

Observation of interconfigurational $f-d$ electronic transitions of lanthanide and actinide ions in a LiCl-KCl melt at 450

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1. Introduction

Molten salt based electrochemical processes, so called pyroprocessing, have been proposed as a new option for the advanced spent nuclear fuel cycle [1]. One of the important steps in the pyroprocessing of spent nuclear fuel is electrorefining in molten LiCl based media. During the course of these electrochemical processes, information on the chemical behavior of some lanthanide and actinide elements is of great concern. The knowledge on the electronic states of those ions in molten salt media is essential for understanding their optical, electrochemical properties. An electronic absorption spectroscopic method may be eligible tool for this purpose. However, few studies have been reported yet on the spectrochemical properties of lanthanide and actinide ions in anaerobic high temperature molten salt media.

The present study is focused on the development of spectroscopic method for elucidating the chemical nature of f -electron bearing lanthanide and actinide ions in an effort to obtain a better understanding of their chemical behavior in LiCl-KCl eutectic melt in the context of the pyrochemical processing of spent nuclear fuel.

2. Experimental

All the experiments were carried out in a glove box system. An inert atmosphere was maintained by a purging with purified Ar gas. The LiCl-KCl eutectic (41.5 mole% KCl) mixture (melting point 634 K) was prepared from LiCl (Aldrich) and KCl (Aldrich). The oxygen and H₂O level was maintained to be less than 1 ppm. Spectrometric components were interfaced with the glove box-furnace system. A rectangular quartz cell attached to a long quartz tube was placed at the center of the electric furnace. A light beam (Ocean Optics Inc) was guided into the sample chamber by using an optical quartz fiber. Suitable quartz lens and iris were used to collimate the beam path and adjust the intensity. The experimental apparatus is schematically shown in Figure 1. UV-VIS spectra of the ions were obtained by dissolving lanthanide and actinide trichloride reagents in a LiCl-KCl containing quartz cell at 450

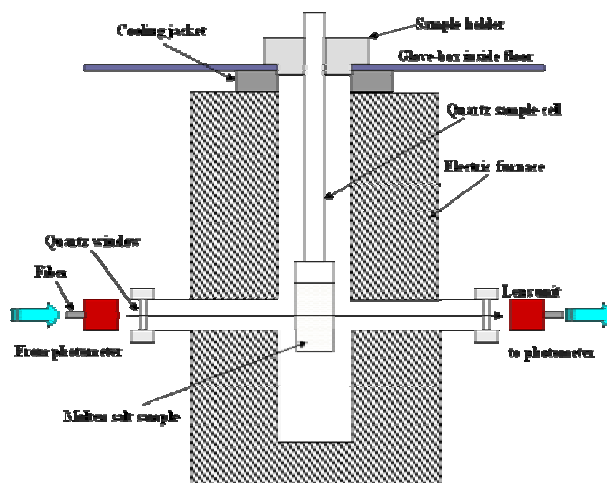


Figure 1. Schematic diagram of reaction system interfaced with spectroscopic measurement unit

3. Results

Within the vacuum UV (VUV) to near infrared energy range, the energy absorption in f -electron bearing ions arises mainly from two types of electronic transitions[2-3].

(1) Intra-configurational transitions: Intra configurational transitions are called $f-f$ transitions and are predominantly electric dipole in nature. They are forbidden to first order by the parity conservation rule and appear on the spectra rather weak and narrow.

(2) Inter-configurational transitions: For ions with f^q ground configuration, the inter-configuration transitions promote one f -electron into unoccupied orbitals of higher-lying configurations. In the energy range considered in UV-VIS spectroscopy, the transitions generally occur between the nf^q and $nf^{q-1}(n+1)d$ configurations of opposite parity ($n=4$ for lanthanides, 5 for actinides). They are called $f-d$ transitions and are orbitally allowed. Consequently, they are much more intense than $f-f$ transitions. These electronic transitions give rise to strong and broad bands.

In general, for trivalent lanthanide ions the quantum-mechanically allowed $4f-5d$ transitions occur in VUV region, making them experimentally less accessible. However, for some divalent lanthanide ions the $4f-5d$ transitions occur at much longer normal UV wavelength ranges. The Eu(II), Sm(II), Yb(II) and the Ce(III) ion

exhibited their characteristic $4f-5d$ transition lines in 200 – 350 nm ranges[4]. Because the $4f-5d$ transition is allowed one, its intensity is stronger than any other parity-forbidden transitions. ($\sim 10^4$ times stronger) Therefore, $4f-4f$ transition lines are almost negligible.

Among the 14 trivalent lanthanide ions, the Ce(III) was the only one which has $4f-5d$ transitions observable in normal UV-VIS spectrometer due to lowest $4f-5d$ energy gap. For europium, samarium, ytterbium the divalent state was stable and some portions of the trivalent species were reduced to divalent state spontaneously.

Unlike the lanthanide ions, for actinide ions the $5f-6d$ transitions occur in UV-VIS ranges. Especially, the U(III) the $5f-6d$ transition lines appeared in as low as 400-600 nm range[5]. Neptunium(III) ion also showed $5f-6d$ transitions at ~ 300 nm region. The electronic transition energy of $5f-6d$ levels was lower than that of $4f-5d$ levels. Figure 2 schematically shows the f-d electronic energy level constructed from the observed UV-VIS spectra of lanthanide and actinide ions in a LiCl-KCl at 450 °C. The analysis of the f-d transitions provides additional information on the oxidation state and coordination environment of the lanthanide and actinide ions.

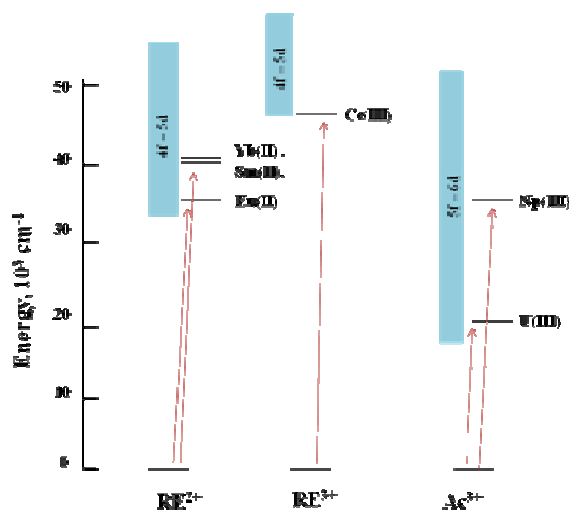


Fig. 2. $f-d$ energy level diagram of lanthanide and actinide ions in a LiCl-KCl melt at 450 °C (constructed from the measured spectra).

4. Conclusions

In this study, we have measured the UV-VIS spectra of lanthanide and actinide (U, Np) ions in a LiCl-KCl eutectic melt at 450 °C. From the spectra, we observed the interconfigurational $4f-5d$ electronic transitions of divalent europium, samarium and ytterbium and trivalent cerium ions on a real time basis. The UV spectra of the Eu, Sm, and Yb ions showed direct evidence of a spontaneous valence reduction to divalent

species. Trivalent actinide ions (U, Np) also showed the $5f-6d$ transition lines at much lower energy than in $4f-5d$ transitions.

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