\eta = 0$) for $^{27}$Al, ($4$ MHz, $\eta = 0.5$) for $^{23}$Na, and ($1.5$ MHz, $\eta = 0.1$) for $^{11}$B. The NQI parameters derived for $^{27}$Al and $^{23}$Na are in close agreement with the values reported in the NMR experiments for alkali aluminoborosilicate glasses. However, the NQI parameter $C_Q = 1.5$ MHz determined for $^{11}$B is noticeably smaller than $C_Q = 2.6$–$2.7$ MHz typically reported from the NMR experiments for trigonal BO$_3$ sites, and larger than $C_Q < 0.5$ MHz for tetrahedral BO$_4$ sites. We speculate that the difference in our ESEEM-derived $C_Q$ may reflect a strong effect on $^{11}$B quadrupolar coupling from Nd$^{3+}$ coordination when forming the Nd–O–B linkages. Lastly, in our ESEEM simulations, for all involved nuclear spins we assume a model of random relative orientations of NQI tensors with respect to the respective hyperfine coupling tensors as appropriate for disordered glass systems.

To help resolving the overlapping signals from $^{23}$Na and $^{27}$Al spins, and thus to allow their independent evaluation, we also perform an additional ESEEM experiment on a glass with the same composition as Nd0.01 but with all Na$_2$O being replaced with an equivalent concentration of K$_2$O (the respective glass is labeled as K-Nd0.01). Figure 3A1
shows the ESEEM spectra and the fits for K-Nd0.001. The first coordination shell parameters (R₁, N₁) for ²⁷Al nuclei in the S₁ centers are thus independently determined from the ESEEM fit of K-Nd0.01, where no interference from ²³Na is present. These ²⁷Al parameters are then used as fixed parameters when fitting the ESEEM effects in the sodium-containing glasses (like LaNd0.001 and LaNd0.1 in Figure 3A2), where both ²⁷Al and ²³Na contribute to the spectra.

**Figure 3A1:** Two-pulse ESEEM for K-Nd0.01, where 25 mol% of Na₂O were replaced with equivalent amount of K₂O. The dominant Nd³⁺ centers in K-Nd0.01 were isolated S₁ centers. (a) The ESEEM decays (solid lines) measured at two field positions, 350 and 550 mT, and their exponential fits (dashed lines). (b) The normalized ESEEM time-domains...
(solid lines), obtained by dividing the measured decays from (a) with their exponential fits. The dashed lines are the ESEEM simulations assuming that each isolated Nd$^{3+}$ center (the S1 center) has on average 0.7 of $^{27}$Al spins at a distance 3.6 Å, and 0.4 of $^{10}$B/$^{11}$B spins at 3.6 Å (Table 3.2). (c) Phase-corrected Fourier Transform (FT) spectra of the experimental (solid lines) and simulated (dashed lines) ESEEM time-domains from (b) showing the peaks from $^{27}$Al, $^{10}$B, and $^{11}$B spins.

**Figure 3A2:** Two-pulse ESEEM for LaNd0.001 (left panels) and LaNd0.1 (right panels), where the dominant Nd species were isolated Nd$^{3+}$ centers (the S1 centers) and dipole-coupled Nd clusters (the S2 centers), respectively. (a) The ESEEM decays (solid lines) measured at two field positions, 350 and 550 mT, marked with blue circles on the EPR spectra in Figures 3.2(e, h). The dashed black curves are exponential fits to the measured decays. (b) The normalized ESEEM time-domains (solid lines), obtained after dividing the measured decays (a) by their exponential fits. The dashed lines are the ESEEM simulations assuming that: (left) each isolated Nd$^{3+}$ center (the S1 center) has on average 0.7 of $^{27}$Al spins at a distance 3.6 Å, four $^{23}$Na spins at 3.2 Å, and 0.4 of $^{10}$B/$^{11}$B spins at 3.6 Å (Table 3.2), and (right) each Nd$^{3+}$ ion in dipole-coupled Nd clusters (the S2 centers) has on
average 0.9 of $^{27}\text{Al}$ spins at a distance 3.6 Å, two $^{23}\text{Na}$ spins at 3.2 Å, and two $^{10}\text{B}/^{11}\text{B}$ spins at 3.6 Å. (c) Phase-corrected Fourier Transformation (FT) spectra of the experimental (solid lines) and simulated (dashed lines) ESEEM time-domains from (b) showing strong overlapping peaks from $^{23}\text{Na}$ and $^{27}\text{Al}$ spins and smaller peaks from $^{10}\text{B}$ and $^{11}\text{B}$ as labeled.
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3.8 Supplementary Information

Figure 3S1: Heat flow versus temperature curves for Nd0 (La$_2$O$_3$-free) and LaNd0 (La$_2$O$_3$-containing) glasses obtained from a differential scanning calorimeter (DSC). The exothermic phase transitions are observed by a positive shift (Exo ↑). $T_p$ refers to the peak temperature of crystallization (an exothermic process) and is only observed in the LaNd0 glass ($T_p = 1043$ K). Both glasses exhibit the characteristic glass transition endotherm (negative dip), the onset of which is reported as the glass transition temperature ($T_g$). $T_g = 824$ K for Nd0 and 840 K for LaNd0.

Figure 3S2: Comparison of the FID-detected and the echo-detected EPR spectra measured for two glasses, Nd0.001 (a) and Nd0.1 (b).
Figure 3S3: Nd/La concentration dependence of spin decoherence times ($T_2$) for EPR-active Nd$^{3+}$ centers in La-free and La-containing glasses measured at 4.6 K.

The $T_2$ times were measured at magnetic field 350 mT where the EPR signal was mostly from the S1 centers (isolated Nd$^{3+}$ centers) at low [Nd$_2$O$_3$] < 0.05 mol%, and the signal had a sizable contribution from the S2 centers (Nd clusters) at high [Nd$_2$O$_3$] > 0.05 mol% (cp. Figure 3.2). The dashed curve is a fit to the data using the equation $1/T_2 = C + R \cdot \sqrt{[\text{Nd}_2\text{O}_3]}$, that takes into account two spectral diffusion mechanisms: the concentration-independent term (C) is from flip-flops of environmental nuclear spins,$^{1,2}$ and the square-root dependent term (R) is from neighboring Nd$^{3+}$ spins undergoing slow spin relaxation.$^3$
Figure 3S4: Variation of a tetrahedral boron fraction ($N_4$) as a function of $R = [Na_2O]/[B_2O_3]$ in sodium borosilicate glasses. Reprinted from Yun, Y. H.; Bray, P. J with permission from Elsevier. The estimated $R'$ values for two glasses examined in this work are $R' = 1.25$ for Nd0, and $R' = 0.43$ for LaNd0, as calculated using the glass compositions (Table 3.1) and the new expression for $R'$ introduced by us in the main text, $[Na_2O]_{ex} = [Na_2O] - [Al_2O_3] - n\cdot[La_2O_3]$, with $n = 2$. The calculated $K = [SiO_2]/([B_2O_3] + [Al_2O_3])$ is equal to 2.75 in both glasses. The respective points, Nd0 (■) and LaNd0 (●), are shown on the plot predicting $N_4 = 0.62$ for Nd0 and $N_4 = 0.4$ for LaNd0, in good agreement with the values 0.66 and 0.37, respectively, measured in our NMR experiments.
Figure 3S5: X-ray diffraction pattern of glass LaNd0.1 heat-treated at 865 K (Tg + 50 K) for 72 hours. The identified phase is lanthanum boron silicate (La$_5$BSiO$_{13}$ – PDF # 00-052-0699).

References

Chapter 4. Impact of RE$^{3+}$, Mo$^{6+}$, and Zr$^{4+}$ on the Structure of Aluminoborosilicate-Based Model Nuclear Waste Glasses

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4.1 Introduction

Although reprocessing of spent nuclear fuel (SNF) generated from civilian power plants is currently not performed in the United States, it is being considered under the transuranic extraction process (TRUEX\textsuperscript{plus}).\textsuperscript{1} However, reprocessing is expected to generate three non-fissionable secondary HLW streams rich in (1) alkalis/alkaline-earths (e.g., $^{137}$Cs, $^{90}$Sr), (ii) rare-earths (RE) (e.g., La, Nd), and (iii) undissolved solids (UDS) (e.g., Mo, Zr) which would require long-term safe disposal.\textsuperscript{2} Therefore, scientists at the U.S. Department of Energy (DOE) are exploring waste forms for the long-term immobilization of the non-fissionable HLW expected from the TRUEX\textsuperscript{plus} process. In this pursuit, the U.S. DOE has recently proposed an alkali alkaline-earth aluminoborosilicate-based glass-ceramic as a potential waste form due to its ability to retain higher concentrations of MoO$_3$ ($\geq$ 4 mol\%) compared to the traditionally employed borosilicate glass, which suffers from poor MoO$_3$ solubility (\~1.5 mol\%).\textsuperscript{1,2} Irrespective of whether glass or glass-ceramic is considered as the final waste form, it critical to evaluate the impact of adding MoO$_3$ and other significant elements present in the HLW on the structure of, borosilicate/aluminoborosilicate glasses, to elucidate the mechanism governing the solubility/retention of MoO$_3$ in these glasses.

In the pursuit of understanding the mechanism governing MoO$_3$ solubility in aluminoborosilicate glasses, in Chapter 2, we reported a study conducted to understand the compositional dependence of MoO$_3$ solubility and retention limits in aluminoborosilicate-based model nuclear waste glasses. It was concluded that Nd$_2$O$_3$, when incorporated into an alkali alkaline-earth aluminoborosilicate glass, tends to increase the solubility of MoO$_3$ by at least 2$\times$ compared to the Nd$_2$O$_3$-free aluminoborosilicate glass. After thoroughly
reviewing the existing literature on MoO$_3$ and RE$_2$O$_3$ containing borosilicate/aluminoborosilicate glasses, we proposed a three-step mechanism governing the solubility of MoO$_3$ in rare-earth (RE) containing aluminoborosilicate-based nuclear waste glasses:

(i) RE$_2$O$_3$ induces phase separation in a homogenous aluminoborosilicate glass, segregating it into borate-rich and silicate-rich domains, where the RE$^{3+}$ preferentially enters the borate-rich domains forming RE-metaborate-like structures ($\text{1BO}_4:\text{RE}:\text{2BO}_3$). Once the concentration of RE$^{3+}$ cations in the glass exceeds its solubility limit in the borate-rich domains, RE$^{3+}$ cations are incorporated in the silicate-rich domains forming some kind of “clusters”.

(ii) When MoO$_3$ is added to the RE$_2$O$_3$-containing phase-separated aluminoborosilicate glass, it preferentially enters the RE-B-rich domains as the molybdate oxyanion (MoO$_4^{2-}$), which is primarily charge compensated by Ca$^{2+}$ and to a lesser extent by Na$^+$ (since most of the Na$^+$ is being used to compensate AlO$_4^{-}$ and BO$_4^{-}$ units).

(iii) MoO$_4^{2-}$ then coordinates with RE’s in the RE-B-rich domains to form a stable RE-Mo-B glassy phase, thus improving MoO$_3$ solubility

As it was essential to understand the structural role of REs in aluminoborosilicate glasses to test the abovementioned hypothesis, in Chapter 3, we reported a study undertaken to investigate the clustering and partitioning mechanism of RE$^{3+}$ cations in peralkaline (Na/Al > 1) sodium aluminoborosilicate glasses. Combining the results from free induction decay (FID)-detected electron paramagnetic resonance (EPR), electron spin echo envelope modulation (ESEEM), and magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopies, we presented an atomic-scale picture of RE$^{3+}$
clustering and coordination in alkali aluminoborosilicate glasses thereby improving on our hypothesis presented in Chapter 2, specifically concerning the mechanism of RE$^{3+}$ incorporation in aluminoborosilicate glasses (step 1 of the three-step mechanism mentioned above). In Chapter 3, it was proposed that RE$^{3+}$ cations exist in alkali aluminoborosilicate glasses in three structural forms: isolated RE$^{3+}$ centers, dipole-coupled RE clusters (RE–O–X–O–RE, X = Si/Al/B), and spin-exchange-coupled RE clusters (RE–O–RE). It was revealed that increasing the RE$_2$O$_3$ concentration promoted extensive RE clustering, with more than 90% REs existing as clusters even at RE$_2$O$_3$ concentrations as low as 0.01 mol%. The isolated RE$^{3+}$ centers were reported to exist in an alkali-Si-rich environment, i.e., depleted of B/Al, and the RE clusters were located in a Na-B-rich environment. Thus, it was proposed that adding increasing concentration of RE$_2$O$_3$ (below their solubility limits) led to the formation of nano-scale RE-Na-B-enriched glassy phases with the leftover glass matrix being depleted of the same elements.

In the compositions investigated in Chapter 3 for understanding the partitioning mechanism of REs, alkaline-earth ions (e.g., Ca$^{2+}$) were intentionally left out to avoid interfering effects from mixed modifier alkalis and alkaline-earths in the aluminoborosilicate glass. Investigations on the quaternary oxide system (Na$_2$O-Al$_2$O$_3$-B$_2$O$_3$-SiO$_2$) allowed an in-depth understanding of the RE$_2$O$_3$ clustering and coordination in aluminoborosilicate glasses which proved to be an essential step in validating a part of our three-step mechanism explaining the role of RE$_2$O$_3$ in improving MoO$_3$ solubility (Chapter 2). However, to exhaustively test the hypothesis, the speciation and coordination environment of RE$^{3+}$ in the presence of MoO$_3$ needs to be investigated. These investigations need to be conducted on glasses whose compositions serve as a model for
the actual HLW glass-ceramic waste form proposed by the U.S. DOE, a complex mixture of more than 25 oxides, including alkalis, alkaline-earths, REs, Mo, and Zr in significant amounts. It also needs to be assessed how REs behave in the presence of other significant elements present in the waste, such as Zr^{4+}, which is known to influence the REs coordination environment in soda-lime aluminoborosilicate glasses, as previously reported in the literature. Accordingly, this work aims to investigate the structure of RE_2O_3, MoO_3, and ZrO_2 containing model HLW-based glasses. The glass compositions investigated in this work have been designed based on a model nuclear waste glass-ceramic composition proposed by the U.S. DOE for HLW immobilization. The glasses are probed by a suite of characterization techniques, including FID-detected EPR, ESEEM, and MAS NMR.

4.2 Experimental details

4.2.1 Glass composition design

The glass compositions investigated in this study have been designed based on a simplified nuclear waste glass-ceramic comprising 11.87 Na_2O–14.1 CaO–5.35 Al_2O_3–9.74 B_2O_3–46.09 SiO_2–5.38 Nd_2O_3–4.13 MoO_3–3.29 ZrO_2 (mol%). The composition of the simplified glass-ceramic has been derived from a more complex glass-ceramic waste form, GC-Mo-Li 6.25, proposed by the U.S. DOE for immobilizing the HLW expected from the proposed Transuranic extraction (TRUEX^{plus}) process, to which simplification has been made such that, Na_2O represents the total fraction of alkali oxides (Na_2O + Li_2O + Cs_2O), CaO represents the alkaline-earth oxides (CaO + BaO + SrO), and Nd_2O_3 represents the fraction of rare earth oxides (Y_2O_3 + La_2O_3 + Ce_2O_3 + Pr_2O_3 + Nd_2O_3 + Sm_2O_3 + Eu_2O_3 + Gd_2O_3).
The baseline glass for this study has a batched composition of 12.5 Na$_2$O–12.5 CaO–5.0 Al$_2$O$_3$–10.0 B$_2$O$_3$–60.0 SiO$_2$ (mol%). Henceforth this glass will be referred to as BL. Three series of glasses referred to as Nd-containing (5 mol% Nd$_2$O$_3$), La-containing (5 mol% La$_2$O$_3$), and LaNd-containing (4.99 mol% La$_2$O$_3$ + 0.01 mol% Nd$_2$O$_3$) have been synthesized by progressively substituting 5 mol% RE$_2$O$_3$, 3 mol% MoO$_3$, and 2–4 mol% ZrO$_2$ for SiO$_2$, in the glass BL, on an equimolar basis. Glasses in the Nd-containing and La-containing series have been labeled as 5RE, REMo, REMoZr$_2$, and REMoZr$_4$, where RE = Nd or La. The glasses in the LaNd-containing series have been labeled as LaNd, LaNdMo, LaNdMoZr$_2$, and LaNdZr$_4$.

The Nd-containing and La-containing glasses have been analyzed by Raman spectroscopy to investigate the structural impact of RE$_2$O$_3$, MoO$_3$, and ZrO$_2$ on the BL glass. Additionally, the BL and the La-containing glasses have been analyzed by $^{11}$B and $^{27}$Al MAS NMR spectroscopy to investigate boron and aluminum speciation. In these glasses, La$^{3+}$ is expected to induce similar structural modifications as Nd$^{3+}$ due to their similar cation field strengths and coordination environment (surrounded by 6–8 oxygens) in the glass.\textsuperscript{5-7} Glasses in the LaNd-containing series have been probed exclusively by FID-detected EPR and ESEEM spectroscopies. In these glasses, the paramagnetic Nd$^{3+}$ acts as a spin probe required for EPR analysis. The concentration of Nd$_2$O$_3$ in these glasses has been kept low (0.01 mol%) since our studies in Chapter 3 revealed that [Nd$_2$O$_3$] > 0.1 mol% were unsuitable for pulsed EPR experiments due to (1) excessive dipole-dipole interactions of paramagnetic Nd$^{3+}$ resulting in a significantly broadened EPR spectra thereby making it impossible to resolve the individual contributions from the different Nd species and (2) very short T$_2$ spin relaxation times (e.g., T$_2 < 100$ ns, below the detection limit of our EPR
experiments), owing to the dipole-dipole interactions, resulting in most of the Nd becoming EPR-invisible. Table 4.1 presents the batched composition of all the glasses investigated in the study.

