

Raman spectroscopic study of the oxidation state of Eu in molten LiCl-KCl

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1. Introduction

Europium can be present in divalent state while many other lanthanides exist in trivalent state. The thermodynamic properties of europium ions have been studied using electrochemical methods, spectroscopic methods, and EPR technique. Although there has been discrepancy of the reduced amount of europium in previous works, the majority of Eu(III) is thought to be reduced to Eu(II) in molten LiCl-KCl spontaneously at relatively low concentration ($< 7.5 \times 10^{-4}$ M) [1].

The Raman spectroscopic studies for rare earth halides and their binary melt systems with alkali halides, LnCl_3 -ACl binary system rich in ACl ($X_{\text{LnCl}_3} < 0.25$, Ln = lanthanides, A = alkali metal), have shown the predominant LnCl_6^{3-} octahedral structure, except for light lanthanides (La, Ce) in arguments [2,3].

Spectroscopy can provide high reliability for the quantitative analysis of such system. The molar absorptivity of Eu(II) at 325 nm is reported as about $1645 \text{ M}^{-1}\text{cm}^{-1}$, which is too high to apply to higher concentration. A high-temperature Raman spectroscopy has been set and employed for analyzing the molecular structure and coordination complex and investigating the oxidation state of europium in molten LiCl-KCl.

2. Experimental

2.1. Sample preparation

Anhydrous LiCl-KCl (LiCl 44wt.%, 99.99% purity), EuCl_3 (99.99% purity), and EuCl_2 (99.99%) purchased from Sigma-Aldrich were used without further purification. Samples were prepared in a hermetically sealed glove box under anhydrous and anaerobic atmosphere of Ar gas (99.9999% purity, H_2O and $\text{O}_2 < 1$ ppm).

The EuCl_3 -LiCl-KCl samples were prepared using the furnace at 773 K, which is attached to the bottom of the glove box under the same inert atmosphere. A crucible made of quartz was used. The melted EuCl_3 -LiCl-KCl was sampled using a thin pyrex tube, and mashed using mortar and pestle.

2.2 Measurement of Raman spectra

A microscopic Raman spectroscopic system for molten salt has been built in the laboratory. DPSS laser (532 nm, continuous wave, 150 mW maximum power at the sample) was used as an excitation source, and the back-scattered Raman signal was measured with an intensified charge coupled device (ICCD, Andor

Technology, iStar) coupled with a Czerny-Turner spectrometer (Andor Technology, shamrock sr-303i). Chloride samples were put into a platinum crucible located on TS1200E temperature-controlled stage (Linkam Scientific Instruments), and the laser was focused with an objective lens. Notch filter and long-wave pass filter were used to suppress the Rayleigh scattering with the cut-off at $\sim 80 \text{ cm}^{-1}$. A $1/4\lambda$ retarder and two polarizers were employed to analyze the isotropic and anisotropic Raman scattering [4,5].

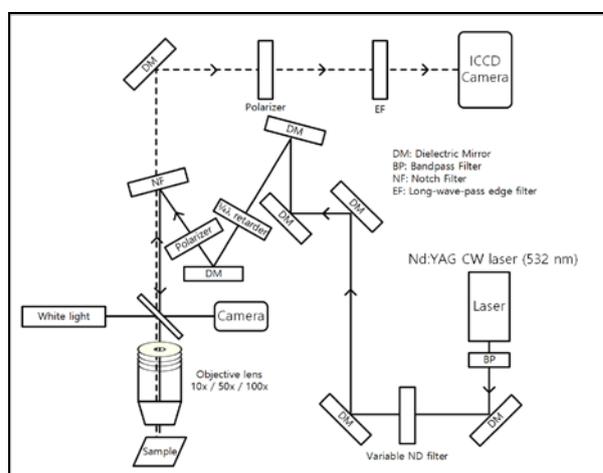


Fig. 1. The design of micro-Raman system

3. Results and Discussion

EuCl_3 -LiCl-KCl was prepared to study the reducing capacity of Eu(III) to Eu(II) at high europium concentration. The amount of sample was decreased after its melting, and it became more significant when the concentration of EuCl_3 was higher. It seems to be vaporized at 500°C .

