Glass Matrix

Continuing Research for Improving Glass Matrix for Vitrification

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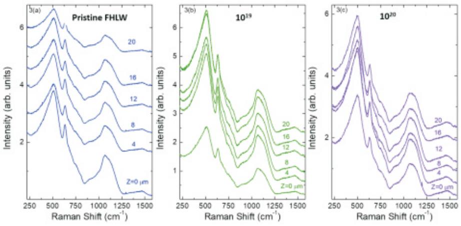

Raman spectra of NBS3 glasses

ABSTRACT

Vitrification forms an important part of the management of high level wastes (HLW). In this article the recent endeavours in the area of glass matrix development and optimization are highlighted. This paper presents recent work on the development of glasses capable of withstanding the alpha damage caused by high loading, which is important to minimize waste volume, and therefore eventual space utilization in the repository. The work presented here shows that even at a simulated α loading of 10^{20} αg^{-1}, there seems to be no detrimental effect on glass leaching.

KEYWORDS: *Glass, Alpha loading, Ion bombardment, Raman spectroscopy, Chemical durability.*

Introduction

The beneficial combination of excellent material properties including high chemical durability, resistance to crystallization/de-vitrification and the ability to accommodate a wide diversity of cations within its structure, combined with ease of handling borosilicate glasses in large scale, remotely handled facilities make them ideal candidates for HLW vitrification [1–3]. With the advent of partitioning, disposal of alpha-bearing wastes is envisaged as a future goal for waste management operations. Indeed, most minor actinides have a life of 10^6 years–10^7 years, during which time the vitreous matrix is likely to receive total alpha dose exceeding 10^{10} Gy. The recoiling daughter nucleus is also expected to create significant, albeit much shorter ranged, damage by initiating displacement cascades in the glass. A combination of these events can potentially cause alterations in the glass structure and lead to crystallization to the detriment of the waste form, with problems including formation of cracks and/or crystalline phases which in turn can increase the vulnerability of the waste form to aqueous attack[4, 5]. In this article, we discuss the role of ion bombardment[4] in actual sodium borosilicate waste glass compositions to simulate alpha loading, and achieve an insight into the structural reasons underlying radiation damage mechanisms. We also present studies of chemical durability to highlight the effect of radiation damage on chemical durability.

Simulation of High Alpha Loading Through Radiation Bombardment

Table 1: Compositions of glasses studied.

(NBS-1 and 3 represent ternary systems while FHLW simulates WIP Trombay glass)

Oxide (Wt. %)	NBS1	NBS3	FHLW glass
SiO_2	52.90	50.89	34
B_2O_3	22.29	29.74	20
Na_2O	24.81	19.67	12
TiO_2	--	--	2
BaO	--	--	8
Waste Oxide	--	--	24

A series of simplified ternary glasses and plant-based compositions with simulated waste loading were chosen for the studies. Table 1 summarizes the compositions used for the present study. The ternary compositions were chosen to highlight the effect of radiation damage on simplified compositions.

The samples chosen were bombarded with He and Xe ions using irradiation conditions as summarized in Table 2. In all cases, alpha loading up to 1020 αg^{-1} has been simulated. Since ion bombardment causes damage on the surface of the sample, confocal Raman spectroscopy was the chosen technique to analyze the samples before and after irradiation. For brevity, we present the Raman spectra of glasses before and after Xe bombardment data in Figs. 1 to 3. Since Xe simulates the recoiling daughter nucleus, it is expected to be the major damage contributor.

The Raman band at ~528 cm^{-1} is attributed to bending and stretching modes of Si–O–Si linkages, and also the stretching modes of Reedmergnerite type structural units. All the glasses also show a sharp Raman peak at 630 cm^{-1}. This is attributed to tetrahedral B in danburite type (Si_2O_7–B_2O_7 rings) structural units. Additionally, the NBS-3 glasses exhibit a pronounced shoulder between 600 cm^{-1} and 800 cm^{-1}. These are attributed to vibration of boroxol rings and B–O$^-$ in

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Table 2: Ion bombardment experiment parameters and the effective α g^{-1} simulated.