4.2.2 Glass synthesis by melt-quenching

High purity powders of Na$_2$SiO$_3$ (Alfa Aesar; > 99%), CaCO$_3$ (Alfa Aesar; > 98%), Al$_2$O$_3$ (Sigma-Aldrich; ≥ 98%), H$_3$BO$_3$ (Alfa Aesar ≥ 98%), SiO$_2$ (Alfa Aesar ≥ 99.5%), La$_2$O$_3$ (Sigma-Aldrich; 99.9%), Nd$_2$O$_3$ (Alfa Aesar; 99%), MoO$_3$ (Alfa Aesar; 99.5%), and ZrO$_2$ (Sigma-Aldrich; 99%) were used as precursors for glass synthesis. The batches corresponding to 70 g of glass were melted in a 90% Pt – 10% Rh crucible covered with a Pt lid (to limit volatilization losses) at 1450–1550 °C for two hours. The melting temperature had to be raised to 1550 °C upon 5 mol% RE$_2$O$_3$ and 2–4 mol% ZrO$_2$ substitution to ensure the ease of pouring the melts. The melts were quenched on a copper plate and cooled to room temperature. After quenching, the LaNd-containing samples were annealed for two hours at temperatures set about 50 °C below the glass transition temperatures (T$_g$) of the corresponding La-containing glasses. Annealing was performed to obtain crack-free samples for EPR analysis. The melt quenched samples were crushed and sieved to a particle size of < 45 µm and analyzed by X-ray diffraction (XRD, PANalytical – X’Pert Pro; Cu Kα radiation; 2θ range: 10° – 90°; step size: 0.01313° s$^{-1}$; dwell time per step: 0.10 s). All the as-synthesized samples were transparent and XRD amorphous, confirming that they were glasses.
**Table 4.1:** Batched compositions of the BL, Nd-containing, La-containing, and LaNd-containing glasses. The compositions are presented in mol%.

<table>
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<th>Mo%</th>
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<th>La-containing</th>
<th>LaNd-containing</th>
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<td>55.0</td>
<td>4.0</td>
<td>4.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

*Note: The table continues with similar entries for other compositions.*
4.2.3 **Raman spectroscopy**

Raman spectra of the BL, Nd-containing and La-containing glasses were acquired at room temperature on an inVia Renishaw confocal Raman spectrometer equipped with a CCD detector. Glasses were probed using a 532 nm line solid-state laser operating at 500 mW power in the frequency range of 200 to 1600 cm\(^{-1}\) with a precision of ± 1 cm\(^{-1}\). The as-collected spectra were processed by correcting for temperature and frequency-dependence of the scattering intensity using the correction factor recommended in the literature \(^8\), followed by the subtraction of a third-order polynomial baseline and normalization to the total unit area. Spectral deconvolutions were performed using the standard Gaussian lineshapes for the bands without constraining the spectral parameters (band positions and FWHM of the bands) while converging the fits.

4.2.4 **\(^{27}\text{Al} \text{ and} ^{11}\text{B MAS NMR}**

\(^{27}\text{Al} 1\text{D} \text{ and Hahn Echo MAS NMR were acquired on the BL and La-containing glasses, whereas} ^{11}\text{B} 1\text{D MAS NMR was acquired only on the La-containing glasses.}^{27}\text{Al} \text{ MAS NMR experiments were performed at 20.0 T on a Bruker Neo spectrometer operating at a frequency of 221.6 MHz and equipped with a double-resonance 2.5 mm rotor diameter probe in which samples were spun at 30 kHz. Spin-lattice relaxation times were estimated using a saturation-recovery and found between 350 ms and 500 ms. Spectra were referenced to a 1M nitric solution of Al(NO\(_3\))\(_3\). One-pulse quantitative spectra were obtained using a pulse length of 0.5 \(\mu\)s at a radio-frequency field of 50 kHz and recycle delay of 0.1 ms. With a spectral width of 100 kHz, the rolling baseline was removed using an iterative baseline correction algorithm \(^9\). 8000 scans were accumulated for each spectrum. The full-echo spectra were obtained using a radio-frequency field of 10 kHz,
selective $\pi/2$ pulses of $8.3 \mu s$, an inter-pulse delay of 25 rotor periods (i.e., $821 \mu s$), and a recycle delay of 1 s. 2000 scans were accumulated for each spectrum. The line shape simulations have been performed using the Gaussian Isotropic Model (GIM) or Czjzek model $^{10}$, based on a statistical distribution of the local environments and implemented in DMFit $^{11}$.

$^{11}$B spectra were acquired at 9.4 T on a Bruker AV 400 WB spectrometer operating at a frequency of 128.4 MHz in a 2.5 mm rotor probe, using $\pi/12$ pulses with a relaxation delay of 3s and 1024 scans at 20 kHz MAS spinning speed. BF3.Et$_2$O was used as a chemical shift reference. The $^{11}$B line shape simulations have been performed using the Q MAS $1/2$ model and Gaussian/Lorentzian functions, respectively, for the $^{11}$B resonances of 3- and 4-coordinated boron species, in DMFit $^{11}$.

4.2.5 \textit{FID-detected EPR and ESEEM}

Pulsed EPR experiments were performed on monolith pieces of the glasses in LaNd-containing series (doped with 0.01 mol\% Nd$_2$O$_3$) with a Bruker EPR spectrometer (Elexsys580E) operating at an X-band frequency of 9.7 GHz. A dielectric resonator (EN-4118X-MD4) and a helium-flow cryostat (Oxford CF935) were used for the EPR experiments, and the spectra were recorded at 4.6 K. The FID-detected EPR and ESEEM simulations were performed using the EasySpin $^{12}$ toolbox developed in MATLAB. Field-sweep EPR spectra were recorded using an FID-detected EPR experiment by applying one excitation $\pi/2$ pulse of duration 400 ns to 1 $\mu$s and integrating an FID signal over 400–800 ns widow. To allow a direct comparison of the signal intensities between different samples, the recorded FID-detected EPR spectra were normalized per sample weight and further corrected for differences in their measured $T_2$ spin relaxation times, taking into account the
initial dead-time of 64 ns in the FID detected window in our experiments. ESEEM experiments were conducted using a two-pulse (Hahn) echo pulse sequence ($\pi/2-\tau-\pi-\tau$-echo) with $\pi/2$ and $\pi$ pulses set to 16 ns and 32 ns, respectively. Before Fourier transformation (F.T.), the measured ESEEM time-domains were normalized by dividing the experimental data with the fit exponential curves followed by subtracting a unit baseline. After F.T., the ESEEM spectra were phase-corrected for the missing dead times (the initial $\tau = 104$ ns) and presented in the cosine F.T. mode.

4.2.6 Density measurements

Density measurements were performed on monolithic glass samples by the Archimedes principle, using D-limonene (specific gravity at 25 °C = 0.84 g/cc) as the immersion fluid. The density values reported for the glasses are an average of five sets of measurements with an uncertainty of ± 0.003 g/cc. Based on the density values, the oxygen molar volume ($V_m^O$) was calculated using the following formula:

$$V_m^O = \frac{\sum_i c_i M_i}{\rho \sum_i n_i c_i}$$

$C_i$ is the molar concentration of the oxide ‘i’ (present in the glass); $M_i$ is the molar weight of the $i^{th}$ oxide; $n_i$ is the $i$th oxide’s oxygen stoichiometry; $\rho$ is the measured density of the glass.

4.2.7 Differential scanning calorimetry

Differential scanning calorimetric (DSC) analysis was performed on the BL, Nd-containing, and La-containing glasses. Glasses were crushed to powders and sieved to a particle size of 850–1000 µm. For DSC measurements, the glass powders were heated in a 90% Pt – 10% Rh crucible covered with a Pt-lid, from room temperature to 1400 °C at a heating rate of 20 °C/min under a constant flow of N$_2$ gas. Measurements were performed
on a simultaneous thermal analyzer, STA-449 F Jupiter, manufactured by Netzsch, Germany. The DSC curves were analyzed only to determine the onset of glass transition ($T_g$). The values of $T_g$ reported in this article are an average of three sets of measurements performed on each glass with an uncertainty of ± 3 °C. The LaNd-containing glasses were not evaluated for their density and $T_g$ as their values were expected to be similar to the corresponding La-containing glasses.

4.3 Results & Discussion

4.3.1 Raman spectroscopy

Figures 4.1a and 4.1b display the baseline subtracted and area-normalized Raman spectra of glasses in the Nd-containing and La-containing series, respectively, overlayed on the spectrum of the BL glass. The spectra in both series of glasses exhibit similar changes with the substitution of 5 mol% RE$_2$O$_3$ (Nd$_2$O$_3$ or La$_2$O$_3$), 3 mol% MoO$_3$, and 2–4 mol% ZrO$_2$ in the BL glass, suggesting that both Nd$^{3+}$ and La$^{3+}$ induce similar modifications in the structure of a soda-lime aluminoborosilicate glass.

![Figure 4.1](image_url)

**Figure 4.1:** Baseline subtracted and area-normalized Raman spectra of (a) Nd-containing glasses and (b) La-containing glasses overlayed on the spectrum of the BL glass.
As seen in Figure 4.1a and 4.1b, the low-frequency end of the spectra of glasses BL and 5RE exhibit broad bands near 500, 635, and 800 cm\(^{-1}\). These bands can be attributed to the mixed stretching, and bending modes of T–O–T linkages (where T = Si/Al), breathing modes of danburite-like rings (consisting of two tetrahedral boron BO\(_4\) and tetrahedral silicon SiO\(_4\)), and symmetric vibrations of trigonal boron (BO\(_3\)) in boroxol rings based on prior literature.\(^8, 13-22\) The spectral deconvolution of the low-frequency region can resolve several other contributions from borate and borosilicate units, as will be revealed in section 4.3.1.1. The bands around 500, 635, and 800 cm\(^{-1}\) appear to be suppressed in the spectra of glasses REMo, REMoZr2, and REMoZr4 (RE = Nd or La). In these glasses, a band evolves at 330 cm\(^{-1}\) which can be assigned to the internal vibrations of the molybdate oxyanion – MoO\(_4^{2-}\).\(^{23-27}\) The prominent peak related to MoO\(_4^{2-}\) evolves at 914 cm\(^{-1}\) and has an associated shoulder at 896 cm\(^{-1}\), which corresponds to the symmetric and asymmetric stretching modes of Mo–O\(^-\), respectively.\(^{23, 24, 28}\) The presence of the highly intense peak at 914 cm\(^{-1}\) obscures the 850–1250 cm\(^{-1}\) region in glasses REMo, REMoZr2, and REMoZr4. In borosilicate/aluminoborosilicate glasses, the 850–1250 cm\(^{-1}\) region is attributed to the stretching modes of Si–O\(^-\) and Al–O\(^-\) in tetrahedral TO\(_4\) units (T = Si/Al).\(^5, 16, 29\) In the BL and 5RE glasses, the band corresponding to TO\(_4\) units is prominent and can be deconvoluted to obtain contributions from several Q\(^n\) speciations (n = 0–4 is the number of bridging oxygens (BO)), where Q\(^n\) could either be SiO\(_4\) or AlO\(_4\) with a specific assignment to Si or Al not being possible due to significant overlap in peak positions. The substitution of 5 mol% RE\(_2\)O\(_3\) to the BL glass (at the expense of SiO\(_2\)) causes broadening of the TO\(_4\) band and a shift in its center of gravity towards a lower frequency (cp. 850–1250 cm\(^{-1}\) region of 5RE with BL in Figure 4.1). Similar spectral transformations were
previously reported in binary alkali silicates and multicomponent alkali alkaline-earth borosilicate glasses in response to rare-earths (e.g., La$^{3+}$, Nd$^{3+}$) being either added to the glass or substituted for the alkali (A$^+$)/alkaline-earth (AE$^{2+}$) cations (e.g., Na$^+$, Ca$^{2+}$).$^5,30,31$

It was proposed that the lower frequency shift was caused due to the partial substitution of RE$^{3+}$ for A$^+/AE^{2+}$ in the next-next neighbor position of Si resulting in the formation of Si–O–RE linkages at the expense of Si–O–A or Si–O–AE linkages.$^5,30,31$ The Si–O–RE linkages led to the weakening of the Si–O$^-$ bond owing to the high cation field strength of RE$^{3+}$ (compared to A$^+$ and AE$^{2+}$), thereby inducing a lower frequency shift of the TO$_4$ band.$^5,30,31$ The formation of Si–O–RE also evolved new peaks corresponding to Q$^n$ linked to RE$^{3+}$, whose peak positions were located towards lower frequencies than the Q$^n$ peaks linked to A$^+/AE^{2+}$ resulting in the broadening of the Raman spectra.$^5,30,31$

The high-frequency region from 1250 to 1600 cm$^{-1}$ is usually assigned to B–O$^-$ stretching modes in chain-type metaborate groups and boroxol rings.$^{13,14,17-21,29}$ This region appears to be suppressed in the currently investigated glasses, except for the BL and 5La, whose spectral deconvolution is discussed below. The Raman spectra of glasses 5Nd, REMo, REMoZr2, and REMoZr4 could not be deconvoluted due to the overwhelming background signal.

4.3.1.1 Raman deconvolution of BL and 5La

The Raman spectral deconvolution of glasses BL and 5La are shown in Figure 4.2, while derived peak positions and relative areas (%) of the peaks are reported in Table 4.2. The peaks are assigned based on Raman bands previously reported in the literature for alkali silicates,$^{30,31}$ alkali borates,$^{13,18}$ alkali borosilicates,$^{16,29}$ and alkali aluminosilicates
glasses. The spectral deconvolution is discussed in terms of the low-frequency (300–850 cm\(^{-1}\)), mid-frequency (850–1250 cm\(^{-1}\)), and high-frequency (1250–1600 cm\(^{-1}\)) region.

**Figure 4.2:** Baseline corrected and area normalized Raman spectra and spectral deconvolution of the B. and 5La glasses. For peak assignments, refer to Table 4.2.

**Low-frequency region (300–850 cm\(^{-1}\))**

In this region, the spectra of both, BL and 5La are fitted with seven peaks referred to as \(\nu_{400}, \nu_{515}, \nu_{586}, \nu_{630}, \nu_{700}, \nu_{755},\) and \(\nu_{800}\) in Table 4.2. The peaks \(\nu_{400}\) and \(\nu_{515}\) are assigned to the mixed stretching/bending modes of \(\text{T–O–T}\), and additionally, \(\nu_{515}\) is assigned to the breathing modes of reedmergnerite-like borosilicate rings consisting of one BO\(_4\) and three SiO\(_4\) units. Reedmergnerite is a mineral of composition \(\frac{1}{2}(\text{Na}_2\text{O}.\text{B}_2\text{O}_3.6\text{SiO}_2)\) which exhibits Raman peaks at 515 and 586 cm\(^{-1}\). The \(\nu_{515}\) peak is assigned to reedmergnerite since the spectra of both, BL and 5La glass, also exhibits a reedmergnerite-
like peak at 575 cm\(^{-1}\) and 580 cm\(^{-1}\), respectively, referred to as \(\nu_{586}\). The peaks \(\nu_{630}, \nu_{700},\) and \(\nu_{755}\) are attributed to the breathing modes of danburite-like rings (two BO\(_4\) and two SiO\(_4\))\(^{14,16,29}\) vibrational modes of BO\(_3\) in chain-type metaborates\(^{13,18}\) and the vibrational modes of BO\(_4\) in six-membered borate rings consisting of both, BO\(_3\) and BO\(_4\) units\(^{29}\), respectively. The low-intensity peak (\(\nu_{800}\)) at 798 and 788 cm\(^{-1}\) in the BL and 5La is assigned to the symmetric vibrational modes of BO\(_3\) in boroxol rings\(^{13,29}\).

The spectral deconvolution of the low-frequency region reveals that the area (%) of reedemergerite-like (\(\nu_{515}, \nu_{586}\)) and danburite-like (\(\nu_{630}\)) peaks decreases with the substitution of 5 mol\% La\(_2\)O\(_3\) in the BL glass (cp. areas of \(\nu_{515}, \nu_{586},\) and \(\nu_{630}\) for BL and 5La in Table 4.2). The decrease indicates a reduced fraction of BO\(_4\) units in the glass 5La compared to BL. The results agree with the lower N\(_4\) value \(\left(\frac{BO_4}{BO_3+BO_4}\right)\) estimated for 5La from \(^{11}\)B MAS NMR analysis (discussed in section 4.3.3, Table 4.4). Since the \(\nu_{515}, \nu_{586},\) and \(\nu_{630}\) peaks correspond to mixed borosilicate units (containing both, SiO\(_4\) & BO\(_4\) units), the lower areas of these peaks suggest a decrease in the relative population of Si–O–[\(^{4}\)B] linkages (where \([^{4}\)B refers to BO\(_4\)) upon La\(_2\)O\(_3\) substitution. Previously, in sodium borosilicate glasses, the lowering of the Si-O-B linkages as determined by \(^{17}\)O NMR was attributed to the unmixing of the homogenous glass into alkali-borate-rich and silicate-rich regions\(^{32}\). It was argued that the unmixing could be viewed as incipient phase separation in the glass\(^{32}\). In Chapter 3, based on combined pulsed EPR and MAS NMR studies, we have shown that incorporating high concentrations of RE\(_2\)O\(_3\) to a homogenous alkali aluminoborosilicate glass results in the segregation of alkali-B-RE-rich nano-scale phases, with the leftover glass matrix being depleted of these same elements, i.e., being enriched in Si. Based on prior literature\(^{32}\) as well as our findings in Chapter 3, and the decrease in
the relative population of Si–O–[4]B linkages observed in our Raman analysis, we propose that RE$_2$O$_3$ (5 mol% La$_2$O$_3$/Nd$_2$O$_3$) addition to a homogenous soda-lime aluminoborosilicate glass (BL) results in the unmixing of the mixed borosilicate region into B-rich and Si-rich phases.

