

Molybdenum in Nuclear Waste Glasses - Incorporation and Redox state

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The composition and structure of the mixed metal molybdates that can form in simulated high level nuclear waste (HLW) glass melts have been studied. It was found that molybdates of a tetragonal scheelite type were formed upon heat treatment of the simulated glass samples (representative of the slow cools experienced by the real vitrified product), and that these compounds are capable of incorporating the majority of the mono, di, and trivalent cations that would be present in a real HLW glass. In addition, it has been shown that altering the redox conditions prevailing upon melting can promote or suppress crystallisation in simplified model waste glasses that contain molybdenum. Experiments to investigate the effect of redox conditions during melting of simulated HLW glass on molybdate formation are also reported.

INTRODUCTION

Borosilicate glasses used for the vitrification of HLW have good long term chemical durability and are able to incorporate a wide range of radionuclides in an amorphous matrix[1-3]. However, depending on the waste loading, redox conditions of the melt and the cooling time of the glass, the amorphous matrix can devitrify which can have a deleterious affect on the glass quality. Redox states (such as Fe^{3+}) in commercial bulk glass compositions have been widely studied (see [4] for example), however less attention has been paid to the effects of redox on nuclear waste glasses. One particular element of interest with multiple oxidation states is Mo. HLW streams (such as the simulated stream used here) that are high in Mo are particularly likely to cause devitrification in borosilicate glasses due to the low solubility of Mo in the glass (approx. 1%[5]). The generic name given to devitrified phases containing molybdenum is 'yellow phase'. Yellow phase accelerates corrosion of the inconel melters in the liquid state and is highly water soluble in the solid state and thus, as it contains a wide range of fission products, yellow phase formation is highly undesirable during HLW vitrification. In the current work the formation of molybdate based crystalline phases in a simulated HLW glass has been studied. The phases have been identified and factors affecting their formation investigated.

EXPERIMENTAL

A series of glasses based a sodium borosilicate base glass composition specified by BNFL and containing a simulated HLW composition were melted (Table 1). Quantities of some elements (such as Ag and Nd) have been boosted to simulate the more costly or radioactive elements (such as Rh, Pd and the actinides) that would be present in a real HLW stream. Although 35wt% is a significantly higher waste loading than is currently used in these glasses, this level of loading (as well as 20wt%) was studied to encourage devitrification and therefore easier phase identification. All of the chemicals were AR>99.5% and where the oxides were unavailable, the corresponding carbonate was used. The batch was preheated overnight to 1000°C at 1°C/min in an alumina crucible, then transferred to an electric furnace with Kanthal

Table 1. Composition of simulated HLW glasses

Oxide	HM4 20% waste (A) Wt %	HM4 35% waste (B) Wt %	Simplified HM4 equivalent to 25% Waste (C) Wt %	Simplified HM4 equivalent to 35% waste (D) Wt %	HM4 1%Mo (E) Wt %
SiO ₂	49.44	40.17	46.35	40.17	61.18
B ₂ O ₃	17.52	14.24	16.43	14.24	21.68
Na ₂ O	8.80	7.15	16.50	14.30	10.89
Li ₂ O	4.24	3.45	Replaced with Na ₂ O	Replaced with Na ₂ O	5.25
Ag ₂ O	1.41	2.47	0	0	0
BaO	0.94	1.64	0	0	0
CeO	1.33	2.33	0	0	0
Cs ₂ O	1.31	2.29	1.94	2.72	0
Gd ₂ O ₃	2.77	4.86	Replaced with Nd ₂ O ₃	Replaced with Nd ₂ O ₃	0
La ₂ O ₃	0.71	1.24	Replaced with Nd ₂ O ₃	Replaced with Nd ₂ O ₃	0
MoO ₃	2.39	4.19	2.99	4.19	1.00
Nd ₂ O ₃	3.00	5.24	8.47	11.85	0
Rb ₂ O	0.16	0.29	Replaced with Cs ₂ O	Replaced with Cs ₂ O	0
Sm ₂ O ₃	0.44	0.77	Replaced with Nd ₂ O ₃	Replaced with Nd ₂ O ₃	0
SrO	0.41	0.73	0	0	0
TeO ₂	0.12	0.21	0	0	0
TiO ₂	0.53	0.94	0	0	0
Y ₂ O ₃	0.25	0.43	0	0	0
ZrO ₂	2.20	3.86	0	0	0
Fe ₂ O ₃	0.33	0.58	0	0	0
NiO	0.09	0.17	0	0	0
Cr ₂ O ₃	0.10	0.18	0	0	0

