Optical Spectra of Several Lanthanide Ions in LiCl-KCl Eutectic Melt at 450℃

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1. Introduction

The use of pyrochemical processing of spent nuclear fuel is emerging as a promising option in the near future. However, rare earth elements (REEs) contained in spent fuel may play a significant role in related pyrochemical processes. Therefore, it is necessary to understand the chemical behavior of the lanthanide elements in high-temperature molten salt media. A UV-VIS spectroscopic method may be used to investigate the chemical behavior of lanthanide ions in molten salt media. Here, we attempted to measure the UV-VIS spectra of several lanthanide ions (Nd, Eu, Ce) in LiCl-KCl eutectic melt at 450 ℃.

2. Experimental and Results

2.1 Sample Preparation

All the experiments were carried out in a glove box system. The inert atmosphere was maintained by purging with purified Ar gas. The LiCl-KCl eutectic (mole ratio of lithium to potassium = 59/41) mixture (melting point 723K) was prepared from A.R. grade reagent. Spectra of Nd(III), Eu(III) and Ce(III) were obtained by dissolving $NdCl_3$, $EuCl_3$ and $CeCl_3$ in LiCl-KCl containing quartz cell at 450 ℃.

2.2 In-situ UV-VIS spectra measurement

The experiment apparatus is schematically shown in Figure 1. Spectrometric components are interfaced with glove box-furnace system. A rectangular quartz cell attached to a long quartz tube (see Figure 1) is placed at the center of the electric furnace. The light beam (Ocean Optics Inc) was guided into the sample chamber by using an optical fiber. Suitable quartz lens and iris were used to collimate the beam path and adjust the intensity.

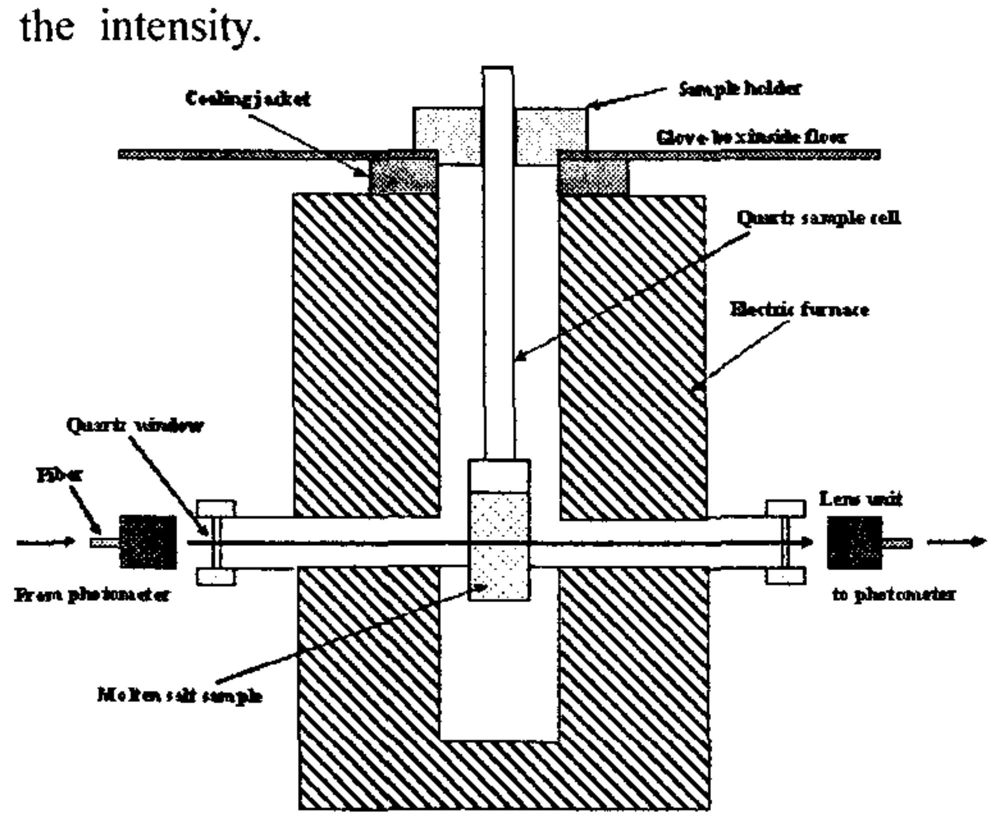

Figure 1. Schematic diagram for UV-VIS spectrum measurements

3. Results

The measured absorption spectra of $NdCl_3$ are shown in Figure 2. The strongest absorption band can be seen at 589 nm. Theses correspond to the transitions from the ground level $^4I_{9/2}$ and to excited level of $^2G_{7/2}$ and $^4G_{5/2}$. The $^4G_{5/2} \leftarrow {}^4I_{9/2}$ transition is known as the hypersensitivity transition. [1]

