Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Impacts of composition and beta irradiation on phase separation in multiphase amorphous calcium borosilicates

Karishma B. Patel[a,*], Bruno Boizot[b], Sébastien P. Facq[a], Sylvain Peuget[c], Sophie Schuller[d], Ian Farnan[a]

[a] Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB23EQ, UK
[b] Laboratoire des Solides Irradiés, CNRS-UMR 7642, CEA-DRF-IRAMIS, Ecole Polytechnique, Université Paris-Saclay, Palaiseau Cedex, 91120, France
[c] CEA, DEN, DE2D, SEVT, LMPA, Marcoule, F-30207 Bagnols-sur-Cèze, France
[d] CEA, DEN, DE2D, SEVT, LDPV, Marcoule, F-30207 Bagnols-sur-Cèze, France

ARTICLE INFO

Keywords:
Nuclear waste materials
Calcium borosilicate glasses
Phase separation
Radiation effects
Microstructure
Crystallization

ABSTRACT

Borosilicate glasses for nuclear waste applications are limited in waste loading by the precipitation of water-soluble molybdates. In order to increase storage efficiency, new compositions are sought out that trap molybdenum in a water-durable $CaMoO_4$ crystalline phase. Factors affecting $CaMoO_4$ combination and glass-in-glass phase separation in calcium borosilicate systems as a function of changing $[MoO_3]$ and $[B_2O_3]$ are examined in this study in order to understand how competition for charge balancers affects phase separation. It further examines the influence of radiation damage on structural modifications using 0.77 to 1.34 GGy of 2.5 MeV electron radiation that replicates inelastic collisions predicted to occur over long-term storage. The resulting microstructure of separated phases and the defect structure were analyzed using electron microscopy, XRD, Raman and EPR spectroscopy prior to and post irradiation. Synthesized calcium borosilicates are observed to form an unusual heterogeneous microstructure composed of three embedded amorphous phases with a solubility limit ~2.5 mol% MoO_3. Increasing $[B_2O_3]$ increased the areas of immiscibility and order of $(MoO_4)^{2-}$ anions, while increasing $[MoO_3]$ increased both the phase separation and crystallization temperature resulting in phases closer to metastable equilibrium, and initiated clustered crystallization for $[MoO_3] > 2.5$ mol%. β-irradiation was found to have favorable properties in amorphous systems by creating structural disorder and defect assisted ion migration that thus prevented crystallization. It also increased reticulation in the borosilicate network through 6-membered boroxyl ring and Si ring cleavage to form smaller rings and isolated units. This occurred alongside an increased reduction of Mo^{6+} with dose that can be correlated to molybdenum solubility. In compositions with existing $CaMoO_4$ crystallites, radiation caused a scattering effect, though the crystal content remained unchanged. Therefore β-irradiation can preferentially prevent crystallization in calcium borosilicates for $[MoO_3] < 2.5$ mol%, but has a smaller impact on systems with existing $CaMoO_4$ crystallites.

1. Introduction

High-level nuclear waste (HLW) has been successfully incorporated into borosilicate glasses and vitrification proves a reliable and established technique [1]. Amorphous structures are ideal waste form candidates as they are able to incorporate a wide array of nuclides with varying charge and are resistant to internal radiation [2]. Moreover, they can be synthesized at reasonable conditions and show good chemical stability when subjected to aqueous environments [1,3]. Though they have proved beneficial in many regards, there are material limitations introduced by insoluble species that can result in unexpected phase separation [4–6] and thus degradation of physical properties [7,8].

