Incorporation of Molybdenum in Nuclear Waste Glasses

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The amount of high level nuclear waste (HLW) that can be vitrified in a given amount of base glass is limited by the solubility of the waste components in that glass. Molybdenum represents a high percentage of mixed oxide fuel HLW and has a low solubility in borosilicate glasses used for HLW vitrification. Mo can combine with other elements in the HLW to form "yellow phase", a crystalline precipitate detrimental to the performance of the vitrified product, when the concentration in the melt exceeds the solubility limit. Experiments were performed to determine the structure of the Mo compounds formed in glasses containing a high percentage of a simulated HLW. It was found that the crystalline phases produced were of a scheelite structured $AB(MoO_4)_2$ type, where the A site is occupied by +1 cations and the B site occupied by +3 cations. There is evidence to suggest that several elements incorporated in the batch have appropriate valance and ionic radii in the vitrified product to occupy these positions.

1. Introduction

Borosilicate glasses have been used as host matricies for the immobilisation of high level nuclear waste (HLW) from power stations and atomic weapon decommissioning for the last 50 years[1]. Borosilicates were chosen due to their ability to incorporate a wide range of elements as found in the typical waste streams created by waste reprocessing, and for their good long term chemical durability, a quality essential for the safe vitrification of long lived radioactive nuclides. One factor that can have a major impact on the chemical stability of a glass is the formation of crystalline phases within that glass.

Hexavalent molybdenum represents a particular problem in HLW vitrification as it is present in high concentrations in the reprocessed waste, and is insoluble in borosilicate waste glasses above levels of approximately 1%[2]. When too much molybdenum is present, it tends to combine with other elements in the glass and form a compound known as "Yellow Phase", which is immiscible with the bulk of the glass, and has a major detrimental effect on the long term chemical durability of the glass.

This work aims to identify to structures formed by molybdenum in a simulated HLW glass using transmission electron microscopy (TEM) and x-ray diffraction (XRD) techniques, in order to allow a better understanding of how to increase the waste loadings of HLW glasses without decreasing their long term durability.

2. Experimental

Glass Melting

A simulated HLW glass was prepared using a composition specified by BNFL. The weight percentage of the simulated waste was increased from 25% to 35% in order to encourage the formation of molybdate phases (see table 1.).

Oxide	Wt (g)	Mol %	Oxide	Wt (g)	Mol %
Base Glass			Nd_2O_3	5.24	1.19
SiO_2	40.2	51.69	Rb_2O	0.29	0.12
B_2O_3	14.2	15.81	RuO_2	2.62	1.52
Na_2O	7.2	8.92	Sm_2O_3	0.77	0.17
Li_2O	3.4	8.91	SrO	0.73	0.54
HLW simulant			TeO_2	0.21	0.10
Ag_2O	2.47	0.82	TiO_2	0.94	0.91
BaO	1.64	0.83	Y_2O_3	0.43	0.15
CeO	2.33	1.15	ZrO_2	3.86	2.42
Cs_2O	2.29	0.63	Fe_2O_3	0.58	0.28
Gd_2O_3	4.86	1.04	NiO	0.17	0.17
La_2O_3	1.24	0.29	Cr_2O_3	0.18	0.09
MoO_3	4.19	2.25	Total	100	100

Table 1. Composition of simulated HLW glass

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 Kenthal SiC elements. The total melting time was 5.5 hours, and an alumina stirring paddle was inserted after 1 hour of melting and rotated at 60rpm to compensate for the lack of convection currents that would be found in a full scale melt. The glass was cast into a preheated steel mould, and annealed at 500°C for 1hour then cooled to room temperature at 1°C/min.

TEM

Samples were cut to a thickness of approximately 1mm using a diamond saw, and then polished on both surfaces using 120, 240, 400, 600, and 1200 grit SiC papers until approximately 30μm thick. They were then glued to 3.05mm copper sample holders using epoxy resin, and milled using a Gatan ion beam miller until perforation gave a small hole in the center surrounded by thin (~30nm) area. The samples were then carbon coated, and viewed in the Phillips 420J TEM using an accelerating voltage of 120kV.

