



Impact of rare earth ion size on the phase evolution of MoO₃-containing aluminoborosilicate glass-ceramics

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HIGHLIGHTS

- Powellite forms on slow cooling when Mo present and incorporates rare earth.
- Oxyapatite (Ca,RE)_{10-x}(Si,B)_{6+x}O₂₆ forms with all rare earths tested with sizes from La to Yb.
- Yb favors keiviite Yb₂Si₂O₇ with minor oxyapatite.
- Oxyapatite does not form when Na is removed from formulation.
- Cations with larger field strength strongly affect molybdate oxyanion vibrations.

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ABSTRACT

Transition metal and rare earth (RE) elements are important fission products present in used nuclear fuel, which in high concentrations tend to precipitate crystalline phases in vitreous nuclear waste forms. Two phases of particular interest are powellite (CaMoO₄) and oxyapatite (Ca₂RE₈(SiO₄)₆O₂). The glass compositional dependencies controlling crystallization of these phases on cooling from the melt are poorly understood. In the present study, the effect of rare earth identity and modifier cation field strength on powellite and apatite crystallization were studied in a model MoO₃-containing alkali/alkaline-earth aluminoborosilicate glass with focus on (1) influence of rare earth cation size (for RE³⁺: Ce, La, Nd, Sm, Er, Yb) and (2) influence of non-framework cations (RE³⁺, Mo⁶⁺, Na⁺, Ca²⁺). Quenched glasses and glass-ceramics (obtained by slow cooling) were characterized by X-ray diffraction (XRD), Raman spectroscopy, X-ray absorption spectroscopy (XAS), and electron probe microanalysis (EPMA). All samples were X-ray amorphous upon quenching, except the Ce-containing composition which crystallized ceria (CeO₂), and the sample devoid of any rare earth cations which crystallized powellite. On heat treatment, powellite and oxyapatite crystallized in the majority of the samples, with the former crystallizing in the volume and the latter on the surface. The EPMA results confirmed a small concentration of boron in the oxyapatite crystal structure. RE cations were incorporated in the glass, as well as in powellite, oxyapatite, and in the case of Yb³⁺, keiviite (Yb₂Si₂O₇). Raman spectroscopy showed that the primary vibration band for molybdate MoO₄²⁻ in the glasses was strongly affected by the ionic field strength of the modifying cations (alkali, alkaline earth, and RE), suggesting their proximity to the MoO₄²⁻ ions in the glass, though the Mo–O bond length and coordination according to XAS suggested little local change.

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1. Introduction

Borosilicate glasses are one of the most suitable matrices for immobilization of nuclear waste worldwide due to their high nuclear waste loading capacity, low tendency for crystallization, high chemical durability, and high self-irradiation resistance [1]. Nuclear waste from reprocessing of used nuclear fuel (UNF) contains a large variety of fission products, including large quantities of the rare-earth (RE) and transition metals (TM), with molybdenum being particularly problematic due to its high fission yield and low solubility in borosilicate glass [2]. In some countries, the research effort is directed towards the development of glass waste forms with no crystallization, or at least minimal crystallization of only durable phases [3]. Another suggested approach being pursued is the development of a glass-ceramic waste form of a desired phase assemblage by controlled crystallization, thus leading to higher waste loading and superior chemical durability in comparison to its glassy counterpart [4–8]. Two crystalline phases of particular interest are powellite (CaMoO_4) and oxyapatite (nominally $\text{Ca}_2\text{RE}_8(\text{SiO}_4)_6\text{O}_2$), which are the primary crystalline phases accommodating Mo and RE ions in these nuclear waste glass-ceramic systems [5].

1.1. Molybdenum in borosilicate glass and glass-ceramics

In order to design a borosilicate-based glassy waste form, it is imperative to understand the compositional and structural drivers governing the solubility of molybdenum oxides in the relevant glass chemistries. Based on the existing literature [9–11], the solubility of MoO_3 in alkali borosilicate glasses is limited to ~1 mass% when no rare earth ions are present (see below) [12]. This threshold limit of MoO_3 solubility affects the total loading of waste into the base glass matrix, which leads to the increase of the total volume of the vitrified waste. Depending on the specific waste stream the maximum waste loading may be as low as ~18 mass%. Higher amounts of MoO_3 (>1 mass%) in borosilicate glass is known to induce phase separation and crystallization [10,13]. The phase separation and crystallization of Mo phases can have a deleterious effect on the durability and safety of the vitrified waste. For compositions rich in alkali, MoO_3 usually phase separates and crystallizes as an alkali molybdate (i.e., Na_2MoO_4) which is soluble in water [14]. Also, the alkali ions in Na_2MoO_4 can be partially or fully replaced by other alkali cations (short-lived ^{137}Cs or long-lived ^{135}Cs) resulting in water-soluble alkali molybdates such as $\text{Cs}_3\text{Na}(\text{MoO}_4)_2$, $\text{CsNaMoO}_4 \cdot 2\text{H}_2\text{O}$ and Cs_2MoO_4 [14–16]. It is known that the distribution of Na^+ in the glass can be controlled, such as with Al_2O_3 , B_2O_3 and CaO , thus forcing molybdate to partition and crystallize powellite (CaMoO_4) which is more durable in water than alkali molybdates [10,17].

