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Determination of the iron oxidation state in iron phosphate glass

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1 Introduction

Iron phosphate glasses ($Fe_{1.2}P_{0.8}O_{4.2}$, IPG) are being considered as the alternative immobilization matrix for high level radioactive waste.[1] Although many studies have investigated the co-ordination and speciation of elements in pristine materials, there are very few X-ray spectroscopic studies concerning the effect of preparation conditions on element speciation in simulated wasteforms. The aqueous durability of iron phosphate glass is known to depend sensitively on the $Fe^{II}/\sum Fe$ ratio: an increase in Fe^{II} is accommodated by the formation of more reactive P-O-P linkages at the expense of more hydrolysis resistant Fe-O-P linkages. It is imperative to understand $Fe^{II}/\Sigma Fe$ ratio in iron phosphate glasses, in order to predict the long term stability.

2 Experiment

Iron phosphate glass of composition 60 mol% P_2O_5-40 mol% Fe_2O_3 was synthesised using $NH_4H_2PO_4$ and Fe_2O_3 as starting precursors. The powder in stoichiometric ratio were mixed and melted at 1150ºC for 4 hrs in recrystallized alumina crucibles in an electric muffle furnace. The glass was cast and annealed at 500 °C for 1 hr. A second sample was melted at 1450 ºC for 4 hrs and then quenched by pouring into water.

Fe K-edge XANES spectra of the cast and quenched iron phosphate was measured in transmission mode at BL-9A, in comparison with Fe^{II} and Fe^{III}-bearing standard. Data reduction and analysis was performed by Athena software package. The pre-edge information was derived by calculating the total integrated area and the centroid (area-weighted average of the pre-edge peak position) of the background subtracted pre-edge.

3 Results and Discussion

Figure 1 shows the pre-edge feature of Fe K-edge XANES for the as-prepared and the quenched samples. Severe differences in the pre-edge region are evident between the as-prepared and quenched sample, suggesting the ratio of Fe^{II} and Fe^{III} in these two samples is different. The centroid position can be used to estimate the average oxidation state of Fe, comparing with the standard samples. As shown in Figure 2, the centroids for ferrous and ferric iron were separated by ~1.4 eV, in agreement with past studies [3]. The as-prepared sample (blue star) located closed to the position of that in the standards of $FePO_4$, $NaFeSi_2O_6$ and $Fe_3(P_3O_7)_2$, which was consistent with the literature on iron phosphate glass [4]. For the quenched IPG sample, the centroid position shifted to around 7111.9 eV. The plotting of the quenched sample in Fig. 2 revealed that the average oxidation state is 2.48+. The reduction in average oxidation state of iron is attributed to formation of additional Fe^{2+} during melting due to the reduction of Fe^{3+} ions.[5] The quenching process has frozen in the high temperature glass state. In the cast glass the iron re-oxidises during the annealing process.

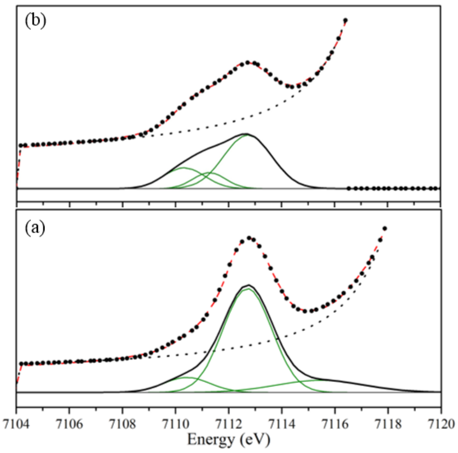

Fig. 1: Pre-edge spectra (Fe K-edge) and the calculated fit; pre-edge for the cast (a) and quenched samples (b).

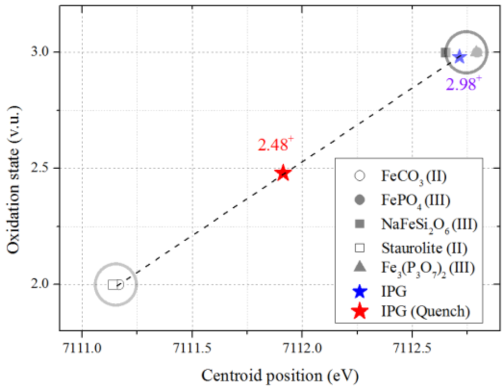

Fig. 2: Pre-edge information for the Fe(II)/(III) standard materials and the glasses of this study.

References

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