Unmixing inducing polymerization of a sodium-molybdenum borosilicate network

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ABSTRACT

Glass network polymerization critically influences rheological behavior and with it the kinetics and dynamics of nuclear waste immobilization. Molybdenum-bearing borosilicate melts may undergo unmixing and rheological changes, which is dominantly controlled by the associated chemical modifications of the melt network. Here, we obtain in-situ (500–940 °C) Raman spectra to probe structural changes of a sodium-molybdenum borosilicate melt undergoing unmixing. The extraction of alkali and molybdenum to form droplets induces polymerization of the residual borosilicate network. Conversely, the opposite phenomenon is observed during droplet re-dissolution. This work provides new insights into the polymerization of a molybdenum-bearing borosilicate composed of two composition sets due to a miscibility gap and has direct contributions for the immobilization of nuclear wastes.

1. Introduction

Glass-ceramics are being actively studied as matrices for nuclear waste immobilization due to their potential for higher waste loading capacity [1]. Glass-ceramic materials are formed by controlled crystallization, in contrast with uncontrolled devitrification processes. Certain Mo-bearing borosilicate melts can have Na-Mo rich crystals such as Na_2MoO_4 and $Na_2Mo_2O_7$ when quenched to the glassy state [2–4]. At high temperatures, due to the way molybdenum is connected to the network [5,6], these crystalline phases have precursors in the form of unmixed liquid droplets [2,3]. In sodium molybdenum borosilicate glass undergoing unmixing, the viscosity, important physical property controlling bubble dynamics [7] for example, rises more than predicted for a homogeneous melt, reflecting the impact of Na_2O and MoO_3 extraction during immiscible liquid droplets formation [2].

Here, we focus on the polymerization behavior of a simplified melt composition serving as an analog for candidate materials for nuclear waste vitrification. Residing in the $SiO_2 - B_2O_3 - Na_2O - Cs_2O - MoO_3$ system, it undergoes unmixing at high temperatures yielding droplets of an alkali-molybdate rich immiscible liquid [8]. We perform in-situ Raman spectroscopy at high-temperatures to observe the structural changes induced during unmixing.

2. Materials and methods

2.1. Glass synthesis and chemical composition

The glasses were synthesized using a mixture of homogenized powder loaded into a Pt-Au crucible and melted at 1300 °C in a muffle furnace in equilibrium with air. The melt was then quenched by casting onto a copper plate. We synthesized a Mo-free glass (named Mo0) and a glass containing 1.0 mol% of MoO_3 (named Mo1). The chemical compositions (Table 1) of the resultant glasses were measured using X-ray fluorescence spectroscopy (XRF) and the amorphous nature was checked via X-ray diffraction (more details are available in Kroeker et al. [8]).

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Table 1

XRF-derived compositions of the studied glasses. The Mo0 sample is MoO_3-free and the Mo1 sample contains 1.0 mol% of MoO_3.

Oxides	Mo0 sample (mol%)	Mo1 sample (mol%)
SiO_2	63.56	62.90
B_2O_3	16.88	16.70
Na_2O	16.57	16.40
Cs_2O	3.00	3.00
MoO_3	0.00	1.00
Total	100.0	100.0

2.2. In-situ high-temperature Raman spectroscopy

In situ Raman spectra were acquired using a LabRam Aramis spectrometer (HORIBA). A 325 nm laser was used to prevent black body radiation from interfering with the Raman signal. In situ measurements were performed using a Linkam apparatus with 20 °C steps. A second order polynomial baseline was fitted using the spectrometer software. Fityk software was used to decompose the spectra [9] and all peaks were modeled by gaussians except the peak at 890 cm^{-1} which was modeled by a Lorentzian function.

2.3. Textural analyses via electronic microscopy

Scanning electron microscopy (SEM) analyses were carried out using a Zeiss Supra 55 operating under 10 kV and equipped with a Bruker Xflash 4010 detector for energy-dispersive X-ray spectroscopy (EDS). Transmission electron microscopy (TEM) analyses were carried out using a JEOL JEM 2010F UPR22. The probe diameter is in the nanometer range and the beam operating voltage is 200 kV. Images were obtained by both microscopy techniques on the Mo1 quenched glass from different heat treatment.

3. Results

Fig. 1 illustrates the Raman spectra obtained at different temperatures. The most prominent spectral features of this family of glass are at (i) 630 cm^{-1}, (ii) 890 cm^{-1}, (iii) in the range between 1000 and 1250 cm^{-1}, and (iv) at 1450 cm^{-1}. The 630 cm^{-1} feature corresponds to danburite-like rings composed of 4 tetrahedra (2 SiO_4 and 2 $[BO_4]^-$), which are linked to a charge compensating atom [10]. Here, we display $[BO_4]^-$ in Fig. 2 as B^4. The feature at 890 cm^{-1} and its left shoulder are related to symmetric stretching vibration of Mo$-$O bonds of molybdate tetrahedra linked to an alkali ion as a charge compensator of the negative charges of the $[MoO_4]^{2-}$, which is similar to the corresponding crystalline Raman spectra of Na_2MoO_4. In this current case, Mo is not linked to terminal oxygens (e.g., Mo $=$ O), due to the absence of vibrational bands at 940–960 cm^{-1} [11,12]. The feature in the range of 1000–1250 cm^{-1} is related to symmetric and antisymmetric stretching vibrations of silicon tetrahedra and the decomposition of this region allows for the evaluation of the glass structure and polymerization, i.e., Q^3/Q^4 ratios [6,10]. The feature at around 1450 cm^{-1} is related to the stretching vibration of trigonal boron BO_3, here displayed as B^3, linked to a $[BO_4]^-$ group [10]. The ratio B^3/B^4 reported in Fig. 2c is the intensities ratio at 1450 cm^{-1} and 630 cm^{-1}. Table s1 displays the evaluated peak features for both studied glasses.

