Ion beam irradiation induced structural modifications in model nuclear waste glasses

An investigation using X-ray Absorption Spectroscopy

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1. Background

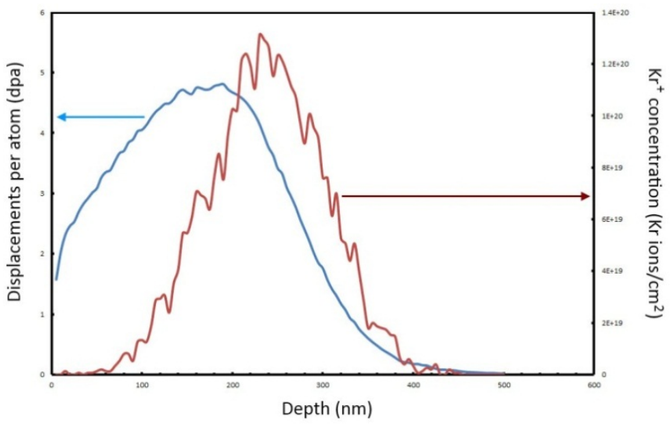
Alkali borosilicate glasses are used to vitrify high level waste (HLW) from reprocessing of spent nuclear fuel. In addition to fission products and minor actinides, cations such as Fe are also present in the waste. α-decay of the actinides produce α-particles (He nuclei) and energetic (~100KeV) daughter recoil nuclei, which transfer energy to the atoms in the glass causing atomic displacements, resulting in collision cascades. Accumulation of this ballistic damage is hypothesised to lead to migration of alkali ions resulting in changes in glass network polymerisation and cation valence state. Alterations to either may have a deleterious effect on the durability of the wasteform and effect its long term performance as an immobilisation matrix. It is therefore important to understand the effects of α-decay on the structure of the glass. This study investigates the effect of simulated α-recoil damage in analogue nuclear waste glasses, using X-ray absorption spectroscopy to examine the co-ordination and valence of Fe.

2. Experimental methods

In this study, results obtained from two glass compositions with different waste loadings are reported. The compositions are given in the table:

Glass	SiO_2 (mol%)	Na_2O (mol%)	B_2O_3 (mol%)	ZrO_2 (mol%)	MoO_3 (mol%)	CeO_2 (mol%)	Fe_2O_3 (mol%)	ZnO (mol%)
DB8	72.18	16.13	9.69	0.50	0.125	0.125	0.625	0.625
DB11	61.87	13.83	8.31	4.00	1.00	1.00	5.00	5.00

Glass batches were melted in Al crucibles at 1300°C, held for 1 hour and stirred for 4 hours. Glasses were cast into blocks and placed in an annealing furnace at 500°C for 1 hour, then cooled at 1°C/min to room temperature. Samples approximately 3mm thick and 1cm in diameter were cut from each glass block and one side polished. X-ray diffraction (XRD) confirmed all samples to be amorphous. The wasteform is expected to receive a dose of about 0.1 - 1.0 displacements per atom (dpa) in its lifetime. Kr^+ irradiation provides an analogue for α-recoil damage [1]. Suitable irradiation conditions were determined using TRIM [2] calculations.



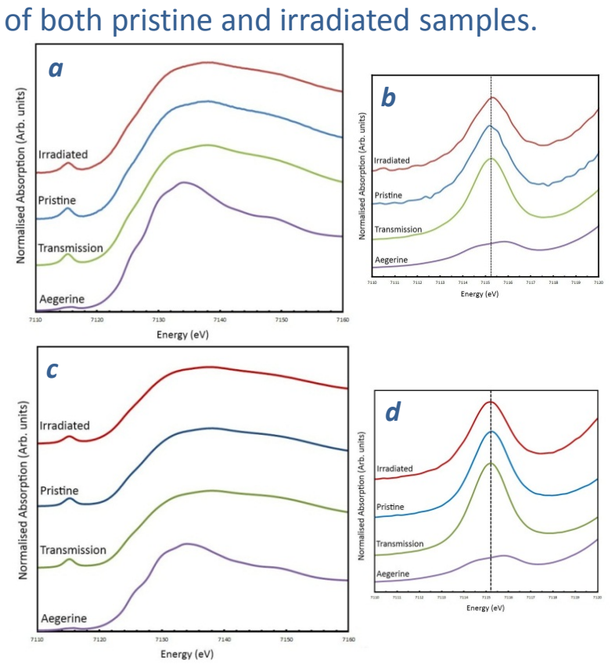
Results from TRIM simulation showing Kr^+ range and dpa produced by $2x10^{-5}$ Kr+ ions/cm² with 450KeV

