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Studies on the chemistry of 4f-block elements in high temperature ionic melt

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1. Introduction

Recently, molten alkaline chloride based melts are considered as a promising reaction media for future nuclear programs and more specifically for spent fuel processing.[1,2] For this, it is necessary to understand the chemical nature of the actinides and lanthanides in high-temperature melt. UV-VIS spectroscopy provides essential information on the behavior of f-block elements in LiCl-KCl melt system. 4f-block elements affect significantly to the pyrochemical processing of spent fuel in high temperature LiCl based ionic melts. Therefore, we report the chemistry of lanthanide elements in LiCl based molten salt media.

2. Experimental

We have studied the chemical behavior of various 4f-block elements with specific focus on Nd and Eu in LiCl-KCl eutectic mixture medium. The LiCl-KCl eutectic (41.5 mole% KCl) mixture (melting point 634 K) was prepared from LiCl (Aldrich) and KCl (Aldrich). Dried salts were mixed and melted under purified Ar atmosphere. $EuCl_3$ and $NdCl_3$ were obtained from Alfa Aesar Co. Ltd. (99.99% purity). Li_2O were purchased from Aldrich Co. Ltd. All the chemicals were used without further purification. All the experiment and sample preparations were carried out in an Ar-atmosphere glove box in which the oxygen content and moisture levels were maintained below 3ppm. The oxygen and H_2O level was maintained to be less than 2 ppm. A home built UV-VIS spectrophotometer system was used to measure the electronic spectra in high temperature and inert conditions. The light beam passes through an optical fiber into the sample chamber. Suitable quartz lens and iris were used to collimate the beam path and adjust the intensity. (See Figure 1) An Electron paramagnetic resonance (EPR) and luminescence spectroscopic method provides additional information on the exact nature of lanthanide elements in specific conditions.

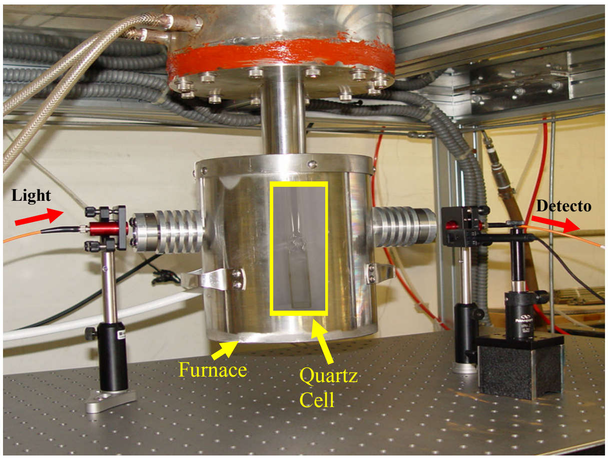

Figure1. Glove box/ Furnace / Spectrophotometer interface for measuring electronic spectra in high temperature molten salt media.

3. Results and Discussion

Lanthanide oxides are insoluble in LiCl-KCl eutectic melt except for the case of europium oxide with appreciable solubility in the same condition.[3] By using the hardware system described in an earlier section, we were able to collect suitable spectroscopic results.[4] The possible reaction of U(III) with lanthanide oxides are of great concern for the electrorefining purification process of metallized uranium. We obtained electronic spectra of U(III), Nd(III) and other lanthanide elements. The reaction of U(III) with lanthanide oxides in LiCl-KCl eutectic melt was studied by on-line monitoring the electronic spectra. Trivalent uranium reacted with lanthanide oxides, which are insoluble, forming insoluble uranium phase and free Ln(III) ions. This poses an important implication for the electrorefining, electrowinning process of spent nuclear fuel. EPR and Luminescence spectra provide additional evidence on the different redox behavior in LiCl-KCl eutectic melt. In the case of europium, the redox behavior is differently with the choice of ion sources. When oxide form is used, europium exist predominantly as divalent Eu(II). However, $EuCl_3$ was used as, europium ion exists as mixed valence state Eu(II)/Eu(II).

Figure 2 shows the luminescence spactra of europium ions

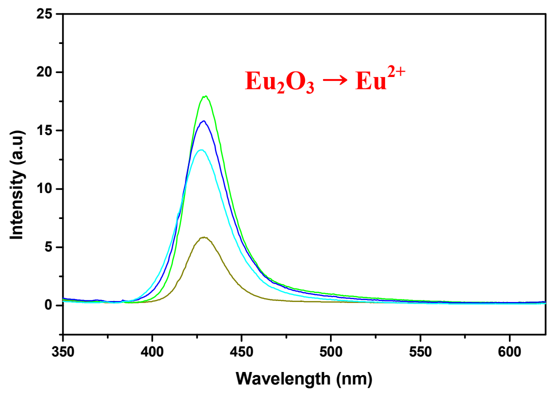

Figure 2a Luminescence spactra of europium ions when oxide form was used as ion source.

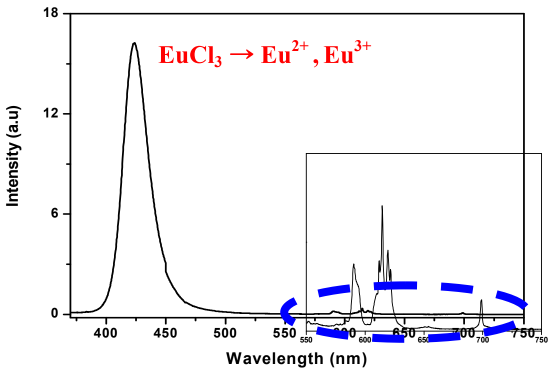

Figure 2b Luminescence spactra of europium ions when oxide form was used as ion source.

The possible reaction of dissolved lanthanide ions with dissolved oxide ion is also of concern in the electrorefining process. Lanthanide ions reacted with oxide ion to form insoluble corresponding oxides. Those chemical reactions were in-situ monitored by applying UV-VIS spectroscopic method described above.

4. Conclusions

UV-VIS spectroscopy combined with fiber optics technology provided an efficient tool for the on-line quantification and speciation of f-block elements in molten salt media.

EPR and Luminescence Spectroscopic tools are sensitive and effective tool for characterizing certain lanthanide ions(f-block elements) in molten salt media. By appying these spectroscopic tools combined with conventional measurement method, the dissolution behavior and chemical reactions of lanthanide elements was clearly understood. This information may have significant implications for the refinement of pyroprocessing technology of spent nuclear fuel in molten salt media.

Acknowledgement

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