**Table 4.2: Raman peak shifts (cm$^{-1}$) and peak areas (%) for the spectra of glasses BL and 5La, derived from the spectral deconvolution shown in Figure 4.2.**

<table>
<thead>
<tr>
<th>Peak assignment</th>
<th>BL</th>
<th>5La</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Raman shift</td>
<td>Area (%)</td>
</tr>
<tr>
<td>v$_{690}$ T–O–T (T = Si/Al)</td>
<td>440</td>
<td>7.5</td>
</tr>
<tr>
<td>v$_{515}$ T–O–T (reedmengerite-like rings (1BO$_4$, 3SiO$_4$))</td>
<td>512</td>
<td>7.8</td>
</tr>
<tr>
<td>v$_{586}$ reedmengerite-like rings (1BO$_4$, 3SiO$_4$)</td>
<td>575</td>
<td>3.9</td>
</tr>
<tr>
<td>v$_{630}$ danburite-like rings (2BO$_4$, 2SiO$_4$)</td>
<td>635</td>
<td>8.5</td>
</tr>
<tr>
<td>v$_{700}$ chain-type metabolates (BO$_4$)</td>
<td>701</td>
<td>3.0</td>
</tr>
<tr>
<td>v$_{755}$ Six-membered borate rings (BO$_4$)</td>
<td>756</td>
<td>2.5</td>
</tr>
<tr>
<td>v$_{800}$ Boroxol rings (BO$_3$)</td>
<td>798</td>
<td>1.5</td>
</tr>
<tr>
<td>v$_{910}$ Q$^1$ (Na, Ca)</td>
<td>907</td>
<td>1.1</td>
</tr>
<tr>
<td>v$_{960}$ Q$^2$ (Na, Ca)</td>
<td>963</td>
<td>8.7</td>
</tr>
<tr>
<td>v$_{1020}$ Si–O$^0$ (bridging O) in Q$^1$, Q$^2$, and Q$^3$</td>
<td>1018</td>
<td>10.3</td>
</tr>
<tr>
<td>v$_{1050}$ Q$^3$ (Na, Ca)</td>
<td>1067</td>
<td>21.1</td>
</tr>
<tr>
<td>v$_{1110}$ Q$^{4,II}$</td>
<td>1117</td>
<td>9.4</td>
</tr>
<tr>
<td>v$_{1120}$ Q$^{4,1}$</td>
<td>1167</td>
<td>4.9</td>
</tr>
<tr>
<td>v$_{1410}$ $^{[3]}$B–O–$^{[4]}$B (chain-type metabolate)</td>
<td>1408</td>
<td>2.6</td>
</tr>
<tr>
<td>v$_{1450}$ $^{[3]}$B–O–$^{[4]}$B (chain-type metabolate)</td>
<td>1451</td>
<td>3.5</td>
</tr>
<tr>
<td>v$_{1500}$ Boroxol rings (BO$_3$)</td>
<td>1503</td>
<td>3.7</td>
</tr>
</tbody>
</table>

La$_2$O$_3$ substitution also decreases the relative area of v$_{755}$ and v$_{800}$ peaks which correspond to the vibrational modes of BO$_4$ in six-membered borate rings (which include both BO$_3$ and BO$_4$ units) and BO$_3$ in boroxol rings, respectively. The decrease in v$_{755}$ peak area is consistent with the lower N$_4$ estimated for 5La from $^{11}$B MAS NMR analysis.
However, the decrease in $\nu_{800}$ peak area, i.e., BO$_3$ in ring-type structures, is surprising. As will be revealed in our discussion of the high-frequency Raman region (1250–1600 cm$^{-1}$), the peak corresponding to $^{[3]}$B–O$^{[3]}$B ($^{[3]}$B refers to tri-coordinated boron) linkages ($\nu_{1450}$) involving chain-type metaborates exhibits a higher area upon La$_2$O$_3$ substitution. The decrease in $\nu_{800}$ along with the increase in $\nu_{1450}$ indicates the interconversion of BO$_3$(ring) (BO$_3$ units in boroxol rings) to BO$_3$(non-ring) (BO$_3$ units in chain-type metaborates) units upon La$_2$O$_3$ substitution.

**Mid-frequency region (850–1250 cm$^{-1}$)**

The 850–1250 cm$^{-1}$ region is fitted with six peaks for both glasses. The peaks $\nu_{910}$, $\nu_{960}$, and $\nu_{1060}$ are assigned to Q$^1$, Q$^2$, and Q$^3$ units, respectively, linked either to Na$^+$ or Ca$^{2+}$. The peaks $\nu_{1110}$ and $\nu_{1150}$ are assigned to Q$^{4,1}$ (A$_1$ stretching mode of Q$^4$ units), and Q$^{4,II}$ units (stretching modes of Q$^4$ exhibiting slightly lower Si–O–Si angles than those contributing towards Q$^{4,1}$) of SiO$_4$. The peak $\nu_{1020}$ is assigned to stretching modes of silica linked to bridging oxygen (Si–O$^0$). Additionally, the $\nu_{1020}$ in the 5La glass is also assigned to Q$^3$(La), i.e., Q$^3$ units linked to La$^{3+}$. The assignment of the $\nu_{1020}$ peak to Q$^3$(La) is based on a prior study reporting the Raman spectra of La$_2$O$_3$-K$_2$O-SiO$_2$ glasses. In this study, the peak corresponding to Q$^3$(La) was observed at 1030 cm$^{-1}$ and was located towards the lower frequency side of the peak corresponding to Q$^3$(K) (Q$^3$ linked to K) (1060–1080 cm$^{-1}$). It was argued that La–O$^-$ bonds being stronger than the K–O$^-$ bonds (due to the higher cation field strength of La$^{3+}$), tend to weaken the Si–O$^-$ bonds, thereby lowering the spring constant of the harmonic oscillator and shifting the Q$^3$(La) peak towards the lower frequency. A similar effect is observed in our 5La glass wherein the substitution of 5 mol% La$_2$O$_3$ broadens the 850–1250 cm$^{-1}$ band and shifts its center of gravity towards...
lower frequency due to the evolving $Q^3\ (\text{La})$ peak. Another plausible reason for the lower frequency shift observed in the 850–1250 cm$^{-1}$ band could be an increase in the effective mass around the Si–O$^-$ harmonic oscillator due Si-O-La formation since, La$^{3+}$ has a higher atomic mass than Na$^+$/Ca$^{2+}$. An increase in the effective mass is known to decrease the vibrational frequency of bonds, thus shifting the Raman peak towards a lower frequency.

Based on spectral deconvolution of the mid-frequency region, it can be concluded that substituting 5 mol% La$_2$O$_3$ for SiO$_2$ causes the depolymerization of the silicate network as evidenced by the lowering of the peak area corresponding to $Q^4\ (\nu_{1150} \& \nu_{1110})$ and an increase in the area of $\nu_{960}\ (Q^2)$ and $\nu_{910}\ (Q^1)$ peaks in the 5La glass. The tendency of RE$_2$O$_3$ to depolymerize the silicate/borosilicate network has been previously reported based on similar Raman spectral transformations observed in alkali silicate$^{31}$ and multicomponent alkali alkaline-earth aluminoborosilicate glasses.$^5$ The increase in $\nu_{1020}$ peak (jointly assigned to Si-O$^0$ and $Q^3\ (\text{La})$) and the corresponding decrease in $\nu_{1060}$ peak ($Q^3\ (\text{Na, Ca})$) upon La$_2$O$_3$ substitution could be due to the formation of Si–O–La linkages at the expense of Si–O–Na (or Si–O–Ca) linkages in the glass network.

High-frequency region (1250–1600 cm$^{-1}$)

The high-frequency region of the Raman spectra of BL and 5La represents peaks from the B–O$^-$ stretching vibrations of BO$_3$ linked to BO$_4$, i.e. $[3]B–O–[4]B\ (\nu_{1410})$ and $[3]B–O–[3]B\ (\nu_{1450})$ units in chain-type metaborate-like structures, and BO$_3$ in boroxol ring units ($\nu_{1500}$). Spectral deconvolution reveals a shift in the $\nu_{1410}$ and $\nu_{1450}$ peaks towards a lower frequency with the substitution of 5 mol% La$_2$O$_3$. The shift is more prominent for $\nu_{1410}$ than $\nu_{1450}$ (cp. $\nu_{1410}$ and $\nu_{1450}$ peak positions in Table 4.2). As discussed for the shift observed in the mid-frequency region corresponding to the $Q^n$ units, the shift in the high-frequency
region could be due to the lowering of spring constant (bond weakening) or higher effective mass around the B–O harmonic oscillator forming $[^3]B–O–[^4]B/[^3]B–O–[^3]B$ linkages. The observed transformations indicate changes in the neighborhood of boron upon La$_2$O$_3$ substitution.

The substitution of 5 mol% La$_2$O$_3$ causes an increase in the $\nu_{1450}$ peak area from 3.5% in BL to 5.9% in 5La glasses. As discussed in the low-frequency region, this increase correlates with the decrease in the peak areas of mixed borosilicate ring units containing BO$_4$ entities ($\nu_2$, $\nu_{586}$, $\nu_{635}$) and BO$_3$ in boroxol rings ($\nu_{800}$), suggesting that La$_2$O$_3$ substitution causes an interconversion of BO$_4$ and BO$_3$(ring) units to BO$_3$(non-ring) units.

4.3.2 $^{27}$Al 1D and Hahn full echo MAS NMR spectroscopy

Figure 4.3a shows the $^{27}$Al 1D MAS NMR spectra of BL and La-containing glasses. The spectra reveal a broad peak around 58 ppm assigned to AlO$_4$ and a bump around 28 ppm, clearly distinguished in the $^{27}$Al Hahn full echo MAS NMR spectra, shown in Figure 4.3b. The $^{27}$Al Hahn full echo spectra of all glasses exhibit an intense peak around 58 ppm with two progressively less intense shoulders around 28 and 0 ppm. The three peaks are assigned to four, five-coordinated, and six-coordinated aluminum (AlO$_4$, AlO$_5$, and AlO$_6$, respectively) based on prior literature.$^{33}$

The simulation of $^{27}$Al Hahn echo spectra allows estimating for each Al species its relative population (%), mean isotropic shift ($\delta_{iso}$), and mean quadrupolar coupling constant ($C_Q$) (Table 4.3). The spectral simulations confirm that only a minor population of Al$^{3+}$ exists as AlO$_5$ (2.7–4.2%) and AlO$_6$ (0.2–0.4%) in the investigated glasses. It is also revealed that the population of AlO$_5$ and AlO$_6$ shows a significant increase (1.4× for AlO$_5$ and 2× for AlO$_6$) upon La$_2$O$_3$ substitution (cp. 5La and BL in Table 4.2) but exhibit no
further change upon MoO$_3$ and ZrO$_2$ substitution (LaMo, LaMoZr2, and LaMoZr4 in Table 4.2). Previous studies on RE-containing aluminosilicate glasses revealed a decrease in the fraction of high-coordinated Al species (AlO$_5$/AlO$_6$) as RE$_2$O$_3$ was substituted for SiO$_2$.\textsuperscript{33-35} It was argued that RE$^{3+}$ act as charge compensators for three neighboring AlO$_4^−$ in these glasses and thus, increasing the RE$_2$O$_3$ concentration stabilizes more AlO$_4$ units in the glass.\textsuperscript{33-35} The discrepancy between our findings and prior literature possibly arises due to the additional presence of Na$^+$ and Ca$^{2+}$ in our BL and 5La glasses. Since La$^{3+}$ exists in an aluminoborosilicate glass in a higher coordination environment (surrounded by 6–8 oxygens),\textsuperscript{5, 36} it requires charge compensation from Na$^+$/Ca$^{2+}$ to be completely integrated into the glass network. Thus, the presence of La$^{3+}$ could induce a competition between LaO$_6^{3−}$ (assuming La$^{3+}$ to exist in a six-coordination environment), AlO$_4^−$, and BO$_4^{−}$ for Na$^+/Ca^{2+}$ charge compensation, thereby converting some of the AlO$_4$ units into higher coordinated Al speciations (AlO$_5$/AlO$_6$). To further explore such a competition between RE$^{3+}$ and Al$^{3+}$ for modifier cations, more systematic studies need to be conducted on aluminoborosilicate-based glass systems in a broad compositional space and varying [RE$_2$O$_3$]/[Al$_2$O$_3$] ratios.

La$_2$O$_3$ substitution also affects the mean isotropic shift ($\delta_{iso}$) and mean quadrupolar coupling constant ($C_Q$) of the La-containing glasses. The peaks corresponding to AlO$_4$ and AlO$_5$ units shift towards a higher ppm (positive $\delta_{iso}$), and $C_Q$ increases upon 5 mol% La$_2$O$_3$ substitution. The effect is more pronounced for AlO$_5$ than AlO$_4$, as revealed by $\delta_{iso}$ shifting from 26.9 to 29.3–29.8 ppm and $C_Q$ increasing from 2.50 to 3.67–4.06 MHz when comparing the AlO$_5$ peak of BL and 5La. Such changes in $\delta_{iso}$ and $C_Q$ with La$_2$O$_3$ substitution also hint towards an increased disorder around AlO$_4$ and AlO$_5$ units.
Figure 4.3: (a) $^{27}\text{Al}$ one pulse MAS NMR and (b) $^{27}\text{Al}$ Hahn full echo MAS NMR of BL and La-containing (5La, LaMo, LaMoZr2, and LaMoZr4) glasses acquired at 20.0 T.

Table 4.3: $^{27}\text{Al}$ Hahn echo MAS NMR spectral parameters and fractional population of AlO$_4$, AlO$_5$, and AlO$_6$ (%) in BL and La-containing glasses. The isotropic chemical shift ($\delta_{\text{iso}}$) is in ppm and quadrupolar coupling constant ($C_Q$) in MHz.

<table>
<thead>
<tr>
<th>ID</th>
<th>AlO$_4$</th>
<th>AlO$_5$</th>
<th>AlO$_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$%\pm 0.6 , \delta_{\text{iso}} \pm 0.02 , C_Q \pm 0.01$</td>
<td>$%\pm 0.2 , \delta_{\text{iso}} \pm 0.12 , C_Q \pm 0.10$</td>
<td>$%\pm 0.1 , \delta_{\text{iso}} \pm 0.10 , C_Q \pm 0.41$</td>
</tr>
<tr>
<td>BL</td>
<td>97.1</td>
<td>60.5</td>
<td>4.41</td>
</tr>
<tr>
<td>5La</td>
<td>95.7</td>
<td>61.6</td>
<td>4.54</td>
</tr>
<tr>
<td>LaMo</td>
<td>96</td>
<td>61.1</td>
<td>4.43</td>
</tr>
<tr>
<td>LaMoZr2</td>
<td>95.7</td>
<td>61.5</td>
<td>4.52</td>
</tr>
<tr>
<td>LaMoZr4</td>
<td>95.4</td>
<td>61.8</td>
<td>4.69</td>
</tr>
</tbody>
</table>

4.3.3 $^{11}\text{B}$ MAS NMR

$^{11}\text{B}$ MAS NMR spectra of the BL glass and the La-containing glasses are shown in Figure 4.4. The spectrum of BL glass in Figure 4.4 is simulated at 9.4 T based on the experimentally acquired spectrum at 16.4 T previously reported in Chapter 2. The $^{11}\text{B}$

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2 Refer to the $^{11}\text{B}$ MAS NMR spectrum of the glass Ca-Mo-0 (BL glass in this chapter) in chapter 2
spectra of all glasses reveal two prominent features: a narrow peak around 0 ppm is from BO₄, and a broad shoulder from 3 to 17 ppm is from BO₃. The BO₄ peak shifts towards higher ppm with the substitution of 5 mol% La₂O₃ for SiO₂ and further exhibits minimal change with MoO₃ and ZrO₂ substitution. A similar higher ppm shift in BO₄ was reported for borosilicate/aluminoborosilicate glasses in which Na⁺ was replaced by high field strength cations like La³⁺ and Ca²⁺. The shift was attributed to changes in the neighborhood of boron atoms.

**Figure 4.4:** ¹¹B 1D MAS NMR spectra of the BL and La-containing glasses. The model spectrum of BL glass is simulated at 9.4 T, based on the previously measured experimental spectrum of the same glass at 16.4 T (reported in Chapter 2, where the glass is labeled as Ca-Mo-0). The spectra of La-containing glasses are experimentally measured at 9.4 T.

