

Chemical Behavior of Europium Ion in a LiCl-KCl Eutectic Melt

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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 pose a potential problem for related pyrochemical processes. [1] Therefore, it is necessary to understand the chemical behavior of the actinides and lanthanides in high-temperature melt. In high temperature molten salt, europium oxide exhibited abnormal behavior in solubility and redox chemistry. The solubility of europium oxide was measured to be ~3 orders of magnitude higher than those of other lanthanide oxides. It is necessary to get further insight on the chemical behavior of europium ion in those conditions. [2]

Here, we report some basic chemical redox properties of europium ion and its reactivity with oxide ion in a LiCl-KCl eutectic melt at 450 ° C.

2. Experimental

All the experiments were carried out in an Ar atmosphere glove box to avoid exposure to oxygen and water. 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. The oxygen and H₂O level was maintained to be less than 2 ppm. Eu₂O₃, EuCl₃ was obtained from Alfa Aesar Co. Ltd. (99.99% purity).

A Bruker EMX spectrometer operating at X-band frequency was used for recording EPR spectra.

3. Results

Spontaneous reduction of Eu(III) to Eu(II):

Most lanthanide ions exist as trivalent oxidation states. However, we identified the stable divalent europium dissolved in LiCl-KCl molten salt by applying electron paramagnetic resonance (EPR) and luminescence spectroscopic methods. [2]

In high temperature and inert molten salt media, europium oxide (Eu₂O₃) dissolves appreciably and europium ion exists as divalent state.[2] It means spontaneous self-reduction to divalent state. It is known that among the 14 lanthanide elements, Eu²⁺, Yb⁺² and Sm⁺² are accessible in divalent form in solution. Eu(II) is easily accessible lanthanide among three elements. This special redox property of europium ion may be

attributable to its electronic configuration of 4f electrons. [3]

The redox behavior appeared differently with the choice of europium ion sources. When europium oxide form is used, europium ion exists predominantly as divalent Eu(II). [2] However, when EuCl₃ was used as a starting material, europium ion existed as mixed valence state Eu(II)/Eu(III). The ratio may depend on the chemical conditions and can be determined by quantitative analysis of EPR measurement and total Eu ion measurement by ICP-AEC method. [4]

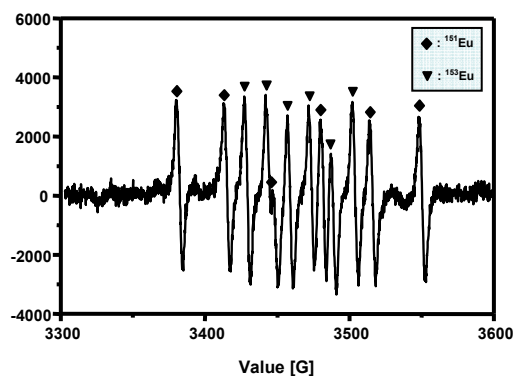
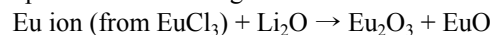


Figure 1. EPR spectrum originating from divalent europium oxide (EuO) formed by reacting Eu(III)/Eu(II) with Li₂O.

Reaction with oxide ion:

Europium ion reacts with oxide ion, O²⁻, to form europium oxide. When EuCl₃ was used as a starting material, europium ions exist both as Eu(III) and Eu(II) in LiCl-KCl at 450 ° C. When Li₂O is added to this, insoluble europium oxide product (denoted as product1) is formed. Figure 1 shows the EPR spectrum of product1. It exhibits the characteristic lines of Eu(II) species. The spectral lines are from divalent EuO. The trivalent Eu₂O₃ form is EPR silent. Figure 2 represents the XRD pattern of product1 showing the diffraction patterns from both Eu₂O₃ and EuO.

From all of these results, the reaction may be expressed as following scheme:



One of the notable features in Figure 1 is its clearly resolved hyperfine absorption lines at room temperature. It means that the EuO product is discretely formed and

its size is much smaller than sub-nano level. Otherwise, the dipolar line broadening effect originating from the neighboring Eu(II)-Eu(II) inter spin interaction would blurred out the resolved hyperfine lines.

By applying this reaction, it will be possible to produce sub-nano EuO crystal.

The specific spectroscopic and redox property of divalent Eu(II) may be attributable to the related properties basically originating from its electron configuration $4f^7$. [3]

(3) P.Dorenbos, "Energy for the first $4f^7-4f^65d$ transition of Eu^{2+} in inorganic compounds", J.Luminescence 104, 239 (2003)

(4) Y. J. Park, T. J. Kim, Y. H. Cho, Y. J. Jung, H. J. Im, K. Song, K. Y. Jee, "Application of an Electron Paramagnetic Resonance Technique to Quantitative Measurements of Eu(II) in a Molten Salt", Proceedings of the Korean Nuclear Society Autumn Meeting, PyeongChang, Korea, October 25-26 (2007)

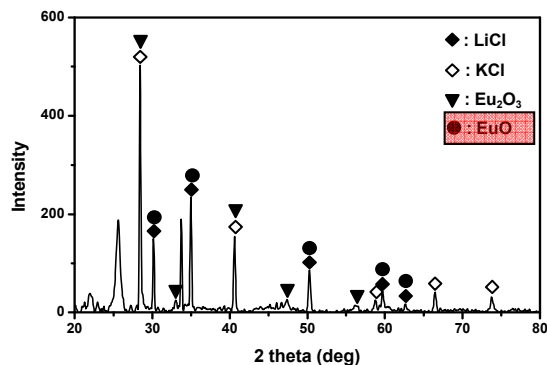
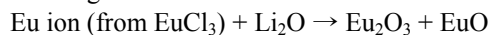


Figure 2. X-ray diffraction pattern for the reaction product (Eu_2O_3 , EuO)

4. Conclusions

Among 14 lanthanide elements Eu(II) is most easily accessible divalent lanthanide in high temperature molten salt media. The redox behavior of europium appeared differently with the choice of europium ion sources. Europium ion reacts with oxide ion, O^{2-} , to form europium oxide. When EuCl_3 was used as a starting material, both mixed valence oxide is formed by following scheme:



REFERENCES

- (1) T. Usami, M. Kurata, T. Inoue, H.E. Sims, S.A. Beetham., J.A. Jenkins, J. Nuclear Materials 300(2002) 15
- (2) T. J. Kim, Y. H. Cho, I. K. Choi, J. K. Kang, K. Y. Jee, "EPR and luminescence studies of Eu(II) magnetically diluted in LiCl-KCl salt", J. Luminescence. 127, 731-734 (2007)