Ion	Charge State	Deck (kV)	Energy (keV)	Beam Current (A)	Flux (ions per cm^2s)	Total Fluence on Sample (ions/cm^2)	Exposure Time(h)	Effective (α g^{-1})
Xe	6	350	2100	10^{-9}	10^{10}	10^{15}	280	10^{19}
Xe	6	350	2100	10^{-9}	10^{10}	10^{16}	2800	10^{20}
He	2	350	750	10^{-6}	10^{12}	10^{15}	0.3	10^{19}
He	2	350	750	10^{-6}	10^{12}	10^{16}	3	10^{20}

Table 3: Normalised Na release rates

Glass Name	Normalized Na release (ppm cm^{-2})				
	Pristine	He-Bombarded		Xe-Bombarded	
		10^{19} α g^{-1}	10^{20} α g^{-1}	10^{19} α g^{-1}	10^{20} α g^{-1}
NBS1	4359	4065	4055	4211	4108
NBS3	881	874	880	1213	1336
FHLW	183	196	192	230	224

metaborate groups. The broad band between 900 cm^{-1} and 1200 cm^{-1} is a convolution of Q^n Si species [6–8].

In case of NBS1 glass, no significant change in the Raman spectra is evident. However, in case of NBS3, a sharp peak is observed in the Q^3 region at a depth of ~12 µm. It maybe mentioned here that the typical penetration depth of Xe into a glass is ~0.5 µm. Therefore, it is unclear how damage was created at such depth in the material. Clearly, further studies are essential to probe the same. It is likely that damage cascades may have deposited energy deep into the material or some heating may have resulted from bombardment, which could have altered the sample. However, it is clear that such a change is not observed in case of the FHLW multi-component system, where the irradiation effects are minimal.

Leaching Studies

Since the final consideration of the effect of radiation damage remains the chemical durability, samples were mounted in a suitable resin such that only the damaged surface remains exposed to the liquid. Short term degradation of one week was observed since the goal is to observe the leaching behaviour of the ion damaged layer only. The degradation experiments were carried out at a temperature of 90°C with the samples placed in sealed containers. A schematic diagram of the sample as mounted is presented in Fig.4. The leaching behaviour of the bombarded samples was compared with the pristine samples to obtain the Na^+ ion concentration in the leachate normalized to sample area exposed.

In terms of degradation behaviour, the initial samples obtained from He and Xe bombarded samples were compared and the results in terms of normalized Na^+ release rates are presented in Table 3.

As evident in Table 3, Na leach rate seems increased in case of the NBS3 samples under Xe bombardment. However, comprehensive investigation with further experiments is essential to confirm this finding. Confirming the absence of significant alteration observed in Raman spectroscopy measurements, FHLW glass does not seem to show a significant change in the normalized leach rate. This effect is most likely due to the multi-component nature of FHLW glasses.

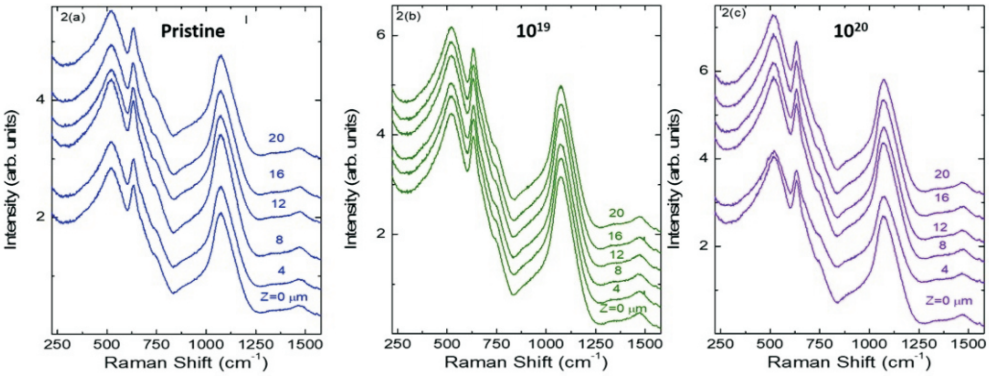

Fig.1: Raman spectra of NBS1 glasses-Pristine (left), 10^{19}αg $^{-1}$(middle) 10^{20} αg $^{-1}$ (bottom). The depth of the measured spectrum is indicated beside the relevant trace.