Spectral deconvolution is performed on ¹¹B spectra to quantify the N₄ fraction (Table 4.4). For the BL glass, deconvolution is performed by considering two contributions each for BO₃ and BO₄, while for the La-containing glasses, a single contribution is considered for both boron species. The estimated N₄ from the BL glass model spectrum
(0.48, Table 4.4) agrees with the estimated N₄ obtained from the experimental spectrum of Ca-Mo-0 presented in Chapter 2 (0.48–0.49), justifying the adequacy of the model. The substitution of 5 mol% La₂O₃ results in a decrease in N₄ from 0.48 in BL to 0.28 in 5La. The interconversion of BO₄ to BO₃ was observed previously in borosilicate/aluminoborosilicate glasses when La³⁺ or other high field strength cations (e.g., Ca²⁺) were added to these glasses or substituted for the alkali ions (e.g., Na⁺). The interconversion was attributed to the high field strength cations' preference for forming highly charged NBOs rather than charge compensating the BO₄⁻ units. However, Na₂O and CaO are kept constant (12.5 mol% each) in both BL and 5La glass, suggesting that sufficient amounts of these ions to charge compensate the BO₄ units in the glass completely. Yet, a significant decrease is observed in the N₄ fraction, suggesting that the boron environment is being depleted of the charge compensating ions (Na⁺ or Ca²⁺) upon La₂O₃ substitution. In Chapter 2, based on combined ESEEM and MAS NMR analysis, we presented an alternate mechanism responsible for lowering of N₄ in RE-containing peralkaline sodium aluminoborosilicate glasses. It was proposed that REO₆³⁻ competed with AlO₄⁻ and BO₄⁻ anionic species in the glass for associating with the Na⁺, required to maintain its local charge balance. Accordingly, the order of preference for Na⁺ charge compensation was reported to be AlO₄⁻ > REO₆³⁻ > BO₃⁻, with each RE³⁺ requiring 2–4 Na⁺ for their complete integration into the glass network. The lowering of N₄ due to RE₂O₃ addition was then attributed to fewer Na⁺ being available for BO₄⁻ charge compensation. A similar global competition between AlO₄⁻, BO₄⁻, and LaO₆³⁻ units mainly for Na⁺ and a lesser extent for Ca²⁺ appears to exist in our 5La glass, causing a decrease in N₄.
The $^{11}$B spectral deconvolution also reveals that MoO$_3$ substitution only has a modest impact on the boron speciation. Literature suggests that MoO$_4^{2−}$ is preferentially accommodated in the depolymerized region of an alkali/alkaline-earth aluminoborosilicate glass. In this region, MoO$_4^{2−}$ is compensated by A$^+$ or AE$^{2+}$ and does not directly link with the glass network forming B$^{3+}$/Al$^{3+}$/Si$^{4+}$ cations. The insignificant change observed in the N$_4$ fraction of our LaMo glass with respect to the 5La glass can be due to its association with Na$^+$/Ca$^{2+}$, which are either leftover after compensating the AlO$_4^−$, BO$_4^−$, and REO$_6^{3−}$ units or were acting as modifiers in the silicate network. Upon substituting 2–4 mol% ZrO$_2$, the N$_4$ fraction decreases to 0.24 in the glass LaMoZr2 and remains unchanged in LaMoZr4. Zr$^{4+}$ is known to exist in octahedral coordination (surrounded by six oxygens) in aluminoborosilicate glasses, with a net charge of −2e (ZrO$_6^{2−}$). It has been suggested that in an alkali alkaline-earth aluminoborosilicate glass, ZrO$_2$ addition lowers the N$_4$ fraction since ZrO$_6^{2−}$ favorably competes with BO$_4^−$ for A$^+$/AE$^{2+}$ charge compensation.

Table 4.4: $^{11}$B MAS NMR spectral fitting parameters and the estimated N$_4$ [BO$_4$/BO$_3$ + BO$_4$] for the BL and La-containing glasses.

<table>
<thead>
<tr>
<th>ID</th>
<th>BO$_3$</th>
<th>BO$_4$</th>
<th>N$_4$ ± 2 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$δ_{iso}$ ± 0.5 (ppm)</td>
<td>$C_q$ ± 0.2 (MHz)</td>
<td>$δ_{iso}$ (ppm)</td>
</tr>
<tr>
<td>BL</td>
<td>17.8</td>
<td>2.7</td>
<td>-1.76</td>
</tr>
<tr>
<td>5La</td>
<td>17.8</td>
<td>2.6</td>
<td>-0.49</td>
</tr>
<tr>
<td>LaMo</td>
<td>17.4</td>
<td>2.6</td>
<td>-0.52</td>
</tr>
<tr>
<td>LaMoZr2</td>
<td>17.7</td>
<td>2.6</td>
<td>-0.35</td>
</tr>
<tr>
<td>LaMoZr4</td>
<td>17.7</td>
<td>2.6</td>
<td>-0.33</td>
</tr>
</tbody>
</table>
4.3.4 **FID-detected EPR**

Figure 4.5 displays the FID-detected EPR spectra of the LaNd-containing glasses (LaNd, LaNdMo, LaNdMoZr2, and LaNdMoZr4) doped with 0.01 mol% Nd2O3, as well as the spectrum of glass Nd0.001 with a nominal composition of 25 Na2O–10 Al2O3–10 B2O3–55 SiO2–0.001 Nd2O3 (mol%), initially reported in Chapter 3. In Chapter 3, based on EPR spectral simulation, the signal of Nd0.001 was attributed to isolated Nd3+ centers (referred to as the S1 centers) i.e., spin S = 1/2 with a rhombic g-factor = (3.5, 1.94, 1.0), and a g-factor strain, δg = (0.8, 0.3, 0.5). It was revealed that the EPR signal at such a low Nd2O3 concentration of 0.001 mol% led to all the Nd in the glass Nd0.001 being EPR-detectable, i.e., ~100% of Nd in the glass contributed towards the EPR signal corresponding to isolated Nd3+ (S1) centers.

A comparison of the spectra of Nd0.001 with the LaNd-containing glasses (Figure 4.5) reveals that although the Nd2O3 concentration increases by 10× from 0.001 mol% in Nd0.001 to 0.01 mol% in the LaNd-containing series, the overall EPR signal intensity decreases by ~1.5–2.2×. The lower signal intensity of LaNd-containing glasses indicates a substantial Nd population in these glasses, which does not contribute towards the EPR signal. A similar presence of EPR-undetectable Nd was detected at Nd2O3 ≥ 0.01 mol% and also after 5 mol% La2O3 addition in the peralkaline sodium aluminoborosilicate glasses investigated in Chapter 3. In Chapter 3 it was discussed that the EPR-silent Nd exists in a clustered arrangement in which two or more Nd3+ interact via strong spin-exchange interactions, thereby making them EPR-silent. Two possible configurations were
hypothesized for such strong spin-exchanged Nd clusters: (1) short-range NN\textsuperscript{3} clusters with Nd\textsuperscript{3+} interconnected by bridging oxygens (Nd–O–Nd), and (2) longer-range NNN\textsuperscript{4} clusters with Nd\textsuperscript{3+} bridged via diamagnetic La\textsuperscript{3+} (Nd–O–La–O–Nd). While the Nd–O–Nd type clusters were the only EPR-silent entities in the La\textsubscript{2}O\textsubscript{3}-free glasses, both Nd–O–Nd and Nd–O–La–O–Nd type clusters co-existed in the La\textsubscript{2}O\textsubscript{3}-containing glasses. Further, since the La\textsubscript{2}O\textsubscript{3} concentration was at least 50× higher than the Nd\textsubscript{2}O\textsubscript{3} concentration in the glasses investigated in Chapter 3, most EPR-silent Nd clusters expected in these glasses were Nd–O–La–O–Nd. Accordingly, we attribute the EPR-silent Nd in the LaNd-containing glasses to Nd clusters in which two or more Nd\textsuperscript{3+} interact via strong spin-exchange interactions and exist in configurations of the type Nd-O-Nd (Nd:Nd 3–4 Å) and Nd-O-La-O-Nd (Nd:Nd 4–5.5 Å). Henceforth in this study, we refer to these EPR-silent Nd clusters as S3 clusters.

The EPR spectra of the LaNd-containing glasses exhibit similar spectral lineshapes suggesting that the signal arises from similar Nd\textsuperscript{3+} species. The spectra reveal a low field shoulder at $g = 4.23$ assigned to Fe\textsuperscript{3+}, arising as an impurity either from the precursors used for glass synthesis or from the metallic sample holder used for cutting glass specimen for EPR analysis. Additionally, after 3 mol% MoO\textsubscript{3} substitution, the spectra of glasses LaNdMo, LaNd2Zr, and LaNd4Zr, reveal a sharp peak at $g = 1.91$ attributed to Mo\textsuperscript{5+}. The fraction of Mo\textsuperscript{5+} is estimated to be 0.003% of the total MoO\textsubscript{3} concentration based on the EPR spectral simulation discussed in section 4.3.4.1. Further, although the Nd\textsubscript{2}O\textsubscript{3} concentration is kept constant (0.01 mol%) for all the LaNd-containing glasses, a decrease

\textsuperscript{3} NN – next nearest neighbor
\textsuperscript{4} NNN – next-next nearest neighbor
in the signal intensity is observed after ZrO$_2$ substitution in glasses LaNdMoZr$_2$ and LaNdMoZr$_4$. The lowering of the EPR-signal intensity indicates that ZrO$_2$ is promoting the formation of EPR-silent S3 clusters.

![Figure 4.5: FID-detected EPR spectra of LaNd-containing glasses: LaNd, LaNdMo, LaNdMoZr$_2$, and LaNdMoZr$_4$ doped with 0.01 mol% Nd$_2$O$_3$. The spectral intensities in each sample were normalized per unit sample weight and also corrected for differences in spin relaxation times and other instrumental settings as described in the experimental section. All the spectra were acquired at 4.6 K.](image)

Chapter 3 presented a mechanistic model explaining the high tendency for RE$^{3+}$ to cluster in alkali aluminoborosilicate glasses. The tendency for REs to cluster is controlled by a competition between AlO$_4$$^-$, BO$_4$$^-$ and REO$_6$$^{3-}$ anionic species for charge compensation by the Na$^+$ ion. The preference for Na$^+$ charge compensation follows the order AlO$_4$$^-$ > REO$_6$$^{3-}$ > BO$_4$$^-$. In glasses LaNdMoZr$_2$ and LaNdMoZr$_4$, there is an additional presence of Zr$^{4+}$ apart from Al$^{3+}$, B$^{3+}$, and RE$^{3+}$. Based on prior literature, ZrO$_6$$^{2-}$ requires the charge compensation from either two Na$^+$ or one Ca$^{2+}$ present in the glass for maintaining its charge neutrality. Thus, ZrO$_6$$^{2-}$ competes with REO$_6$$^{3-}$ and BO$_4$$^-$ for the
Na⁺/Ca²⁺ in these glasses. Given the simultaneous presence of ZrO₆²⁻, REO₆³⁻, AlO₄⁻, and BO₄⁻ units in our glasses LaNdMoZr2 and LaNdMoZr4, even stronger competition for Na⁺ or Ca²⁺ charge compensation is expected to exist than what was observed in our RE₂O₃ containing sodium aluminoborosilicate glasses investigated in Chapter 3. Such a competition would further promote clustering of EPR-silent (S3) RE clusters in these glasses.

It can be observed in Figure 4.5 that the spectra of glasses LaNdMo, LaNdMoZr2, and LaNdMoZr4 have their EPR signals shifted slightly towards a higher magnetic field when compared to the signal of LaNd0.001. A similar spectral shift was observed in our sodium aluminoborosilicate glasses with increasing Nd₂O₃ and La₂O₃ concentrations (Chapter 3). Based on previous studies, and the spectral decomposition of the FID-detected spectra of the RE₂O₃ containing sodium aluminoborosilicate glasses presented in Chapter 3, we had attributed the shift to the presence of EPR-detectable Nd clusters (referred to as S2) with strong dipolar-coupling (weaker exchange-coupling) between the Nd³⁺ within the cluster. These clusters were hypothesized to be NNN clusters, i.e., Nd-O-X-O-Nd, wherein X = B/Al/Si. We hypothesize a similar presence of dipole-coupled S2 clusters in our LaNd-containing glasses contributing towards the slight high-field shift in the spectra of LaNdMo, LaNdMoZr2, and LaNdMoZr4 glasses.

4.3.4.1 FID-detected EPR spectral decomposition

Based on the above discussion of the observed spectral changes in the EPR signal of the LaNd-containing glasses and our previous quantitative EPR analysis performed on RE₂O₃ containing sodium aluminoborosilicate glasses in Chapter 3, we deconvoluted the FID-detected EPR spectra of LaNd-containing glasses using a two-component model as
shown in Figure 4.6. The EPR spectra of the LaNd-containing glasses are decomposed into signal S1 arising from the isolated Nd$^{3+}$ centers and signal S2 from the dipole-coupled Nd clusters. Signal S2 also accounts for the presence of the Fe$^{3+}$ impurity ($g = 4.23$) and a sharp peak arising from Mo$^{5+}$ ($g = 1.91$) estimated to be 0.003% of the total MoO$_3$ concentration. The blue circles with perpendicular lines at 350 and 550 mT correspond to the center of gravity of signal S1 and S2, respectively. The overall EPR signal is a simple weighted sum of S1 and S2.

![Figure 4.6](image)

**Figure 4.6:** Spectral decomposition of FID-detected EPR signal of LaNd-containing glasses. The spectra for the glasses have been deconvoluted using two components (a) S1 (isolated Nd centers) depicted by the dotted red line and (b) S2 (Nd clusters) depicted by the dotted yellow line. Additionally, the fraction of isolated Nd$^{3+}$ centers (S1) and dipole-coupled Nd clusters (S2) have been estimated for each glass. The spectra of all glasses also feature a low field shoulder at $g = 4.23$ attributed to Fe$^{3+}$. The spectra of glasses LaNdMo, LaNdMoZr2, and LaNdMoZr4 additionally exhibit a sharp peak at $g = 1.91$ from Mo$^{5+}$ whose estimated concentration is 0.003% of the total MoO$_3$ concentration in these glasses.
The spectral decomposition reveals that signal S1 (isolated Nd$^{3+}$ centers) dominates the overall EPR signal for all glasses with only trace contributions from the signal S2 (dipole-coupled S2 clusters) (Figure 4.6). Also, it can be observed that the majority of the Nd$^{3+}$ in these glasses are EPR-silent since the combined EPR signal from S1 and S2 (EPR-detectable Nd) accounts for only 5.5–8.5% of the total Nd$^{3+}$ content in these LaNd-containing glasses. Further, it can be observed that the EPR signal (S1 + S2) decreases abruptly for the glass LaNd2Zr (Figure 4.6c), the reasons for which are unclear at this point and would require further studies. Based on this reduced signal for LaNd2Zr (Figure 4.6c), it appears that glass containing 2 mol% ZrO$_2$ (LaNdMoZr2) has a higher tendency for RE clustering than the glass containing 4 mol% ZrO$_2$ (LaNdMoZr4). To probe the coordination environment of the EPR-visible Nd centers, a two-pulse ESEEM experiment has been performed on the LaNd-containing glasses.

### 4.3.5 ESEEM spectroscopy

Figures 4.7a and 4.7b present the ESEEM spectra of LaNd-containing glasses (LaNd, LaNdMo, LaNdMoZr2, and LaNdMoZr4) acquired at two magnetic fields, 350 and 550 mT. The spectra of all glasses measured at both fields represent the signal from only the S1 centers (isolated Nd$^{3+}$) since these are the dominant species observed in the FID-detected EPR signal shown in Figure 4.6. The ESEEM spectra resolve several peaks from the magnetic isotopes $^{10}$B (nuclear spin $I = 3$, natural abundance 20%), $^{11}$B ($I = 3/2$, 80%), $^{23}$Na ($I = 3/2$, 100%), and $^{27}$Al ($I = 5/2$, 100%), as marked in Figure 4.7. The signal from $^{43}$Ca ($I = 7/2$, 0.135%) and $^{29}$Si ($I = 1/2$, 4.68%) could not be detected due to their low natural abundance. Our ESEEM spectra show no resolvable contribution from $^{139}$La spins, even though the natural abundance of this isotope (99.9%) and its spin ($I = 7/2$) are both
high. The lack of detectable ESEEM signal from $^{139}$La spins in the currently investigated glasses is consistent with our previously reported ESEEM spectra for the Nd$_2$O$_3$ and La$_2$O$_3$ containing sodium aluminoborosilicate glasses in Chapter 3. A similar argument presented in Chapter 3 would be responsible for the absence of $^{139}$La ESEEM signatures.

![ESEEM spectra](image)

**Figure 4.7:** ESEEM spectra of glasses LaNd, LaNdMo, LaNdMoZr2, and LaNdMoZr4 obtained at (a) 350 mT and (b) 550 mT.

The ESEEM spectral simulation is performed using the two-shell model approximation proposed by Dikanov et al., described in Appendix 3.1 in Chapter 3. Based on the ESEEM simulation, the proximity distance ($R_1$) and the number of nuclei ($N_1$) in the first coordination shell (3–4.5 Å) around the isolated Nd$^{3+}$ (S1 centers) of the LaNd-containing glasses are reported in Table 4.5.

The ESEEM data (Table 4.5) reveals that the first-shell coordination environment of the isolated Nd$^{3+}$ (S1 centers) in glasses LaNd, LaNdMo, and LaNdMoZr4 is surrounded by on average 1.5 boron ($^{10/11}$B), 2 sodium ($^{23}$Na), and 0.7 aluminum ($^{27}$Al). The glass LaNdMoZr2 (containing 2 mol% ZrO$_2$) has a slightly different first-shell coordination environment for its isolated Nd$^{3+}$ centers (S1), slightly enriched in boron (1.7 $^{10/11}$B) and depleted of aluminum (0.5 $^{27}$Al). It is important to note that although the $^{29}$Si signal is
absent in the ESEEM spectra of the investigated glasses, their presence in the first coordination shell environment around the Nd$^{3+}$ cannot be discounted. Assuming a six-coordination environment for the RE$^{3+}$ (Nd$^{3+}$, La$^{3+}$) in these glasses, and considering the ESEEM results (Table 4.5), it can be suggested that the first coordination shell of the Nd$^{3+}$ in the isolated centers (S1) must have on average 3.8 Si for charge neutralization.