SiC elements. The total melting time was 5.5 h, and an alumina stirring paddle was inserted after 1 h of melting and rotated at 60rpm to compensate for the lack of convection currents in the crucible which occur in full scale melts at the Sellafield vitrification plant. Some glasses were sparged with O₂, compressed air or N₂/5%H₂ during melting. For these glasses, a pure alumina tube was inserted into the glass melt to a depth of approximately 10mm from the base of the crucible and connected to the appropriate gas cylinder depending upon the atmosphere required. The gas flow rate was 5l/min. The glasses were cast into a preheated steel mould and annealed at 550°C for 1h then cooled to room temperature at 1°C/min. The glasses were examined using X-ray powder diffraction (XRD) and Electron Spin Resonance (ESR) Spectroscopy (done at the University of Birmingham). XRD samples were ground to a fine powder (<200µm), front loaded into an aluminium sample holder, and scanned using a Philips PW1373 X-ray Powder Diffractometer. Cu/Kα radiation was used at 50kV, with a step size of 0.02°, and scanning speeds between 2 and 0.5°/min depending on the level of resolution required. ESR samples were ball milled using alumina balls to a fine powder (<75µm) and were analysed using a Bruker ESP 300 spectrometer at a frequency of 9.89GHz. Some ceramic powders of AMoO₄ scheelite-type phase were synthesized to help interpret the diffraction data obtained from the glass samples (see Table 2). Oxides or carbonates of these elements were mixed with the appropriate quantities MoO₃ to form 10g of the end product, and then ground using an agate mortar and pestle. The resulting batch was placed in a small alumina crucible and covered with an alumina lid to minimize volatilization and prevent contamination, heated to 700°C at 5°C/min held for 10 hrs and cooled back down to room temperature. The samples were then reground to increase reactivity, and reheated using the same schedule.

Table 2 – Compositions of synthesised molybdates

$\text{AgGd}(\text{MoO}_4)_2$	$\text{LiNd}(\text{MoO}_4)_2$	$\text{Li}_{0.5}\text{Na}_{0.5}\text{Nd}(\text{MoO}_4)_2$	$\text{KBa}_{0.5}(\text{MoO}_4)$
$\text{AgLa}_{0.5}\text{Gd}_{0.5}(\text{MoO}_4)_2$	$\text{NaNd}(\text{MoO}_4)_2$	$\text{Li}_{0.5}\text{K}_{0.5}\text{Nd}(\text{MoO}_4)_2$	$\text{K}_{0.25}\text{Ba}_{0.5}\text{La}_{0.25}(\text{MoO}_4)_2$
$\text{AgCe}(\text{MoO}_4)_2$	$\text{KNd}(\text{MoO}_4)_2$	$\text{Li}_{0.5}\text{Rb}_{0.5}\text{Nd}(\text{MoO}_4)_2$	$\text{Na}_{0.25}\text{Sr}_{0.5}\text{Nd}_{0.25}(\text{MoO}_4)_2$
	$\text{RbNd}(\text{MoO}_4)_2$	$\text{Li}_{0.5}\text{Cs}_{0.5}\text{Nd}(\text{MoO}_4)_2$	$\text{Na}_{0.25}\text{Ba}_{0.5}\text{Nd}_{0.25}(\text{MoO}_4)_2$
	$\text{CsNd}(\text{MoO}_4)_2$		

RESULTS

Glass B (35% waste) phase separated upon cooling and an EDS analysis of the crystalline phase showed that it was higher in Mo than the amorphous matrix. A sample of this glass was heat treated for 48h at 650°C to encourage growth of the crystalline phase to aid XRD analysis (see Fig 1) as this schedule had been found (by previous experiments) to give maximum devitrification in the glass. The XRD and EDS data indicate that the major crystalline phase in the glass is a scheelite-type molybdate of the $\text{AB}(\text{MoO}_4)_2$ type where A and B are +1 and +3 alkali metal and lanthanide cations respectively. However, due to the large number of ions that could potentially occupy the A and B sites it was not possible to positively identify the phase. XRD of the prepared molybdate phases (Fig 2) showed that it is possible to accommodate +1, +2 and +3 cations into the scheelite structure to form an $\text{AB}_2\text{C}(\text{MoO}_4)_4$ compound such as $\text{NaSr}_2\text{Nd}(\text{MoO}_4)_4$ or $\text{KBa}_2\text{La}(\text{MoO}_4)_4$.

