Characteristics of *f-d* Transitions of Lanthanide Ions in High Temperature Molten Salt Media and its Measurements

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1. Introduction

The rare earth elements (REEs) contained in a spent fuel may play a significant role in the related pyrochemical processes [1]. Therefore, it is necessary to understand the chemical behavior of the lanthanide elements in a high-temperature molten salt media.

2. Experimental

All the experiments were carried out in a glove box system. 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 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

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

3. Result and Discussions

From the optical spectroscopy point of view, lanthanides and actinide behave differently from the other elements. Indeed, the *f*-orbitals (l=3) which are under completion across the series and contain the unpaired optically active electrons are protected by the most outer *s* and *p* shells and therefore, can be considered as belonging to the core shells.

Within the vacuum UV (VUV) to near-IR energy range, the energy absorption in *f*-compounds arises mainly from two types of electronic transitions.

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 but this selection rule is partly relaxed by the admixture of opposite parity configuration states into f^{q} state functions. The mixing is due to the perturbing crystal field (CF) potential. The, these transitions are called forced electric dipole transitions and they appear on the spectra rather weak and narrow. Allowed magnetic dipole transitions are in general one order of magnitude weaker in intensity.

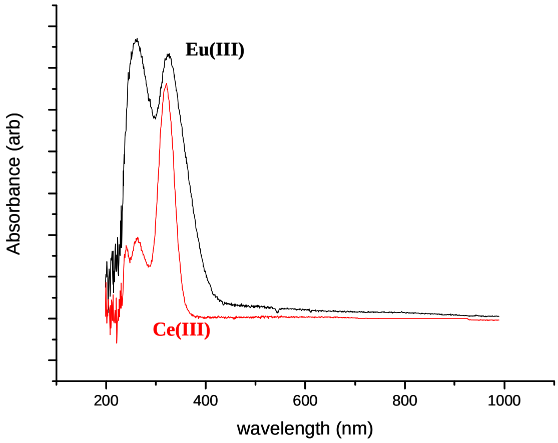

Fig. 2. Absorption Spectra of Eu(II) and Ce(III) in LiCl-LCl at 450 ℃

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 optical spectroscopy, the transitions generally occur between the nf^{q} and $nf^{q-1}d$ configurations of opposite parity. 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 broad bands mainly vibronic in nature. Figure 2 shows the absorption spectra of Eu(II) and Ce(III).

The Eu^{2+} ion produces two broad optical absorption band due to transitions from the $4f^{7}$ (^{8}S) ground state of Eu^{2+} to states in the $4f^{6}5d$ configuration. [3]

The energy of the *f-d* transition of Ce^{3+} is generally the smallest in Ln^{3+}-series. Figure 3 show the f-d transition line arising from divalent samarium ion.

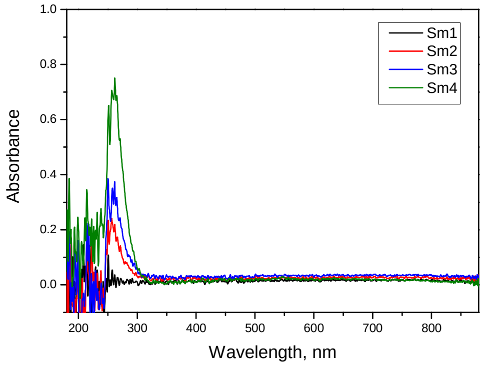

Fig. 3. Absorption spectrum for samarium in various concentrations

Much less known about is the inter-configurational *4f-5d* transitions, especially in high temperature molten salt media. The lack of research on *f-d* transitions is partly caused by the fact that the transitions lie generally in the UV and vacuum UV (VUV) regions, making them experimentally difficult to achieve. Also, successful measurement of UV-VIS spectra in an in-situ manner implies that the absorption spectroscopic method may be applied to monitor the relevant pyrochemical processes by selecting suitable key ions and spectroscopic properties.

4. Conclusions

Electronic absorption spectra arising from *f-d* transitions from Eu(II), Sm(II) and Ce(III) were recorded in UV region in an in-situ manner in LiCl-KCl melt at 450℃.

Acknowledgements

This study has been accomplished under the fund of the Mid- and Long-Term Nuclear Research and Development Program by the Korean Ministry of Education, Science and Technology..

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