XRD

Samples for XRD were broken down first using a percussion mortar, then ground to a fine powder (<200μm) using an agate mortar and pestle. They were then front loaded into an aluminum sample holder and scanned using a Phillips PW1373 X-ray Powder Diffractometer. CuKα 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.

Molybdate Production

Some ceramic powders were synthesized to help interpret the data obtained from the glass samples. The powders produced were of the $AB(MoO_4)_2$ type where A=Li, Na, K, Rb, Cs or Ag (or combinations of these elements) and B=Ce, La, Sm, Nd, Gd or Y (or combinations of these elements). Oxides or carbonates of these elements were mixed with the appropriate quantities MoO_3 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 as just described. The samples were ground to a powder for XRD analysis.

3. Results

Glass Melting

The cast block showed evidence of phase separation in the form of yellow streaking within the bulk of the dark purple block. XRD analysis of the glass revealed the presence of a crystalline phase (Fig. 1), and the particles responsible for the crystalline peaks were photographed using the TEM (Fig. 2) and found to be approximately 0.175μm in size.

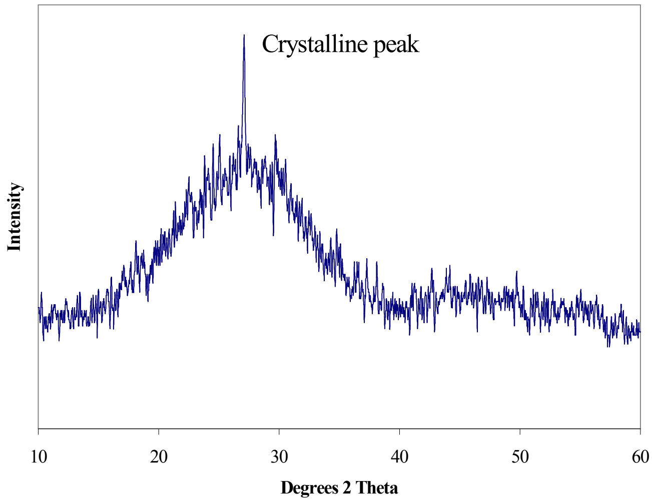

Fig.1 XRD trace of as-cast HLW glass

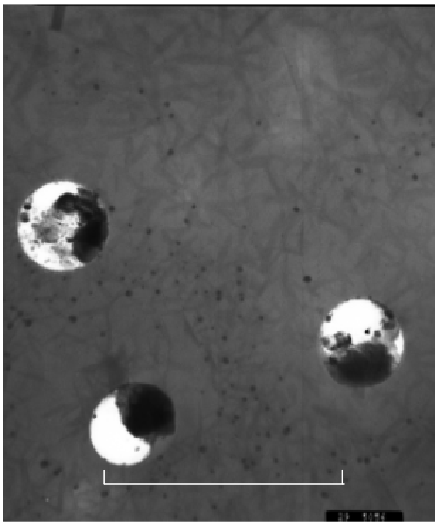

Fig.2 Spherical crystallites observed in HLW glass. Scale bar = 0.5μm

EDS analysis showed that the particles were higher in Mo than the glass matrix, although their small size limited the amount of information available from this sample.

In order to increase the amount of crystallinity and therefore aid analysis, a sample of the glass was heat treated for 48hrs at 600°C. XRD showed this sample to contain a greater volume of crystalline material (Fig. 3). Silver metal is present in the sample, but the majority of the peaks are caused by a molybdate of the $AB(MoO_4)_2$ type. These molybdates have a scheelite ($CaWO_4$) structure with a tetragonal unit cell (space group of $I4_1/a$)[3]. In the molybdate form, WO_4^{2-} tetrahedra are replaced by MoO_4^{2-} tetrahedra, and Ca^{2+} by a distribution of +1 and +3 cations. It is also noted in the literature that vacancies on the +1 sites can be present, with the charge difference being accounted for by an excess of +3 cations. There is a wide range of elements within the batch which are likely to be found in the appropriate oxidation state to fit into the scheelite structure. These are shown in table 2.

