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Peculiar temperature-dependent fluorescence of $EuCl_3$ in LiCl molten salt as a result of phase changes

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ABSTRACT

Fluorescence spectra were obtained *in situ* as a function of temperature (ranging from room temperature to 956 K) from a melt of $EuCl_3$ and LiCl. Three different characteristic Eu^{2+} fluorescence bands, associated with phase changes, were observed. The critical fluorescence dependence on temperature appearing in the blue fluorescence were resulted from the radiative relaxation from $4f^65d^1$ excited state to $4f^7$ ($^8S_{7/2}$) ground state of Eu^{2+}, which was reduced from Eu^{3+} of $EuCl_3$ at high temperature. The fluorescence studies could provide information regarding the phase changes estimated as the stable dihalide, aggregation, and precipitation states of Eu^{2+} in alkali halide not only crystallic but also fluidic melting matrix.

1. Introduction

The understanding and knowledge regarding the melts of rare-earth halides and alkali halides are important in extracting rare metals through electrochemical methods during the electrorefining step of pyrochemical processing, and in solidifying alkali halide based waste produced from the recycle processing of spent fuel [1].

The spectrophotometric properties of alkali halides doped with europium ions (Eu^{2+}, Eu^{3+} or both) have been investigated by several research groups [2,3]. In these papers, electrolytic reduction, radiolysis, and methallothermic reduction are well-known methods that can be used to generate Eu^{2+}, Sm^{2+} and Yb^{2+} ions from the oxidation state +3 of the corresponding rare-earth elements [4]. In the meantime, the reaction of lithium (including sodium partially) and europium has been given particular attention compared to other alkali metals because of the production of eutectics (such as $EuCl_2+LiCl$) from these halides. The formation of the lithium- and europium-ion combined compounds has not been observed [5], the reasons of which are explained below:

When the ratio between the ionic radius of a doping ion (r^{2+}) and the radius of a host (matrix) cation (r^+) is above 1.2 ($r^{2+}/r^+>1.2$), a Suzuki phase of the divalent cation in the alkali halides is not produced, as the formation of a Suzuki phase is suppressed by the large anion displacement. Here, 'a Suzuki phase is a type of composition of $6NX\cdot MX_2$ compounds, or in other words, $M_6N\square X_8$, in which N, M, X, and □ are alkali metals, divalent metals, halides, and cation vacancies' [6]. As an example in which a Suzuki phase is not formed, a $SrCl_2/NaCl$ system, in which the ionic radius of Sr^{2+} is very similar to that of Eu^{2+}, was reported to produce a second-phase precipitate [2]. Coherently, when the ratio of ionic potentials (IP) of alkali metal ion (M^+) to lanthanide ion (Ln^{2+}) [in binary common anion molten-salt systems, and not in small amounts (impurity) of lanthanide ion doping systems],

$$\begin{aligned} IP_{M+}\ /\ IP_{Ln2+} &= (z_{M+}/\ r_{M+})\ /\ (z_{Ln2+}/\ r_{Ln2+}) \\ &= (1\ /\ r_{M+})\ /\ (2\ /\ r_{Ln2+}) \\ &\qquad (z_i:\ \text{charge of i ion and } r_i:\ \text{radius of i ion}) \end{aligned}$$

was in the range of $IP_{M+}/IP_{Ln2+}>0.850$ or $0.627<IP_{M+}/IP_{Ln2+}<0.691$, eutectic mixtures were reported. The following is reported data on a LnX_2–MX binary system producing the following eutectics: $EuCl_2$–LiCl, $IP_{M+}/IP_{Ln2+}=0.939$; $EuCl_2$–NaCl, $IP_{M+}/IP_{Ln2+}=0.681$ [7]. On the one hand, in (pseudo) binary common anion molten-salt systems, several compounds of stoichiometry M_2LnCl_4, MLn_2Cl_5, and $MLnCl_3$ for $LnCl_2$–MCl systems [7], and M_3LnCl_6, M_2LnCl_5, and $M_2Ln_2Cl_7$ for $LnCl_3$–MCl systems have been reported to exist in alkali halides of KCl, RbCl, and CsCl [8,9].

For Eu^{2+} and (or) Eu^{3+} in LiCl molten-salt systems, information is rare, and these compounds have yet to be confirmed through structural measurements. Therefore, we are interested in fluorescence measurements in studying and understanding the intermediate states formed in $EuCl_2$/LiCl (or $EuCl_3$/LiCl) eutectics.

2. Experimental

2.1. Equipment setup

A temperature controlled furnace system was installed underneath a glove box through a furnace sized hole. The furnace had 1-inch quartz

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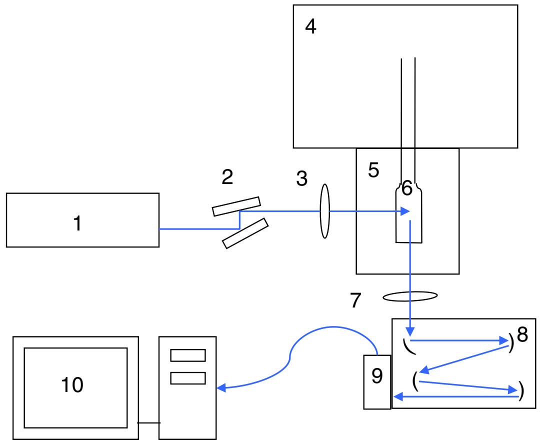