Irradiations were carried out at the Ion Beam Centre at Helmholtz Zentrum Dresden Rossendorf (HZDR). Samples were irradiated with $2x10^{15}$ Kr^+ ions/cm², with energy of 450KeV and at room temperature. Un-irradiated (pristine) samples were kept for comparison. Fe K-edge X-ray absorption spectra (XAS) were acquired on beam line 11.1R at ELLETRA synchrotron light source.

3. XANES Results

TRIM results (above) indicated the formation of a damage region extending from the surface to a depth of about 300nm. Total Electron Yield (TEY) XAS measurements were made to probe the surface region of both pristine and irradiated samples.

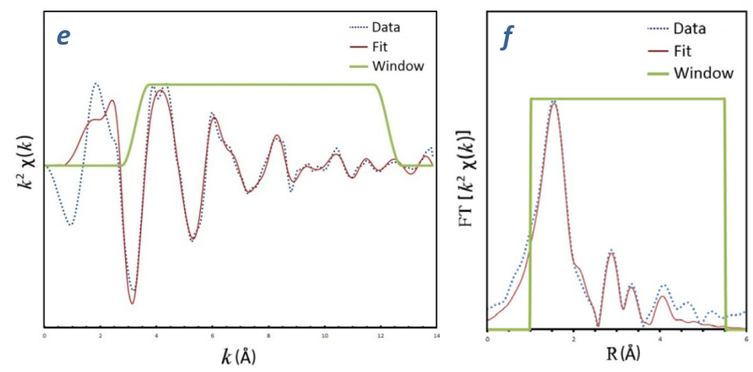
Transmission measurements of the pristine sample and the $NaFeSi_2O_6$ crystalline mineral standard (aegerine) containing Fe^{3+} in 6-fold co-ordination were also made. Fe K-edge X-ray Absorption Near Edge Structure (XANES) spectra were obtained for DB8 (figure a), and DB11 (figure c). The location and intensity of pre-edge peak in the pristine and irradiated samples for both DB8 (figure b) and DB11 (figure d) are the same suggesting no change in Fe valence or co-ordination as a consequence of irradiation.



4. XAFS Results

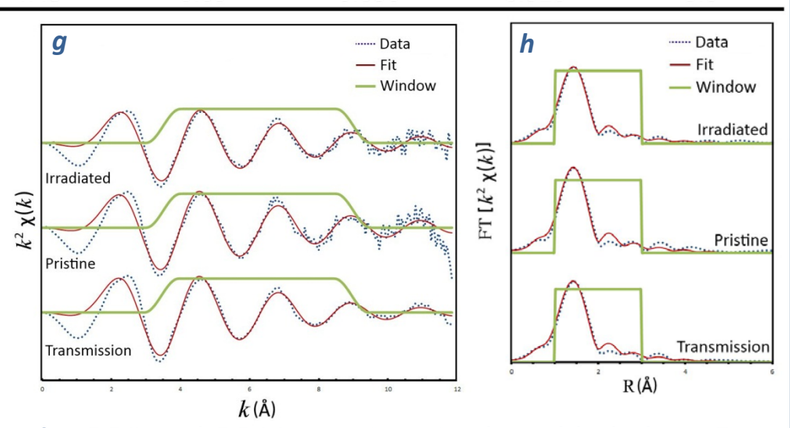
X-ray absorption fine structure (XAFS) spectra gives information about short range structure. To determine Fe co-ordination in the glass samples, the parameter S_0^2 was first calculated using XAFS data obtained from the aegerine standard. To calculate S_0^2, a model from [3] was fitted to the aegerine data, shown in k (figure e) and R (figure f):