Table 4.5: Proximity distances ($R_1$) and numbers of nuclear spins ($N_1$), including $^{10/11}\text{B}$, $^{23}\text{Na}$, and $^{27}\text{Al}$, in the first (proximal) coordination shell of Nd$^{3+}$ ions in the S1 and S2 centers, as derived from the ESEEM simulations.

<table>
<thead>
<tr>
<th></th>
<th>$^{10}$B or $^{11}$B</th>
<th>$^{23}$Na</th>
<th>$^{27}$Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1 centers</td>
<td>$R_1 = 3.6 , \text{Å}$</td>
<td>$R_1 = 3.2 , \text{Å}$</td>
<td>$R_1 = 3.6 , \text{Å}$</td>
</tr>
<tr>
<td>(LaNd, LaNdMo, LaNdMoZr4)</td>
<td>$N_1 = 1.5$</td>
<td>$N_1 = 2$</td>
<td>$N_1 = 0.7$</td>
</tr>
<tr>
<td>S1 centers</td>
<td>$R_1 = 3.6 , \text{Å}$</td>
<td>$R_1 = 3.2 , \text{Å}$</td>
<td>$R_1 = 3.6 , \text{Å}$</td>
</tr>
<tr>
<td>(LaNdMoZr2)</td>
<td>$N_1 = 1.7$</td>
<td>$N_1 = 2$</td>
<td>$N_1 = 0.5$</td>
</tr>
</tbody>
</table>

The coordination environment of the S1 (isolated Nd$^{3+}$) centers observed in these LaNd-containing glasses (Table 4.5) is significantly different from the environment reported in Chapter 3 for glasses $[25 \text{Na}_2\text{O}– 10 \text{Al}_2\text{O}_3– 10 \text{B}_2\text{O}_3– 55 \text{SiO}_2]_{(100-x-y)} \times \text{Nd}_2\text{O}_3$. $y \text{La}_2\text{O}_3$ (x = 0–0.1 mol%, y = 0–5). For the glasses investigated in Chapter 3, each isolated S1 center had on average 4 Na, 0.4–0.7 Al, and 0.2–0.4 B in their first-shell coordination. Thus, the environment of S1 in those RE$_2$O$_3$ containing sodium aluminoborosilicate glasses was concluded as being Na/Si-rich. The environment of isolated S1 centers in the LaNd-containing glasses is significantly depleted of Na (by two-folds) compared to the S1 centers for the glasses investigated in Chapter 3. The Na depletion can be due to the additional presence of Ca in these glasses, which would also be involved in the charge compensation
of isolated Nd\textsuperscript{3+}, although ESEEM cannot detect its presence due to the low natural abundance of the paramagnetic \textsuperscript{43}Ca nuclei (0.135%).

4.3.6 *Density, oxygen molar volume, and glass transition temperature*

Figures 4.8a, 4.8b, and 4.8c display the evolution of density, oxygen molar volume \(V_m(O)\), and glass transition temperature \(T_g\), respectively, of the Nd-containing and La-containing glasses, as well as the BL glass. All three properties (density, \(V_m(O)\), and \(T_g\)) exhibit a likewise trends for both sets of glasses with the progressive substitution of 5 mol\% \(\text{RE}_2\text{O}_3\) (\(\text{RE} = \text{Nd or La}\)), 3 mol\% MoO\(_3\), and 2–4 mol\% ZrO\(_2\). These observations support the similar Raman spectral evolutions observed for these glasses (Figure 4.1), confirming that both Nd\textsuperscript{3+} and La\textsuperscript{3+} have a similar impact on the structure of the BL glass.

As observed in Figure 4.8a, the density increases sharply with the substitution of \(\text{RE}_2\text{O}_3\) (5RE), and then more gradually with the substitution of MoO\(_3\) (REMo) and ZrO\(_2\) (REMoZr\(_2\) and REMoZr\(_4\)). A higher density for these glasses with respect to the BL glass can be attributed to the higher molecular weights of Nd\(_2\)O\(_3\) (336.48 g/mol), La\(_2\)O\(_3\) (325.8 g/mol), MoO\(_3\) (143.94 g/mol), and ZrO\(_2\) (123.218 g/mol) as compared to SiO\(_2\) (60.08 g/mol).

\(V_m(O)\) is calculated based on the density and batched glass composition (Figure 4.8b). \(V_m(O)\) increases steadily with the substitution 5 mol\% \(\text{RE}_2\text{O}_3\) and 3 mol\% MoO\(_3\) for SiO\(_2\) in the BL glass for both series of glasses. Previously, an increase in \(V_m(O)\) was observed for a binary sodium silicate glass with the substitution of La\(_2\)O\(_3\) for SiO\(_2\) on an equimolar basis.\textsuperscript{49} The increase was attributed to the higher number of bonds formed as each SiO\(_4\) tetrahedron was replaced by two higher-coordinated lanthanum-oxygen units (6–8 oxygens surrounding the La\textsuperscript{3+}).\textsuperscript{49} In our 5RE glasses, 5 mol\% SiO\(_2\) is being replaced
by RE$_2$O$_3$ resulting in many more bonds being formed in the glass network, which explains the higher $V_m$(O) of the 5RE glasses. The increase in $V_m$(O) observed for the REMo glasses could be due to MoO$_4^{2-}$ causing the depolymerization of the aluminoborosilicate network as previously proposed by Short et al.\textsuperscript{38} and thus opening up the network. Eventually, upon the substitution of 2–4 mol\% ZrO$_2$, a steady decrease in $V_m$(O) is observed for glasses REMoZr$_2$ and REMoZr$_4$. The decrease in $V_m$(O) with increasing ZrO$_2$ concentration suggests that the oxygen atoms network becomes increasingly more compact for glasses REMoZr$_2$ and REMoZr$_4$, as has also been previously observed by Quintas et al.\textsuperscript{4} for ZrO$_2$ addition to a RE-containing soda-lime aluminoborosilicate glass.

Figure 4.8c depicts the evolution of $T_g$ for the BL, Nd-containing, and La-containing glasses. The $T_g$ has been derived from the onset of the endothermic dip in the heat flow versus temperature curves of these glasses obtained using DSC, and their values are reported in Table 4S1. Based on Figure 4.8c and Table 4S1, it can be observed that $T_g$ increases from 578 °C in the BL glass to 603 °C (5Nd) or 596 °C (5La) after the substitution of 5 mol\% Nd$_2$O$_3$ or La$_2$O$_3$ for SiO$_2$. A similar increase in $T_g$ with rare-earth (RE$_2$O$_3$) addition to alkali (A)/alkaline-earth (AE) silicates, regardless of the cation being replaced (A/AE/Si),\textsuperscript{49-51} and multicomponent alkali alkaline earth aluminoborosilicate glasses were reported in the literature.\textsuperscript{6, 52} In these glasses, the increase in $T_g$ with increasing RE$_2$O$_3$ concentration was attributed to the higher cation field strength of the trivalent RE$^{3+}$ resulting in stronger RE–O$^-$ bonds being formed at the expense of the weaker A–O$^-$ / AE–O$^-$ bonds.\textsuperscript{6, 49-52} Raman analysis for the BL and 5La glasses presented in section 4.3.1.1 indeed suggested the formation of Si–O–La linkages at the expense of Si–O–Na or Si–O–Ca linkages with La$_2$O$_3$ substitution for SiO$_2$. The stronger Si-O-La linkages would have
contributed towards an increase in $T_g$. The presence of AlO$_5$ and AlO$_6$ units could also contribute towards an increase in $T_g$ as reported in the literature.$^{33-35}$ However, the fractional population of AlO$_5$ and AlO$_6$ in our 5La glass are very low (AlO$_5$ = 3.9% and AlO$_6$ = 0.6%) to alone cause the observed ~18 °C increase in $T_g$ with respect to the BL glass. Nevertheless, the increase in $T_g$ of 5RE glasses seems to be a cumulative effect of the formation of strong RE–O–Si linkages and higher coordination aluminum speciations (AlO$_5$ and AlO$_6$) in the glass.

The substitution of 3 mol% MoO$_3$ in glasses 5Nd and 5La causes an abrupt decrease in $T_g$ to 588 °C in NdMo or 582 °C in LaMo. A decrease in $T_g$ with MoO$_3$ addition was previously observed in sodium borosilicate glasses with increasing MoO$_3$ concentration (0–4 mol%).$^{53}$ Regarding MoO$_3$ in alkali alkaline-earth borosilicate/aluminoborosilicate glasses, literature reveals$^{27, 54, 55}$ that Mo tends to depolymerize the aluminoborosilicate glass and increase its susceptibility towards a crystallization. Thus, in REMo glasses, the decrease in $T_g$ with MoO$_3$ addition can be attributed to the Mo$^{6+}$ ions inducing depolymerization of the glass network.

Eventually, the substitution of 2 and 4 mol% ZrO$_2$ increases the $T_g$ steadily for the glasses RE2Zr and RE4Zr where RE = Nd or La. A similar observation was reported by Quintas et al. in their ZrO$_2$ containing soda-lime aluminoborosilicate glasses.$^4$ Based on Raman and MAS NMR analysis and optical basicity considerations, Quintas et al.$^4$ argued that the ZrO$_6^{2-}$ in these glasses was charge compensated by Na$^+$. Some of the charge compensating Na$^+$ were initially (before ZrO$_2$ addition) acting as a modifier in the silicate network of the aluminoborosilicate glass. Hence, ZrO$_2$ addition reduced the NBO content, thereby reticulating the silicate network, which raised the $T_g$ of the glass. A similar
structural reorganization appears to be induced by ZrO$_2$ in our REMoZr2 and REMoZr4 glasses leading to an increase in their $T_g$.

**Figure 4.8**: Variation of (a) density, (b) $V_m(O)$ (oxygen molar volume), and (c) $T_g$ (glass transition temperature) of the Nd-containing and La-containing glasses.
4.4 Impact of RE$^{3+}$, Mo$^{6+}$, and Zr$^{4+}$ on the Na$_2$O-CaO-Al$_2$O$_3$-B$_2$O$_3$-SiO$_2$ glass

The impact of adding 5 mol% RE$_2$O$_3$ (Nd$_2$O$_3$/La$_2$O$_3$), 3 mol% MoO$_3$, and 2–4 mol% ZrO$_2$ by replacing an equimolar concentration of SiO$_2$ on the structure of 12.5 Na$_2$O–12.5 CaO–5.0 Al$_2$O$_3$–10.0 B$_2$O$_3$–55.0 SiO$_2$ (mol%) model nuclear waste glass is investigated using combined Raman, MAS NMR, FID-detected EPR, and ESEEM spectroscopies. The RE-, Mo-, Zr-free BL glass is homogenous, as per the criterion proposed for designing homogenous alkali aluminoborosilicate glasses, specifically $[\text{Na}_2\text{O}]_{\text{ex}}/[\text{Al}_2\text{O}_3] > 0.5$, where $[\text{Na}_2\text{O}]_{\text{ex}} = [\text{Na}_2\text{O}] - [\text{Al}_2\text{O}_3]$. This criterion has been further modified by Caurant et al. to account for the presence of CaO, specifically glasses with $([\text{Na}_2\text{O}] + [\text{CaO}])_{\text{ex}}/[\text{Al}_2\text{O}_3] > 0.5$ should be considered homogenous. The BL glass has $[\text{Na}_2\text{O}]_{\text{ex}}/[\text{Al}_2\text{O}_3] = 0.75$, and $([\text{Na}_2\text{O}] + [\text{CaO}])_{\text{ex}}/[\text{Al}_2\text{O}_3] = 2$, and is thus homogenous and not expected to exhibit any microscopic glass-in-glass phase separation.

RE$_2$O$_3$ substitution to the homogenous BL glass is observed to cause an unmixing of the borate-rich and silicate-rich regions, based on the reduced fractional population of Si-O-$^{[4]}$B linkages in 5La than BL, as estimated from the Raman spectra analysis discussed in section 4.3.1.1. The $^{11}$B/$^{27}$Al MAS NMR studies reveal that the addition of La$_2$O$_3$ reduces the N$_4$ fraction (decreases the population of BO$_4$ units) from 48% in BL to 28% in 5La, and also cause a slight increase in the population of AlO$_5$ and AlO$_6$ units in the 5La glass. The decrease in N$_4$ and the increase in AlO$_5$/AlO$_6$ species suggests that RE$^{3+}$ tends to redistribute the network modifying Na$^+$ and Ca$^{2+}$ and thus limits their availability for the BO$_4^-$ and, to a lesser extent, the AlO$_4^-$ anionic species. The quantitative FID-detected EPR spectral analysis reveals a high tendency for the RE$^{3+}$ to cluster in the aluminoborosilicate glass matrix. Even at 0.01 mol% Nd$_2$O$_3$ concentration, more than 90% of Nd$^{3+}$ in the LaNd
glass exist as dipole-coupled (S2) and spin-exchange-coupled clusters (S3). Extensive RE clustering indicates a non-uniform distribution of these ions in the alkali alkaline-earth aluminoborosilicate glass.

The first-shell coordination of the isolated S1 (Nd$^{3+}$), as revealed from the ESEEM analysis, contains on average 1.5 B, two Na, and 0.7 Al. Although Si cannot be detected due to the low natural abundance of $^{29}$Si nuclei, on average, 3.8 silicon can be expected (assuming RE$^{3+}$ exists in a six-coordination geometry) in the first-shell coordination of the S1 center for maintaining the charge balance around the Nd$^{3+}$. Thus, it can be suggested that the isolated S1 centers are preferentially located in a Na-B-Si-rich environment. In RE$_2$O$_3$ doped sodium aluminoborosilicate glasses, investigated in Chapter 3, the isolated S1 centers were located in an environment that contained more Na (on average 4) and very few (0.2–0.4 B). As the concentration of RE$_2$O$_3$ in these glasses were raised, REs were observed to cluster into EPR-detectable S2 and EPR-silent S3 forms, with the environment of RE$^{3+}$, progressively becoming richer in B and depleted of Na. Based on this trend and the significant Na depletion and B enrichment observed for the S1 centers in the LaNd glass, we propose the EPR-detectable S2 and EPR-silent S3 clusters in the LaNd glass to be located in a more B-enriched and Na-depleted environment. Combining our Raman, MAS NMR, and EPR analysis, we thus propose that RE$^{3+}$ preferentially enter the Na-B-Si-rich region of the alkali alkaline-earth aluminoborosilicate glass where they exist as isolated RE$^{3+}$ centers. However, the tendency to form these isolated RE$^{3+}$ centers only exist at very low RE$_2$O$_3$ concentrations due to the limited availability of Na. At higher RE$_2$O$_3$ concentrations, most RE$^{3+}$ prefer to form RE-RE clusters with strong exchange-coupling between the RE$^{3+}$ within the cluster. These RE clusters are located in a B-rich environment
with few Na and can be viewed as nano-scale glass phases of RE-Na-B dispersed in the leftover RE-B-depleted glass matrix.

The substitution of MoO$_3$ in the 5RE glass is observed to cause minimal changes in the speciation of $^{11}$B/$^{27}$Al and the clustering tendency of RE$^{3+}$ in our glasses. These results can be viewed in terms of the previously reported structural role for MoO$_3$ in alkali/alkaline-earth aluminoborosilicate glasses.$^{27,38,54}$ Accordingly, Mo is known to enter as MoO$_4$$^{2-}$, which is accommodated in the depolymerized region of the aluminoborosilicate glass. In this depolymerized region, MoO$_4$$^{2-}$ is charge compensated by Na$^+/Ca^{2+}$ and does not directly link to the network forming B, Al, Si atoms. Our REMo glasses exhibit a decrease in their $T_g$ compared to the Mo-free, 5RE glasses. The lowering of $T_g$ suggests the depolymerization of the aluminoborosilicate network when 3 mol% MoO$_3$ is added to 5RE glasses. The insignificant changes observed in the $^{11}$B/$^{27}$Al speciations upon MoO$_3$ addition suggest that MoO$_4$$^{2-}$ does not scavenge the Na$^+/Ca^{2+}$ required for its local charge compensation from BO$_4^-$ or AlO$_4^-$.

Further, the possibility of MoO$_4$$^{2-}$ scavenging its Na$^+/Ca^{2+}$ from the Si-O-Na/Ca linkages also seems unlikely, as such a mechanism would have caused a reticulation of the silicate network due to removal of NBO’s and thus would have raised the $T_g$ of the REMo glasses. We thus hypothesize that MoO$_4$$^{2-}$ achieves its local charge compensation from the RE$^{3+}$ ions, which are a part of the RE-B-Na nano-scale glass phases, as mentioned in the previous paragraph. Thus, MoO$_4$$^{2-}$ oxyanions enter the phase separated RE$_2$O$_3$ containing alkali alkaline-earth aluminoborosilicate glass and are accommodated in the RE-B-Na-rich domains forming a RE-Mo-B-Na glass phase.

