Effect of $V_2O_5$ on crystallization tendency and chemical durability of Mo-bearing aluminoborosilicate glass

Qihui Lian, Xingquan Zhang, Hongjia Ji, Pengpeng Yu, Xiaofeng Guo, Wei Wan, Haifeng Liu, Kui Zheng, Yongchang Zhu, Haibin Wang and Jichuan Huo

1 State Key Laboratory of Environment-friendly Energy Materials, Southwest University of Science and Technology, Mianyang 621010, People’s Republic of China
2 Institute of Quartz and Special Glasses, China Building Materials Academy, Beijing, 100024, People’s Republic of China
3 Key Laboratory of Inorganic Materials Preparation and Synthesis, Mianyang Normal University, Mianyang, Sichuan 621010, People’s Republic of China
4 Authors to whom any correspondence should be addressed.

E-mail: zxqli@163.com and huojichuan@swust.edu.cn

Keywords: high-level liquid waste, molybdenum oxide, borosilicate glass, solubility, chemical durability

Abstract

The effect of $V_2O_5$ addition on molybdates crystallization tendency, glass structure and chemical durability of aluminoborosilicate glass belonging to SiO$_2$-B$_2$O$_3$-CaO-Na$_2$O-Al$_2$O$_3$-MoO$_3$ system has been studied. The results confirm that $V_2O_5$ addition can effectively suppress the crystallization tendency of powellite and enhance the molybdenum solubility in the glass. The MoO$_3$ solubility limit is found to be 2.8 mol% in the $V_2O_5$-containing aluminoborosilicate glass. Raman results reveal that $V_2O_5$ addition seems to modify the local structural environment of isolated MoO$_4$ units and increase their chemical disorder in the glass, which is favored for molybdenum incorporation in the glass. The molar volume and glass transition temperature of samples are found to depend on $V_2O_5$ content. Product consistency test (PCT) results show that the normalized leaching rates of the $V_2O_5$-containing aluminoborosilicate glass maintain at a fairly low level compared with standard borosilicate glassy waste form.

1. Introduction

Highly radioactive liquid waste (HLW) resulting from spent nuclear fuel reprocessing is highly hazardous to human beings and the environment, due to its radioactivity and biological toxicity. The safe disposal of HLW has drawn a great deal of attention from the public and governments [1–6]. Currently, vitrification is a worldwide recognized method to immobilize HLW, and borosilicate glasses have been employed to immobilize HLW on an industrial scale in several countries [7–9].

Higher concentration of molybdenum is usually present in HLW streams resulting from the reprocessing of commercial spent nuclear fuel due to the high burn-up. Based on previous studies, molybdenum has a very low solubility in alkali borosilicate glass under usual elaboration conditions. Above the solubility limit, a molybdate salt phase (‘yellow phase’) is usually separated from glass melt during the melting stage. This yellow phase is dominated by crystals of alkali molybdates (Na$_2$MoO$_4$), which would gather radioactive elements like $^{137}$Cs, $^{90}$Sr and minor actinides. On account of the solubility of Na$_2$MoO$_4$ in water, the yellow phase can severely decrease the chemical durability of nuclear waste forms. In addition, the yellow phase would also corrode melter liners and impede the vitrification process [10–12].

Mo cations primarily exist as a hexavalent state Mo$^{6+}$ in borosilicate glasses prepared in oxidizing or neutral conditions and take the form of [MoO$_4$]$^{2-}$ tetrahedra, which locate in the alkali and alkaline earth enriched depolymerized regions of the glass network [13–16]. In order to improve the solubility of MoO$_3$ via suppressing the formation of yellow phase in borosilicate glass, a number of studies have been conducted by developing new or modified glass formulation [17–21]. The strategies include adding proper amount of rare earth (e.g., Nd and La)
or high field strength modifiers such as Li [20], Mg [21] to the components, adjusting the ratio of Ca to Na and Na to B of the components [22–26], and increasing the B2O3 level [27] in borosilicate glass.