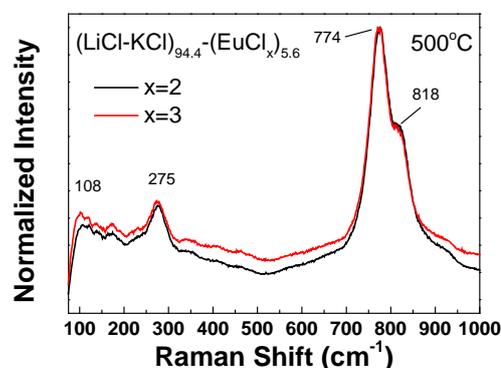


Fig. 2. Raman spectra of $(\text{LiCl-KCl})_{94.4}-(\text{EuCl}_x)_{5.6}$ ($x = 2, 3$) at 500°C

The europium concentrations of initial sample and remaining sample after vaporization were compared using ICP-OES analysis. The concentration of Eu was almost not changed while significant amount of the sample was vaporized, implying that Eu is vaporized together with LiCl-KCl.

Fig. 2 shows the Raman spectra of two samples whose EuCl_x content in LiCl-KCl was kept constantly at 500 °C. One was prepared using EuCl_2 , and the other EuCl_3 . If there is no vaporization or redox reaction, it is not possible that those two spectra are almost the same because of the inevitable structural difference. The results strongly support that the trivalent europium is vaporized with chloride ions and the left europium ions exist in divalent state mostly.

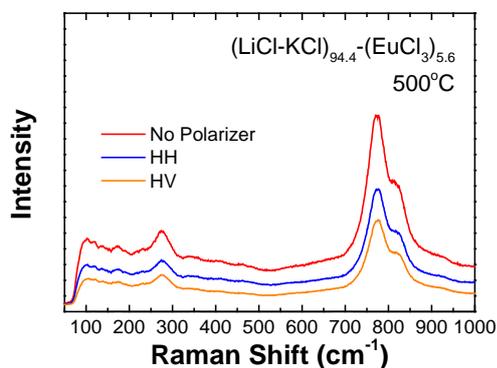


Fig. 3. Raman spectra of $(\text{LiCl-KCl})_{94.4}-(\text{EuCl}_3)_{5.6}$ with polarization at 500 °C

The symmetry of molecular vibration was studied by depolarization ratios of Raman bands defined as Eq. (1).

$$\rho_p = \frac{I_{\perp}(\omega)}{I_{\parallel}(\omega)} \quad (1)$$

Fig. 3 shows the Raman spectra with the use of polarizers. The term ρ_p indicates a measure of symmetric vibration, e.g. 0.75 for non-totally symmetric vibration and 0 for totally symmetric vibration. All the vibrations have depolarization ratio larger than about 0.6 and can be concluded to be asymmetric (Fig. 4).

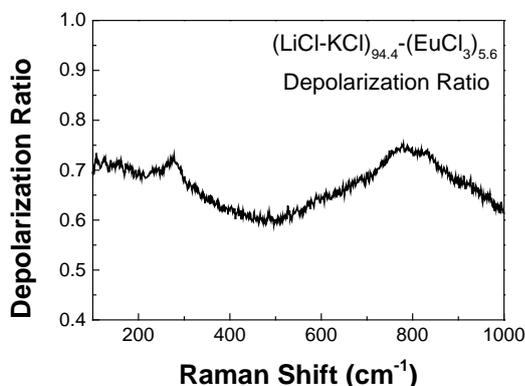


Fig. 4. The depolarization ratio of $(\text{LiCl-KCl})_{94.4}-(\text{EuCl}_3)_{5.6}$ at 500 °C

4. Conclusions

Raman spectroscopy was employed to investigate the oxidation state of EuCl_x in LiCl-KCl at 500 °C. The Raman scattering results suggest the majority of trivalent europium is reduced to divalent state with the composition change by vaporization. The Raman bands show highly asymmetric structure, quite different from regular octahedral structure.

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