

## Application of an Electron Paramagnetic Resonance Technique to Quantitative Measurements of Eu(II) in a Molten Salt

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### 1. Introduction

Application of a pyrochemical process is an active option for reprocessing spent nuclear fuels. In this pyrochemical process, molten salt based electrochemical processes have been proposed as a promising method in which actinides are separated and recycled from lanthanides in molten chlorides.[1,2] Although the oxides of actinides and lanthanides are sparingly soluble in molten salts, the solubility of the europium oxides showed several orders of a magnitude higher than that of the other lanthanide oxides in LiCl-KCl eutectic melts at 723 K, in our previous work.[3] Some portion of Eu(III) ions were found to be reduced to Eu(II) in LiCl-KCl eutectic melts at 723 K. However, the detailed information such as the extent of an europium reduction or the mechanism is not known yet. Knowing the redox behavior of lanthanide ions in molten chlorides gives important information to enhance the separation efficiency in the electrorefining and electrowinning processes.

In this work, electron paramagnetic resonance(EPR) technique was applied to the quantitative and non-destructive analysis of Eu(II) and Eu(III) in LiCl-KCl eutectic melts. The ICP-AES technique was additionally adopted to analyze the total concentration of europium, since EPR is sensitive only for detecting the Eu(II) ion.

### 2. Experimental

#### 2.1 Sample preparation

The LiCl-KCl eutectic (41.5 mole% KCl) mixture was prepared from lithium chloride (99.9+%, Aldrich) and potassium chloride (99+%, Aldrich). EuCl<sub>2</sub> and EuCl<sub>3</sub> were obtained from Alfa Aesar Co. Ltd. (99.99% purity). All the sample preparation experiments of dried salts were carried out inside the glovebox under a purified Ar atmosphere. The oxygen and H<sub>2</sub>O level in the glovebox was maintained to be less than 2 ppm. The EuCl<sub>2</sub> or EuCl<sub>3</sub> dissolved in molten salt was equilibrated at 723 K for 10 hours with frequent stirring. The solidified molten salt sample at room temperature was then ground into fine powder and transferred into a quartz tube for an EPR measurement. After the EPR measurement, the molten salt sample was diluted with 5

ml of water for the analysis of the total amount of europium by using the ICP-AES.

#### 2.2 Instrumental method of EPR spectrometry

The EPR spectra of the sample in LiCl-KCl matrix were recorded at room temperature on a Bruker EMX spectrometer at X-band frequency with 100 kHz field modulation. A modulation amplitude of 5G, microwave power attenuation of 5 to 15dB and a sweep width of 300 G were used. Typical value of the receiver gain was  $6.32 \times 10^3$ . The modulation amplitude and microwave power settings were chosen such that neither an over-modulation nor saturation occurred. All the instrumental parameters except for the receiver gain were kept the same for all the different experimental series. The samples were taken from molten LiCl-KCl eutectic melt and cooled (hereafter referred as molten salt sample otherwise being stated). EPR measurements were carried out with about 50 mg of each sample inserted into a quartz tube and sealed to prevent it from contacting with air.

### 3. Results and discussion

The Eu(II) is EPR active since it shows a paramagnetic property with an electron configuration  $4f^7$  and  $^8S_{7/2}$  ground levels.[4-6] The typical EPR spectrum of Eu<sup>2+</sup> dissolved in LiCl-KCl matrix at room temperature exhibits a well-resolved hyperfine structure with 12 absorption lines as shown in Fig. 1. These 12 absorption lines are contributed to two magnetically non-equivalent pairs of europium ions, <sup>151</sup>Eu and <sup>153</sup>Eu isotopes, respectively. Eight absorption lines in the middle area were slightly overlapped or close to each other when compared to the first or the last absorption line. Therefore the first absorption line was chosen for the quantitative analysis throughout this experimental work.

Calibration standard samples were prepared by adding known amount of Eu(II) chloride into LiCl-KCl eutectic molten salts at 723 K. The plot of the EPR intensity against the absolute amount of Eu(II) provided a good linearity ( $R^2=0.9968$ ).

As reported in the previous work[3], the fluorescence spectrum of the europium molten salts showed a distinct reduction from Eu(III) to Eu(II) in LiCl-KCl eutectic molten salts at 723 K. The EPR technique established

in this work was applied to determine the extent of a reduction of Eu(III) in LiCl-KCl eutectic melt at 723 K. As a result, approximately 50 percent of Eu(III) was found to be reduced to Eu(II) in a LiCl-KCl eutectic melt. As a conclusion, EPR method can be used to measure rapidly and non-destructively the content of Eu(II) in solid matrices.

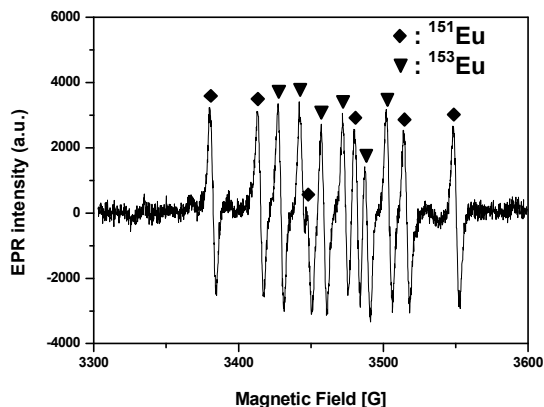


Fig. 1. Typical EPR spectrum of Eu(II) in LiCl-KCl eutectic melts

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