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Spectroscopic Approach for Studying the Lanthanide Ions in Molten Salt Media: UV-VIS, EPR and Luminescence Study

Y.H.Cho, T.J. Kim, I.K. Choi, K.Y. Jee
Korea Atomic Energy Research Institute, Yuseong P.O Box 105, Daejeon, Rep. of Korea

1. Introduction

Recently, molten salt based electrochemical processes have been proposed as a promising method for future nuclear programs and more specifically for spent fuel processing [1-2]. For this, it is interesting to understand the chemical nature of the actinides and lanthanides in the molten salt at high temperature. Several spectroscopic methods provide an effective way for studying the electronic nature of these f-block elements, enabling quantification and speciation of the corresponding elements. UV-VIS, Electron paramagnetic resonance (EPR) and luminescence spectroscopic methods have been applied to elucidate the nature of the dissolved lanthanide ions in molten salt media.

2. Methods and Results

Home-built UV-VIS spectrometer combined with optical fiber technology was used to measure the lanthanide behavior in LiCl-KCl melt at 723 K. A Bruker EMX spectrometer operating at X-band frequency was used for recording EPR spectra. An Edinburgh FS920 fluorometer with the excitation sources from a 450 W Xe-lamp and Hamamatsu R955 PMT was used for recording luminescence spectra.

2.1 UV-VIS spectra

Figure 1 presents the Nd(III) species (wavelength~ 700 – 900 nm region). This spectra were obtained by *in-situ* monitoring of the reaction of U(III) with Nd_2O_3. It shows the changes in U(III) and Nd(III) simultaneously.

The intensity of U(III) peak decreases as the reaction proceeded, and consequently the intensity of Nd(III) peak increased. In general, molar extinction coefficient of lanthanides are much lower than U(III). The Nd(III) spectra showed the same features as reported in recent journal.[3-5] The characteristic peak patterns of Nd(III), which are attributed to the $^4G_{5/2}$, $^2G_{7/2} \leftarrow {}^4I_{9/2}$ transitions, are clearly seen.

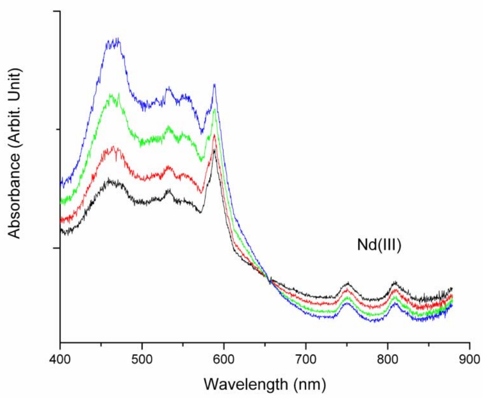

Figure 1. On-line monitoring of theUV-VIS spectra for the reaction of U(III) with Nd_2O_3 in molten salt.

2.2 EPR spectra

Figure 2 shows the EPR spectrum of europium dissolved in LiCl-KCl matrix at room temperature. The spectrum exhibits a well-resolved hyperfine structure centered at g~ 1.989. It looks like having 12 absorption lines. However, the spectrum actually consisted of two sets of six EPR lines attributable to two magnetically non-equivalent pair of Eu^{2+} ions. $^{151,153}Eu$ nucleus has different magnetic property, i.e. g_n, causing different hyperfine splitting[6].

From an analysis of the observed EPR spectrum, the hyperfine splitting constant of ^{151}Eu, A(^{151}Eu), was evaluated to be ~33.4 gauss and ^{153}Eu, A(^{153}Eu), to be ~ 14.8 gauss. Bruker WIN-EPR and Simfonia programs were used for data processing and analyzing the EPR results. One of the notable features of EPR spectrum of Eu(II) is its clearly resolved absorption peaks at room temperature. It means that dissolved paramagnetic Eu(II) ions are uniformly distributed and located into the LiCl-KCl lattice sites throughout the molten salt matrix.

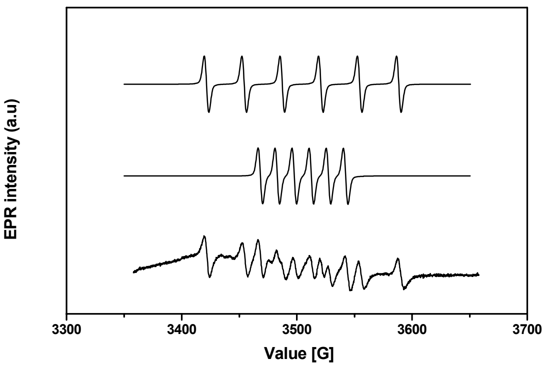

Figure 2. . EPR spectra of Eu^{2+} in LiCl-KCl matrix at room temperature

2.3 Luminescence Spectra

The spectrum exhibits a strong band centered at 430 nm. This broad and intense band is attributed to the transition from $4f^65d^1$ lowest excited state to $^8S_{7/2}$ ground state[6]. As this luminescence of Eu(II) is very intense due to the partially-allowed transitions, it can be used as an indicator for the existence of Eu(II) ions. The characteristic feature of Eu(III) emission spectra is sharp lines ranging from 520 to 720 nm, which are associated with transitions from the excited $^5D_1$ and $^5D_0$ levels to ^7F_J levels[7].

3. Conclusion

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. The EPR and luminescence studies provided detailed information regarding the nature of some lanthanide ions in molten salt.

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