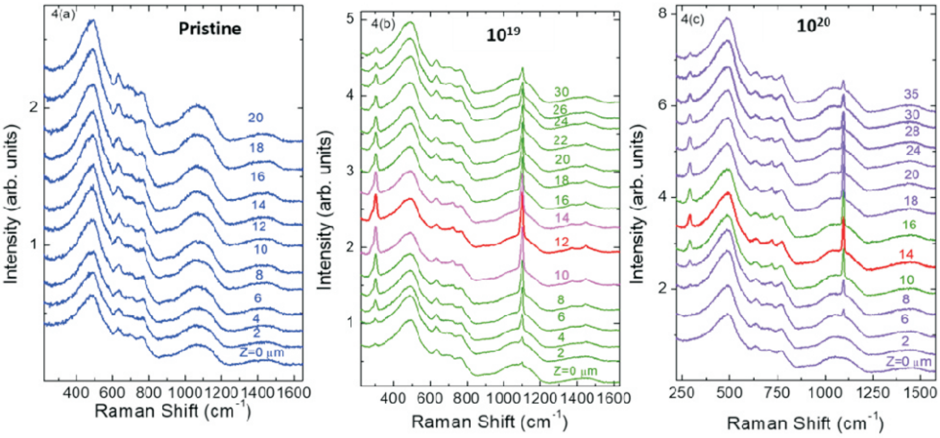

Fig.2: Raman spectra of NBS3 glasses-Pristine (left), 10^{19}αg $^{-1}$(middle)10^{20} αg $^{-1}$(bottom). The depth of the measured spectrum is indicated beside the relevant trace. Note the emergence of a sharp peak indicating possible crystallization.

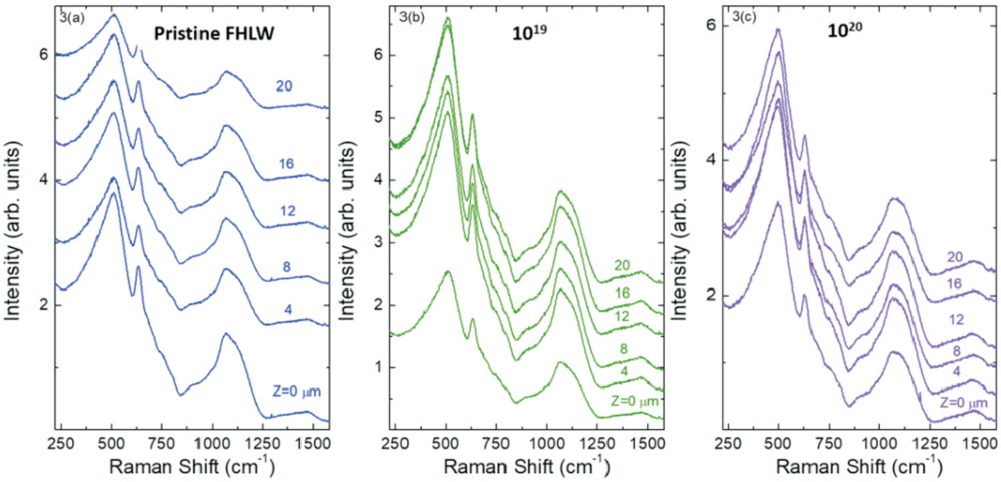

Fig.3: Raman spectra of FHLW glasses-Pristine (left), 10^{19}αg $^{-1}$(middle)10^{20} αg $^{-1}$ (right). The depth of the measured spectrum is indicated beside the relevant trace.

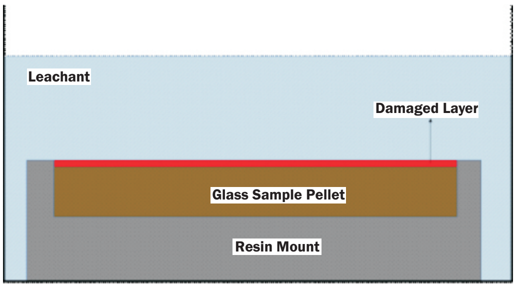

Fig.4: Schematic figure showing short term leaching test configuration to allow leaching of damaged layer.

Conclusions

- The studies presented confirmed that simplified glasses with a higher B_2O_3 percentage are susceptible to radiation damage from recoiling species. However, this effect is mitigated in multi-component glasses as typical in waste management applications

- Further studies into the effect of multi-component versus ternary systems will be required to fully understand this phenomenon

- Bombardment and characterization studies allied to degradation properties suggest that even at an α loading ~10^{20} α.g^{-1}, no deleterious effects on leaching properties are evident.

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