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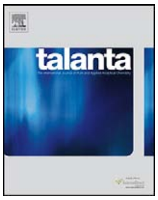

Temperature dependence of fluorescence for $EuCl_3$ in LiCl–KCl eutectic melt

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ABSTRACT

The fluorescence of $EuCl_3$ in LiCl–KCl eutectic melt according to temperature changes was investigated, and the spontaneous partial reduction of Eu^{3+} to Eu^{2+} at high temperature was confirmed by the fluorescence results. The fluorescence decreases when the temperature increases, and this was examined in detail. The studies of fluorescence provided information regarding the chemical and physical behavior of europium ions in the molten salt according to the temperature changes. It is applicable for monitoring species and concentrations and estimating the approximate chemical structure of the ions in molten salts.

1. Introduction

The recent increase in the amount of Nuclear Power Plants requires the development of adequate methods for the increased reliability of nuclear reactors, effectiveness improvement of nuclear fuel consumption, and a corresponding decrease in radioactive waste volumes. Based on these necessities, there have been many efforts to effectively treat the wastes of spent fuel which is composed of U_3O_8, trance uranium oxide, Cs, Sr, Ba, and various lanthanides elements [1], and to re-use the spent fuel as a nuclear fuel. As a result of this, pyrochemical process (which is an electrolytic separation of uranium from irradiated spent nuclear fuel at a high temperature) was considered as an alternative dry processing technique compared to the aqueous processing of plutonium uranium extraction (PUREX; which is a chemical separation of uranium and plutonium by solvent extraction steps involving the dissolution of the fuel elements in concentration nitric acid) in the treatment of the spent nuclear fuel [2]. In pyrochemical processing, reusable products and minimum amounts of waste are generated through high-temperature LiCl or LiCl–KCl molten-salt electrolytes at over 723 K. In the molten-salt electrolytes, several species of lanthanides, which are less reduced during the electrolytic reduction step in the pyrochemical process of spent fuel, are dissolved and affect the production-efficiency of the reusable uranium product. Therefore, it was necessary to understand the chemical and physical behaviors of the lanthanides in the high-temperature molten-salt electrolytes. From this perspective, the research in this paper has concentrated on spectroscopic methods.

In studying the chemical constitution and electronic structure of f-elements in molten-salt media, not only electrochemical [3] but also spectroscopic approaches have been achieved by using methods such as Raman scattering [4], X-ray absorption fine structure (XAFS) [5], electron paramagnetic resonance (EPR) [6] and UV–vis absorption [7]. In a previously published paper [8], the fluorescence of Tb^{3+} and Sm^{3+} in LiCl–KCl molten salt was observed at room temperature. However, *in situ* and on-line measurements of the lanthanide ions in high temperature for a practical application in pyrochemical processing or molten-salt media were not discussed in detail. Moreover, to date, the fluorescence measurements of $EuCl_3$ in LiCl–KCl eutectic melt according to temperature changes have not been reported. Therefore, these results will be discussed.

2. Experimental

A temperature controlled furnace system was installed underneath a glove box and was connected through a furnace-sized hole. The furnace was specially designed for the simultaneous spectroscopic measurements of the absorption and fluorescence as shown in Fig. 1 [8]. All the experiments were performed in the furnace, and chemicals were handled in the glove box where both the oxygen and moisture contents in the argon atmosphere were maintained at lower than 2 ppm.

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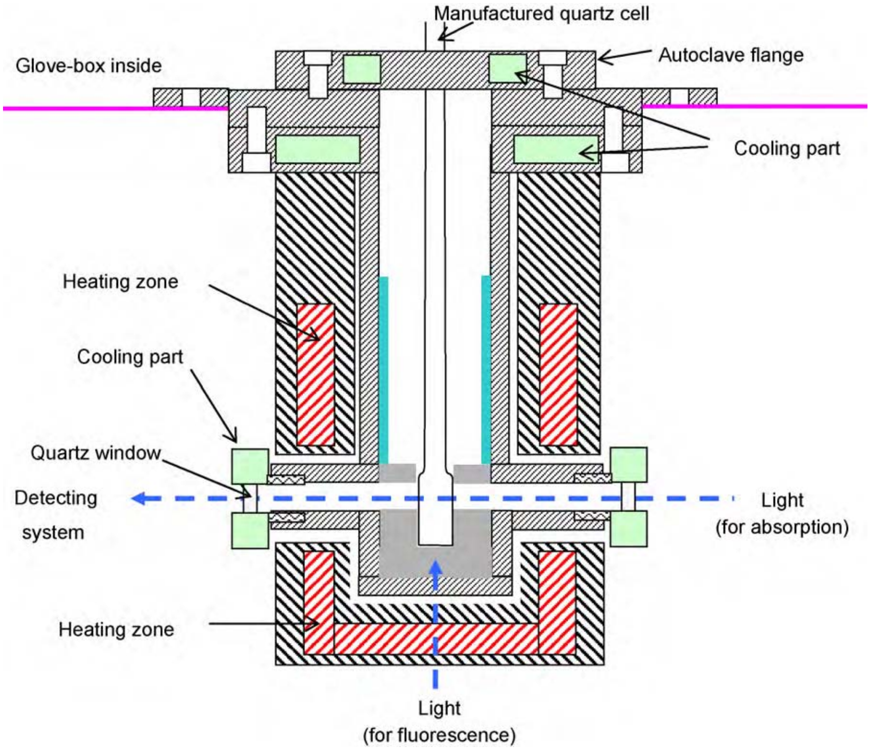