In the fitted model, co-ordination number and degeneracy of the paths were fixed while S_0^2 was allowed to refine. For the best fit S_0^2 = 0.84 ± 0.08. The results of the fit are given in the table below:



Path	Model	R_i (Å)	±	σ_i^2 (Å²)	±	N_i
Fe – O1	2.03	2.01	0.02	0.011	0.001	6.0
Fe – Si	3.19	3.13	0.05	0.006	0.005	6.0
Fe – Na	3.17	2.98	0.19	0.002	0.004	3.0
Fe – Fe	3.19	3.16	0.03	0.002	0.003	2.0
Fe – O2	3.73	3.71	0.02	0.018	0.005	10.0
Fe – Si	4.46	4.43	0.03	0.006	0.005	2.0
Fe – O3	4.52	4.43	0.09	0.030	0.026	8.0

The first Fe-O shell was then fitted to the glass samples fixing S_0^2 (0.84) and allowing the co-ordination number to refine. The model fits for k and R for DB8 are shown in figures g and h, respectively.



The fitted model parameters for DB8 and DB11 are given in the table below. ***Fe is calculated to be 4-fold co-ordinated in both compositions and in both pristine (DB8a and DB11a) and irradiated (DB8b and DB11b) samples, within experimental error. The Fe-O bond length (R_o) is the same in all case within error.***

Glass	*R-factor*	E_0 (eV)	±	R_O (Å)	±	σ_O^2 (Å²)	±	N_O	±
DB8a (Trans)	0.011	-0.21	2.08	1.88	0.057	0.006	0.002	4.53	0.72
DB8a (TEY)	0.011	-0.26	2.01	1.88	0.059	0.004	0.002	4.18	0.64
DB8b (TEY)	0.007	0.47	1.53	1.87	0.060	0.004	0.002	3.74	0.45
DB11a (Trans)	0.016	-0.09	1.58	1.86	0.071	0.004	0.001	3.81	0.42
DB11a (TEY)	0.013	-0.38	1.42	1.87	0.068	0.004	0.001	3.91	0.39
DB11b (TEY)	0.012	-1.23	1.36	1.87	0.062	0.005	0.001	3.70	0.34

5. Conclusions

- XAS was used to investigate the effect of simulated α-recoil damage (simulated by K^+ ion irradiation) on Fe co-ordination and valence in simple sodium borosilicate glasses.
- The location and intensity of the pre-edge peak in the XANES spectra were identical for both glass compositions and for both pristine and irradiated samples, suggesting that the irradiation had no effect on Fe valence.
- The fitted model parameters using XAFS data showed Fe to be 4-fold co-ordinated in both glass compositions and for both pristine and irradiated samples. The results also showed the Fe-O bond length to be the same for both compositions, with no variation between pristine and irradiated samples.
- From these results, we conclude that $2x10^{15}$ Kr^+ ions/cm², with energy of 450KeV, used to simulate α-recoil damage, has no effect on Fe co-ordination and valence in simple sodium borosilicate glasses.

References

[1] **Krypton irradiation damage in Nd-doped zirconolite and perovskite**, C. Davoisne *et al, Journal of Nuclear Materials 415 (2011) 67–73.*

[2] **The Stopping and Range of Ions in Solids**, J.F. Ziegler, *et al* Pergamon press, New York, 1985. http://www.srim.org/>.

[3] **Synthesis and structural properties of clinopyroxenes of the hedenbergite** , G. J. Redhammer *et al,* (2000) European Journal of Mineralogy (1,1989-) 12, 105-120

Acknowledgements

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