Recently, a potential glass waste form based on iron–phosphate (40Fe2O3–60P2O5) has been developed by Hsu et al [28] to immobilize HLW with high content of MoO3. No phase separation was observed in this iron-phosphate glass when the MoO3 content reaches up to 30 wt%. Moreover, Mo cations can bond well with phosphate units in the glass structure, which indicates that the compatibility of molybdenum and phosphate tetrahedrons is better than that of molybdenum and silicate tetrahedrons. However, due to the poor thermal and chemical durability properties, phosphate glass is undesirable in nuclear industry. Therefore, to address these problems during nuclear waste immobilization, it is felt prudent to develop borosilico-vanadate glasses based on the similar ‘crystallo-chemical’ features of V2O5 and P2O5. This glass matrix may not only present the ability to incorporate high content of MoO3 but also have better chemical durability and thermal stability than phosphate glass. Vanadium ions in alkali borosilicate glass mainly occupy V(VI)O4 units and the introduction of V2O5 can modify the structural around B- or Si-centred structural units induced by Mo ions [15, 29]. Therefore, it is expect that vanadium addition can suppress the preference of alkali ions for Mo(V)O4, owing to equivalent or even higher priority of alkali ions coordination with V(VI)O4 units, which would enhance the solubility of MoO3 in borosilicate glass and suppress the formation of yellow phase precipitation. However, a detailed description the effect of V2O5 addition on structure and physical properties (e.g., chemical durability, density, molar volume and glass transition temperature) of Mo-bearing borosilicate glass is still missing.

The aim of this work is to evaluate the influence of V2O5 content on crystallization tendency and microstructure of a modified aluminoborosilicate, which contains simultaneously MoO3 and V2O5. For the purpose, a Mo-enriched aluminoborosilicate glass composition has been chosen in the SiO2–B2O3–Na2O–CaO–Al2O3–MoO3 system, which is derived from a more complex glass envisaged to immobilize Mo-enriched HLW. Accordingly, two series of aluminoborosilicate glasses have been synthesized and characterized. The structural re-adjustments influence on the glass properties has also been studied.

2. Experimental

For this work, two series of glass (Vx–M2 and My–V3) were synthesized by melt quenching method.

Series Vx–M2: (1−x/100) (58.76 SiO2−13.86 B2O3−11.30 Na2O−2.85 Al2O3−11.23 CaO−2.00 MoO3− x V2O5 (x = 0, 0.6, 1.2, 1.8, and 3.0, mol%));

Series My–V3: (1−y/100) (58.16 SiO2−13.72 B2O3−11.18 Na2O−2.82 Al2O3−11.11 CaO−3.00 V2O5−y MoO3 (y = 2.0, 2.5, 2.8, and 3.0, mol%).

The raw materials of SiO2, CaCO3, Al2O3, H3BO3, Na2CO3, MoO3, and V2O3 with purity higher than 99 wt% were mixed by ball-milling for 3 h. Compositions of batches were given in table 1. The obtained samples were dissolved in nitric acid and the solution was analyzed for Si, B, Ca, Al, Na, Mo and V by inductively coupled plasma–atomic emission spectroscopy [21, 30]. The obtained results showed good agreement between experimental and nominal glass compositions. For each oxide, the relative molar loss during melting was always lower than 3% of the nominal composition values, which indicates that only weak loss of volatile oxides such as B2O3, Na2O and V2O3 occurred during melting. About 50 g of the mixture was heated in alumina crucibles to dissociate the carbonates and borate and then melted isothermally for 3 h at 1300 °C to form homogeneous melts, followed by quenching of the melts into water. The quenched samples were crushed and melted again at 1300 °C for 2 h to ensure homogeneity, then poured onto a preheated steel plate.

X-ray diffraction (XRD) data was collected on an X’ Pert PRO diffractometer using Cu-Kα radiation (λ = 1.54187 Å) [31, 32]. For XRD measurement, powdered samples with particle size ≤ 80 μm were used. Raman spectra were measured using a micro Raman spectrometer. The microstructure and microtopography of the obtained samples were studied on a Zeiss Ultra 55 field emission scanning electron microscope in the backscattered electron mode. Glass transformation temperature of the samples was determined by differential temperature analysis (DTA, SDT Q600, TA Instruments Inc.) with heating at 20 °C/min in air. Bulk densities of the obtained samples were determined using Archimedes method.

The chemical durability of the obtained samples was evaluated by PCT method according to ASTM C1285-14 [33]. The samples were crushed into granules, selected by sieving (75–150 μm), cleaned with deionized water and dried. Then 3 g sample was soaked in 80 mL deionized water (pH = 7) in Teflon reactors and kept in an oven at 90 ± 1 °C. Leachates were taken from the reactors at the end of 1, 3, 7, 14, 28 days respectively. These powdered samples were cleaned with absolute ethanol, dried and then mixed with new deionized water after each removal of leachate. The ion concentrations in leachate were obtained by inductively coupled plasma (ICP) analysis using an iCP A 6500 spectrometer (Thermo Fisher Company, USA). The normalized leaching rate LR, was calculated according to the following equation:
3. Results and discussion

The effect of V$_2$O$_5$ content on the crystallization tendency of the glass has been qualitatively estimated on the basis of XRD analysis as shown in figure 1. It can be found that all samples exhibit a broad peak in the 2$_\theta$ ranges of 15°-35°, which is regarded as the characteristic amorphous nature pattern of the samples. For the samples with $x = 0$, the diffraction peaks can be indexed to powellite phase CaMoO$_4$. However, the intensity of these diffraction peaks progressively decreases with increasing V$_2$O$_5$ content, and no more CaMoO$_4$ phase is detected for samples with more than 1.8 mol% V$_2$O$_5$, which indicates that the incorporation of V$_2$O$_5$ in aluminoborosilicate glass can clearly increase the solubility of MoO$_3$.

