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Raman and X-ray absorption spectroscopy studies of chromium–phosphorus interactions in high-bismuth high-level waste glasses

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ABSTRACT

High-level waste (HLW) glasses containing bismuth, phosphorus, and chromium were investigated using Raman and X-ray absorption spectroscopy (XAS). The novel and practically important occurrence of foaming on *cooling* of these melts is associated with P and Cr from the HLW. In response, glasses were synthesized where Bi_2O_3 and P_2O_5 contents were varied independently. Relationships between P and Cr were found, where as P_2O_5-content increases, chromate Cr–O stretch Raman modes diminish intensity, while Cr XAS shows that Cr reduces, from 50% Cr^{6+} + 50% Cr^{3+} to nearly 20% Cr^{6+} + 80% Cr^{3+}, explaining the chromate mode behavior. In the most P_2O_5-rich glass, the chromate Cr–O distance increases by approximately 0.10 Å, which may indicate bonding between CrO_4 and PO_4 tetrahedra, similar to that in chromo-phosphates. The presence of chromo-phosphate domains in HLW melts can be linked to oxygen generation as a source of the foaming.

1. Introduction

As a result of the use of the bismuth phosphate process as the first large-scale method for extraction of plutonium from dissolved spent nuclear fuel, a significant amount of high-level waste (HLW) that is rich in bismuth (Bi) and phosphorus (P) was accumulated at the Hanford site in Washington state from activities performed in support of the US defense program. All of the Hanford HLW is destined for treatment by vitrification and the compositional diversity of these wastes presents many unique challenges for glass formulation. Motivated by the substantial economic benefits of achieving high waste loadings in glass [1,2], high-loading glasses have been developed for a range of Hanford HLW streams [2] and for Bi–P-rich streams in particular [2,3]. In those studies, a novel phenomenon of foaming of the melt during *cooling* was observed for certain high Bi–P HLW glass formulations when they were exposed to the controlled cooling process that simulates the canister centerline cooling (CCC) rate [2,3]. This behavior is clearly of significant practical significance since it could potentially lead to foaming of the HLW melt out of the canister during cooling. A phenomenological model was proposed that was based on the observation that melt foaming was largely associated with the presence of both phosphorus and chromium (Cr) from the HLW in the glasses [3]. Observations from scanning electron microscopy of some HLW glass samples also indicated a Bi to P association [3]. In the present work, Raman spectroscopy and X-ray absorption spectroscopy (XAS) were used to investigate how Bi, Cr, and P glass components are incorporated into the glass structure and any potential interactions among them. This information is then used to develop a refined model to explain the observed melt foaming phenomenon. Moreover, it is of interest to explore the interaction at the microscopic scale of these three elements in borosilicate glass systems to aid in the development of Bi–P HLW glass formulations that can incorporate a maximum amount of waste without excessive crystallization or foaming.

An initial model to explain the chemistry behind the melt foaming [2,3] began with the concept that P_2O_5 can stabilize Cr^{6+} by forming chromo-phosphate species in the melt. As the temperature decreases during CCC, chromo-phosphates decompose, with the formation of sodium-pyrophosphate ($Na_4P_2O_7$) along with the reduction of Cr^{6+} to Cr^{3+} that reacts with NiO in the melt to crystallize spinels. The foaming was hypothesized [3] to be due to oxygen generation associated with the Cr reduction and spinel crystallization according to the equation:

$$Na_3PCr^{6+}O_7(m) + 1/2NiO(m) \rightarrow Na_3PO_4 + 1/2NiCr_2^{3+}O_4(sp) + 3/4O_2(g). \quad (1)$$

In this case, phosphate acts as a vehicle to preserve Cr^{6+} for later reduction at lower temperature when crystallization is more

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favorable, rather than reduction taking place at the glass melting temperature. These ideas were used to design glass composition modifications that were effective in mitigating the observed foaming behavior [3].

This paper reports the second part of a study characterizing Bi–P HLW glasses. The earlier work focused on the valence and local environment of Bi in representative Bi–P HLW glasses [4] by using Bi L_{III}-edge X-ray absorption spectroscopy (XAS). XAS analyses indicate nearly identical Bi valence and structural environments in all glasses studied, despite their diverse compositions and significant differences in P_2O_5-content. XAS also indicated that Bi acts as a borosilicate network modifier, where no structural correlation with phosphate was found [4]. On the other hand, in agreement with the phenomenological model [3], a relationship between chromium and phosphorus was observed from the Raman spectra of these glasses [4]. In response to the above observations, Cr K-edge XAS and Raman spectroscopy measurements were performed on four HLW borosilicate glasses that contain Cr_2O_3 and P_2O_5 at relatively high concentrations with respect to the saturation of these two components in the melt, but at relatively low concentrations with respect to the major chemical components in the glass (Table 1). For these glasses, P_2O_5 and Bi_2O_3 concentrations were varied while the Cr_2O_3 content was similar.