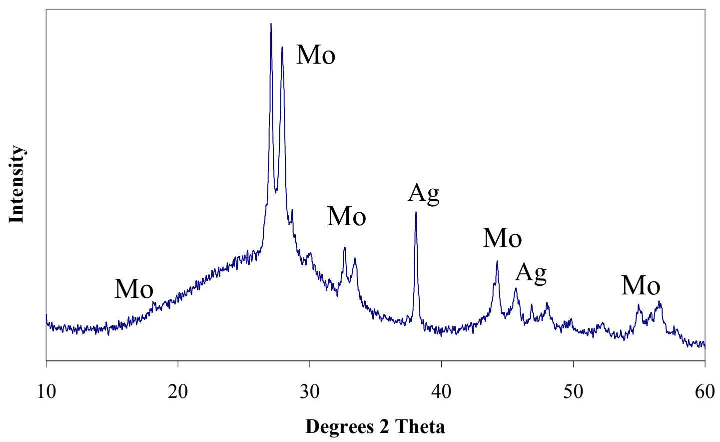

Fig. 3 XRD of HLW glass after heat treatment molybdate peaks are labeled Mo.

Ion	Radius (Å)
Li^+	0.88
Na^+	1.16
Rb^+	1.63
Cs^+	1.84
Ag^+	1.29
Y^{3+}	1.02
La^{3+}	1.19
Ce^{3+}	1.15
Nd^{3+}	1.12
Sm^{3+}	1.1
Gd^{3+}	1.08

Table 2. Radii of ions likely to be found in simulated HLW glass

Molybdate Production

Due to the wide range of ions which are capable of occupying the A and B sites in scheelite structured molybdates, it was theorized that it would be possible to mix 2 or more similarly sized ions on the A or B site and retain the tetragonal structure. Initially, 3 Ag molybdates were synthesized using Gd, Ce and a stoichimetric mixture of Gd and La for the +3 sites. $AgCe(MoO_4)_2$ was used as a control to confirm the firing schedule used as the pattern for this molybdate was available in the JCPDS XRD database. Table 3 compares the 2θ and d-spacing values for AgLa, AgGd and $AgLa_{0.5}Gd_{0.5}(MoO_4)_2$ molybdates.

	Degrees 2 Theta	(CuK∝)		d-spacing	
AgGd	$AgLa_{0.5}Gd_{0.5}$	AgLa	AgGd	$AgLa_{0.5}Gd_{0.5}$	AgLa
28.666	28.407	28.046	3.112	3.139	3.179
34.197	33.892	33.511	2.62	2.643	2.672
46.858	46.415	45.912	1.937	1.955	1.975

Table 3. Comparison of the 3 most intense peaks on the XRD traces of selected Ag molybdates

As can be seen, as the ionic radii of the ion on the B site increases, the angle at which reflection occurs decreases indicating that the distance between the atomic planes increases and that the size of the unit cell is proportional to the size of the ions within it. It can also be seen that if the B site is equally occupied by a mixture of two ions, the d-spacings for that cell lie approximately ½ way between those for the pure $AB(MoO_4)_2$ compounds. The literature[4] indicates that ion size is a limiting factor in determining which ions will form a scheelite structure with molybdenum. This theory was tested by mixing combinations of +1 alkali earth ions (Li – Cs) on the A site of an $ANd(MoO_4)_2$ molybdate. Fig. 4 shows the XRD results of these experiments.