Figure 2 shows BSE images of the as-prepared samples with different content of V$_2$O$_5$. For the samples with 0 mol% V$_2$O$_5$, it can be found that numerous Mo-rich white globules are homogeneously dispersed throughout the matrix of glass with grain size of about 200 nm in diameter. This should be related to the fact that the crystallization of CaMoO$_4$ resulted from liquid-liquid phase separation during melt cooling. With increasing the matrix of glass with grain size of about 200 nm in diameter. This should be related to the fact that the V$_2$O$_5$ content, the size of the globules remains conformably but the number of the globules reduces in the sample with 3.0 mol% V$_2$O$_5$, no vibration bands corresponding to MoO$_4$ tetrahedral entities in aluminoborosilicate glass respectively. For the samples with more than 1.8 mol% V$_2$O$_5$, no more globules are observed, which means that no phase separation and crystallization occurs during melt cooling and the obtained glass is homogeneous. These results are consistent with the obtained XRD data and indicate that V$_2$O$_5$ addition in aluminoborosilicate glass can inhibit the crystallization tendency of molybdate salt phases.

Table 1. Compositions of V$_x$-M2 (x: mol% V$_2$O$_5$) and M$_y$-V3 (y: mol% MoO$_3$) series glass.

| Batch name | SiO$_2$ | B$_2$O$_3$ | Na$_2$O | Al$_2$O$_3$ | CaO | MoO$_3$ | V$_2$O$_5$ |
|------------|--------|----------|--------|------------|-----|---------|----------|
| V0-M2$^a$  | 58.76  | 13.86    | 11.30  | 2.85       | 11.23 | 2.00    | 0.00     |
| V0-M2$^b$  | 59.11  | 13.64    | 11.01  | 2.81       | 11.45 | 1.98    | ---      |
| V0.6-M2$^c$| 58.41  | 13.78    | 11.23  | 2.84       | 11.16 | 1.99    | 0.60     |
| V0.6-M2$^d$| 59.06  | 13.41    | 11.02  | 2.89       | 11.06 | 1.98    | 0.58     |
| V1.2-M2$^c$| 58.05  | 13.69    | 11.16  | 2.82       | 11.10 | 1.98    | 1.20     |
| V1.2-M2$^d$| 58.71  | 13.35    | 10.88  | 2.75       | 11.26 | 1.97    | 1.17     |
| V1.8-M2$^c$| 57.70  | 13.61    | 11.09  | 2.80       | 11.03 | 1.96    | 1.80     |
| V1.8-M2$^d$| 58.19  | 13.36    | 10.94  | 2.83       | 10.96 | 1.94    | 1.78     |
| V3.0-M2$^c$| 57.00  | 13.45    | 10.96  | 2.77       | 10.89 | 1.94    | 3.00     |
| V3.0-M2$^d$| 57.51  | 13.14    | 10.77  | 2.72       | 10.98 | 1.92    | 2.96     |
| M2.0-V3$^a$| 57.00  | 13.45    | 10.96  | 2.77       | 10.89 | 2.00    | 2.94     |
| M2.0-V3$^b$| 57.43  | 13.03    | 10.83  | 2.71       | 11.10 | 1.99    | 2.91     |
| M2.5-V3$^a$| 56.71  | 13.38    | 10.90  | 2.75       | 10.84 | 2.50    | 2.93     |
| M2.5-V3$^b$| 56.76  | 13.18    | 10.68  | 2.81       | 11.17 | 2.49    | 2.91     |
| M2.8-V3$^a$| 56.33  | 13.34    | 10.87  | 2.75       | 10.80 | 2.80    | 2.92     |
| M2.8-V3$^b$| 57.07  | 13.07    | 10.59  | 2.72       | 10.89 | 2.77    | 2.89     |
| M3.0-V3$^a$| 56.42  | 13.31    | 10.85  | 2.74       | 10.78 | 3.00    | 2.91     |
| M3.0-V3$^b$| 56.86  | 13.02    | 10.61  | 2.79       | 10.87 | 2.98    | 2.87     |

*a* Nominal composition

*b* Composition analyzed by ICP-AES

Not analyzed

$$LR_i = \frac{C_i}{f_i \cdot \frac{SA}{V} \cdot \Delta t}$$

where $C_i$ is the concentration of the $i$-th element in the leachate (g l$^{-1}$), $f_i$ is the weight fraction of the $i$-th element in the obtained samples, $V$ is the volume of the solution (L), $SA$ is the powered samples surface area (m$^2$), and $\Delta t$ is the duration of the experiment days. $SA$ was determined using a surface area analyzer in a BET nitrogen adsorption. The $SA$ and $SA/V$ ratio are about 0.07 m$^2$ g$^{-1}$ and 2625 m$^2$ m$^{-1}$, respectively.