The substitution of ZrO$_2$ to the RE$^{3+}$ and Mo$^{6+}$ containing REMo and LaNdMo glasses reveals significant structural modification occurring in the aluminoborosilicate
network. 2 mol% ZrO₂ substitution decreases the fraction of N₄ from 32% in LaMo to 25% as observed in LaMoZr2 glass as per our ¹¹B MAS NMR analysis (section 4.3.3; Table 4.4). Further, 2 mol% ZrO₂ addition also reveals an increase in the fraction of EPR-silent (S3) Nd clusters from ~92% in LaNdMo to ~95% in LaNdMoZr2 glass. As mentioned above, RE clustering is promoted due to a competition between several anionic species (AlO₄⁻, BO₄⁻, REO₆³⁻) for the charge compensating Na⁺/Ca²⁺ in the glass. Given this competition and a reduced N₄ fraction observed for our LaMoZr2 glass (compared to 5La glass), it can now be proposed that Zr⁴⁺ also enters the competition for the charge compensating ions along with Al³⁺, B³⁺, and RE³⁺ hence decreases the N₄ and promotes RE clustering. Although, further increasing the ZrO₂ concentration to 4 mol% does not cause a change in either N₄ or the clustering tendency of REs.

4.5 Conclusion

In this work, a suite of characterization techniques including Raman, MAS NMR, FID-detected EPR, and ESEEM spectroscopies are employed to understand the impact of adding RE₂O₃, MoO₃, and ZrO₂ on the structure of alkali alkaline-earth aluminoborosilicate-based mode nuclear waste glasses. The substitution of RE₂O₃ is observed to induce an unmixing of the homogenous alkali alkaline-earth aluminoborosilicate glass into borate-rich and silicate-rich regions. It is also observed that Nd³⁺ is non-uniformly distributed in the glass and speciates into three different forms: isolated Nd³⁺ centers, dipole-coupled Nd clusters (Nd-O-X-O-Nd, where X = B/Al/Si), and spin-exchanged-coupled Nd clusters of two types – Nd-O-Nd and Nd-O-La-O-Nd. The majority of REs in the alkali alkaline-earth aluminoborosilicate glass exist as spin-exchanged coupled RE clusters, as quantitative EPR spectral analysis estimates more than
90% of Nd$^{3+}$ to exist as the exchange-coupled clusters. ESEEM analysis of the EPR-active isolated Nd$^{3+}$ centers suggest their first-shell coordination environment to be rich in sodium (two Na) and boron (1.5 B). The environment of Nd clusters is argued to become more enriched in boron and depleted of sodium as clustering of RE$^{3+}$ lowers their dependence on Na$^+$ charge compensation. The substitution of MoO$_3$ to the RE$_2$O$_3$ containing alkali alkaline-earth aluminoborosilicate glass lowers the $T_g$, suggesting that MoO$_4^{2-}$ depolymerizes the glass network. Further, MoO$_4^{2-}$ causes an insignificant change in the fractional population of BO$_4$, i.e., it does not scavenge the Na$^+$/Ca$^{2+}$ around the boron and thus is proposed to coordinate with RE$^{3+}$ for maintaining its charge balance. ZrO$_2$ substitution is found to decrease the fractional population of BO$_4$, increase the $T_g$, and promote RE$^{3+}$ clustering, although only up to 2 mol% [ZrO$_2$] and further increasing the concentration to 4 mol% does not induce these changes.

Based on these results and our understanding of RE partitioning and clustering in sodium aluminoborosilicate glasses discussed in Chapter 3, a mechanism governing the incorporation of RE$^{3+}$ and Mo$^{6+}$ in these alkali alkaline-earth aluminoborosilicate-based model nuclear waste glasses is proposed:

(i) RE$^{3+}$ phase separates a homogenous alkali alkaline-earth aluminoborosilicate glass into borate-rich and silicate-rich phases and preferentially clusters into the borate-rich phase. RE$^{3+}$ thus forms RE-B-rich nanoscale glass phases non-uniformly distributed within a glassy matrix depleted of the same elements (RE, B).

(ii) MoO$_4^{2-}$ enters the phase separated RE$_2$O$_3$ containing alkali alkaline-earth aluminoborosilicate glass and preferentially enters the RE-B-rich phases, forming
RE-Mo-B phases within the glass. The charge neutrality of MoO$_4^{2-}$ in these phases is achieved by charge compensation from the RE$^{3+}$. 
Reference


4.7 Supplementary Information

*Table 4S1*: Glass transition temperature recorded for BL, Nd-containing, and La-containing glasses using differential scanning calorimetry.

<table>
<thead>
<tr>
<th>Glass</th>
<th>( T_g )</th>
</tr>
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<tbody>
<tr>
<td>BL</td>
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</tr>
<tr>
<td>5Nd</td>
<td>603</td>
</tr>
<tr>
<td>NdMo</td>
<td>588</td>
</tr>
<tr>
<td>NdMoZr2</td>
<td>596</td>
</tr>
<tr>
<td>NdMoZr4</td>
<td>607</td>
</tr>
<tr>
<td>5La</td>
<td>596</td>
</tr>
<tr>
<td>LaMo</td>
<td>582</td>
</tr>
<tr>
<td>LaMoZr2</td>
<td>587</td>
</tr>
<tr>
<td>LaMoZr4</td>
<td>601</td>
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</tbody>
</table>
Chapter 5. Ruthenium Solubility and its Impact on the Crystallization behavior and Electrical Conductivity of MoO$_3$-containing Borosilicate-Based Model High-Level Nuclear Waste Glasses

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Abstract
The present study focuses on investigating the solubility of RuO$_2$ in a borosilicate-based model high-level waste glass and understanding its impact on the crystallization behavior and electrical conductivity of the resulting vitrified waste forms. The solubility limit of RuO$_2$ in the investigated glass composition has been determined to be 460 ppm by weight. The higher concentration of RuO$_2$ results in sub-micron sized Ru-rich inclusions in the glassy matrix, which eventually agglomerate to form needle-like and polyhedral RuO$_2$ crystals. It is observed that RuO$_2$ selectively promotes the crystallization of the rare-earth apatite phase over powellite. The as-synthesized RuO$_2$-containing glasses exhibit semiconducting behavior with a similar level of electrical conductivity below the glass transition. The percolation of non-uniformly distributed RuO$_2$ inclusions may result in a formation of short-range low-resistive conduction pathways in the host glass matrix leading to an apparent metallic-like behavior of selected thin samples with the highest ruthenium content.
5.1 Introduction

The United States, as of 2016, has accumulated around 77,900 metric tons (MT) heavy metal (MTHM) of spent nuclear fuel generated from commercial nuclear power production, which is stored in temporary on-site facilities across the country.\(^1\) As a significant fraction of this spent fuel is fissionable and thus, can be reused for power generation, the U.S. Department of Energy (DOE) is considering its reprocessing by the Transuranic Extraction (TRUEX\(^{\text{plus}}\)) process.\(^2\) The TRUEX\(^{\text{plus}}\) process is expected to generate the following three secondary HLW streams: (i) alkalis (A)/alkaline-earth (AE) (e.g., \(^{137}\)Cs, \(^{90}\)Sr)-rich, (ii) rare-earths (RE) (e.g., La, Nd)-rich, and (iii) undissolved solids (UDS) (e.g., Mo, Zr, platinum group metals), which have to be safely disposed to avoid risks of environmental contamination due to spillage.\(^2,3\) While borosilicate glass is the most widely accepted matrix for immobilization of HLW worldwide, including the United States (for legacy defense waste),\(^4\) the low solubility of UDS, specifically MoO\(_3\) and platinum group metals (PGM), in the borosilicate glass matrix limits the waste loading, thus, making it a less attractive option for the immobilization of the nuclear waste. Due to this reason, the US DOE is considering alternative waste forms with higher waste loadings and comparable or better long-term performance, than borosilicate glass, and ease of processing, to immobilize the projected commercial wastes. (compared to borosilicate glass), ease of processing, and comparable or better long-term performance (in comparison to borosilicate glass) to immobilize the projected commercial wastes.\(^2\) In this pursuit, the US DOE has proposed a borosilicate-based glass-ceramic with expected waste loading of \(~45\) mass\% (compared to \(~18\) mass\% for borosilicate glass) for the immobilization of the commercial HLW.\(^2\) The proposed glass-ceramic is expected to improve the retention of
MoO$_3$ by undergoing a controlled crystallization process into the targeted phase of powellite (AEMoO$_4$), rare-earth apatite (AE$_3$RE$_{(10-x)}$Si$_6$O$_{26}$), and rare-earth borosilicates (RE$_5$BSi$_2$O$_{13}$). However, the presence of PGM, in particular, ruthenium oxide, is still a challenge due to their very low solubility, high density, and high electrical conductivity in the glass melt, thus, impacting the rheology of the melt and the performance of the waste melter. According to an estimate, the total concentration of PGM in the HLW is expected to be ~7.4 kg/tU where ruthenium oxide will constitute more than 45% of the total PGM concentration. If overlooked, the issues related to the presence of PGM, especially ruthenium oxides, can affect the functionality of the glass-ceramic and degrade the performance of the melter used for their processing. Thus, understanding the behavior of UDS like Ru in borosilicate glasses and glass-ceramics is highly relevant for designing optimized nuclear waste form compositions.

In the preface to the technical details of this work, it is essential to understand the challenges Ru poses for HLW immobilization in borosilicate glasses/glass-ceramics. Ru is reported to exist in multiple oxidation states of 0, III, IV, VI, VII, and VIII in glasses depending on the chemistry and oxygen partial pressure of the melt. In HLW glasses, Ru has been reported to exist primarily as RuO$_2$ (IV) and may contain a minor concentration of metallic Ru (0). Ru (IV) has been reported to be the stable oxidation state of ruthenium in borosilicate melts and is known to be sparingly soluble in the melts with limits ranging from tens to a few thousand parts per million (ppm) by weight. Above its solubility limit, it precipitates in the borosilicate melt and forms polyhedral or needle-like RuO$_2$ crystals with rutile structure which exhibit high density ($\rho_{\text{RuO}_2} = 6.97 \text{ g/cm}^3$) and metal-like conductivity ($\sigma = 2.5 \times 10^4 \Omega^{-1} \text{ cm}^{-1}$). Once formed, these
crystals are stable up to 1200 °C and decompose at 1580 °C which is above the highest operating temperatures of the melters used in HLW vitrification (~1150 °C – Joule Heated Ceramic-lined Melters (JHCM); 1300–1400 °C - Cold Crucible Induction Melters (CCIM)). Further, due to their high density, the precipitated RuO₂ crystals eventually settle to the bottom of the melter. As the sedimentation continues, they form highly conducting layers between the electrodes, which can cause short-circuiting of the JHCM melters. Although short-circuiting of electrodes during the processing of the U.S. HLW glass-ceramics can be avoided by using CCIM melters (as they do not employ metallic electrodes to melt the raw material batch), the presence of RuO₂ crystals in the melt could potentially alter the crystalline phase assemblage of the glass-ceramic waste form. RuO₂ crystals, when dispersed in the melt, can act as nucleating sites for other crystalline phases during cooling of the melt in steel canisters, as has been previously reported for spinel and acmite crystallization in defense based HLW in the U.S. This may lead to uncontrolled devitrification, thereby affecting the long-term chemical durability of borosilicate glass and glass-ceramic waste forms.

Thus, irrespective of the choice of melters and whether a borosilicate glass or glass-ceramic is used for HLW immobilization, the behavior of RuO₂ in these waste forms needs to be investigated in the context of its solubility in borosilicate glass, its impact on crystalline phase evolution upon exceeding the solubility limit, and the electrical conductivity of the waste form. Accordingly, this article reports on the impact of ruthenium oxide (RuO₂) on the crystallization behavior and electrical conductivity of model commercial HLW glasses.
5.2 Experimental Details

5.2.1 Composition design and glass synthesis by the melt-quench technique

The baseline sample chosen for this study (Ru-0) has a batched composition of 12.5 Na$_2$O– 12.5 CaO– 5.0 Al$_2$O$_3$– 10.0 B$_2$O$_3$– 3.0 MoO$_3$– 5.0 Nd$_2$O$_3$– 4.0 ZrO$_2$– 48.0 SiO$_2$ (mol.%). This composition is a simplified version of the complex HLW glass-ceramic composition (GC-Mo-Li 6.25$^3$) proposed by the U.S. DOE for the HLW immobilization. RuO$_2$ was added to the baseline composition by exchanging with SiO$_2$ in the amounts 0.05, 0.1, 0.2, and 0.3 mol.%. The melt-quenched samples are labeled as ‘Ru-x,’ where x is the batched concentration of RuO$_2$ in mol.%. Table 5.1 presents the batched compositions of the melt-quenched samples.

High purity powders of SiO$_2$ (Alfa Aesar ≥ 99.5%), Na$_2$SiO$_3$ (Alfa Aesar > 99%), Al$_2$O$_3$ (Sigma-Aldrich ≥ 98%), H$_3$BO$_3$ (Alfa Aesar ≥ 98%), Nd$_2$O$_3$ (Alfa Aesar 99%), MoO$_3$ (Alfa Aesar ≥ 99.5%), ZrO$_2$ (Sigma-Aldrich; 99%), and RuO$_2$ (Sigma-Aldrich; 99.9%) were used as precursors. Homogeneous mixtures of batches were melted in Pt-Rh (10 wt.% Rh) crucibles covered with Pt-lid (to limit the volatilization) at 1500–1550 °C for 2 hours. The melts were then poured on a copper plate and allowed to cool to room temperature in ambient conditions. The compositions with a higher concentration of RuO$_2$ (for example, Ru-0.2 and Ru-0.3) showed an apparent increase in the melt-viscosity resulting in higher melting temperatures. The experimental compositions of the as-synthesized samples were analyzed using PerkinElmer Optima 8300V ICP-OES (Inductively coupled plasma optical emission spectroscopy).
Table 5.1: Batched composition of the melt-quenched samples.

<table>
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<tr>
<th>Label</th>
<th>%</th>
<th>Na₂O</th>
<th>CaO</th>
<th>Al₂O₃</th>
<th>B₂O₃</th>
<th>MoO₃</th>
<th>ZrO₂</th>
<th>Nd₂O₃</th>
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<tr>
<td></td>
<td>mol.</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Ru-0</td>
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<td>12.50</td>
<td>5.00</td>
<td>10.00</td>
<td>3.00</td>
<td>4.00</td>
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<td></td>
<td>wt.</td>
<td>9.48</td>
<td>8.58</td>
<td>6.24</td>
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<td>35.29</td>
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<td>5.00</td>
<td>10.00</td>
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<td>4.00</td>
<td>5.00</td>
<td>47.95</td>
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<td>35.24</td>
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5.2.2 Differential scanning calorimetry (DSC)

DSC analysis was performed on powders (particle size: 850–1000 µm) of the melt-quenched samples using a Simultaneous Thermal Analyzer (STA 449F5 Jupiter; Netzsch) from 100 to 1100 °C (Pt-crucible) at a heating rate of 10 °C/min under a constant flow of N₂ gas. The thermal parameters, including the glass transition (T_g), the onset of crystallization (T_c), and the peak of crystallization (T_p1 and T_p2) temperatures are reported and represent an average of three scans. The T_g and T_c were obtained from the onset of the endothermic dip and the first exothermic peak, appearing in the scans, respectively. The estimated standard deviation of the values reported is within ± 3 °C range.

5.2.3 Crystalline phase-evolution by isothermal heat-treatments

The crystallization was induced in bulk pieces of the melt-quenched samples by heating from room temperature to 715 °C, followed by soaking for 1, 3, 6, 12, and 24 hours, respectively. The isothermal heat treatment temperature (715 °C) was selected based on the T_c observed in the DSC scans. The heat-treated samples were cooled down to room
temperature by placing the samples in the ambient atmosphere (outside the furnace) post their isothermal heat treatment durations.

5.2.4 X-ray diffraction (XRD)

The qualitative phase analysis was performed on fine powders (< 45 µm) of the melt-quenched and heat-treated (715 °C, 1–24 h) samples using a PANalytical X’Pert Pro X-ray diffractometer with Cu Kα radiation (1.5406 Å) and a Bragg-Brentano geometry. The XRD scans were obtained at a voltage of 45 kV and current of 40 mA in a 2θ range of 10–90°, a step-size of 0.013°, and a dwell time of 0.1 seconds at each step. The quantitative phase analysis on the crystallized samples was performed using the Rietveld – Reference Intensity Ratio method. The samples for Rietveld analysis were prepared by crushing and sieving them to powders with particle size < 45 µm and mixing with 10 wt.% Al₂O₃ (NIST SRM 676A) as an internal standard. Higher-resolution XRD scans in the 2θ range of 10–90°, a step-size of 0.026°, and a dwell time of 1.16 seconds at each step was acquired for the Rietveld refinement. Crystalline phases were identified using the International Center for Diffraction Data (ICDD) database. The value of the R-factor for the Rietveld refinement of the heat-treated samples was < 5.0 for all the samples.

5.2.5 Scanning electron microscopy – energy dispersive X-ray spectroscopy

SEM-EDS analysis was performed on the polished and chemically etched (2 vol.% HF for 1 min) pieces of melt-quenched and isothermally heat-treated samples. The chemically etched samples were sputtered with a ~20 nm thick gold coating to make them electrically conducting. The samples were observed under the ZEISS Sigma Scanning Electron Microscope (SEM) attached with an Oxford Instruments EDS detector.
5.2.6 Electrical conductivity measurements

The electrical conductivity (σ) was studied in the temperature range 50–600°C (below T_g). The measurements were performed by AC impedance spectroscopy (IS, Keysight E4284A precision LCR meter, frequency range 20 Hz–2 MH, AC voltage 1V) using disk- and bar-shaped samples cut from the melt-quenched samples and polished to a regular geometric shape. The values of bulk resistance were obtained by the analysis of complex impedance spectra using ZView software. At lower temperatures, when the resistance of samples was too high for reliable IS measurements (i.e., when log σ (S/cm) ≤ -7), the values of conductivity were determined by a 2-probe DC technique (short-term measurements using currents ≤ 1 µA). 2 to 6 samples of each glass composition were investigated. The studies were performed using two different electrode/sample/electrode geometries (Figure 5S1 – Supplementary information): across the plane (⊥, the distance between electrodes L ≤ 3 mm) and along the plane (∥, L > 5 mm). Porous silver electrodes (Sigma Aldrich Ag paste, sintering at 450 °C for 30 min, used for measurements only at T ≤ 400°C) or platinum electrodes (Heraeus CL11-534 Pt paste, sintering at 600°C for 30 min, used for measurements up to 600°C) were applied on the corresponding surfaces of the samples.