The waste loading in French nuclear waste glass R7T7 is limited to 18.5 wt% fission products [9], which corresponds to ~1 mol% MoO_3 [10]. Above this solubility limit, it is possible for metastable phases to form leading to crystallization of molybdenum-rich phases [11,12]. The production of alkali molybdates (Na_2MoO_4, Cs_2MoO_4), known as yellow phase, are particularly problematic owing to their high water solubility and ability to act as carriers for radioactive cesium and strontium [1,13]. This ability thus creates a contamination risk during final geological deposition by increasing corrosion probabilities [14,15]. While formation of yellow phase can prove detrimental to chemical durability, alkaline earth molybdates ($CaMoO_4$) are

---

[*] Corresponding author.
E-mail address: kp391@cam.ac.uk (K.B. Patel).

http://dx.doi.org/10.1016/j.jnoncrysol.2017.06.018
Received 25 April 2017; Received in revised form 14 June 2017; Accepted 15 June 2017

Please cite this article as: Patel, K.B., Journal of Non-Crystalline Solids (2017), http://dx.doi.org/10.1016/j.jnoncrysol.2017.06.018

comparatively water durable and are stable following synthesis in a borosilicate matrix [12,14,15].

Selective and controlled formation of secondary phases can be useful to accommodate waste streams with a high concentration of insoluble elements while maintaining physiochemical properties. This notion has led to a renewed interest in glass ceramic (GC) materials. GCs contain a combination of vitreous and crystalline phases that can be compositionally induced during glass synthesis, or through a separate heat treatment. They can also be specifically manufactured by dispersing solid particles in a liquid [1]. These structures are ideal candidates for legacy waste containing refractory oxides or for post operation clear out, where waste has high molybdenum or alkali concentrations that would otherwise require unacceptably high melting temperatures. They are also useful to trap volatile elements such as Cs in a crystalline framework, which would otherwise prove problematic in conventional high temperature vitrification techniques.

Molybdate formation in particular can be controlled by composition [10,16,17], external heat treatments [12,18,19], redox chemistry [20,21], or by controlled cooling during synthesis [11]. Compositionally, the preferential charge balancing of $(BO_4)^-$ and $(MoO_4)^{2-}$ anionic entities by Na^+ and Ca^{2+} cations can determine molybdate speciation and network connectivity [22]. Due to charge, mobility, size and sterics $(BO_4)^-$ prefers Na^+ ions as charge balancers. This preference thus enables the incorporation of Ca^{2+} ions into molybdates [4,23,24]. It is observed that an increase of B_2O_3 will reduce the tendency of Na_2MoO_4 crystallization and increase the crystallization of $CaMoO_4$ in soda-lime borosilicates [10,24]. A similar effect has also been observed when the concentration of CaO is increased, owing to a corresponding reduction of $(BO_4)^-$ species [10,22]. Increasing the quench rate to 10^4 °C.min^{-1} has also been observed to promote the growth of $CaMoO_4$ over alkali molybdates and increase molybdenum solubility up to 2.5 mol% MoO_3 [12].

While composition and quench rate can directly influence molybdate speciation, redox chemistry is known to affect molybdenum solubility. Molybdenum can exist in several oxidative states (Mo^{6+}, Mo^{5+}, Mo^{4+}, Mo^{3+}), but in oxidizing or neutral conditions molybdenum ions will be primarily hexavalent [21]. The high field strength of Mo^{6+} exerts a strong ordering effect on the surrounding oxygen atoms and results in tetrahedral $(MoO_4)^{2-}$ units [15,16,24]. These tetrahedra remain unconnected to both the glassy framework and to each other, and are found embedded in a cationic lattice located in non-bridging oxygen (NBO) channels according to Greaves' structural model [25]. In this configuration, cations are octahedrally coordinated and bound to $(MoO_4)^{2-}$ entities by weak long-range ionic forces [17]. A reducing environment on the other hand, is found to promote molybdenum species in lower oxidative states that subsequently increases the solubility of molybdenum groups in borosilicates and silicates [15,21].

Though these relationships have been investigated in soda-lime borosilicates, very little research describes the simplified calcium borosilicate system. It is imperative to understand this system if we are to drive the selective formation of $CaMoO_4$ at high concentrations of MoO_3 in nuclear waste materials. This study seeks to address the effect of preferential charge balancing of $(BO_4)^-$ and $(MoO_4)^{2-}$ units in the absence of Na^+ alkali ions to determine the specific effect of $[B_2O_3]$ on the precipitation of $CaMoO_4$ and subsequent response of the residual matrix. This investigation further seeks to investigate how ionizing irradiation will alter both the crystalline and amorphous microstructures in terms of promoting or remediating phase separation.

