Fluorescence Spectroscopic Characteristics of Tb$^{3+}$ and Sm$^{3+}$ in LiCl-KCl Molten Salts

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Laser-induced fluorescence was applied for the detection of lanthanide ions such as Tb$^{3+}$ and Sm$^{3+}$ in a pyrochemical processing. The fluorescence signals of Tb$^{3+}$ and Sm$^{3+}$ in LiCl-KCl molten salts were successfully observed at room temperature. Moreover, the fluorescence method was identified to be sensitive enough to detect a trace of Eu$^{2+}$, originated from a reduction of Eu$^{3+}$ contained in a LiCl-KCl eutectic reagent at a given high temperature molten salt condition. The non-destructive and direct fluorescence measurement can be an alternative method in on-line and in situ determination of the species and concentrations of lanthanides in a molten salt along with absorption measurement.

Key Words: Fluorescence, Lanthanides, Pyrochemical Processing, Electrorefining

1 Introduction

Pyrochemical processing can be simply described as an actinides separation processing at a high temperature by an electrochemical method. The recovery of uranium and the volume reduction of transuranic (TRU) elements for re-use as a nuclear fuel, as well as for nuclear disposal purposes are the advantages of pyrochemical processing has over several other spent fuel treatment techniques. Actinide ions dissolved in LiCl-KCl molten salts at 450 °C are recovered as pure actinide metals at a cathode through an electrorefining step of pyrochemical processing, and at that time, the lanthanide species dissolved in the LiCl-KCl molten salts play an important role in effective metal purification during the electrorefining step. Therefore, to understand the chemical and physical behavior of lanthanides in molten salts, to develop an on-line spectroscopic measurement system, and to study their behavior according to temperature changes, are essential, in addition to the electrochemical tools. Here, we will especially discuss the fluorescent behavior of lanthanides in a LiCl-KCl molten salts medium.

It is well known that the 4f electrons of lanthanides are shielded by the filled 5s and 5p electrons, and the 4f orbitals penetrate a xenon core, so electronic spectra and magnetic properties are rarely affected by the ligands bound to it or the environment. Moreover, many lanthanide ions are luminescent and produce characteristic f-f transition peaks of their ions.11 The fluorescence of lanthanides in various solutions and solids has been studied extensively, but a study in high temperature molten salts has not been reported yet. In this paper, we will especially discuss the fluorescent behavior of Tb$^{3+}$ and Sm$^{3+}$ dissolved in LiCl-KCl molten salts.

2 Experimental

The temperature controlled furnace system was installed in a glove box, and the furnace was specially designed for simultaneous absorption and fluorescence spectroscopic measurement as shown in Fig. 1. All the experiments and chemicals were performed and handled in the furnace and the glove box. Both the oxygen and moisture contents in the argon atmosphere of the glove box were maintained at lower than 2 ppm. Anhydrous LiCl-KCl (44 wt.% LiCl, 99.99%, Aldrich) eutectic, ultra dry lanthanide compounds, such as SmCl$_3$ (99.99%, Alfa Aesar) and TbCl$_3$ (99.99%, Alfa Aesar) were used as received.

The fluorescence spectra were recorded on-line after around 0.007 g of SmCl$_3$ or TbCl$_3$ was completely dissolved in about 6 g of LiCl-KCl eutectic at 465 °C as an initial material in a specially manufactured quartz cell.

Fig. 1 Spectroscopic measurement system for measuring fluorescence using pulsed N$_2$ laser operation (337 nm excitation).
The original 1 cm rectangular quartz fluorescent cell had been attached to a long neck circular quartz tube using hydrogen gas, and it was placed at the center of the electric furnace.

An Edinburgh FS920 fluorometer with the excitation sources from a 450 W Xe lamp (Oriel 66021) and He-Cd laser (Kimmon, 325 nm excitation) equipped with a Hamamatsu R955 PMT was used for the measurement of the lanthanide fluorescence at room temperature.

Fluorescence spectra were also measured on a SpectroPro 2300i - PMT detector with a N₂ laser (LSI, 337 nm excitation) as an excitation source for the comparison of the lanthanide fluorescence results obtained by using the He-Cd laser. The fluorescence signal was collected by a collection lens and optical fiber.