5.3 Results and discussion

5.3.1 Physical appearance of the melt-quenched samples

Figure 5S2 presents the photographs of the melt-quenched samples, displaying a change in coloration and transparency with increasing RuO_2 concentration. As compared to the RuO_2-free baseline sample (Ru-0), which has a purple hue (due to Nd_2O_3) and is transparent, the sample with 0.05 mol.% RuO_2 (Ru-0.05) shows a distinct change in
coloration to a reddish-brown hue with a visible loss of transparency. Increasing the RuO₂ concentration above 0.05 mol.% results in increasingly opaque samples with dark brown/black color. The change in coloration and an increase in opacity with RuO₂ addition is a preliminary and qualitative indicator of increasing RuO₂ concentration in these samples.

5.3.2  Amorphous/crystalline nature of the melt-quenched samples

Figure 5.1 presents the XRD patterns of the melt-quenched samples. Up to the batched RuO₂ concentration of 0.2 mol.% (up to Ru-0.2), the samples are XRD amorphous. An increase in the batched RuO₂ concentration to 0.3 mol.% results in three low-intensity XRD peaks positioned around 2θ = 28°, 35.05°, and 54.5° corresponding to the (110), (101), and (211) diffraction planes of rutile phase of RuO₂, respectively.

![Figure 5.1: XRD patterns of the melt-quenched samples. The diffraction peaks in the pattern of Ru-0.3 are assigned to the rutile phase of RuO₂ (PDF# 01-071-02273).](image)
Figures 5.2(a-d) present the SEM micrographs of the melt-quenched samples Ru-0.05, Ru-0.1, Ru-0.2, and Ru-0.3, respectively. The SEM micrograph of Ru-0.05 (Figure 5.2a) shows no evidence of crystallinity, and in conjunction with the XRD data (Figure 5.1), we conclude the sample Ru-0.05 is amorphous. The micrograph of Ru-0.1 (Figure 5.2b) reveals the presence of tiny particles scattered on the sample surface. Further increasing the batched concentration of RuO₂ to 0.2 mol.% increases the number density of these particles as is evident from the SEM micrograph of the sample Ru-0.2 (Figure 5.2c). The higher magnification image (10× magnified) of the sample Ru-0.2 presented in the inset of Figure 5.2c shows sub-micron particles with a globular morphology dispersed or embedded in the glassy phase. Although based on the XRD data of sample Ru-0.3, it is highly likely that the observed particles embedded in the glassy matrix of samples Ru-0.1 and Ru-0.2 are RuO₂ inclusions, it is difficult to ascertain their crystalline character based on the XRD and SEM data. The EDS point and area scans (not shown) of these samples’ surfaces do not show the preferential enrichment of Ru or other elements in the sub-micron sized particles possibly due to the lower spatial resolution of the EDS detector thus, preventing their chemical identification. Therefore, a transmission electron microscopy (TEM) analysis may be required to identify their chemical and structural make-up. Eventually, the SEM micrograph of the sample Ru-0.3 shows the presence of needle-like (4–10 µm) and polyhedral (1–3 µm) crystals scattered on the surface of the sample (Figure 5.2d). These crystals are agglomerates consisting of sub-micron size globules (Figure 5.2d inset) like the ones observed in Ru-0.2 (Figure 5.2c inset). The elemental mapping of the microstructure of Ru-0.3 performed by EDS is presented in Figure 5.3. As evident from the EDS elemental mapping, the needle-like and polyhedral crystals on the surface of Ru-
0.3 are enriched in Ru and depleted in Na, Ca, Si, Al, and Nd. Since the XRD pattern of Ru-0.3 shows peaks for RuO$_2$ (rutile phase) and prior literature reports that RuO$_2$ forms needle-like or polyhedral crystals in borosilicate-based glasses,$^{11}$ it can be concluded that the crystals observed in the SEM image of Ru-0.3 correspond to the rutile phase of RuO$_2$.

Here it should be noted that though Zr and Mo appear to be uniformly distributed on the surface of the sample Ru-0.3 (even in the regions covering the RuO$_2$ crystals), their relative concentrations cannot be accurately detected by EDS analysis as the peaks corresponding to the characteristic X-ray energies of Zr ($L_\alpha = 2.042$ keV) and Mo ($L_\alpha = 2.293$ keV) are masked by the strong signal of the gold nano-layer (Au, $M_\alpha = 2.120$ keV) deposited on the sample to make it electrically conducting.

**Figure 5.2:** SEM micrographs of the melt-quenched samples: (a) Ru-0.05; (b) Ru-0.1, indicating tiny white particles scattered on its surface; (c) Ru-0.2, indicating streaks of tiny white globular particles (inset: a 10X magnified image of the sample); and (d) Ru-0.3, Ru-0.3, showing the presence of hexagonal and needle-like sub-micron sized RuO$_2$ crystals.
Thus, based on the combined XRD and SEM-EDS analysis of the melt-quenched samples, it is safe to assume that in the sample containing 0.05 mol.% RuO$_2$ (batched), all the ruthenium is dissolved in the glass structure. Above the solubility limit of 0.05 mol.% (batched), the excess RuO$_2$ remains undissolved in the glass matrix. It exists as Ru-enriched domains, which increase in size and eventually crystallize to RuO$_2$ crystals with a growing concentration of RuO$_2$.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure53.png}
\caption{EDS elemental map of the melt-quenched sample Ru-0.3. The map shows preferential ruthenium enrichment in the needle-like and polyhedral crystals.}
\end{figure}

5.3.3 RuO$_2$ concentration analysis by ICP-OES

Table 5.2 reports the experimentally analyzed compositions (wt.%) of the melt-quenched samples. For all the samples, the experimentally determined concentration of RuO$_2$ is significantly lower than the batched concentration. Even in the sample with the lowest amount of batched RuO$_2$ (Ru-0.05), the experimental concentration (0.046 wt.%, Table 5.2) is ~43% lower than the batched concentration (0.081 wt.%, Table 5.1). Further, the experimental RuO$_2$ concentration increases with increasing the batched RuO$_2$ concentration and is highest in the sample Ru-0.3 (experimental: 0.203 wt.% vs. batched:
0.49 wt.% (Table 5.1 and 5.2) which includes both solubility and retention. The difference in the analyzed and batched RuO$_2$ concentration can be attributed to the volatilization of RuO$_2$ during melting in a temperature range of 1500–1550 °C. As previously reported by Schreiber et al.,$^9$ Ru is extremely volatile at the high-temperature processing conditions utilized in HLW vitrification (~1150 °C in JHCM, and 1300–1400 °C in CCIM). In the present study, though lower temperatures could have reduced the volatilization of RuO$_2$, temperatures below 1500 °C significantly increased the melt-viscosity, thus, making it difficult to pour the melts out of the crucible.

**Table 5.2:** Compositions (wt.%) of the melt-quenched samples determined by ICP-OES analysis.

<table>
<thead>
<tr>
<th>Label</th>
<th>Na$_2$O</th>
<th>CaO</th>
<th>Al$_2$O$_3$</th>
<th>B$_2$O$_3$</th>
<th>MoO$_3$</th>
<th>ZrO$_2$</th>
<th>Nd$_2$O$_3$</th>
<th>SiO$_2$</th>
<th>RuO$<em>2$ (X$</em>{RuO2}$)</th>
<th>X$_{Total}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru-0</td>
<td>9.32</td>
<td>8.56</td>
<td>5.85</td>
<td>8.33</td>
<td>5.17</td>
<td>6.34</td>
<td>20.74</td>
<td>35.2</td>
<td>-</td>
<td>99.54</td>
</tr>
<tr>
<td>Ru-0.05</td>
<td>9.11</td>
<td>8.75</td>
<td>5.7</td>
<td>8.17</td>
<td>5.657</td>
<td>6.39</td>
<td>20.47</td>
<td>35.7</td>
<td>0.046</td>
<td>100</td>
</tr>
<tr>
<td>Ru-0.1</td>
<td>8.95</td>
<td>8.36</td>
<td>5.8</td>
<td>7.75</td>
<td>5.24</td>
<td>6.26</td>
<td>19.94</td>
<td>34.9</td>
<td>0.067</td>
<td>97.27</td>
</tr>
<tr>
<td>Ru-0.2</td>
<td>8.9</td>
<td>8.59</td>
<td>5.49</td>
<td>8.07</td>
<td>5.34</td>
<td>6.31</td>
<td>20.16</td>
<td>35.9</td>
<td>0.189</td>
<td>98.94</td>
</tr>
<tr>
<td>Ru-0.3</td>
<td>8.65</td>
<td>8.54</td>
<td>5.45</td>
<td>7.89</td>
<td>5.34</td>
<td>6.31</td>
<td>20.11</td>
<td>35.5</td>
<td>0.203</td>
<td>97.96</td>
</tr>
</tbody>
</table>

Based on the ICP-OES, XRD, and SEM data, the solubility of RuO$_2$ in the MoO$_3$-containing baseline glass is ~460 ppm (0.046 wt.%) by weight. Previously, Yamashita and Yamanaka$^6$ have reported a RuO$_2$ solubility of 0.025 wt.% in a 7.7 Na$_2$O– 7.6 Li$_2$O– 4.0 CaO– 3.7 Al$_2$O$_3$– 15.7 B$_2$O$_3$– 2.8 ZnO– 58.4 SiO$_2$ glass. Please note that for the convenience of readers, the results in the following sections have been discussed based on the batched RuO$_2$ concentrations.
5.3.4  *Impact of RuO$_2$ on the crystalline phase evolution*

The DSC scans of the melt-quenched samples are presented in Figure 5.4, and the derived thermal parameters from these scans are reported in Table 5.3. The scans of all the samples show an endothermic region characteristic of the glass transition ($T_g$) region around 625 °C. Heating the samples above their glass transition region leads to the crystallization of at least two phases exhibited by the broad exothermic peaks observed around 735 °C and 800 °C. RuO$_2$ addition does not seem to affect the position of the first crystallization peak ($T_{p1}$). However, RuO$_2$ addition (above 0.1 mol.% batched) appears to impact the crystalline phase growing in the second crystallization curve, as is evident from the lowering of the peak temperature of crystallization ($T_{p2}$), thus, implying its possible role as a nucleating agent. The identity of the crystalline phases formed in the DSC analysis has been investigated by isothermal heat treatment of the samples at 715 °C, followed by their characterization using XRD and SEM-EDS, as discussed below.

Figure 5.5 presents the results of the quantitative phase analysis of the isothermally heat-treated samples demonstrating high amorphous character (> 75 wt.%) in all the samples. The qualitative phase analysis (shown in Figure 5S3) reveals that only two crystalline phases, CaMoO$_4$ (powellite) and Ca$_{2.2}$Nd$_{7.8}$(SiO$_4$)$_6$O$_{1.9}$ (Nd-apatite), evolve in these samples. Although the RuO$_2$ phase was detected in the melt-quenched sample Ru-0.3 (Figure 5.1 and Figure 5.2), its presence could not be confirmed in the isothermally heat-treated Ru-0.3 samples (Figure 5.5). It can be observed that in the samples heat-treated for 1 hour (Figure 5.5a), the crystallization of Nd-apatite is only observed in samples with RuO$_2$ concentration > 0.1 mol.%, *i.e.*, Ru-0.2 and Ru-0.3. An increase in the isothermal heat-treatment duration above 1 h results in the crystallization of both, the Nd-apatite phase
and powellite phase in all the samples, where the weight fraction of Nd-apatite increases with increasing RuO$_2$ concentration in the glasses. Based on the above XRD results, it can be concluded that though RuO$_2$ addition promotes the crystallization of the Nd-apatite phase, it does not affect the crystallization of the powellite phase. Similar behavior of RuO$_2$, i.e., selectively promoting the crystallization tendency of Nd-apatite over powellite, has been reported by Chouard et al.\textsuperscript{17} in Mo, Nd, and Ru containing soda-lime borosilicate glasses.

\textbf{Figure 5.4:} DSC curves of the melt-quenched samples recorded at a heating rate of 10 \textdegree C/min.
Table 5.3: Thermal parameters of onset of glass transition ($T_g$), the onset of crystallization ($T_{c1}$), and the peak of crystallization ($T_{p1}$ & $T_{p2}$) obtained from differential scanning calorimetry of the melt-quenched samples.

<table>
<thead>
<tr>
<th>Label</th>
<th>$T_g \pm 3$ ($^\circ$C)</th>
<th>$T_{c1} \pm 3$ ($^\circ$C)</th>
<th>$T_{p1} \pm 1$ ($^\circ$C)</th>
<th>$T_{p2} \pm 1$ ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru-0</td>
<td>602</td>
<td>714</td>
<td>735</td>
<td>805</td>
</tr>
<tr>
<td>Ru-0.05</td>
<td>606</td>
<td>711</td>
<td>736</td>
<td>813</td>
</tr>
<tr>
<td>Ru-0.1</td>
<td>611</td>
<td>714</td>
<td>737</td>
<td>811</td>
</tr>
<tr>
<td>Ru-0.2</td>
<td>606</td>
<td>717</td>
<td>741</td>
<td>785</td>
</tr>
<tr>
<td>Ru-0.3</td>
<td>610</td>
<td>712</td>
<td>737</td>
<td>790</td>
</tr>
</tbody>
</table>

To gain further insights into the crystallization behavior of the melt-quenched samples, the photographs of the 1-hour and 3-hour isothermally heat-treated samples have been captured and presented in Figure 5.6a and Figure 5.6b, respectively. The baseline sample, Ru-0, and the sample containing the lowest RuO$_2$ batched concentration (Ru-0.05) appear translucent after 1 hour of heat treatment at 715 $^\circ$C (Figure 5.6a). There are no visible traces of surface or bulk crystallization in these samples. However, an isothermal heat-treatment for 3 hours at 715 $^\circ$C turns the Ru-0 and Ru-0.05 samples opaque (both from the surface and in the interior), suggesting that they have undergone bulk crystallization (Figure 5.6b). White patches (WP) can be observed on the surface of samples Ru-0.1, Ru-0.2, and Ru-0.3 after 1 hour (Figure 5.6a) and 3 hours (Figure 5.6b) of heat-treatment at 715 $^\circ$C, suggesting that these samples have undergone surface (as well as bulk) crystallization.
Figure 5.5: Quantitative XRD analysis results of isothermally heat-treated samples at 715 °C for (a) 1 h, (b) 3 h, (c) 6 h, (d) 12 h, (e) 24 h.

In order to study the morphology of the crystalline phases on the surface and in the bulk of the heat-treated samples, the SEM micrographs have been collected on a single sample, Ru-0.1, obtained after undergoing isothermal crystallization. Figure 5.7(a-e) presents the SEM micrographs of Ru-0.1 obtained after 1 to 24 hours of isothermal heat-treatment. A careful observation of the micrograph of the 1 h heat-treated sample presented in Figure 5.7a suggests that two different crystalline morphologies exist in the corresponding glass-ceramic. The first morphology represented by region 1 (Figure 5.7a, column C) exhibits a leaf-like aggregated microstructure present on the sample surface (WP, Figure 5.7a) and the other morphology represented by region 2 (Figure 5.7a, column B) exhibits a dendritic microstructure in the bulk. The SEM micrographs of all the remaining glass-ceramics obtained after 3 to 24 h of heat-treatments have a similar crystalline microstructure represented by region 1 in Figures 5.7(b-e). The higher
magnification images of the region 1 presented in column C of Figures 5.7(b-e) suggest that its microstructure consists of leaf-like aggregates similar to that of region 1 (WP) in the 1-hour heat-treated sample (Figure 5.7a, column c). The dendritic microstructure observed in region 2 of the 1 h heat-treated sample (Figure 5.7a) is not revealed for the other heat-treated samples, possibly because the phase is growing in the bulk and the surface crystalline layer will have to be removed to observe its microstructure.

Figure 5.6: Photographs of the isothermally heat-treated samples (a) 715 °C for 1 hour and (b) 715 °C for 3 hours.
Figure 5.7: Micrographs of the Ru-0.1 glass-ceramic isothermally crystallized for (a) 1 h, (b) 3 h, (c) 6 h, (d) 12 h, and (e) 24 h. Images in column A have been captured at 250× for all samples. Images in column B have been captured at 1000× for all samples except for the 12 h sample (d) which is at 2500×; Images in column C have been captured at 15000× except for the 1 hour sample (a) which is at 50,000×. Images have been obtained on a FE-SEM in the InLens mode.

