Local Structural Analysis around Zr and Cs in Iron Phosphate Glasses

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For the encapsulation of high-level radioactive waste from pyroprocess, iron phosphate glass has high affinity to contain waste salts as main constituents of glass. This fact attracts attention to this system as suitable vitrification media, because this glass system is also known to have high loading capacity of nuclear wastes. In addition, this glass system has another advantage of chemical stability comparable or higher than borosilicate glass system.

Among fission products, zirconium has been considered to be difficult to dissolve into iron phosphate glass. According to the previous study, Zr ions in glass are stabilized by the coexistence of alkali ions, Cs_2O, which is also one of radwastes from the nuclear power plant. Moreover, the chemical stability of the glasses depends in the concentration of these waste elements.

In this study, the coordination structure around the Zr and Cs atoms in iron-phosphate glass have been evaluated by EXAFS structural analysis of the glass samples with different Cs_2O in order to clarify the role of these elements in the glass proerties.

The base composition of the iron phosphate glass is $1Cr_2O_3$-$3(CoO)_2$-$4.5Al_2O_3$-$28Fe_2O_3$-$65P_2O_5$ (in mol%). 2 mass% of ZrO_2 with 2, 4, 8 and 16 mass% of Cs_2O, as well as 4 mass% of ZrO_2 with 0, 2, 4, 8, 16, 25 and 40 mass% of Cs_2O were added to this iron phosphate glass matrix. The samples were obtained by stirring and melting at 1300 ºC for 2 hours using an electric furnace, followed by quenching and rate cooling. These samples were subjected to EXAFS measurement by transmission or fluorescence methods at BL-27B of High Energy Accelerator Research Organization PF or BL-5S1 of Aichi synchrotron light center. The obtained data have been analysed by EXAFS analysis program WinXAS version 3.02. An EXAFS oscillation was extracted using the cubic spline method and the structure function was obtained by the Fourier transformation. Structural parameters were derived from fitting based on EXAFS equation.

In the EXAFS oscillation of Zr, there is not any remarkable difference irrespective of ZrO_2 concentration. Zr-O distance showed certain dependency on Cs_2O concentration below 16 mass%. When Cs_2O concentration is higher than 16 mass%, oscillations become identical. It is considered that the influence of Cs addition on the local structure of Zr almost disappeared at high Cs_2O concentration region.

EXAFS analysis of Cs showed that the distance from the nearest neighbor (Cs-O) gradually becomes shorter as the Cs_2O concentration increases. Particularly in the case of the glasses with 2 mass% of ZrO_2 concentration, Cs-O peak shifted greatly between 8 and 16 mass% of Cs_2O concentration. In the case of 4 mass% ZrO_2 glasses, the shift was found between 16 and 25 mass% of Cs_2O concentration. It can be said that local structural correlation of Zr and Cs exist in iron-phosphate glass indicating the solubility and stability of Zr and Cs in this glass system.