Internal radiation from nuclear waste will constitute localized high-energy input events that can significantly alter the structure of a material. For the first 100 to 300 years of high-level waste storage, β-decay will provide a higher ionization dose than α-decay [26], thus resulting in significant alteration to the encapsulating structure. The dose from β-decay will then reach a plateau from 100 to 10^6 years of storage given current waste loading for French nuclear waste glasses. In organized systems such as metals or crystals, accelerated external radiation used to replicate these events can induce dislocations and eventual cracking along stress planes, as well as swelling and void formation [7,26]. These phenomena also take place in glasses irradiated by electrons where they are initiated by the formation of point defects [27,28]. These composition dependent defects can further lead to the release of charge compensators that can enable alkali migration and formation of alkali clusters [28], as well as the creation of molecular oxygen [29] following either β or x-ray irradiation [30,31]. Alkali migration and clustering can foster the creation of a precursor environment for molybdate formation; hence, it is a factor governing precipitation during long-term storage. Accumulated defects can also lead to glass-in-glass phase separation [26,32]. Alteration to the internal structure and connectivity of amorphous phases is of significance, as modification can result in changes to macroscopic properties such as density and hardness [33,34].

Molybdate formation and radiation effects on homogeneous borosilicates have been independently examined, but very few studies correlate the effects of radiation on phase separation and even fewer investigate the calcium borosilicate system. In this study, we segregate the effects of changing $[B_2O_3]$ and $[MoO_3]$ independently on the microstructure and solubility of molybdenum entities on a fundamental level to better understand the tendencies of internal phase separation. This study further attempts to determine if internal radiation produced from radioisotope β-decay on the order of 100 to 10^6 years of storage will induce, propagate or anneal glass-in-glass or crystalline phase separation in these samples, thus providing a window to long-term structural projections in these systems.

2. Experimental

2.1. Glass compositions and synthesis technique

In this study we synthesized several non-active glasses and glass GCs to test the solubility of molybdenum in calcium borosilicates and the durability of precipitated crystalline phases as a function of $[B_2O_3]$ and $[MoO_3]$ when subjected to β-irradiation. Table 1 provides the normalized glass compositions prepared.

The CB series tests the effect of increasing $[B_2O_3]$, while the $[SiO_2]/[CaO]$ ratio remained constant and with a fixed amount of MoO_3 and Gd_2O_3. This series will be used to determine how the concentration of boron will affect the Ca^{2+} ion distribution and preferential charge balancing when the molybdenum content is around its solubility limit and no alkalis are present. Gadolinium was included as a spectroscopic probe for EPR measurements, but rare earths can also be considered as actinide surrogates, indicating incorporation sites of actinide species. The composition of CBO was determined based on the eutectic point of the SiO_2 – CaO system [35] and was used as a marker for boron incorporation sites.

The CM series tests the effect of increasing $[MoO_3]$ in a calcium borosilicate matrix normalized to inactive French nuclear waste glass

Table 1
Sample composition in mol%.

Series	Sample ID	SiO_2	B_2O_3	Na_2O	CaO	MoO_3	Gd_2O_3
CB	CBO	59.41	–	–	38.94	2.50	0.15
	CB7	78.07	7.00	–	12.28	2.50	0.15
	CB15	71.16	15.00	–	11.19	2.50	0.15
	CB23	64.16	23.00	–	10.09	2.50	0.15
CM	CaBSi	67.74	20.97	–	11.29	–	–
	CM1	67.07	20.76	–	11.18	1.00	–
	CM2.5	66.05	20.44	–	11.01	2.50	–
	CM7	63.00	19.50	–	10.50	7.00	–
M	CM5	65.00	22.00	–	8.00	5.00	–
	CM7	63.00	19.50	–	10.50	7.00	–
	CN10	49.90	13.29	10.78	16.03	10.00	–