

5f-6d Electronic Transitions in U(III) Ion in LiCl-KCl Eutectic Melt at 450 °C

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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. In the final step (electro refining and winning), uranium originally in the spent nuclear fuel, exists predominantly as trivalent state, U(III). Therefore, it is necessary to understand the spectro-chemical behavior of the U(III) species in high-temperature molten salt media. UV-VIS spectroscopic method was used to investigate the chemical behavior of U(III) ion in molten salt media. Here, we attempted to measure and analyze the UV-VIS spectra of U(III) in LiCl-KCl eutectic melt at 450 °C. Most of the spectroscopic studies of lanthanide and actinide ions have been focused on the f-f transitions. These transitions are in principle forbidden quantum mechanically and thus show weak intensities. However, f-d transitions are allowed and are sensitive to very low concentration and contains valuable information on the state of ions. 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. Until now, no results have been reported on the f-d transitions in actinide ions in high temperature molten salt media. Here, we report the in-situ measurement of 5f-6d transitions in U(III) ion in LiCl-KCl melt at 450 °C.

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 U(III) were obtained by oxidizing the U metal using CdCl₂ in a LiCl-KCl medium at 450 °C.

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.

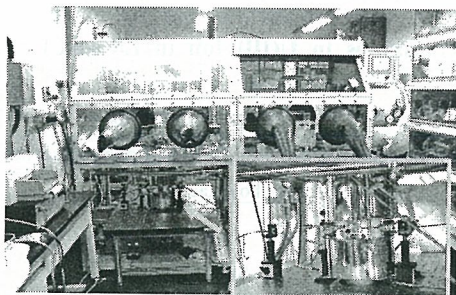


Fig. 1. Glove interfaced with reaction vessel and spectroscopic components.

3. Results

The measured absorption spectra of U(III) are shown in Figure 2. Although the UV-VIS spectra of U(III) was introduced recently by Prof. Yamana's group (Kyoto University), no attempt to interpret the spectra has been made and remains unsolved. The U(III) spectra (Figure 2) matched well with those of Prof. Yamana's group (by private communications). It shows the strong absorption band with peak at 000 and 000 nm region. This peaks are attributable to $5d^3 - 5f^26d^1$ inter-configurational transitions. In the $5f^3$ electronic configurational in a octahedral ligand-field symmetry, it splits the $6d^1$ electronic state into a t_{2g} lower and e_g upper energy state. This accounts for the spectral patterns of U(III) species. The transition energy of $5d^3 - 5f^26d^1$ appeared at much lower position than its isoelectronic $4f3$ species Nd(III) of $4d^3 - 4f^2d^1$ transitions.

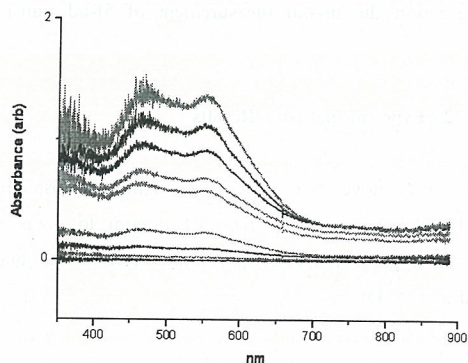


Figure 2. In-situ absorption spectra of U(III) ion with varying concentrations in LiCl-KCl at 450°C.

3. Conclusions

The electronic absorption spectra of U(III) ion originating from $5d^3 - 5f^26d^1$ transitions are measured in LiCl-KCl high temperature melt at 450 °C.

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