4. Discussion

At temperatures above 630 °C, the peak intensity of the Mo$-$O vibration at 890 cm^{-1} increases, reaching its maximum value at 740 °C (Fig. 2a). This behavior is related liquid–liquid unmixing to form liquid droplets containing a relatively high concentration of Mo$-$O bonds, whereby higher peak intensity reflects a higher abundance of the bonds and therefore higher fractions of unmixed liquid droplets. Note that the
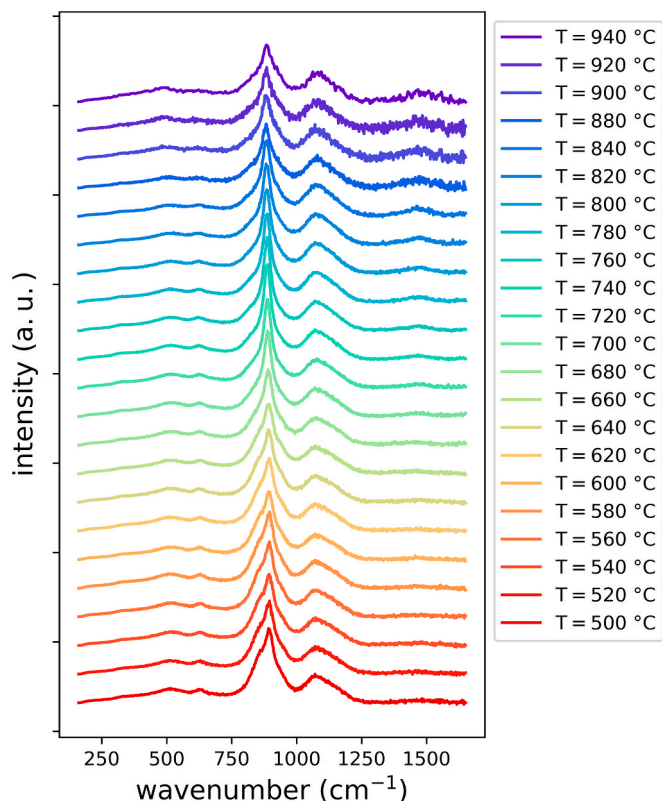

Fig. 1. Raman spectra of the *Mo* 1 at high temperature region (500 – 940 °C) in which unmixing and droplet dissolution occur. Spectra shifted vertically for visual inspection.

peak position of this band closely resembles that of the crystalline phase Na_2MoO_4 [13]. At temperatures higher still (>740 °C), there is an inflection and the peak intensity decreases due to dissolution of the droplets, as Mo solubility goes up. This continues until the system re-homogenizes to a single liquid phase (above 880 °C). Upon complete re-homogenization of these droplets, the intensity of the Mo $-$O symmetric vibration band further decreases with temperature increase. We observe a minor frequency shift related to this peak (Fig. 1).

The intensity ratio of the Q^3/Q^4 species ratio (Fig. 2b) was obtained after deconvolution of the bands located at about 1000–1250 cm^{-1}. The Mo0 sample (no phase separation) demonstrates a slightly increase in the Q^3/Q^4 ratio with increasing temperature. In contrast, the sample containing molybdenum (Mo1) exhibits different behavior. At temperatures above 630 °C, the Q^3/Q^4 remains constant, reflecting a relatively polymerization of the silicate network due to departure of sodium and molybdenum during unmixing counterbalancing the depolymerization observed in Mo0 sample. At temperatures above ca. 740 °C, the Q^3/Q^4 ratio increases (depolymerization) more for the Mo1 sample than for the Mo0 composition. This behavior is mainly linked to re-homogenization of the droplets and the corresponding return of alkali and molybdenum to the matrix. After complete re-mixing of the droplets, the Mo1 system continues to depolymerize as temperature increases, while the Mo0 presents a nearly constant ratio. The initial homogeneous glass and final homogeneous melt (i.e., below 630 °C and above 880 °C respectively) differences in Q^3/Q^4 ratios, suggesting that the Mo addition polymerizes the silicon network due to the need of charge compensation by the $[MoO_4]^{2-}$ units [4,5]. The inset images of Fig. 2b, obtained by TEM (570 and 900 °C) and SEM (700 and 800 °C), illustrate the microstructures of the molybdenum-bearing sample.

