

Local structure analysis of light elements included in simulated radioactive waste glasses by soft X-ray absorption fine structure

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The disposal of radioactive waste generated from nuclear facilities is one of the important research topics in the field of nuclear energy. The “vitrification technology” using borosilicate glass is thought to be effective for immobilizing high-level radioactive liquid waste (HLLW). In order to further improve this technology, it is necessary to analyze chemical state of the light element components contained in the sample in detail. In this study, as part of a study to investigate measures for suppressing precipitates from the glass structure, B K-edge XAFS measurement of the glass frits and the simulated waste glass samples was performed. The aim of this study is to investigate the influence of B-composition on the local structure around B atom.

The samples used for the measurement were 14 borosilicate glass frits and 8 glasses mixed, heated and melted with simulated HLLW. The composition of the frit glass and the sample name are based on the PF-xx series of the composition of the vitrified solid material. S-xx series mean excluding CaO and ZnO from PF-xx series. B-xx series mean the increased B amount of PF-xx series. BS-xx series means excluding CaO and ZnO from the B-xx series. The composition in which 0% weight of Na₂O is represented by yy-N0, 10% weight is represented by yy-N10, and Li₂O is excluded at the 10% Na₂O with excluded Li₂O is expressed as yy-Li.

The simulated waste glass sample yy-xx-W was prepared by mixing the simulated high-level radioactive waste solution prepared with the non-RI nitrate reagent so that the waste liquid component contained in the glass was 30 wt% in terms of oxide (yy-N0, yy-Li). B K-edge XAFS measurement was performed in the vacuum chamber at the beamline BL-11, SR center, Ritsumeikan University at room temperature in a partial fluorescence yield method. From the XANES spectra, the two peaks derived from the 3-coordinate sp² structure (BO₃) and the 4-coordinate sp³ structure (BO₄) were analyzed. The peak area ratio of BO₄ / BO₃ was calculated to compare glass composition dependency.

Comparing the BO₄ / BO₃ ratios of the four

samples of glass frit PF-Nx series (PF-N0, PF-N2, PF-N4, PF-N10), as Na₂O increases, BO₄ / BO₃ ratio increased. It is confirmed that as the amount of Na in the glass increases, the ratio of the tetracoordinate sp³ structure (BO₄) of B-O increases and the ratio of the three coordination sp² structure (BO₃) decreases. Similarly, when yy-N0 and yy-N10 of other glass frit series are compared, the BO₄ / BO₃ ratio of yy-N10 with larger amount of Na is higher than that of yy-N0. Therefore, Na in borosilicate glass acts on the transition from the three-coordinate sp² structure of BO to the four-coordinate sp³ structure. However, since the BO₄ / BO₃ ratio of the yy-Li series containing the same 10 wt% Na₂O content and excluding Li₂O is lower than the yy-N10 series including Li₂O, not only Na but also alkaline components such as Li can influence the transition. Comparing 8 samples of the simulated waste glass and the raw material glass 8 not containing the waste liquid component, the BO₄ / BO₃ ratio was higher in the simulated waste glass than in all the compositions. It is considered that this waste liquid component acts on the transition like the alkaline component.

Variation of BO₄ / BO₃ ratio due to alkaline components and waste liquid components of S - xx series and BS - xx series excluding CaO and ZnO is different from PF - xx series and B - xx series. In the case of the raw glass composition, the change of the BO₄ / BO₃ ratio due to the alkali component such as Na is larger in the S-xx series than in the PF-xx series, and larger in the BS-xx series than in the B-xx series. In the case of simulated waste glass, the BO₄ / BO₃ ratio of the yy-N0-W composition of the PF-xx series and the B-xx series is lower than the yy-Li-W composition excluding Li₂O, and the tendency is opposite in the S-xx series and the BS - xx series.

Reference

- (1) M. E. Fleet, S. Muthupari, *J. Non-Crystalline Solids*, **1999**, 255, 233.