

Structural Analysis of Molten CeCl_3 - NaCl - CsCl System by High-energy X-ray Diffraction Measurements

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Introduction

Molten NaCl - 2CsCl has been an useful electrolytic bath for new pyrochemical separation process in nuclear fuel cycle. However, the low electric current efficiency of the process is a critical problem for the practical use. It is important to investigate the local structure of actinide ion in the NaCl - 2CsCl melt in order to elucidate the mechanism of the process. For the preliminary experiments, CeCl_3 was selected as a model material of actinide chlorides in the process. The structure of molten CeCl_3 - NaCl - 2CsCl system was investigated by high-energy X-ray diffraction (HEXRD) measurements with 30keV photon energy. In this study, the XRD measurements were performed by transmission method with silica glass capillary for the melt container at 923K.

Experimental

The sample of NaCl - 2CsCl and 0.1CeCl_3 - $0.9(\text{NaCl}-2\text{CsCl})$ were prepared from anhydrous NaCl , CsCl and CeCl_3 . The mixture was injected into a silica glass capillary with 1mm diameter and 0.01mm thickness. The capillary was set on an alumina holder in furnace and heated up to 923K as shown in Figure 1. The HEXRD patterns were measured by the transmission mode with the multi-axis diffractometer at BL19B2 beamline with 30keV photon energy. The XRD was measured in a interval of 0.2 degree from 2 to 30 degree and 0.4 degree from 30 to 80 degree of 2θ , respectively. The intensities were accumulated by fixed time method.

Results and discussion

The observed XRD data were corrected for absorption, background, incoherent scattering. The corrected data were normalized to electron units by high-angle method. The RDFs were calculated by the Fourier transformation of the reduced interference functions.

Figure 2 shows the correlation functions, $g(r)$ for NaCl - 2CsCl and 0.1CeCl_3 - $0.9(\text{NaCl}-2\text{CsCl})$

melts at 923K. For both $g(r)$ s, a peak were found at 3.4Å which are assigned to Cs-Cl correlation. For NaCl - 2CsCl melt, a shoulder were found around 2.2Å. It is assigned to Na-Cl correlation.

For the latter melt, a broad shoulder was found around 2.8 Å. It is assigned to Ce-Cl correlation. The Na-Cl correlation was overlapped with the Ce-Cl correlation and the main peak around 3.4 Å shifted to short distance due to the overlapping of the Ce-Cl correlation.

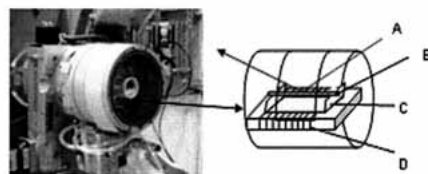


Figure 1 Schemes of furnace and sample holder for HEXRD measurement at 923K. A: X-ray beam, B: Silica glass capillary, C: Alumina holder, D: Platinum heater.

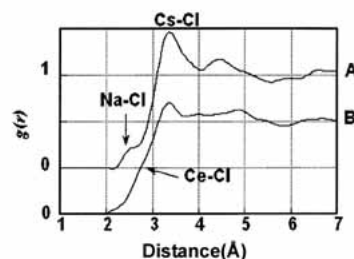


Figure 2 Correlation functions, $g(r)$ at 923K for (A) NaCl - 2CsCl melt and (B) 0.1CeCl_3 - $0.9(\text{NaCl}-2\text{CsCl})$ melt.

Investigation of local structure of Er-doped silicate glasses for optical amplifier

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WDM is a common method used in telecommunication and erbium-doped fiber amplifier (EDFA) is a widely used WDM amplifier. Nowadays, EDFA with high performances, that is, broadband gain and high efficiency, becomes essential because the amount of data in telecommunication increase in every year. As a candidate for WDM amplifier with high performance, we have developed new silicate glass with large amount of La_2O_3 in composition. In this glass, La^{3+} ion may play an important role to achieve the good dispersion of Er^{3+} ions, but details are still unclear. Since determination of the origin is important for the purpose of further improvement, we have tried to investigate the local structure around Er^{3+} ions in glasses by XAFS measurements. In our previous works (2004A0288-NI- and 2004A 0810-RI-np-TU), we found that the first coordination structures of La^{3+} ions are similar to that of La_2O_3 crystals, in contrast, that of Er^{3+} greatly depends on the glass composition. In addition, La^{3+} and Er^{3+} ions are located in similar sites. In the present work, for the purpose of examination of concentration quenching effect from the structural viewpoint, dependence of the local structure around Er^{3+} ions on the content of Er_2O_3 was investigated for conventional silicate glasses.

XAFS measurements at the K-edge of Er^{3+} ions in glasses of sodium-silicate glass (sample A) and sodium-alumino-silicate glass (sample B) with the Er_2O_3 content of 0.15-1.0 mol% were executed.

Figures 1 and 2 show Fourier transformed EXAFS spectra measured at the K-edge of Er^{3+} ions in sample A and B, respectively. In

the case of sample B, two peaks around 2Å are definitely separated for $x=0.15$ and 0.3, but the separation becomes smaller for $x=1.0$. This change was not observed by the measurement at the L_{III} -edge because of the limitation of range in measurement. In contrast, any changes in shape of peaks are observed for sample A. This suggests the structural change with the Er_2O_3 content occurs for sample B. To understand the relationship between structural change and concentration quenching, further works are needed.

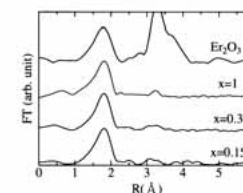


Fig.1 Fourier transformed EXAFS data of Er_2O_3 crystal and sample A with the Er_2O_3 content of 0.15, 0.3 and 1.0 mol%.

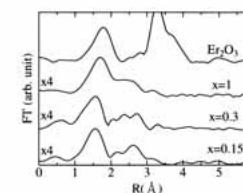


Fig.2 Fourier transformed EXAFS data of Er_2O_3 crystal and sample B with the Er_2O_3 content of 0.15, 0.3 and 1.0 mol%.