Simplified Batches

To assist the analysis of redox effects on the simulated HLW glasses, simplified batches of the glass (Table 1) were melted under oxidising (O_2), neutral (air) and reducing ($\text{N}_2/5\%\text{H}_2$) atmospheres. Only the reduced 25wt% waste glass and the oxidised 35wt% waste glass showed evidence of the presence of crystalline material (Fig 3). XRD indicated the presence of Mo metal and $\text{Nd}_2\text{Mo}_3\text{O}_9$, however a conclusive identification could not be made on the basis of this data due to the small number of weak reflections observed. To encourage growth of crystalline phases, the glasses were heat treated for 48h at 650°C (Fig. 4). Of the 25wt% waste glasses, the oxidised melt showed the most devitrification, and the crystallised phase had good matches for $\text{Nd}_2\text{Mo}_3\text{O}_9$ and $\text{Na}_{0.5}\text{Nd}_{0.5}\text{MoO}_4$. A small amount of devitrification occurred in the air melt but not enough to identify the phase using the ICDD database. Heat treatment did not change the phase observed in the reducing atmosphere melt.

All of the 35wt% waste samples showed significant amounts of devitrification on heat treatment. The phase developed in the 35wt% waste glass appears to be the same as in the 25wt% waste glass. In the air melt, the majority of reflections are indicative of a scheelite-type molybdate phase. The reducing atmosphere melt exhibited significant devitrification and the large number of reflections observed in the XRD pattern suggests the presence of more than one crystalline phase. However, no matches could be obtained for these reflections using the ICDD database.

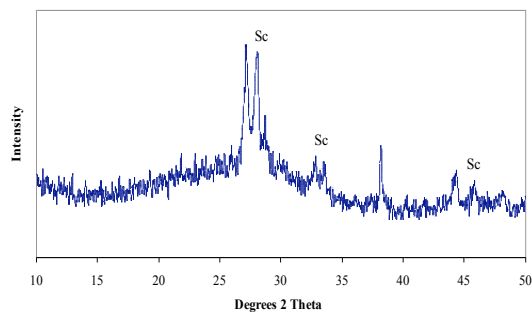


Fig.1: HM4 B after 48hrs at 650°C.
Sc = scheelite molybdate phase

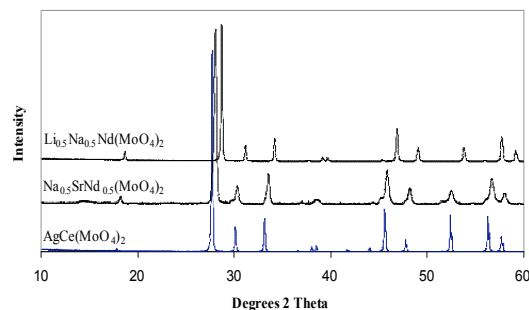


Fig.2: Synthesised scheelite molybdates

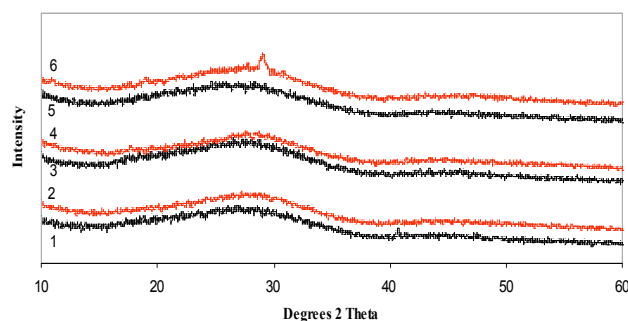


Fig.3: As cast glasses C and D

1, 3 & 5: Glass C melted under $N_2/5\%H_2$, Air and O_2 respectively
2, 4 & 6: Glass D melted under $N_2/5\%H_2$, Air and O_2 respectively

