Raman Spectroscopic Study of Eu(II) and Yb(II) in Molten LiCl-KCl Eutectic

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1. Introduction

Molten salts have been widely studied for a broad application since they typically provide superior properties, such as good electrical conductivity, high energy density, excellent radiation resistance, nonflammability, etc. The efficiency of molten salts in diverse applications depends on the solvation of metal ions in molten salts, *i.e.* the local structure of liquid [1]. In molten alkali chloride melts, some of lanthanide elements (Sm, Eu, Tm, and Yb) can be present in the divalent state, while other lanthanides mostly exist in the trivalent state.

In this work, the Raman study of $EuCl_2$-LiCl-KCl and $YbCl_2$-LiCl-KCl system were performed to gain the structural information of divalent lanthanide ions in molten LiCl-KCl.

2. Experimental

2.1 Sample preparation

$EuCl_3$, $EuCl_2$ and $YbCl_3$ (99.99% purity) were purchased from Sigma-Aldrich. Yb(II) was prepared by the electrochemical reduction of Yb(III) using a potentiostat (Bio-Logic Science Instruments, SP240). Tungsten was used as a working electrode and a counter electrode, and the detailed electrochemical system has been described in [2]. All experimental procedures including sample handling were conducted in a glove box under argon atmosphere (H_2O, O_2 < 1 ppm)

2.2 Raman spectroscopic system for molten salt

An in-situ Raman spectroscopic system for molten salt built in our laboratory uses a 532 nm light of the DPSS laser (CNI Optoelectronics Technology, MLL-U-532) with a maximum power of 400 mW as excitation source. The laser beam was focused into the inside of sample through an optical furnace window. The back-scattered Raman signal was measured with an intensified CCD (Andor Technology, iStar) coupled with a Czerny-Turner spectrometer (Andor Technology, shamrock sr-303i).

3. Results and Discussions

3.1 Raman spectra of Eu(III) and Eu(II)

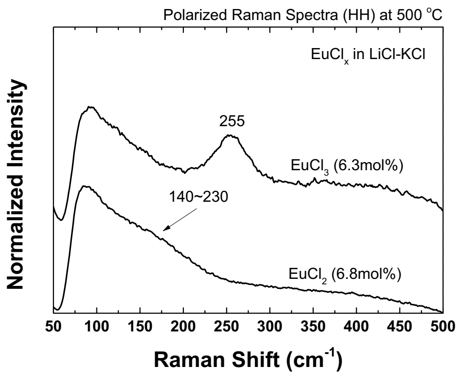

Fig. 1. Raman spectra of $EuCl_3$ and $EuCl_2$ in LiCl-KCl eutectic salt at 500°C.

The trivalent lanthanide ions in alkali chloride melts are known to be present as $LnCl_6^{3-}$ with the octahedral coordination environment [3]. Fig. 1 shows the Raman spectra of Eu(II) and Eu(III) in a linear polarized mode of HH. $EuCl_3$ (6.3mol%) in LiCl-KCl eutectic salts has the $\nu_1(A_{1g})$ peak of the octahedral symmetry (O_h) at 255 cm^{-1}. On the other hand, $EuCl_2$ (6.8mol%) in the same chloride eutectic revealed a relatively broad peak in the range of 140 to 230 cm^{-1}, as shown in Fig. 1.

3.2 Raman spectra of Yb(III) and Yb(II)

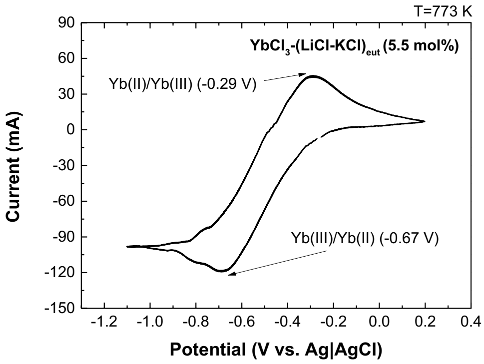

Fig. 2. Cyclic voltammogram of $YbCl_3$ in LiCl-KCl molten salt at 5.5mol% and 773 K.

$YbCl_3$ (5.5mol%) in LiCl-KCl eutectic salts showed the $\nu_1(A_{1g})$ peak at 262 cm^{-1}. The reduction and oxidation peaks were found from the cyclic voltammogram of $YbCl_3$-LiCl-KCl consistently (Fig. 2), as reported by Smolenski et al. [4]. The polarized Raman spectrum of Yb(II) was measured in the course of chronoamperometry at the reduction potential of -0.67 V (vs. 1wt.% Ag|AgCl).

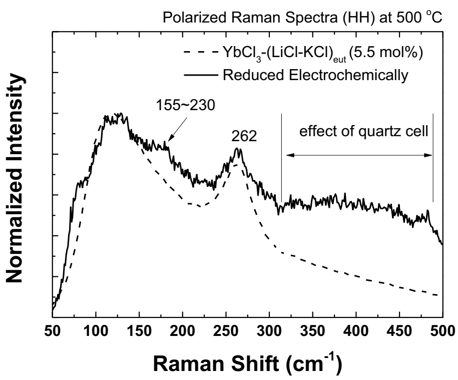

Fig. 3. Raman Spectra of $YbCl_3$ before and after electrochemical reduction.

Fig. 3 shows Raman spectra of electrochemically reduced $YbCl_3$-LiCl-KCl sample. The total applied electric charge of 154 C in the present work induces a reduction of initially prepared Yb(III) by 44%, so that the $\nu_1(A_{1g})$ peak of $YbCl_6^{3-}$ could be observed as well. The reduced Yb(II) has a weak but broad Raman band between 155 and 230 cm^{-1}, similar to Eu(II). It implies that Ln(II) has different coordination environment in LiCl-KCl system, compared to Ln(III).

4. Conclusions

The vibrational modes of $EuCl_3$ and $YbCl_3$ are associated with the octahedral local structure of $LnCl_6^{3-}$. The Raman bands of $EuCl_2$ and $YbCl_2$ show a change in their molecular structure, which should be further identified using computational chemistry.

ACKNOWLEDGEMENT

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