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Detection of Fluorescence for Lanthanides in LiCl-KCl Molten Salt Medium

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1. Introduction

In the electrorefining step of the pyrochemical process, actinide ions dissolved in the LiCl-KCl eutectic salt are recovered as pure actinide metals at a cathode for a re-use as a nuclear fuel from the aspect of its nonproliferation of the nuclear fuel cycles. The lanthanide species dissolved in the LiCl-KCl eutectic salt play an important role in an effective metal purification during the electrorefining step, so it is necessary to understand the chemical and physical behaviors of lanthanides in molten salt.

The in situ spectroscopic measurement system and studies according to temperature changes are essential for better understandable information. To our knowledge, the absorption studies of lanthanides at high temperatures have been reported before [1], but the fluorescence studies of those at high temperature are not reported yet. We will discuss here the fluorescence behaviors of lanthanides in LiCl-KCl molten salt medium according to a changing temperature.

2. Experimental

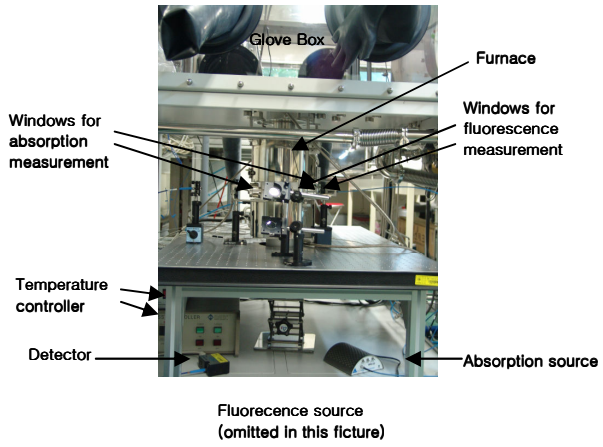

Fig. 1. Spectroscopic measurement system for measuring absorption and fluorescence of molten salt according to temperature changes (especially at high temperature)

Lanthanide-ion fluorescence of an f-f transition was measured at various temperatures in the range of room temperature to 465°C. A He-Cd laser (LiCONix, 442 nm) and a N_2 laser (LSI, 337 nm) were used as the excitation sources for the measurements of the fluorescence. All experiments were performed in a glove box controlled under Ar-atmosphere and equipped with a temperature controlled furnace system as shown in Figure 1. The furnace was specially designed for the simultaneous spectroscopic measurements of absorption and fluorescence. Anhydrous LiCl-KCl (44 wt.% LiCl), and ultra dry lanthanides chlorides of $SmCl_3$ (99.99%), $TuCl_3$ (99.99%), and $EuCl_3$ (99.99%) were used as received from Alfa Aesar.

3. Results and discussion

The fluorescence of lanthanide-ions, which is a radiative emission from an excited electronic state to a ground state, is weak due to Laporte-forbidden transitions. Nevertheless, the fluorescence of the lanthanides was measured only when the sample was solidified from the melt as shown in Fig. 2 and Fig. 3.

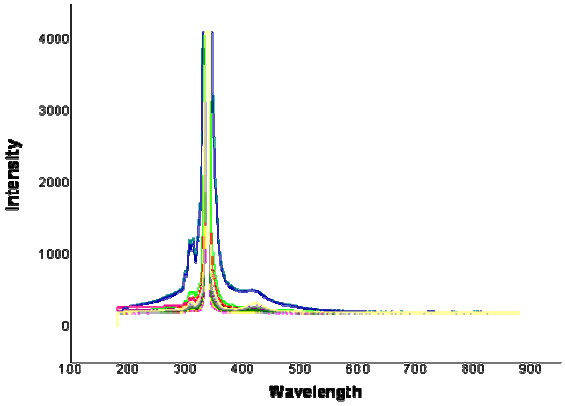

Fig. 2. Fluoresce spectra of $EuCl_3$ in LiCl-KCl eutectic measured in the range of room temperature to 465°C (λ_{exe} = 337 nm)

The fluorescence peak measured at 428 nm was recognized as the transition from the lowest $4f^6 5d^1$ excited state to the $^8S_{7/2}$ ground state [2]. At high temperature of molten salt medium, the fluorescence of lanthanides may be lost possibly by a quenching (thermal or dynamic) of the f-elements [3]. In addition, the bubbles may contributed to the enhancement of the quenching of fluorescence. The temperature, where the fluorescence, was lost was identified to be different depending on the elements.

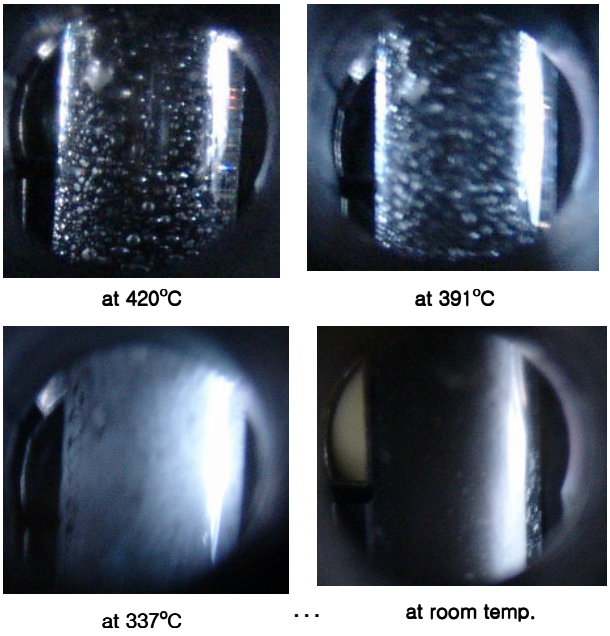

Fig. 3 Photos of $EuCl_3$ in LiCl-KCl eutectic taken in the range of room temperature to 465°C

We will make efforts to find proper components (act as 'antennas'), which absorb enough energy for excitation and then transfer energy to the lanthanide with an appropriate radiative transition fluorescence [4]. In this way, on-line monitoring of chemical species for lanthanides elements in molten salt media can be accomplished.

4. Conclusion

The fluorescence behaviors of lanthanides in LiCl-KCl molten salt medium at high temperature were discussed, and the possible method to control the quenching of the fluorescence in molten salt at high temperature was also suggested.

Acknowledgement

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