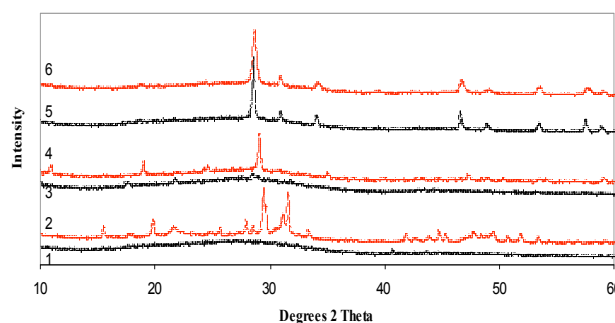


Fig.4: Heat treated glasses C and D

ESR Studies

As controls for the ESR experiments, batches of the HM4 base glass containing 1wt% MoO_3 (see Table 1) were melted in oxidising (O_2), neutral (air) and reducing ($N_2/5\%H_2$) conditions. The ESR spectra of the glasses melted under oxidising/neutral conditions were ESR silent, consistent with the presence of $Mo^{6+}(4d^0)$ species (inset in Fig 5). The reducing melt showed a strong signal at $g=1.9059(1)$ (Fig. 5), indicating that at least partial reduction of Mo^{6+} to $Mo^{3+}(4d^3)$ had occurred, in agreement with previous studies [6].

The 35wt% waste simplified batches showed the same trend in that only in the reduced melt had the molybdenum been reduced to Mo^{3+} (Fig. 6). This trend was also mimicked by the 20wt% full waste stream glasses in which a resonance for Mo^{3+} can be seen at $g=1.9061(1)$ in the reduced glass against a strong iron induced background (Fig 7). The Mo^{3+} resonance is not present in the air atmosphere melt of the same batch (Fig 8).

DISCUSSION

Both the full waste stream and simplified waste stream glass compositions yielded scheelite-type molybdate phases upon heat treatment. These phases are analogous to the yellow phases often produced during the melting of full scale HLW simulant glasses [5], although the differences in composition and waste loading of the simulated HLW streams leads to differences in the