Fig. 1. Schematic diagram of the optical cell and furnace for spectroscopic measurements according to the temperature changes.

The following components of fluorescence measurement were interfaced with the glove box-furnace system. Fluorescence spectra according to temperature changes were measured 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), and the laser beam was guided into the sample in the furnace. An Edinburgh FS920 fluorometer with the excitation sources from a 450 W Xe lamp (Oriel 66021) and alternatively an He–Cd laser (Kimmon, 325 nm excitation) equipped with a Hamamatsu R955 PMT was also used for the measurement of the europium ions' fluorescence at room temperature. The light beams and the fluorescence signals were guided and collected by optical fibers and collection lens. A small hole (only for a thermocouple connection to the Yokogawa temperature controller) was made at the opposite side to the entrance of the excitation light beam, and the thermocouple was slightly touched at the surface of the fluorescence cell for the sample temperature reading. A good linearity of actual reading temperature vs. controller setting temperature was found, and the controller setting temperature of 873 K provided an actual reading temperature of 738 K with almost invariable stability (±1.0 K). The temperature increase was programmed from room temperature to 738 K (controller setting temperature: 873 K) with a 20 min duration.

Anhydrous LiCl–KCl eutectic (beads, 99.99% purity, 44 wt.% LiCl, molar ratio ca. 1.5 to 1, Aldrich) and ultra dry $EuCl_3$ (99.99% purity, Alfa Aesar) were used as received. Fluorescence spectra were recorded on-line according to the temperature changes and were obtained by dissolving 0.035 g of $EuCl_3$ in about 6.112 g of LiCl–KCl eutectic in the specially manufactured quartz cell. An original rectangular quartz fluorescence cell was welded to a long neck quartz tube for the preparation of the manufactured quartz cell, and it was placed at the center of the electric furnace. The melting point of LiCl–KCl eutectic is 630 K, so each europium compound was completely dissolved in the LiCl–KCl eutectic at 738 K first, and then it was cooled down to room temperature before the fluorescence tendency of the europium compound in LiCl–KCl eutectic melt according to the temperature changes was observed.

3. Results and discussion

It has been known that the study of the position, intensity and splitting pattern of the peaks in the fluorescence spectra of certain compounds can provide information about the valence states and the environment of their existing ions [6,9]. These phenomena can also be supported by the energy level diagram of the ions.

Eu^{2+} and Eu^{3+} in chloride eutectic melts exhibited very broad absorption bands, in which their maximums and the tails of the bands were at ca. 325 and 305 nm each and to over 430 nm both [10], so the molten salt composed of $EuCl_3$ in LiCl–KCl eutectic melt was excited with a proper 337 nm N_2 laser for the study of its fluorescence. Fig. 2 shows the observed fluorescence spectrum

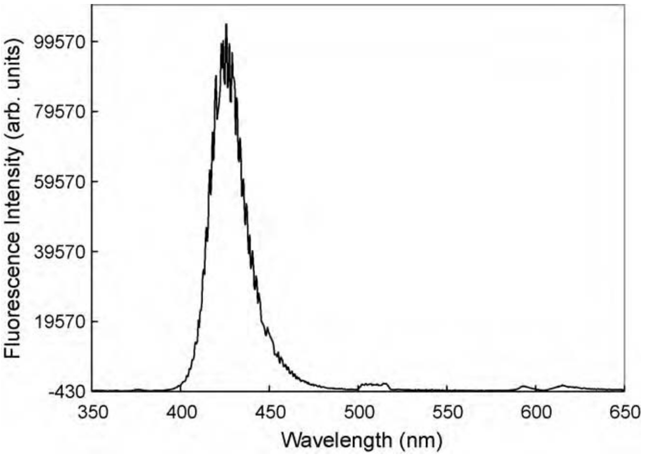

Fig. 2. Fluorescence spectrum of $EuCl_3$ in LiCl–KCl molten salt measured at room temperature over the wavelength region from 350 to 650 nm (λ_{exc} = 337 nm).