3. Results and discussion

The effect of V$_2$O$_5$ content on the crystallization tendency of the glass has been qualitatively estimated on the basis of XRD analysis as shown in figure 1. It can be found that all samples exhibit a broad peak in the 2$_\theta$ ranges of 15°-35°, which is regarded as the characteristic amorphous nature pattern of the samples. For the samples with $x = 0$, the diffraction peaks can be indexed to powellite phase CaMoO$_4$. However, the intensity of these diffraction peaks progressively decreases with increasing V$_2$O$_5$ content, and no more CaMoO$_4$ phase is detected for samples with more than 1.8 mol% V$_2$O$_5$, which indicates that the incorporation of V$_2$O$_5$ in aluminoborosilicate glass can clearly increase the solubility of MoO$_3$.

Figure 2 shows BSE images of the as-prepared samples with different content of V$_2$O$_5$. For the samples with 0 mol% V$_2$O$_5$, it can be found that numerous Mo-rich white globules are homogeneously dispersed throughout the matrix of glass with grain size of about 200 nm in diameter. This should be related to the fact that the crystallization of CaMoO$_4$ resulted from liquid-liquid phase separation during melt cooling. With increasing V$_2$O$_5$ content, the size of the globules remains conformably but the number of the globules reduces in the samples from $x = 0$ to $x = 1.2$ mol% (as shown in figures 2(a)$-$(c), respectively). When the V$_2$O$_5$ content reaches up to 1.8 mol%, no more globules are observed, which means that no phase separation and crystallization occurs during melt cooling and the obtained glass is homogeneous. These results are consistent with the obtained XRD data and indicate that V$_2$O$_5$ addition in aluminoborosilicate glass can inhibit the crystallization tendency of molybdate salt phases.

Figure 3 shows Raman scattering spectra of the two extreme samples ($x = 0$ and $x = 3.0$) of the Vx-M2 series. It should be noted that each spectra was normalized to the total area. For the sample with 0 mol% V$_2$O$_5$, the vibration bands at 390, 793, 864, and 878 cm$^{-1}$ are related to the Mo(VI)O$_4$ units in CaMoO$_4$ [23]. While, the vibrations modes around 322 cm$^{-1}$ and 914 cm$^{-1}$ are corresponding to the bending vibrations ($v_2$) and stretching vibrations ($v_1$) for the Mo(VI)O$_4$ tetrahedral entities in aluminoborosilicate glass respectively. For the sample with 3.0 mol% V$_2$O$_5$, no vibration bands corresponding to Mo(VI)O$_4$ units in CaMoO$_4$ are detected by Raman spectroscopy, which is in agreement with the crystallization study presented above. Raman active modes
were obtained by fitting the measured spectra according to the assignments recommended in [34]. Introduction of V$_2$O$_5$ to the glass adds vanadate V–O stretch modes near 865 cm$^{-1}$ and OV–O bend modes near 370 cm$^{-1}$ to the spectra. In addition, other peaks corresponding to Q-species of SiO$_4$ tetrahedra, and B–O stretching vibrations of BO$_4$ units are also present [35].

![Figure 1. XRD patterns of V$_x$-M2 (x: mol% V$_2$O$_5$) series samples.](image)

Figure 1. XRD patterns of V$_x$-M2 (x: mol% V$_2$O$_5$) series samples. (a) $x = 0$, (b) $x = 0.6$, (c) $x = 1.2$, (d) $x = 1.8$ and (e) $x = 3.0$.

Figure 2. BSE images of V$_x$-M2 (x: mol% V$_2$O$_5$) samples. (a) $x = 0$, (b) $x = 0.6$, (c) $x = 1.2$, (d) $x = 1.8$ and (e) $x = 3.0$.