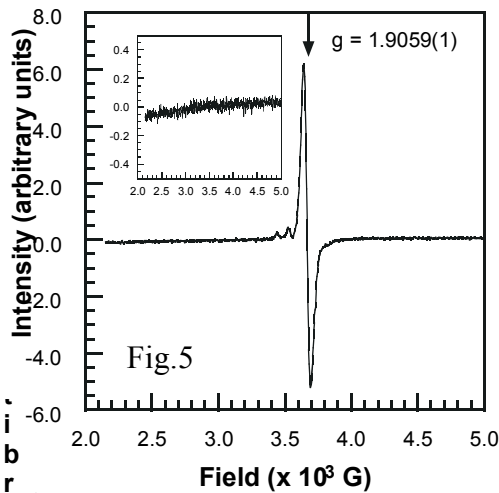


Fig.5

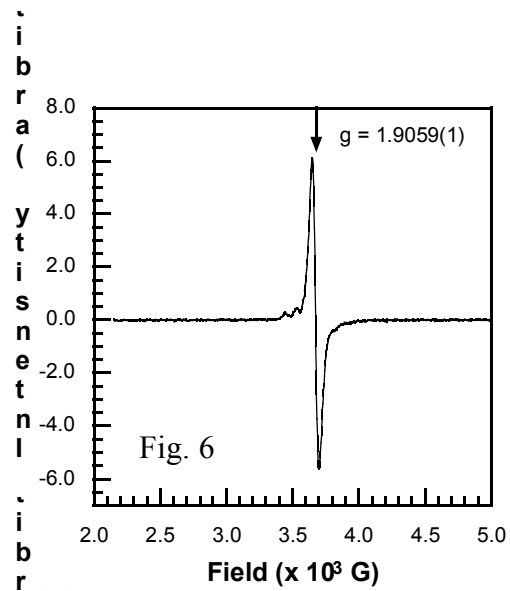


Fig. 6

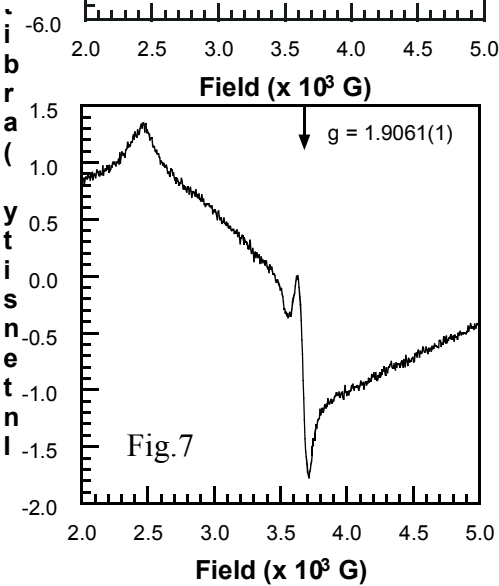


Fig.7

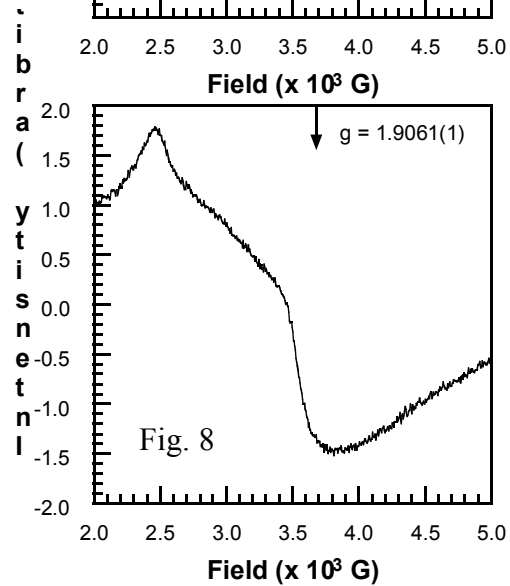


Fig. 8

Fig.5 ESR Spectra of glass E melted in $N_2/5\%H_2$ and Inset: Glass E melted in air

Fig.6: ESR spectra of glass D melted in $N_2/5\%H_2$

Fig.7: ESR spectra of glass A melted in $N_2/5\%H_2$

Fig.8: ESR spectra of glass A melted in air

composition of the yellow phases formed in the full scale melts and the lab. scale melts performed in this work. Scheelite-type molybdates are capable of incorporating a wide range of ions of varying valencies on the A site of the unit cell, and this range appears to be limited by the geometric mean radii of the ions on the site. Muller [7] defines the limiting radii as 1.14\AA to 1.5\AA (for 8-fold co-ordination) with Mo^{6+} on the B site of an ABO_4 scheelite, although the molybdates synthesised in this work show that that range can be extended to 0.957\AA to 1.55\AA . Ions with radii smaller than 0.957\AA (e.g. Li^+ , I.R. 0.88\AA) can be incorporated on the A site of scheelite molybdates when combined with larger ions providing the mean geometric radii of all of the ions on the A site is within the limiting range.

For scheelite-type molybdates to form, Mo has to be present as Mo^{6+} . Reducing the valency of Mo^{6+} should both eliminate the possibility of scheelite molybdate formation in the glass and increase the solubility of Mo in the matrix by reducing the field strength around the ion [5].

Previous ESR studies [6,8] of soda-lime-silica glasses doped with more than 0.4% MoO₃ have shown that even under oxidising conditions some of the Mo is present as Mo³⁺ or Mo⁵⁺ (although the existence of Mo³⁺ at room temperature has been queried by some workers [9]). However, in the present study the ESR spectra of alkali borosilicate glasses containing 1wt% Mo melted under oxidising or neutral conditions were found to be ESR silent, consistent with the presence of Mo⁶⁺ only (Fig 6). ESR spectra of the same glass melted under reducing conditions indicate that at least partial reduction of Mo⁶⁺ to Mo³⁺ has occurred. Further work, including Mo-K-edge XANES studies, is in progress to assess the extent of reduction of Mo⁶⁺ to Mo³⁺ under reducing conditions. ESR studies of the simplified 35% waste glass (D) demonstrated that (at least) partial reduction of Mo⁶⁺ to Mo³⁺ had occurred. A heat treated sample of this glass showed that no scheelite molybdate had formed, although other crystalline phases (yet to be identified) did form in the glass. However, heat treatment of the reduced glass C (25 % waste) showed no further devitrification upon heat treatment compared to the as-cast state, whereas the neutral and oxidised melts of this glass both led to significantly more crystalline material upon heat treatment than was present in the as-cast blocks. The ESR experiments performed on the neutral and reducing atmosphere glass A melts show that the Mo⁶⁺ to Mo³⁺ reduction under a N₂/5%H₂ atmosphere holds true for glasses containing the full simulated waste stream.

CONCLUSIONS

Melting simulated HLW glasses under a reducing atmosphere leads to (partial) reduction of Mo⁶⁺ to Mo³⁺. XRD studies of simplified waste composition glasses indicate that this reduction is sufficient to prevent the formation of scheelite-type molybdate compounds (which are analogous to detrimental yellow phase compounds found in full scale simulated HLW glasses) in the glass.

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