In alkali borosilicate glasses, the molybdenum cation exists primarily in +6 oxidation state (as molybdate oxyanion), and in the dilute limit as an MoO_4^{2-} tetrahedron, based on evidence from Mo K-edge X-ray absorption [18,19], and molybdate vibrational frequency changes with the average charge density of modifier [19]. Molybdate oxyanions are thought to be located in the depolymerized region of the glass structure surrounded by alkali and alkaline-earth cations [12]. Recent *ab initio* molecular dynamics simulations have shown that when Li^+ is substituted for Na^+ , however, some longer Mo–O bonds result in connection with the borosilicate network and an effective Mo^{5+} charge [20].

1.2. Rare earth cations (RE^{3+}) in borosilicate glass and glass-ceramics

Molybdate and RE ions interact strongly in borosilicate glasses,

with the latter exerting a significant impact on the solubility of former (increases to 3–5 mass%) in the glass structure [1,21]. However, the mechanism of their interaction resulting in higher solubility of molybdenum in borosilicate glasses is still debated [11]. The most well-known hypothesis is the close relationship between RE^{3+} and $[\text{MoO}_4]^{2-}$ tetrahedral entities in the depolymerized region of the glassy network, where the RE^{3+} ions tend to disperse any molybdate clusters leading to an increase in the molybdenum solubility in the glassy waste form. The removal of RE^{3+} from the glassy matrix (for example, by crystallization of rare-earth containing oxyapatite phase) results in the crystallization of alkali/alkaline-earth molybdate phases [1,21,22]. Further, both RE (Nd, Gd, etc.) [10,23–25] and actinide ions [26] can be incorporated in the powellite crystal structure, as well as the related Na–Nd molybdate scheelite structure [27,28].

The sequence of crystallization of oxyapatite and powellite is highly dependent on several parameters. Generally, for a glass containing both MoO_4^{2-} and RE^{3+} , the crystallization (upon heating from room temperature) initiates through the formation of powellite in the volume followed by oxyapatite on the surface [21], while this sequence reverses during crystallization from the melt under slow cooling [11]. In fact, molybdate crystalline phases (Na_2MoO_4 , CaMoO_4) have been suggested as nucleation sites for apatite crystals [21]. However, as mentioned above, this sequence of crystalline phase assemblage is subject to change based on the glass/melt chemistry and thermal conditions.

Most studies of oxyapatite crystallization in nuclear waste glass have focused on Nd_2O_3 as the primary RE oxide addition, and the phase produced is $\text{Ca}_2\text{Nd}_8(\text{SiO}_4)_6\text{O}_2$ [1,2,4,29]. The stoichiometry of this phase is variable, with a tendency to be Ca-rich, Nd-poor, and O-poor, i.e., $\text{Ca}_{2+x}\text{Nd}_{8-x}(\text{SiO}_4)_6\text{O}_{2-0.5x}$ [30,31], though likely the stoichiometric range is quite large, including Ca-absent Nd-only versions of the crystal [32]. The $\text{Ca}_2\text{Nd}_8(\text{SiO}_4)_6\text{O}_2$ oxyapatite has been well-studied for radiation damage due to its chemical and structural similarity to target phases for actinide immobilization [33,34].

The composition of RE oxyapatite can be quite variable, and many synthetic pure phase RE oxyapatites have been reported containing Ca (or Ba, Sr, Mg, or Pb), including La, Nd, Sm, Dy, Er, Lu, as well as Y [35]. Several studies have been conducted looking at the compositions of oxyapatites crystallizing from the simulated nuclear waste glass. In complicated starting glass compositions, energy dispersive spectroscopy (EDS) has shown that multiple RE cations, for example, Y^{3+} , La^{3+} , $\text{Ce}^{3+}/\text{Ce}^{4+}$, Pr^{3+} , Nd^{3+} , Sm^{3+} , along with alkali (for example, Na^+), and alkaline earth ions (for example, Ca^{2+} , Sr^{2+}) can simultaneously incorporate into the oxyapatite structure [5]. In comparing La, Nd, and La + Nd in Na–Ca aluminoborosilicate glasses, it was observed that the amount of RE_2O_3 that could be accommodated in the glass before apatite crystallization was higher for La than Nd, and that overall apatite composition depended on the RE cation present [36].

According to a study conducted on elucidating the effect of the RE identity and heat treatment protocol on the oxyapatite crystallization in a Mo-free Na–Ca aluminoborosilicate glass [37], crystallization behavior of glasses depends on the ionic radii of the rare-earth cation, where the smaller the size of the rare-earth cation, the more sluggish is the tendency towards crystallization. This effect was most pronounced for the smallest sized RE^{3+} ions (Lu^{3+} , Yb^{3+} , Er^{3+} , Y^{3+}), where no crystals were seen on slow cooling of the melt, a minor amount of crystallization was viewable in monolithic samples (under an electron microscope) when heated from room temperature, and crystals in amounts detectable by XRD were obtained only in glass-ceramics produced through nucleation and crystallization in glass powders. Similar results have also been reported by Goel et al. [38] for rare-earth containing alkaline-earth

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