Figure 3(b) shows Raman scattering spectra of the samples with varying concentrations of V$_2$O$_5$. It can be found that the intensity of the bands corresponding to Mo(VI)O$_4$ units in CaMoO$_4$ progressively decreases with increasing the content of V$_2$O$_5$, and no more CaMoO$_4$ was detected with more than 1.8 mol% V$_2$O$_5$. This indicates that introduction of V$_2$O$_5$ to aluminoborosilicate glass can enhance the solubility of MoO$_3$. Earlier EXAFS and NMR studies suggested that Mo(VI)O$_4$ tetrahedra are isolated from the borosilicate network and are surrounded by alkali/alkaline-earth cations. The changes of cation-type and the average charge density of the alkali and alkaline earth cations neighboring molybdate tetrahedra can modify the environment around molybdate tetrahedra in the glass structure [36]. The enhancement of MoO$_3$ solubility in aluminoborosilicate glass resulted from V$_2$O$_5$ addition may be attributed to modifications of the environment around Mo(VI)O$_4$ tetrahedra in the glass structure. Suzuki et al. [35] has examined the chemical state of vanadium ions in the multicomponent borosilicate glass and found that V(V)O$_4$ is present as the dominant state. In addition, V(V)O$_4$
tetrahedra in borovanadate and borosilicate glasses are partially present as isolated ion species and acts as a network modifier in low contents [29, 34]. When V(V)O₄ tetrahedra are present in molybdenum-bearing borosilicate glass, the following priority is found for the alkali ion coordination: AlO₄ > VO₄ > MoO₄⁻² > SiO₄ (Q² or Q³) or BO₄ [35]. V(V)O₄ tetrahedra can strongly modify the distribution of the network modifying cations in glassy network and suppress the preference of the alkali/alkaline-earth cations only around Mo(VI)O₄ tetrahedral. In addition, earlier Raman studies of vanadate-molybdate crystals revealed that (Mo, V)O₄ tetrahedra share oxygen atoms with (Li, Mg)O₆ octahedra and other six-coordinated Li, Mg-environments [37]. Therefore, the Vanadium ions added to the glass may locate in the nearness of the molybdate entities, which could disturb the clusterization tendency of Mo(VI)O₄ units. Consequently, these modifications of the environment around Mo(VI)O₄ tetrahedra in the glass structure would suppress the crystallization tendency of molybdate salt phase and improve MoO₃ solubility in aluminoborosilicate glass. In order to understand more precisely the relationship between molybdenum and vanadium in the glass structure, further structural characterization such as NMR (⁹⁵Mo, ¹¹B, ²⁷Al, ²³Na and ²⁹Si) will be performed in the following work.

To determine the MoO₃ solubility limit within the studied aluminoborosilicate glass, samples were prepared with incremental additions of MoO₃ up to 3 mol%. Figure 4 shows XRD and Raman scattering spectra of Vₓ-M2 (x: mol% V₂O₅) series samples. It can be found that no crystalline phase is formed other than glass phase even MoO₃ addition up to 2.8 mol% in V₂O₅-containing aluminoborosilicate glass. When the content of MoO₃ is close to 3 mol%, the powellite phase CaMoO₄ is detected. These results indicate that V₂O₅ addition can obviously enhance the solubility of MoO₃ in aluminoborosilicate glass and V-containing borosilicate glass samples can accommodate up to 2.8 mol% of MoO₃.

The density of the Vₓ-M2 series samples was measured at room temperature by the Archimedes method. The molar volume (Vₓ) of each sample was evaluated using the following formula:

\[
V_M = \frac{x_i M_i}{\rho}
\]

Where \(x_i\) is the molar fraction and \(M_i\) is the molecular weight of the ith component, and \(\rho\) is the density. Figure 5 (a) shows the density and molar volume of the Vₓ-M2 series samples as a function of V₂O₅ content. It can be observed that density slightly decreases with increasing V₂O₅ content, where as molar volume increases. Similar results has been observed in V₂O₅ loaded soda-lime silicate glasses [38, 39], which indicates that the network structure of the glass is more open and the structure becomes loosely packed. Previous reports revealed that incorporation of V₂O₅ into silicate glasses results in the reconversion of BO₄ tetrahedra to BO₃ triangles by the breaking of B-O-B linkages and the formation of nonbridging oxygens (NBOs) [34, 35]. The increase in molar volume may be regarded as an outcome of the regular evolution of more NBOs, which is characteristic of alteration of the volume concentration. To get better insight, by virtue of the approximated values of the density and molar volume, the molar volume of oxygen (Vₒ) (volume of glass in which 1 mol of oxygen is confined) and the oxygen packing density (OPD) were calculated using the following formula [40, 41]:

\[
\text{OPD} = \frac{V_o}{\rho}
\]
Figure 4. XRD patterns and Raman spectra of M_{y}-V_{3} (y: mol% MoO_{3}) glasses (P: Mo-O vibration modes related to CaMoO_{4}).