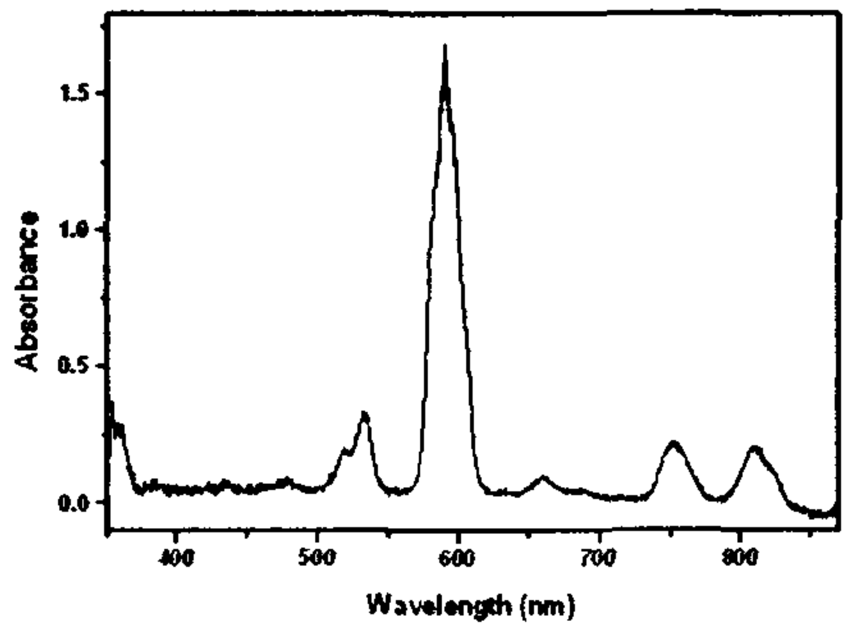

Figure 2. *In-situ* absorption spectra of Nd(III) ion in LiCl-KCl at 450℃.

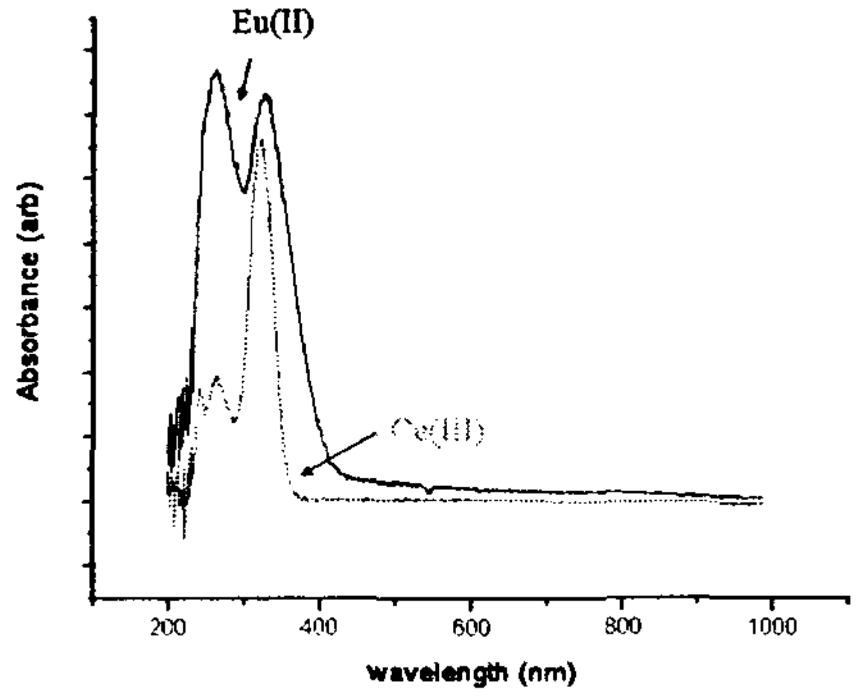

Figure 3. *In-situ* absorption spectra of Eu(II) and Ce(III) ion in LiCl-KCl at 450℃.

The absorption spectra of europium and cerium ion are shown in Figure 3. The origin of the spectral lines are different from those of Nd(III). It is known as interconfigurational $4f^7$->$4f^6 5d^1$ and $4f^1$->$4f^0 5d^1$ (f-d) transitions for Eu(II) and Ce(III), respectively.[2] It is not surprising that the absorption line at 263nm and 328 nm are from divalent-europium ion. This means that tri-valent $EuCl_3$ is converted spontaneously into divalent-europium ion. This confirms the results of our previous EPR study.[3] The strong absorption band at 320 nm in Figure 3 is from f-d transition in Ce(III). In general f-d transitions lie in the UV and more higher energy (vacuum UV) regions. It is expected that the f-d transition lines of the heavier trivalent lanthanide ion will appear at more higher vacuum UV range, making it difficult to measure.

3. Conclusions

In Eu(II) and Ce(III) ions, f-d transition lines were in-situ measured at high temperature molten salt medium. Trivalent europium ion is easily reduced to divalent ion.

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