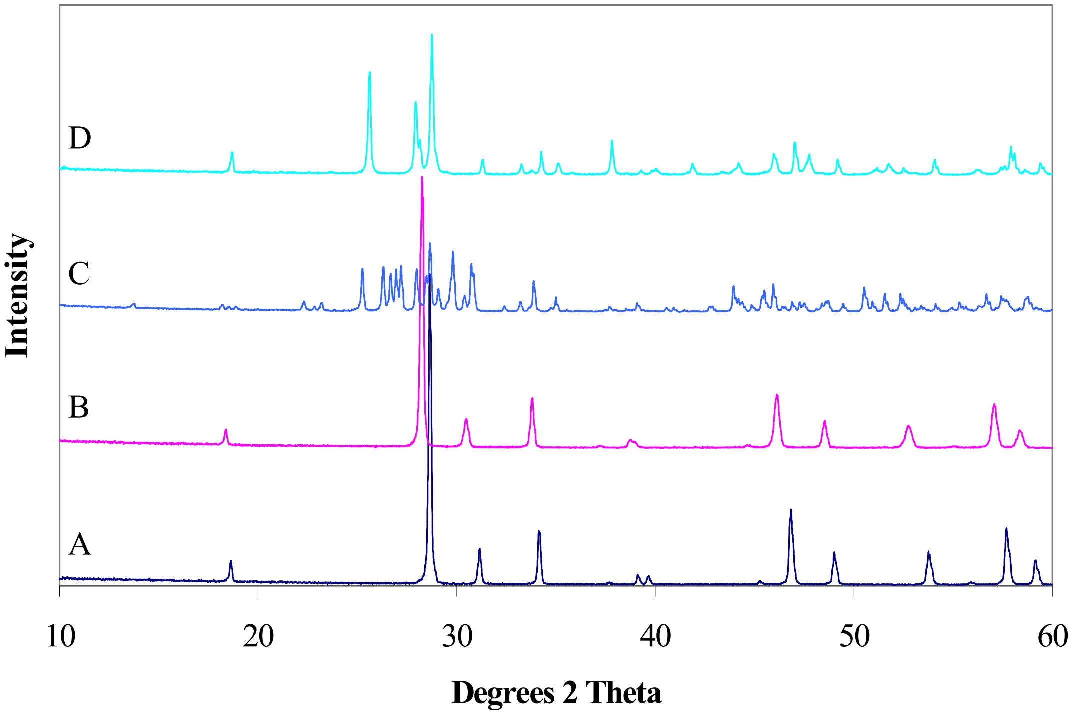

Fig. 4. XRD Traces of $Li_{0.5}X_{0.5}Nd(MoO_4)_2$ molybdates. For 'A' X=Na, 'B' X=K, 'C' X=Rb, 'D' X=Cs

The LiNa and LiK neodymium molybdate compositions have formed single phase scheelite structured powders upon sintering, indicating that the unit cell is not being over strained by the size difference of Li and K (0.64Å). However, the LiRb composition with a size difference between Li and Rb of 0.75Å) formed a multi-phase powder upon sintering, as did the LiCs composition. $LiNd(MoO_4)_2$ is present in trace D, thus giving the pattern the characteristic scheelite shape. On comparing the geometric mean ion radii (i.e. converting the $Li_{0.5}X_{0.5}Nd(MoO_4)_2$ formulas into ABO_4, where $Li_{0.5}X_{0.5}Nd$=A and Mo=B) to the structure field map in [4], it shows that scheelite structured molybdates would be expected for the LiRb and LiCs compositions and not for the LiNa and LiK compositions. These results would indicate the opposite, although it must be remembered that coordinating 3 different ions in the same unit cell is likely to affect the ionic radii of those elements, thus making the calculated radii inaccurate.

The results show that it is possible to mix 2 ions on both the +1 and +3 sites of $AB(MoO_4)_2$ compounds and retain the scheelite structure found in the simulated HLW glass samples. However, there is a limit to the difference in size of the equally charged ions that can form these compounds and maintain the $I4_1/a$ geometry. It can be inferred from this data that within the size constraints, it should be possible to mix several +1 and +3 ions in any one scheelite structure, although further work needs to be done to verify this assumption.

4. Conclusion

When the waste percentage of a simulated HLW glass is increased to 35wt%, crystalline phases are precipitated in the glass. Heat treatment of the glass (c.f. extremely slow cools in nuclear waste containment vessels) produces a scheelite structured molybdate as the major crystalline phase. Many of the mono and trivalent species present in the glass are capable of substituting into this structure.

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