Figure 5. (a) Density (ρ) and molar volume (V_{M}) and (b) oxygen molar volume (V_{O}) and oxygen packing density (OPD) of the V_{x}-M_{2} (x: mol% V_{2}O_{5}) series samples.
where M is the molecular mass of the glass sample and n is the number of oxygen atoms per formula units. Figure 5(b) shows the molar volume of oxygen and OPD of the Vx-M series samples as a function of V₂O₅ content. It can be observed that the molar volume of oxygen increases and the OPD decreases with a rise in the concentration of V₂O₅. It is generally believed that OPD is presentation of the compactness of glass structure and is dependent on the number of bridging and non-bridging oxygen atoms. The behavior of the molar volume of oxygen and OPD with increasing V₂O₅ content indicates that the glass network is more open and the structure turns out to be less tightly packed because of the re-arrangement of NBOs\(^{[42]}\). The glass transition temperature (\(T_g\)) values of these samples determined by differential temperature analysis are 582.42 °C, 577.94 °C, 564.36 °C, 561.52 °C, and 560.26 °C respectively. It can be found that \(T_g\) of these samples decreases with increasing V₂O₅ content, which is also attributed to the influence of V₂O₅ addition on the glass network structure.

The leaching properties of the as-prepared samples were examined by PCT tests. The calculated normalized leaching rates of Si (\(LR_{Si}\)), Ca (\(LR_{Ca}\)), Mo (\(LR_{Mo}\)) and V (\(LR_{V}\)) of all glass present a gradual downward trend with increasing leaching time in the first 14 days and remain basically unchanged after 14 days. This should be due to the passivation layer formed on the sample surface. In addition, the normalized leaching rates of V₂O₅-containing samples are slightly lower than that of V₂O₅ freeing samples in the first 14 days. While, the normalized leaching rates at 28 days of all samples are almost equal. This indicates that V₂O₅ addition has no obvious effect on the leaching properties of aluminoborosilicate glass. After 28 days, the \(LR_{Si}, LR_{Ca}, LR_{Mo}\) and \(LR_V\) of the sample with 3 mol% V₂O₅ are about 1.21 x 10⁻³ g·m⁻²·d⁻¹, 6.24 x 10⁻⁴ g·m⁻²·d⁻¹, 1.35 x 10⁻³ g·m⁻²·d⁻¹, and 9.54 x 10⁻⁴ g·m⁻²·d⁻¹ respectively, which are lower than those of the standard borosilicate glassy waste form\(^{[43]}\).

4. Conclusion

V₂O₅-containing aluminoborosilicate glass was proposed and synthesized using melt quenching method to enhance the MoO₃ solubility in glass matrix. V₂O₅ can effectively suppress the crystallization tendency of powellite phase CaMoO₄ and improve the solubility of MoO₃ in aluminoborosilicate glass. V₂O₅-containing
aluminoborosilicate can accommodate 2.8 mol% of MoO₃. The probable explanation for the enhancement of MoO₃ solubility in aluminoborosilicate glass by V₂O₅ addition could be (1) the depletion of alkali/alkaline-earth ions in Mo(VI)O₄ surrounding (2) the increase of the dispersion of Mo(IV)O₄ units in the glass. The molar volume and glass transition temperature of samples are found to depend on V₂O₅ content. After 28 days, the normalized leaching rates of all modified aluminoborosilicate glass maintain at a fairly low level compared with standard borosilicate glassy waste form. Results of this initial investigation indicate that V₂O₅-containing aluminoborosilicate glass is potential hosts for the immobilization of Mo-bearing high-level nuclear waste. This work will continue to be investigated by focusing on understanding more precisely the relationship between molybdenum and vanadium in the glass structure.

Acknowledgments

This research was supported by the National Natural Science Foundation of China [11702268] and the Postgraduate Innovation Fund Project by Southwest University of Science and Technology [19ycx0005].

ORCID iDs

Xingquan Zhang @ https://orcid.org/0000-0003-2012-6615
Kui Zheng @ https://orcid.org/0000-0001-5541-1980

References

[1] Lutze W and Ewing R C 1988 Radioactive Waste forms for the Future (Amsterdam: North-Holland)

[2] Ojovan M I and Lee W E 2007 New Developments in Glassy Nuclear Waste forms (New York: Wiley)

[3] Molin S, Micheal I O, Hyatt N C and Hand R J 2015 MoO₃ incorporation in magnesium aluminosilicate glasses J. Mater. Res.