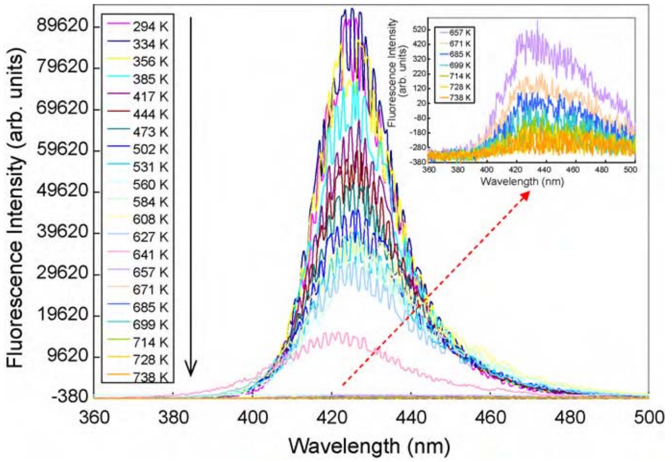

Fig. 3. Fluorescence spectra of $EuCl_3$ in LiCl–KCl molten salt measured in the range of room temperature to 738 K focused on Eu^{2+} fluorescence area (when increase the temperature) ($\lambda_{exc} = 337$ nm).

over the wavelength region from 350 to 650 nm at room temperature, and the fluorescence peak at ca. 425 nm was much higher than those that appeared in the range of 580–650 nm more than 73 times. A strong blue color, which is an evidence of the fluorescence at around 425 nm, was observed through the quartz window of the temperature-controlled furnace when the laser beam was guided to the sample. For a detailed examination of each peak, as shown in Fig. 3, a series of fluorescence spectra during temperature changes were obtained after the measurement was focused on the range of 360–500 nm, where an intensive peak appeared in Fig. 2. The peak intensities generally decreased when the temperature was increased. The fluorescence, especially, dramatically decreased when the sample melted at around 633 K, which is very close to the melting point (630 K) of LiCl–KCl eutectic, and then the intensities of the fluorescence peaks became low and decreased constantly. It was possible to detect the fluorescence peak until 738 K. Where the temperature decreased from 738 K to room temperature, the same tendency was observed. This intense band was attributed to the transition from the $4f^65d^1$ lowest excited state to the $^8S_{7/2}$ ground state of Eu^{2+}, and the unusual high fluorescence compared to other known lanthanide ions' was caused from the parity-allowed transition. Actually, the transition from $^6P_{7/2}$, which is the lowest excited state for a $4f^7$ electron configuration of Eu^{2+}, to $^8S_{7/2}$, is the spin and parity forbidden, and the probability of the f-f transition is known to be low and was not observed in the present work. Due to the strong fluorescence of the transition from the $4f^65d^1$ lowest excited state to the $^8S_{7/2}$ ground state, it was expected that the crystal field induced from around Eu^{2+} would affect the structure [6].

Fig. 4 gives the fluorescence spectra from Eu^{3+} of the molten salt composed of $EuCl_3$ in a LiCl–KCl eutectic melt upon 337 nm excitation, and unlike Eu^{2+}, the splitting pattern of Eu^{3+} fluorescence peaks were expected to provide more information about its symmetry and structural configuration. To the best of our knowledge, the spectra presented in Figs. 3 and 4 are the first observed full fluorescence-changes of europium ions in a high temperature LiCl–KCl eutectic melt according to temperature changes, and the data explain the chemical reduction of Eu^{3+} in eutectic melt at high temperature.