2. Experimental

2.1. Sample details

2.1.1. Crystalline standards

Raman measurements were made on crystalline Na_2SO_4 and $HNa_2PO_4{\cdot}2(H_2O)$ (dorfmanite) powders, where the dorfmanite sample was initially Na_3PO_4 powder (both original reagents from Alfa-Aesar). Na_2SO_4 and dorfmanite contain Na^+ bonded to isolated sulfate and phosphate tetrahedra, respectively [5,6], and are used here to model possible environments in the glasses, which have Na^+ as the dominant network modifying cation (Table 1). Both dorfmanite [6] and Na_3PO_4 [7] contain PO_4 tetrahedra bonded to Na^+ within similar distance ranges. The two crystalline standards measured for Cr XAS include: uvarovite ($Ca_3Cr_2Si_3O_{12}$) (NMNH #106331 from Finland) that contains $Cr^{3+}O_6$ octahedra [8], and crocoite ($PbCrO_4$) (NMNH #157582 from Australia) that contains $Cr^{6+}O_4$ tetrahedra [9]. These two XAS standards were ground to powders, where particle diameters are near one absorption length at the Cr K-edge energy to minimize self absorption effects from the samples being too thick. For the XAS measurements, each sample consisted of one layer of particles deposited between two pieces of transparent tape. Phase identification of all crystalline standards was verified by powder X-ray diffraction (XRD).

2.1.2. Glasses

Two well-characterized Cr-containing Na–Li–Mg-borosilicate glasses (A177 and A305) were originally part of a Cr redox series studied by Schreiber and Hockman [10] (Table 1). These two borosilicate glasses were measured by Raman spectroscopy to illustrate chromate Cr–O stretch modes. Both glasses were synthesized at 1150 °C, in O_2 ($-\log fO_2 = 0$) and in a CO_2–CO gas mixture ($-\log fO_2 = 8.5$), respectively, and as a result, each glass has a different Cr valence distribution: 69% Cr^{6+} + 31% Cr^{3+} for A177 (with chromate) and 97% Cr^{3+} + 3% Cr^{2+} for A305 (without chromate) [10]. Since these glasses were acquired after the XAS measurements were completed for this study, only the Raman spectra of these samples are presented.

The Bi HLW glasses measured were synthesized from reagent grade chemicals and were prepared as 400-gram batches in Pt–Au crucibles [3], where the bulk glass fragments were taken from portions of the quenched homogeneous glass (Table 1). These glasses include: an original Bi HLW formulation, HLW-Bi–F2, a

Table 1
Major oxide compositions (wt.%) of the glasses investigated. Values determined for the HLW-glasses are from XRF and DCP-AES analyses. Other components include: BaO, La_2O_3, PbO, and ZrO_2. Uncertainties for the HLW-glass compositions are within ±10% of the values reported.

Glass	Cr_2O_3	P_2O_5	Network modifiers		Transition metals		Network formers		SO_3	Other components	Total
HLW-Bi–BiP0	0.77	0	Bi_2O_3	0	Fe_2O_3	8.41	Al_2O_3	12.89	0.37	0.54	99.94
			CaO	1.01	NiO	2.28	B_2O_3	16.19			
			Li_2O	0.18	TiO_2	0.19	SiO_2	37.27			
			K_2O	0.52	ZnO	0.19					
			MgO	0.50							
			Na_2O	18.62							
HLW-Bi–Bi0	0.70	5.78	Bi_2O_3	0	Fe_2O_3	7.44	Al_2O_3	11.78	0.34	0.45	99.16
			CaO	0.94	NiO	1.95	B_2O_3	15.33			
			Li_2O	0.17	TiO_2	0.18	SiO_2	35.61			
			K_2O	0.49	ZnO	0.18					
			MgO	0.48							
			Na_2O	18.13							
HLW-Bi–F2[a]	0.77	5.35	Bi_2O_3	8.13	Fe_2O_3	8.00	Al_2O_3	10.91	0.40	0.52	99.91
			CaO	0.94	NiO	2.24	B_2O_3	14.30			
			Li_2O	0.16	TiO_2	0.19	SiO_2	32.11			
			K_2O	0.46	ZnO	0.21					
			MgO	0.43							
			Na_2O	14.79							
HLW-Bi–2P	0.69	8.67	Bi_2O_3	7.10	Fe_2O_3	7.35	Al_2O_3	10.43	0.31	0.46	99.93
			CaO	0.87	NiO	1.95	B_2O_3	13.84			
			Li_2O	0.16	TiO_2	0.17	SiO_2	31.70			
			K_2O	0.43	ZnO	0.17					
			MgO	0.41							
			Na_2O	15.22							
A177[b] and A305[b]	Cr 1.0	0	Li_2O	5.7	TiO_2	1.0	B_2O_3	14.7	0	1.0	101.0
			MgO	2.0			SiO_2	57.9			
			Na_2O	17.7							

[a] Sample has minor amounts of crystalline Fe-silicate phases.
[b] Glasses from Schreiber and Hockman have SRL131 glass frit 131 composition [10].