[4] Donald I W 2010 Waste Immobilization in Glass and Ceramic Based Hosts, Radioactive, Toxic and Hazardous Wastes (Chichester, UK: Wiley)

[5] Remanian M, Bhowmik S, Varshney I and Jayaranayan K 2018 Poly(aryl ether ketone) based individual, binary and ternary nanocomposites for nuclear waste storage: mechanical, rheological and thermal analysis Mater. Res. Express 5 105306

[6] Mail I T, Tran T D, Itaka T and Nguyen V H 2017 Computer simulation of CaSiO₃ glass under compression: correlation between Si-Si pair radial distribution function and intermediate range order structure Mater. Res. Express 4 065201

[7] Ojovan M I, Lee W E and Lee W 2005 “An Introduction to Nuclear Waste Immobilization” (Amsterdam: Elsevier)

[8] Short R J 2004 Incorporation of molybdenum in nuclear waste glasses PhD Thesis The University of Sheffield(UK)

[9] Pegg I L 2015 Turning nuclear waste into glass Phys. Today 68 33–9

[10] Xu K, Pearce D A, Hrma P, Schweiger M J and Kruger A A 2015 Rhenium volatilization in waste glasses J. Nucl. Mater. 464 382–8

[11] Nicoleau E, Schuller S, Angeli F, Charpentier T, Jollivet P, Alexandre L G, Fournier M, Mesbah A and Vasconcelos, F 2015 Phase separation and crystallization effects on the structure and durability of molybdenum borosilicate glass J. Non-Cryst. Solids 427 120–33

[12] Kroezer S, Schuller S, Wren J E C, Greer B J and Mesbah A 2016 133Cs and 23Na MAS NMR spectroscopy of molybdate crystallization in model nuclear glasses J. Am. Ceram. Soc. 99 1557–64

[13] Caurant D, Majérus O, Fadel E, Quintas A, Charpentier T and Neville D 2010 Structural investigations of borosilicate glasses containing MoO₃ by MAS NMR and Raman spectroscopies J. Nucl. Mater. 396 94–101

[14] Magnin M, Schuller S, Caurant D, Majerus O, Ligny D D and Mercier C 2009 Effect of compositional changes on the structure and crystallization tendency of a borosilicate glass containing MoO₃ Ceram. Trans. 207 59–67

[15] McKeown D A, Muller I S, Matlock K S and Pegg I L 2002 X-ray absorption studies of vanadium valence and local environment in borosilicate waste glasses J. Non-Cryst. Solids 298 160–75

[16] Calas G, Grand M L, Galoisy I and Ghaled, D 2003 Structural role of molybdenum in nuclear glasses: an EXAFS study J. Nucl. Mater. 322 15–20

[17] Brehat A, Patil D, Kamat H, Youngman R E, Thirion I M, Mauro J C, Corkhill C L, McCloy J S and Goel A 2018 Compositional dependence of solubility/retention of molybdenum oxides in aluminoborosilicate-based model nuclear waste glasses J. Phys. Chem. B 122 1714–29

[18] Chouard N, Caurant D, Majerus O, Dussossoy J L, Leduc F, Peugeot S, Hadj-Campos R and Rams 2011 Feudalized oxide on the solubility of MoO₃ in an aluminoborosilicate glass J. Non-Cryst. Solids 357 1775–82

[19] Kossoy A, Schulze R, Tang M, Safarik D J and McCabe R J 2013 Nd–Mo–borosilicate glass–ceramic: synthesis, characterization and response to ionizing radiation J. Nucl. Mater. 437 216–21

[20] Szumera M 2014 Structural investigations of silicate–phosphate glasses containing MoO₃ by FTIR, Raman and 31P MAS NMR spectroscopies Spectrochim. Acta, Part A 130 1–6

[21] Prakash A D et al 2019 Studies on modified borosilicate glass for enhancement of solubility of molybdenum J. Non-Cryst. Solids 510 172–8

[22] Konstantinou K, Sushko P V and Duffy D M 2016 Modeling the local atomic structure of molybdenum in nuclear waste glasses with ab initio molecular dynamics simulations Phys. Chem. Chem. Phys. 18 26212–32

[23] Tan S, Michel F O, Hyatt N C and Hand R J 2015 MoO₃ incorporation in magnesium aluminosilicate glasses Journal of Nucl. Mater. 458 335–42

[24] Quintas A, Charpentier T, Majerus O, Caurant D, Dussossoy J L and Vermaut P 2007 NMR study of a rare-earth aluminoborosilicate glass with varying CaO–Na₂O ratio Appl. Magn. Reson. 32 613–34