The chemistry of the microstructures observed in the SEM micrographs of the isothermally heat-treated Ru-0.1 glass-ceramics has been confirmed using EDS maps obtained for the 1 h and 6 h samples presented in Figure 5.8 and Figure 5S4, respectively.
It reveals the dendritic microstructure (Region 2) in the 1 h heat-treated Ru-0.1 glass-ceramic to be enriched in neodymium (Nd) and deficient in silicon (Si), and sodium (Na). Calcium (Ca), which is present in both the powellite and the Nd-apatite phase, appears to be uniformly distributed in the sample. Although molybdenum (Mo) and zirconium (Zr) appear to be uniformly distributed across the sample, the overlapping of their respective L\text{α} peaks with the M\text{α} peak of the gold coating prevents their assignment specifically to the dendritic crystals. However, combining the results from the quantitative XRD (Figure 5.5a), SEM (Figure 5.7a), and EDS (Figure 5.8) for Ru-0.1 (715 °C, 1 hour), the dendritic crystals can be identified as the powellite phase which crystallizes in the bulk of the sample. This assignment of the powellite’s bulk crystallization tendency is also supported by quantitative XRD results of samples Ru-0 and Ru-0.05 heat-treated for 1 hour at 715 °C (Figure 5.5a) and their photographs presented in Figure 5.6a. The prior literature, including our study based on similar glass compositions, reports the dendritic morphology of powellite\textsuperscript{18} and its bulk crystallization tendency\textsuperscript{17, 19, 20}. Also, as shown in the literature, Nd is known to enter the crystal structure of powellite\textsuperscript{17-21}, thus, resulting in the Nd-enriched crystalline microstructure.

Although the EDS maps (Figure 5.8 and Figure 5S4) do not confirm the identity of the leaf-like crystalline phase (Region 1) forming the white patches on the surface of Ru-0.1, its chemistry can be attributed to the Nd-apatite phase as it is the only other primary phase evolving in these samples (RuO\textsubscript{2} is present in minor amounts) and whose crystal fraction increases with the increase in heat-treatment duration as has been shown by quantitative XRD (Figure 5.5). Prior studies have also reported the Nd-apatite phase to crystallize on the surface of glasses.\textsuperscript{17, 19} Here it should be noted that though the SEM
images of sample Ru-0.1 (715 °C, 1 h) show the presence of Nd-apatite on its surface, we could not confirm this result from XRD (Figure 5.5a and Figure 5S3) most likely due to its low concentration in the sample.

**Figure 5.8:** EDS map indicating the distribution of elements on the surface (1) and in the bulk (2) of the sample Ru-0.1 obtained after 1 hour of heat-treatment at 715 °C.

5.3.5  **Impact of RuO$_2$ on the electrical conductivity of the as-synthesized samples**

Figure 5.9a and 5.9b shows typical examples of complex impedance spectra of melt-quenched glass samples. The spectra comprise a single slightly depressed semicircle assigned to the bulk resistance of the samples (capacitance in the order of $10^{-11}$ F/cm) and a low-frequency spike visible at higher temperatures. The latter is characteristic of ionic conductors and is attributed to the electrode response.

The temperature dependence of the electrical conductivity of the melt-quenched glasses below $T_g$ is given in Figure 5.10a. Some scattering in the conductivity values, up to 2–4 times, can be observed for different samples of each glass compositions. Nevertheless, all glasses demonstrate very similar conductivity levels and Arrhenius behavior in the studied temperature range with an activation energy of $83 \pm 3$ kJ/mol. This
seems reasonable considering very minor modifications in the chemical composition of the glasses.

Figure 5.9: Typical impedance spectra of melt-quenched glass samples recorded at (a) 600 and (b) 370 °C; (c) an example of impedance spectrum of low-resistivity Ru-0.3 sample recorded at 370 °C in ⊥ configuration.
At the same time, a different electrical behavior has been observed for selected samples of Ru-0.3, a glass with the highest RuO$_2$ addition. When studied in $\perp$ geometry, these samples exhibit metallic-like behavior (Figure 5.10b) with electrical conductivity decreasing on heating and apparent conductivity values substantially higher compared to other samples (3–3.5 orders of magnitude at 400 °C). The corresponding impedance spectra (see an example in Figure 5.9c) are typical for metallic conductors (with a high-frequency inductance contribution originating from the wire current collectors). A similar phenomenon of electrical conductivity showing a weak temperature dependence in the low-temperature range has been reported previously for a complex HLW borosilicate-based glass-composite containing 1.3 vol.% of needle-like RuO$_2$ crystals. The conductivity of this Ru-containing glass-composite below $T_g$ has been claimed to be dominated by electronic transport through long chains of interconnected RuO$_2$ crystals separated by an insulating barrier (glass matrix) whose thickness is on the order of ~1 nm. The abnormal behavior of electrical conductivity for selected Ru-0.3 samples observed in the present work also can be attributed to similar effects. As an example, Figure 5.11 illustrates the distribution of Ru in the glass matrix of one polished Ru-0.3 sample used for the conductivity measurements (s3 in Figure 5.10b). The EDS maps collected at lower magnifications (Figure 5.11a and 5.11b) depict a non-uniform dispersion of ruthenium crystals in the glassy matrix with specific zones (circled in white) being more concentrated in Ru. The EDS maps with higher magnifications (Figure 5.11c and 5.11d) suggest a certain degree of interlinking of these Ru particles at least within 4–10 µm range.
Figure 5.10: (a) Temperature dependence of electrical conductivity of melt-quenched glasses; (b) selected examples of electrical conductivity data measured for three different Ru-0.3 glass samples using along the plane (∥) and across the plane (⊥) sample geometries with different distances (L) between the electrode.
Figure 5.11: SEM micrographs with overlaid EDS elemental maps of polished glass sample Ru-0.3-s3 (see Figure 5.10) recorded with an incremental increase in magnification from (a) to (d).

Based on the analysis of electrical conductivity data and the localized clustering of RuO₂ in the matrix of Ru-0.3 glass, one can conclude that crystalline RuO₂ inclusions may percolate to create low-resistance conduction pathways across the glass matrix of Ru-0.3. Ruthenium dioxide is known to possess high metallic-like electronic conductivity with $\sigma \approx 10^3$ S/cm reported for porous ceramics at 50°C\(^2\) and $2 \times 10^4$ S/cm for single crystals at 20°C\(^2\). However, the distribution of RuO₂ inclusions in the glass matrix is very non-uniform, and the crystals are interlinked only on a short-range. At the same time, the percolation of conductive clusters on a long-range does not happen. This explains high apparent values of electrical conductivity obtained for selected thin Ru-0.3 samples in $\perp$. 
geometry (L ≤ 3 mm) (Figure 5.10b), whereas the same samples exhibit semiconducting
high-resistivity behavior in the course of measurements in \( \parallel \) configuration (L > 5 mm).

5.4 Conclusion

The article reports the solubility limit of RuO\(_2\) in a MoO\(_3\)-containing borosilicate-

based model HLW glass. Further, an attempt has been made to understand the impact of

RuO\(_2\) on the crystalline phase evolution and electrical conductivity of the HLW glasses.

Accordingly, RuO\(_2\) has been systematically added to a baseline glass with the composition

12.5 Na\(_2\)O– 12.5 CaO– 5.0 Al\(_2\)O\(_3\)– 10.0B\(_2\)O\(_3\)– 3.0 MoO\(_3\)– 5.0 Nd\(_2\)O\(_3\)– 4.0 ZrO\(_2\)– 48.0 SiO\(_2\)

by partial substitution of SiO\(_2\), in batched amounts ranging from 0.05 to 0.3 mol.\%.

Significant volatilization of RuO\(_2\) is observed from the glass melts. The combination of

ICP-OES, XRD, and SEM-EDS reveals the solubility of RuO\(_2\) in the glass to be 0.046 wt.%

(460 ppm). Further, an increase in the RuO\(_2\) concentration results in sub-micron sized Ru-

rich inclusions heterogeneously dispersed in the host glass matrix which eventually

agglomerate to form needle-like and polyhedral RuO\(_2\) crystals (in the sample with highest

RuO\(_2\) concentration). RuO\(_2\) acts as a nucleating agent, promoting the crystallization of the

Nd-apatite (Ca\(_{2.2}\)Nd\(_{7.8}\)(SiO\(_4\))\(_6\)O\(_{1.9}\)) phase but does not tend to affect the crystallization

behavior of powellite (CaMoO\(_4\)) phase. The electrical conductivity measurements suggest

that all RuO\(_2\) containing samples show a temperature-dependent Arrhenius behavior. At

the same time, the percolation of non-uniformly distributed RuO\(_2\) inclusions may result in

a formation of short-range low-resistive conduction pathways with metallic-like electronic

conductivity in the glass matrix, as observed for selected Ru-0.3 samples.
Acknowledgements
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Supplementary Information
The online version of this article contains supplementary information including a schematic of the electrode/sample geometries used for electrical conductivity measurement; photographs of the melt-quenched samples; XRD plots of heat-treated samples; EDS map of Ru-0.1 isothermally heat-treated at 715 °C for 6 h.
References


Chapter 6. Conclusion

With rapid technological advancement, the reliance on nuclear energy, a clean source of energy, is expected to increase manifolds in the near future. The demand for high volumes of electricity is expected to drive the construction of new nuclear power plants with higher capacities, thereby increasing the generated volume of HLW. For immobilizing the HLW while maintain lower costs of vitrification, it will be of paramount importance to develop advanced waste forms with higher waste loading capacities. In the United States, an alkali alkaline-earth aluminoborosilicate glass-ceramic, with an expected higher waste loading capacity than borosilicate glasses, has been proposed for the immobilization of the projected HLW generated from the reprocessing of the spent civilian nuclear fuel. In the pursuit of developing the advanced waste form, a fundamental understanding of the compositional and structural drivers governing waste loading capacity in corresponding aluminoborosilicate glasses is essential. The work presented in this thesis is one contribution, which evaluates the solubility of MoO$_3$, one of the integral components of HLW, in alkali alkaline-earth aluminoborosilicate glasses and investigates mechanism governing this improved solubility with RE$_2$O$_3$ addition.

By following a systematic tiered approach for designing glass compositions, it is determined, that CaO addition to Na$_2$O-Al$_2$O$_3$-B$_2$O$_3$-SiO$_2$ glasses improves the solubility limit of MoO$_3$, since Ca$^{2+}$ replaces Na$^+$ as the preferred charge compensator for MoO$_4^{2-}$, thus impeding the crystallization of sodium molybdate (Na$_2$MoO$_4$) phase. In addition, a two-fold increase in the solubility limit of MoO$_3$ is confirmed upon 5 mol% Nd$_2$O$_3$ incorporation to a 12.5 Na$_2$O– 12.5 CaO– 5.0 Al$_2$O$_3$– 10.0 B$_2$O$_3$ – 55.0 SiO$_2$ glass. The
increase in MoO₃ solubility with RE₂O₃ addition is explained by the following novel hypothesis:

(i) RE³⁺ induces phase separation in the aluminoborosilicate glass resulting in borate-rich and aluminosilicate-rich regions.

(ii) It enters the borate-rich region forming metaborate-like structures (1BO₄:RE:2BO₃). Further, only when its concentration in the borate-rich region exceeds the solubility limit, does the RE³⁺ enter the aluminosilicate-rich region forming some kind of “clusters”.

(iii) MoO₄²⁻ preferentially enters the RE-B-rich regions in the phase separated glass and forms a stable RE-Mo-B-O glass phase resulting in an increased MoO₃ solubility.

This novel hypothesis is tested partly by investigating the partitioning and clustering behavior of RE³⁺ (RE = Nd and/or La) cations in quaternary Na₂O-Al₂O₃-B₂O₃-SiO₂ glasses. By performing quantitative FID-detected EPR analysis on these glasses it is identified that Nd³⁺ co-exist in three different forms: Isolated Nd³⁺ centers, dipole-coupled Nd clusters (Nd–O–X–O–Nd, where X = Si/B/Al), and spin-exchange-coupled Nd clusters — (Nd–O–Nd) & (Nd–O–La–O–Nd). Higher Nd₂O₃ concentrations (> 0.01 mol%) and La₂O₃ co-doping is found to promote extensive RE clustering. ESEEM analysis of the EPR-detectable Nd reveals a Na/Si-rich environment for the isolated Nd³⁺ centers and Na/Si/B-rich environment for the dipole-coupled Nd clusters. In view of the ESEEM and MAS NMR analysis, it is predicted that the EPR-undetectable exchange-coupled RE clusters exist in a Na/B-rich environment. These observations suggest that clustering of RE³⁺ in alkali aluminoborosilicate glasses is governed by a strong competition between
AlO$_4^-$, BO$_4^-$, and REO$_6^{3-}$ for Na$^+$ charge compensation. Limited availability of Na$^+$ thus forces the isolated RE$^{3+}$ centers to cluster, eventually into nano-scale RE-Na-B-rich phases, with the leftover glass matrix being depleted of the same elements.

The subsequent chapter builds on this improved understanding and presents a structural investigation of MoO$_3$, RE$_2$O$_3$, and ZrO$_2$-containing model nuclear waste glasses in the Na$_2$O-CaO-Al$_2$O$_3$-B$_2$O$_3$-SiO$_2$ system. The substitution of RE$_2$O$_3$ in the baseline 12.5 Na$_2$O–12.5 CaO–5.0 Al$_2$O$_3$–10.0 B$_2$O$_3$–55.0 SiO$_2$ glass is observed to cause the unmixing of the homogenous glass into borate-rich and aluminosilicate-rich regions as evidenced by the combined FID-detected EPR and ESEEM spectroscopies. Nd$^{3+}$ is observed to co-exist as isolated Nd$^{3+}$ centers, dipole-coupled Nd cluster, and spin-exchange coupled Nd clusters. However, it is observed that the environment of isolated Nd$^{3+}$ centers is significantly altered from the glass investigated in chapter 3, being further depleted of sodium and more enriched in boron. The substitution of MoO$_3$ leads to the depolymerization of the glass network, whereas ZrO$_2$ substitution has an opposite effect wherein it reticulates the glass network. Based on these results an improved hypothesis on the increase in MoO$_3$ solubility with RE$_2$O$_3$ is proposed:

(i) Rare earths induce phase separation in an alkali alkaline-earth aluminoborosilicate glass forming borate-rich and aluminosilicate-rich regions wherein the majority of RE$^{3+}$ preferentially cluster in the RE-B-rich glass phase.

(ii) MoO$_4^{2-}$ preferentially enters the RE-B-rich phase and forms a stable RE-Mo-B-rich glass phase within the bulk glass.
(iii) In this RE-Mo-B-rich phase, $\text{MoO}_4^{2-}$ is preferentially charge neutralized by RE$^{3+}$ rather than Na$^+$ which suppresses the crystallization of $\text{Na}_2\text{MoO}_4$ and improves MoO$_3$ solubility.

Finally, this thesis also investigates the solubility of RuO$_2$ and its impact on the crystalline phase evolution of a model aluminoborosilicate-based HLW glass. RuO$_2$ exhibits a very low solubility limit, 460 ppm by weight, in the glass, and above the solubility limit is observed to precipitate as sub-micron-sized Ru-rich inclusions, which at higher RuO$_2$ concentrations (2030 ppm by weight) agglomerate into needle-shaped and polyhedral RuO$_2$ crystals. These crystals act as short-range low-resistive conduction pathways in the host glass matrix as observed by the metal-like conductivity of few select samples with RuO$_2$ concentration above the solubility limit. Further, RuO$_2$ selectively promotes the crystallization of the rare-earth apatite phase in the glass.
Chapter 7. Future Work

The work performed during the course of this doctoral research has explored the structural and compositional drivers governing the solubility of MoO$_3$ in RE$_2$O$_3$-free and RE$_2$O$_3$-containing peralkaline (alkali/Al > 1) aluminoborosilicate glasses. Accordingly, an atomic-scale structural picture of the partitioning and clustering tendency of RE$^{3+}$ in these glasses, and the impact of such structural modifications on the improved solubility of MoO$_3$ is hypothesized. The future work on this topic will be focused on expanding the understanding of RE$^{3+}$ speciation and coordination in metaluminous (alkali/Al = 1) and peraluminous (alkali/Al < 1) aluminoborosilicate glass systems. In the context of the nuclear waste immobilization problem, the motivation for conducting these studies stems from the preliminary results, which have been already, collected, which suggest that MoO$_3$ exhibits higher solubility limits in the RE$_2$O$_3$-containing metaluminous and peraluminous aluminoborosilicate glasses than their corresponding peralkaline counterparts. Notably, in metaluminous glasses, a tendency to accommodate >5 mol% MoO$_3$ without causing visible phase separation or crystallization, has already been confirmed.

Another future research direction for this work could be to conduct systematic studies on RE$_2$O$_3$ containing silica-based glasses with compositions in the binary (e.g. Na$_2$O-SiO$_2$), ternary (e.g. Na$_2$O-Al$_2$O$_3$-SiO$_2$), and quaternary (e.g. Na$_2$O-Al$_2$O$_3$-B$_2$O$_3$-SiO$_2$) silicates, to understand their structure-property relationships. Emphasis would be laid on correlating structural signatures derived from EPR, MAS NMR, Raman, and extended absorption fine structures (EXAFS) spectroscopy. Such an effort could help in explaining some of the anomalous property trends exhibited rare-earth silica-based glasses. For
instance, prior literature suggests that RE$^{3+}$ mainly acts as a network modifier in silicate glasses and tends to depolymerize the glass network. Given the modifier-like behavior of RE$^{3+}$, a decrease in the glass transition temperature ($T_g$) should be expected upon RE$_2$O$_3$ addition. Although, increasing RE$_2$O$_3$ concentration is known to increase the $T_g$ of the glass. Based on the EPR results presented in this thesis, I believe that there is a need to reevaluate the structural role of RE$^{3+}$ in silicate glasses, as this could potentially explain many of their physico-chemical properties thus having a long-term impact on the design and development of functional glasses.