Fig. 1. Block diagram of the experimental set up (1-Nitrogen laser, 2-Mirror, 3-Focusing lens, 4-Glove box, 5-Temperature controlled furnace system, 6-Sample in the manufactured quartz cell, 7-Collection lens, 8-Monochromater, and 9-Photomultiplier tube; SpectroPro 2300i-PMT detector, 10-Computer analysis system).

windows on three sides, perpendicular to each other (front, left, and right sides), and was specially designed for spectroscopic measurements of absorption and fluorescence. The temperature was controlled and monitored using a Yokogawa temperature controller, and a thermocouple was inserted into hole placed at the opposite side of the entrance of fluorescence light in the furnace. The thermocouple touched the surface of a fluorescence cell slightly for a real temperature reading of a sample. A temperature increase was programmed to automatically adjust from room temperature to the target temperature in 20 min. Temperature stability within the melt was maintained at ±1 K during the fluorescence measurements. All of the experiments were performed in the furnace, and chemicals were handled in the glove box where both the oxygen and moisture in the argon atmosphere were maintained at lower than 1 ppm.

2.2. Fluorescence measurements

Fluorescence spectra were measured according to temperature changes on a SpectroPro 2300i — PMT detector (350 nm–1 μm sensitive grating) with the light beam from a N_2 laser (LSI, 337 nm excitation) with a <4 ns pulse width, 75 kW peak power, and 260 μJ pulse energy at 10 Hz. Using an independent mounting and adjustment method, mirrors were adjusted for beam alignment and focusing lens for beam focusing to obtain the optimized signal from the detector. The arrangements of the laser beam, mirror, focusing lens, furnace, collection lens, and detector are shown in Fig. 1. Fluorescence, perpendicular to the laser beam direction, was delivered to the entrance slit of the monochromator through a quartz optical fiber. Ultra dry LiCl (99.995% purity, metal basis, 10 mesh beads, Aldrich) and ultra dry $EuCl_3$ (99.99% purity, Alfa Aesar) were used as received. Samples were prepared through the complete melting of $EuCl_3$ (ca. 0.03688 g) and LiCl (about 5.83057 g) at 953 K, and then cooled down to room temperature. The fluorescence spectra of the prepared melts were recorded according to the temperature changes (from room temperature to 956 K). The melts were located in a specially manufactured quartz cell, in which an original rectangular quartz fluorescence cell was attached to a long neck quartz tube, which was placed at the center of the electric furnace. Details of the manufactured furnace and arrangements of the spectroscopic components were described previously in the figures in [10,11].

3. Results

3.1. Fluorescence tendency of $EuCl_3$ in LiCl molten salt according to temperature changes

It was previously reported in our published paper that the fluorescence of europium ions (both of Eu^{2+} and Eu^{3+}) in LiCl–KCl molten salts constantly decreases according to an increase in temperature, and dramatically decreases at around the melting temperature of LiCl–KCl (630 K). The peak positions of the europium fluorescence were found to be almost independent of the temperature [11]. However, after changing the electrolyte (matrix) from LiCl–KCl to LiCl in this study, the observed Eu^{2+} fluorescence changes (Fig. 2) with increased temperature can be roughly divided into the following three ranges: (i) The peak intensities of the maximum peak position at ca. 409 nm decreased constantly until about 645 K, (ii) then increased to about 804 K with movement of the maximum peak position to ca. 443 nm. (iii) Finally the peak intensities again decreased to 956 K with movement of the maximum peak position to ca. 432.5 nm.

The fluorescence of LiCl molten salt exclusively was carefully checked according to changes in temperature, and very similar spectra

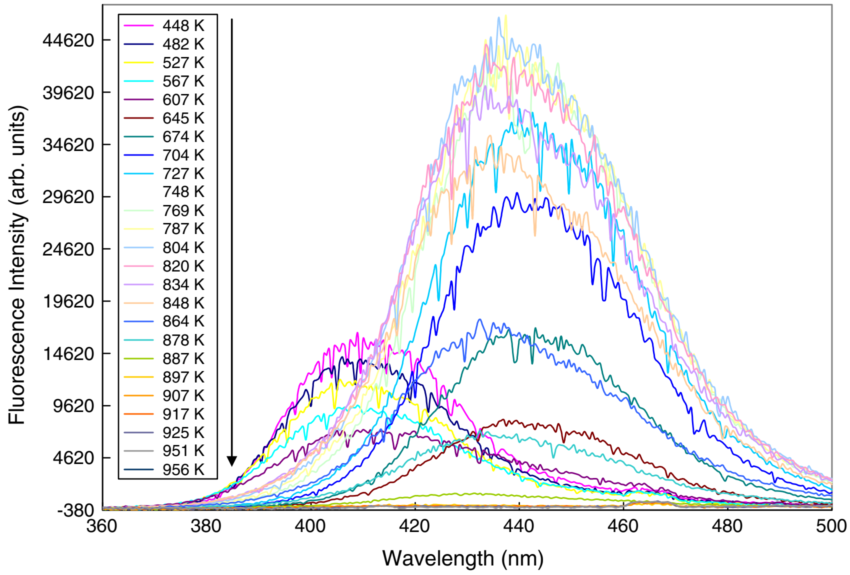

Fig. 2. Fluorescence spectra of $EuCl_3$ in the LiCl molten salt measured from room temperature to 915 K ($\lambda_{exc} = 337$ nm).