Local Structure Analysis of S and Mo in Simulated Nuclear Waste Glasses

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High-level radioactive waste disposed from reprocessing facilities is treated by mixing it with aluminoborosilicate glass beads, melting it in a high-temperature electric furnace, and pouring it into a stainless-steel canister to vitrify it. High-level radioactive liquid waste contains ZrO_2, MoO_3, alkaline earth oxides, rare earth oxides, platinum group metals, their nitrates and sulfates, etc. Aluminoborosilicate glass as a base glass is used in various reprocessing processes, because of its relatively low melting point and excellent chemical durability. Chemical compositions of aluminoborosilicate glasses should be further optimized because there is a growing demand for base glasses that can contain more radioactive waste.

In this study, S *K*-edge and Mo L_3-edge XANES measurements were performed to investigate the chemical state and local structure of S and Mo atoms, which have a strong influence on the chemical durability and crystallization tendency of the simulated nuclear waste glasses.

Fig. 1 shows the normalized XANES spectra. SiB225Al3-mogi to 20-9SS-SSS are simulated nuclear waste glasses. $25La_2O_3$–$75MoO_3$ is a glass synthesized by a levitation technique, $La_2Mo_3O_{12}$ is a crystalline phase with the same composition of the glass, and MoO_3 to H_2MoO_4 are reference samples.

The S content of the samples was very low, and therefore the peak intensities were not high enough to provide any structural and chemical information. However, the fact that no S *K*-edge peaks were detected except for the SiB series and 20-9SS-SSS glasses, which were made from sulfates, indicates that S *K*-edge XANES spectra was useful in determining whether S was present in the glass.

Mo *K*-edge EXAFS and Raman scattering spectroscopy have shown that Mo atoms formed isolated MoO_4^{2-} tetrahedra in the simulated nuclear waste glasses, but information on the second coordination sphere was lacking. The Mo L_3-edge XANES spectra of the simulated nuclear waste glasses obtained in this study showed no significant differences, whereas the spectrum of MoO_3 is clearly different from those of the nuclear waste glasses. This is because the MoO_3 structure is composed of edge-shared MoO_6 octahedra.

The spectra of $25La_2O_3$-$75MoO_3$ glass, $CaMoO_4$, K_2MoO_4, and H_2MoO_4 were also different from those of the simulated nuclear waste glasses, although the main structural unit is isolated MoO_4^{2-} tetrahedron as in the simulated nuclear waste glasses. These results indicate that the Mo L_3-edge XANES spectrum includes information on the second coordination sphere of Mo, but the experimental spectra of the simulated nuclear waste glasses are averaged even if the local structure of Mo atoms should become more diverse in a multi-component system.

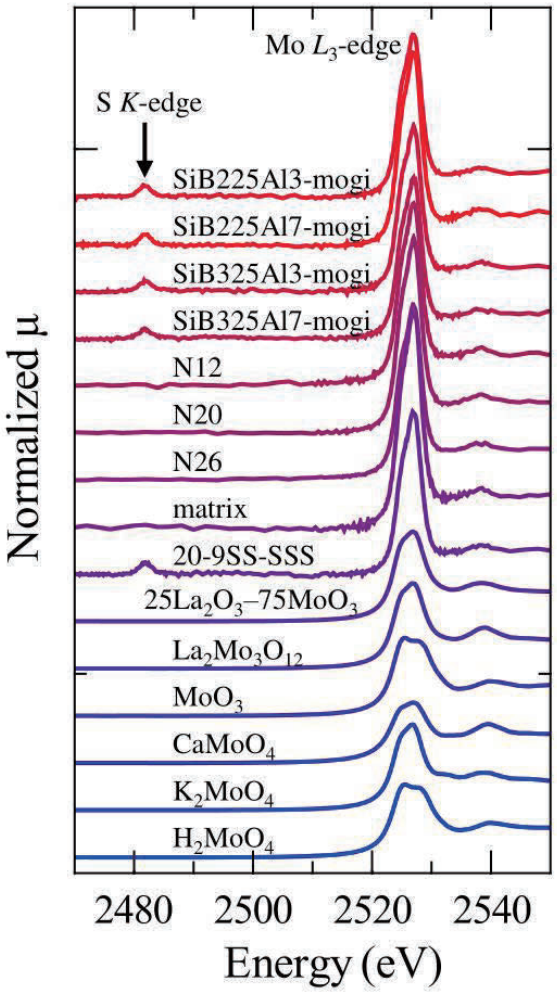

Fig. 1 S *K*-edge and Mo L_3-edge XANES spectra.