The borate network of the Mo0 sample (Fig. 2c) demonstrates an expected increase of the B^3/B^4 ratio (depolymerization) as temperature
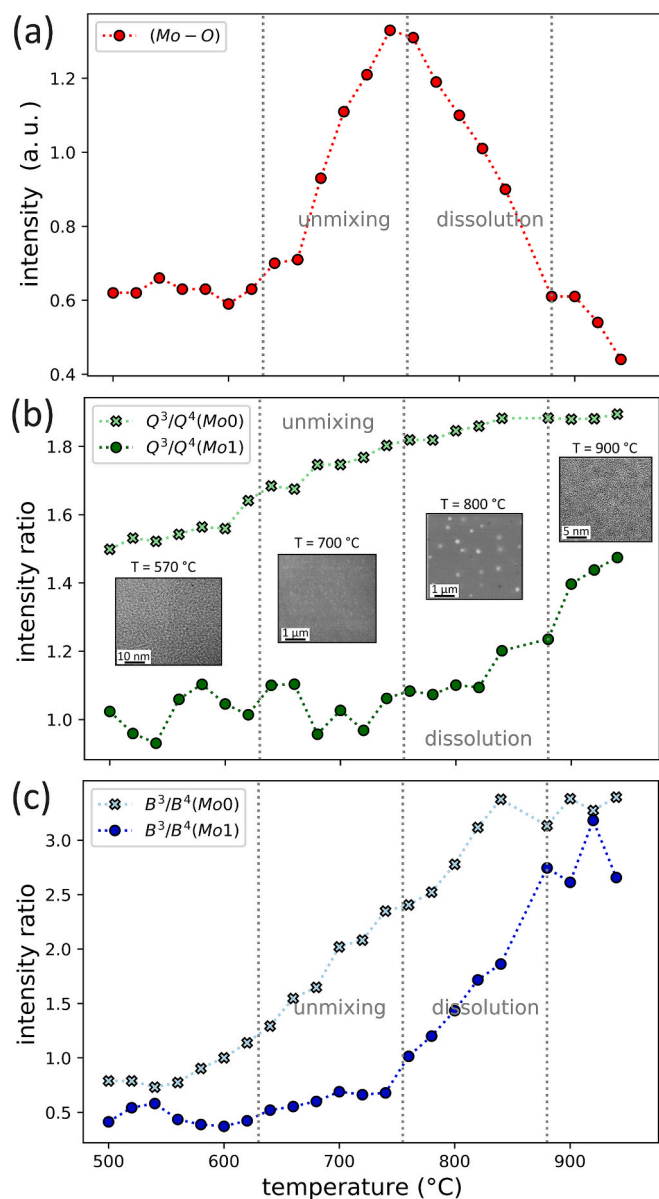
Fig. 2. (a) Intensity of $Mo-O$ as a function of temperature, (b) intensity ratio for Si in terms of Q^3/Q^4 together with the SEM and TEM images obtained after quenching the samples from an isothermal heat treatment at the displayed temperatures (570, 700, 800, 900 °C) for a constant duration of 1 h, and (c) intensity ratio for B network in terms of B^3/B^4.

increases [10,14], whereas the behavior of the Mo1 sample is different. At temperatures above 630 °C, its B^3/B^4 ratio is constant, reflecting a relative polymerization of the borate network during alkali- and molybdenum-rich droplet formation compared with the Mo0 sample. At temperatures above ca. 740 °C, the B^3/B^4 ratio increases again reflecting the depolymerization caused by the return of alkali and molybdenum to the network during droplet re-mixing and phase homogenization of the sample. Comparing the initial homogeneous glass with the final homogeneous melt for the Mo0 and Mo1 samples, the borate network exhibits a lower B^3/B^4 ratio in Mo1 compared to Mo0, agreeing with the charge compensation required by the $[MoO_4]^{2-}$ entities. Moreover, the borate network demonstrates greater sensitivity to the formation and re-dissolution of Mo-bearing droplets when compared to the silicate network (cf. Fig. 2b, 2c).

5. Conclusion

We studied the structure of borosilicate glass containing molybdenum using in-situ Raman spectroscopy at high-temperatures. We observed that this system undergoes polymerization upon formation of droplets enriched in alkali and molybdenum. At higher temperature, these droplets remix and the network matrix undergoes depolymerization.

CRediT authorship contribution statement

Luiz Pereira: Writing – original draft, Visualization, Software, Investigation, Formal analysis, Conceptualization. **Sophie Schuller:** Writing – review & editing, Visualization, Investigation, Formal analysis, Conceptualization. **Adrien Donatini:** Writing – review & editing, Visualization, Software, Investigation, Formal analysis, Data curation. **Fabian B. Wadsworth:** Writing – review & editing, Visualization. **Daniel R. Neuville:** Writing – review & editing, Visualization. **Donald B. Dingwell:** Writing – review & editing, Visualization, Funding acquisition. **Dominique De Ligny:** Writing – review & editing, Visualization, Methodology, Investigation, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matlet.2024.137776.

Data availability

Data will be made available on request.

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