The concentration of an impurity in the LiCl-KCl eutectic reagent was determined by the ICP-MS (Inductively Couple Plasma-Mass Spectroscopy, Varian) method.

3 Results and Discussion

As is well known, europium-ions generally show high fluorescence sensitivity in a solution phase. One of the fluorescence peaks of EuCl₃ in LiCl-KCl molten salts was observed at around 425 nm as shown in Fig. 2, and the peak, including other (more) peaks, was investigated from room temperature to 465 °C. The detailed results for in situ fluorescence studies at a high temperature are in the process of publication in our group. The fluorescence of the europium-ions was generally decreased when the temperature was increased. Based on our previous fluorescence results for europium-ions in a high temperature LiCl-KCl molten salt, we performed experimental studies for other lanthanides, Tb³⁺ and Sm³⁺.

These are known to emit fluorescence in a visible region like europium ions do with a reasonable intensity, so to look into the lanthanides fluorescence in the molten salt media might be possible. Before a detailed in-situ and on-line measurement system is developed to detect the lanthanide ion species and concentrations in high temperature pyrochemical processing, it is necessary to observe the fluorescence of the Tb³⁺ and Sm³⁺ in LiCl-KCl molten salts at room temperature at first, in order to confirm the potentiality to use this method.

The fluorescence measurement of the lanthanide ions was performed after cooling down the samples, in which the lanthanide compounds were completely dissolved in the LiCl-KCl eutectic at 465 °C as the initial material, as explain in the experimental part.

As shown in Fig. 3 and Fig. 4, fluorescence peaks of a high intensity were observed at the position of ca. 425 nm, while several lower intensity peaks were observed from 490 nm to 671 nm and 563 nm to 708 nm, respectively. The intensive peak at 425 nm was identified as originating from Eu²⁺ and was identified to be generated as the relaxation process of Eu²⁺ from the 4f⁵5d⁴(L₆) excited state to the ⁴S₇/₂ ground state. The Eu²⁺ was produced from either Eu²⁺ or a reduction of Eu³⁺ under the used high temperature molten salt conditions. The Eu³⁺ may be introduced as an impurity in the LiCl-KCl eutectic reagent since we used the reagent without any purification. The manufacturing certificate shows that the europium concentration is less than 0.1 ppm, and it was confirmed in our lab by ICP-MS for the LiCl-KCl eutectic reagent used. It was 65.3 ppb of europium in the LiCl-KCl eutectic. This result was verified by measuring the

![Fig. 3](image_url) Fluorescence spectra of TbCl₃ in the LiCl-KCl molten salt at room temperature (λₑₓ = 325 nm) ; (b) is 10 time blow-up of (a).

![Fig. 4](image_url) Fluorescence spectra of SmCl₃ in the LiCl-KCl molten salt at room temperature (λₑₓ = 325 nm) ; (b) is 10 time blow-up of (a).
fluorescence for the LiCl-KCl molten salts only, as shown in Fig. 5. The fluorescence measurement method is sensitive enough to detect a trace amount of Eu$^{2+}$ due to the high fluorescence coefficient of Eu$^{3+}$. We also checked the fluorescence from the manufactured quartz cell itself, and it did not show any fluorescence in the investigated wavelength region.

Figure 3 shows the fluorescence spectra of TbCl$_3$ in LiCl-KCl molten salts upon 325 nm excitation by a He-Cd laser at room temperature. The result of using the 337 nm N$_2$ laser also shows a similar result to the one using the He-Cd laser. The Tb$^{3+}$ fluorescence intensity was very weak to be detected compared with the peak at ca. 425 nm. The fluorescence peaks of the Tb$^{3+}$, which are observed in an area from 490 nm to 671 nm, are associated with the transitions from the excited $^5D_1$ level to $^7F_J$ ($J = 0, 1, 2, 3, 4, 5, 6$) levels. Six emission bands, centered at 490 ($^5D_1$→$^7F_0$), 547 (doublet into 545 and 550 nm; $^5D_1$→$^7F_1$), 586 ($^5D_1$→$^7F_2$), 623 ($^5D_1$→$^7F_3$), 650 ($^5D_1$→$^7F_4$), and 671 ($^5D_1$→$^7F_5$ and $^5D_0$) nm each, can be attributed to Tb$^{3+}$ in the LiCl-KCl molten salt. A similar result was reported for KCl:Tb$^{3+}$ grown crystal. Therefore, we could assign the Tb$^{3+}$ ion in the LiCl-KCl molten salts has a cubic symmetry as was the case of KCl:Tb$^{3+}$ crystal.

