

Local Structure of Sodium Ion in Synthesized Nuclear Waste Glass Analyzed by Soft X-ray Absorption Spectroscopy

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1. Introduction

In Japan, high-level nuclear waste discharged from nuclear power plant is subject to be immobilized into sodium borosilicate glass matrix and then buried into deep underground. For immobilizing high-level nuclear waste into borosilicate glass as much as possible, the optimization of glass composition is required to suppress yellowed phase precipitation, mainly consisting of alkaline molybdate compound (e.g. Na_2MoO_4). It was previously reported that molybdenum ions exist as MoO_4^{2-} in the borosilicate glass¹, and it was suggested that alkaline ions are associated with MoO_4^{2-} superior to other structural units. On the other hand, it has been empirically found that the borosilicate glass containing vanadium oxide shows high filling capacity of nuclear waste without yellowed phase deposition, however its mechanism has not been clarified. We have conducted various kind of structural analysis for the synthesized nuclear waste glass containing vanadium oxide, which have revealed that vanadium ion in the glass exists as V^{5+}O_4 and the distributing tendency of alkaline ions to MoO_4^{2-} is suppressed. However, the structural behavior of alkaline ion is not still clear. This study investigates Na ion distribution in the synthesized nuclear waste glass by soft X-ray absorption spectroscopy, to directly verify that Na ion is preferentially coordinated with oxygen ion of VO_4 rather than that of MoO_4^{2-} .

2. Experimental

The synthesized nuclear waste glass sample consists of Al_2O_3 , B_2O_3 , Li_2O , Na_2O and SiO_2 as main components, which are fundamentals of conventional glass composition used for nuclear waste immobilization. In addition, the synthesized glass sample includes V_2O_5 ,

MoO₃ and other minor elements. Our previous study revealed that these components mainly exist as AlO₄, BO₃, SiO₄, VO₄ network structure or MoO₄²⁻ isolated ion respectively. To investigate Na ion distribution in the synthesized nuclear waste glass, we measured Na K-edge XANES spectrum by both total electron yield (TEY) and fluorescence (PFY) modes. NaAlO₂, Na₂B₄O₇, NaSiO₃, NaVO₃, and Na₂MoO₄ compounds were taken as standard samples corresponding to Na ion distribution to the above structural units respectively. The XANES measurements were conducted by use of soft X-ray XAFS platform (BL-10) in SR center, Ritsumeikan University. These samples were prepared as powders, and taken to the high vacuum (<10⁻⁶ Pa) condition for the XAFS measurements.

3. Results and Discussion

The measured Na K-edge XANES spectra of the synthesized nuclear waste glass and Na-containing compounds as standard samples are presented in **Figure 1**, where PFY mode was adopted. First, the spectra of Na-containing compounds indicate that different Na ion distributions can be clearly recognized by the comparison of the corresponding XANES spectrum structure. Second, it was found that the spectrum structure of the synthesized nuclear waste glass quite resembles that of NaVO₃ rather than Na₂MoO₄, which directly demonstrates that Na ions in the glass are mainly coordinated with oxygen ion of VO₄ structure rather than that of MoO₄²⁻ isolated ion. The above result can explain the suppressing behavior of yellowed phase formation in the vanadium-containing nuclear waste glass.

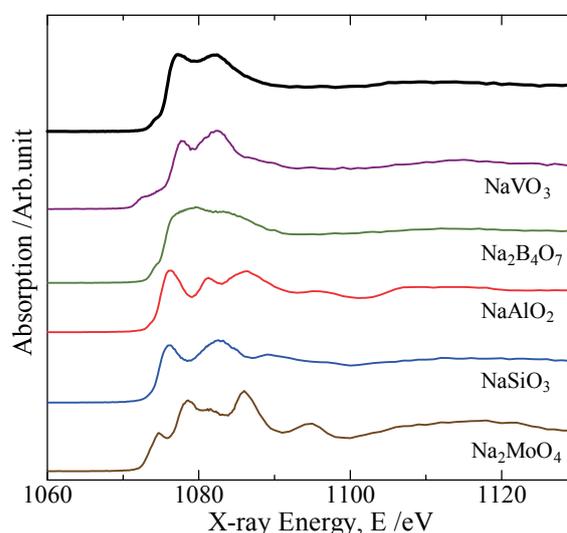


Fig. 1. Observed Na K-edge XANES spectra of synthesized nuclear waste glass and standard samples. (Measured by fluorescence mode)

Acknowledgement

This work was carried out as a part of the research project, "Basic Research Programs for the Next Generation Vitrification Technology", commissioned by the Ministry of Economy, Trade and Industry (METI), in FY2016.

References

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