[25] Quintas A, Majerus O, Caurant D, Dussossoy J L and Vermaut P 2007 Crystallization of a rare earth in rich aluminoborosilicate glass with varying CaO/Na₂O ratio J. Am. Ceram. Soc. 90 712–9
[26] Magnin M, Schuller S, Mercier C, Trebosc J, Caurant D, Majérus O, Angéli F, Charpentier T and Jantzen C 2011 Modification of molybdenum structural environment in borosilicate glasses with increasing content of boron and calcium oxide by $^{95}$Mo MAS NMR J. Am. Ceram. Soc. 94 4274–82

[27] Caurant D, Majérus O, Fadel E, Lenoir M, Gervais C and Pinet O 2007 Effect of molybdenum on the structure and the crystallization of SiO$_2$-Na$_2$O-CaO-B$_2$O$_3$ J. Am. Ceram. Soc. 90 774–83

[28] Hsu J, Bai J, Kim C, Brow R, Szafoi J and Zervos A 2018 The effects of crystallization and residual glass on the chemical durability of iron phosphate waste forms containing 40 wt% of a high MoO$_3$ Collins-CLT waste J. Nucl. Mater. 500 373–80

[29] Sengupta P, Dey K, Halder R, Ajithkumar T, G, Abraham G, Mishra R K, Kaushik C P and Dey G K 2015 Vanadium in borosilicate glass J. Am. Ceram. Soc. 98 88–96

[30] Chouard N, Caurant D, Majérus O, Fadel E, Lenoir M, Gervais C and Pinet O 2007 Effect of molybdenum on the structure and the crystallization of SiO$_2$-Na$_2$O-CaO-B$_2$O$_3$ J. Am. Ceram. Soc. 90 774–83

[31] Hsu J H, Bai J C, Kim C W, Brow R K, Szabo J and Zervos A 2018 The effects of crystallization and residual glass on the chemical durability of iron phosphate waste forms containing 40 wt% of a high MoO$_3$ Collins-CLT waste J. Nucl. Mater. 500 373–80

[32] Sengupta P, Dey K, Halder R, Ajithkumar T, G, Abraham G, Mishra R K, Kaushik C P and Dey G K 2015 Vanadium in borosilicate glass J. Am. Ceram. Soc. 98 88–96

[33] Kidari A, Dussossoy J L, Brackx E, Caurant D, Magnin M and Giboire I B 2012 Lanthanum and neodymium solubility in simplified SiO$_2$-B$_2$O$_3$-Na$_2$O-Al$_2$O$_3$-CaO high level waste glass J. Am. Ceram. Soc. 95 2537–44

[34] Xie R S, Li Y L, Liu H F and Zhang X Q 2017 Insights into the structural, microstructural and physical properties of multiphase powder mixtures J. Alloys Compd. 691 378–87

[35] ASTM C1285-14 2014 Standard Test Methods for Determining Chemical Durability of Nuclear, Hazardous, and Mixed Waste Glasses and Multiphase Glass Ceramics: the Product Consistency Test (PCT) (West Conshohocken, PA: ASTM International)

[36] Gillie L J, deSouza S A, Sheptyakov D, Reeves-McLaren N, Pasero D and West A R 2010 Synthesis, structural characterization and Li$^+$ ion conductivity of a new vanado-molybdate phase, LiMg$_3$VMo$_2$O$_{12}$ J. Solid State Chem. 183 2589

[37] Lu X N, Sun R F, Huang L P, Ryan J V, Vienna J D and Du J C 2019 Effect of vanadium oxide addition on thermomechanical behaviors of borosilicate glasses: toward development of high crack resistant glasses for nuclear waste disposal J. Non-Cryst. Solids 515 88–97

[38] Kundu V, Dhiman R L, Maan A S and Goyal D R 2008 Structural and physical properties of Fe$_2$O$_3$-B$_2$O$_3$-V$_2$O$_5$ glasses Adv. Cond. Matter. Phys. 2008 937054

[39] Mariyappan M, Marimuthu K, Sayyed M I, Dong M G and Kara U 2018 Effect Bi$_2$O$_3$ on the physical, structural and radiation shielding properties of Er$^{3+}$ ions doped bismuth sodiumfluoroborate glasses J. Non-Cryst. Solids 499 75–85

[40] Das A S, Biswas D, Roy M, Roy D and Bhattacharya S 2019 Effect of V$_2$O$_5$ concentration on the structural and optical properties and DC electrical conductivity of ternary semiconducting glassy nanocomposites J. Phys. Chem. Solids 124 44–53

[41] Abdelghany A M and Hammad A H 2015 Impact of vanadium ions in barium borate glass Spectrochim. Acta A 137 39–44

[42] Callebut C, Angeli F, Devreux F, Gin S, Jestin J, Jollivet P and Spalla O 2008 Insight into silicate-glass corrosion mechanisms Nat. Mater. 7 978–83