The Sm$^{3+}$ fluorescence intensity was also very weak, and the peak at ca. 425 nm was relatively intense as shown in Fig. 4. The peaks centered at 563, 600, 650, and 708 nm are generated from Sm$^{3+}$. According to the Sm$^{3+}$ energy level diagram, the emission corresponds to the radiation from the $^4G_{5/2}$ level to the $^4H_J$ ($J = 5/2, 7/2, 9/2, 11/2$). The assignment for fluorescence spectra of Tb$^{3+}$ and Sm$^{3+}$ in Fig. 3 and Fig. 4 is summarized in Table 1. The reduction process is one of the important subjects in lanthanide chemistry in molten salt media. Nevertheless, we were not able to observe any characteristic spectroscopic information for Tb$^{3+}$ and Sm$^{3+}$ in this study (maybe due to the low signal intensity or position of fluorescence peaks (e.g. Near-IR)). Some lanthanides may not go through the reduction process in high temperature molten salt media. An increase of the detection sensitivity for these samples may provide more detailed information in our future work.

### 4 Conclusion

To our knowledge, the fluorescence studies of lanthanides in a LiCl-KCl molten salt have not been reported yet, except for our group. Some lanthanides are sensitive on absorption measurement, and other lanthanides are more sensitive on fluorescence measurement. The spectrum tendency may provide on-line and in situ screening tools for the detection of lanthanides and actinides species and their concentrations in high-temperature molten salt media. High-temperature fluorescence studies for various lanthanides and actinides are in progress.

### Acknowledgement

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### References


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**Table 1** Summarised assignment for fluorescence spectra of Tb$^{3+}$ and Sm$^{3+}$ in Fig. 3 and Fig. 4.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Peak Position (nm)</th>
<th>Intensity</th>
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<tbody>
<tr>
<td>Tb$^{3+}$, $^5D_1$→$^7F_1$</td>
<td>490</td>
<td>strong</td>
</tr>
<tr>
<td>Tb$^{3+}$, $^5D_1$→$^7F_2$</td>
<td>547</td>
<td>very strong</td>
</tr>
<tr>
<td>Tb$^{3+}$, $^5D_1$→$^7F_3$</td>
<td>586</td>
<td>medium</td>
</tr>
<tr>
<td>Tb$^{3+}$, $^5D_1$→$^7F_4$</td>
<td>623</td>
<td>medium</td>
</tr>
<tr>
<td>Tb$^{3+}$, $^5D_1$→$^7F_5$</td>
<td>650</td>
<td>weak</td>
</tr>
<tr>
<td>Tb$^{3+}$, $^5D_1$→$^7F_6$</td>
<td>671</td>
<td>very weak</td>
</tr>
<tr>
<td>Sm$^{3+}$, $^4G_{5/2}$→$^4H_{5/2}$</td>
<td>563</td>
<td>weak</td>
</tr>
<tr>
<td>Sm$^{3+}$, $^4G_{7/2}$→$^4H_{11/2}$</td>
<td>600</td>
<td>very strong</td>
</tr>
<tr>
<td>Sm$^{3+}$, $^4G_{9/2}$→$^4H_{15/2}$</td>
<td>650</td>
<td>strong</td>
</tr>
<tr>
<td>Sm$^{3+}$, $^4G_{11/2}$→$^4H_{19/2}$</td>
<td>708</td>
<td>very weak</td>
</tr>
</tbody>
</table>

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**Fig. 5** Fluorescence spectra of only the LiCl-KCl molten salt at room temperature ($\lambda_{ex} = 325$ nm).