Eu^{3+} has a $4f^6$ configuration with $^7F_0$ as ground state, and the luminescence from Eu^{3+} was very weak due to the Laporte-forbidden transition. However, it produced the characteristic f–f transitions of the Eu^{3+}. The Eu^{3+} fluorescence decreased constantly until about 493 K according to the increasing temperature, and then it was similar from about 503 K until around 633 K. However, the peak shape suddenly changed at about 653 K, and a new peak appeared at around 600 nm, and then peaks changed to an almost base line from about 673 K. Where the temperature decreased, the same tendency was observed. The fluorescence spectra, as seen in Fig. 4, were compared with the one in Fig. 5, which was obtained by our group previously [11] at room temperature upon 325 nm excitation using Cd–He laser. In Fig. 5, the fluorescence peaks were matched with the transitions from the $^5D_0$ level to ^7F_J ($J = 1, 2, 3, 4$) levels. Four clear emission bands, centered at 593 ($^5D_0 \rightarrow {}^7F_1$; doublet), 618 ($^5D_0 \rightarrow {}^7F_2$; doublet of doublet), 653 ($^5D_0 \rightarrow {}^7F_3$; broad weak singlet), and 699 ($^5D_0 \rightarrow {}^7F_4$) nm each, could be attributed to Eu^{3+} in the LiCl–KCl molten salt at room temperature. However, the peak splitting changed to be somewhat broad, occupying the same spectral region according to the temperature increasing as shown in Fig. 4. The peak at 699 nm ($^5D_0 \rightarrow {}^7F_4$) could not be detected with this experiment because a very intensive and broad second order N_2 laser-peak buried the peak. Other peaks expected in the range of 577–581 nm, associated with transitions from the excited $^5D_0$ level to $^7F_0$ ground state were not observed in both cases, explaining that the structure of Eu^{3+} in LiCl–KCl molten salt was not centered [9]. The speculation can also be supported by the result of the $^5D_0 \rightarrow {}^7F_2$ transition, which is very sensitive to the environment. The transition is electric dipole allowed with a low symmetry of the site based on the result of strong fluorescence peak, which is absent if the ion is on an inversion center. On one side, even in low symmetry systems, the $^5D_0 \rightarrow {}^7F_1$ transition is the magnetic dipole allowed, and its radiative transition is relatively insensitive to the environment [12].

Then what is the structure of europium LiCl–KCl molten salt? LiCl and KCl solids each have cubic structures [13], and the structures of $EuCl_3$ and $EuCl_2$ powders were reported as tricapped trigonal prismatic (in detail, $EuCl_3$ has UCl_3 structure, and $EuCl_2$ has $PbCl_2$ structure) which has a nine-coordinate geometry. The large coordination are from bigger europium ionic radii than the transition metals' and the inner f-orbitals, which are shielded from the effects of the surrounding anions. The geometry has been known to be formed from simple polyhedra, which are predicted from electron-pair repulsion models [9]. On the one hand, according to the definition of molten salts by Dr. Cotton et al., 'Molten salts present a kind of extreme of aprotic (does not contain ionizable proton), autoionizing highly polar solvents, and in them, ions predominate over neutral molecules. The alkali metal halides are among the "totally" ionic molten salts' [13]. Moreover it was reported that $2CsCl + LiCl + LnCl_3 \rightarrow Cs_2LiLnCl_6$ were made by fusion, and they possess the six-coordinate elpasolite structure in which the perfectly octahedral $[LnCl_6]^{3-}$ ions occupy sites with cubic symmetry. However, although similar elements and groups were used for the molten salt composed of $EuCl_3$ and LiCl–KCl to the above mentioned one, its structure was not expected to have perfectly octahedral $[EuCl_6]^{3-}$ ions due to the low symmetry analogized from $^5D_0 \rightarrow {}^7F_2$ transition. As a similar example, Dr. T. Fujii et al. [7] suggested that Nd(III) in LiCl–KCl eutectic at the high temperature has a distorted symmetric octahedral coordination in molten elpasolite, based on the comparison of the UV–vis absorption spectra of Nd(III) in LiCl–KCl eutectic and a neodymium compound $Cs_2NaNdCl_6$. The addition of over 60% LiCl made it lose its symmetry to a certain distorted octahedral symmetry [14]. A temperature dependent structure type such as $NaLnCl_4$ (Ln = Eu–Yb, Y) was also reported to have the six-coordinate α-$NiWO_4$ structure at low temperatures and the seven-coordinate $NaGdCl_4$ structure at high temperatures. Eu^{3+} in LiCl–KCl molten salt might be slightly the temperature-dependent structure type too, and the structure turning temperature is expected around the melting point due to the slope of fluorescence intensity changes and a new peak appearance. The exact structure of the europium complex produced from the current molten salt seems complicated, and

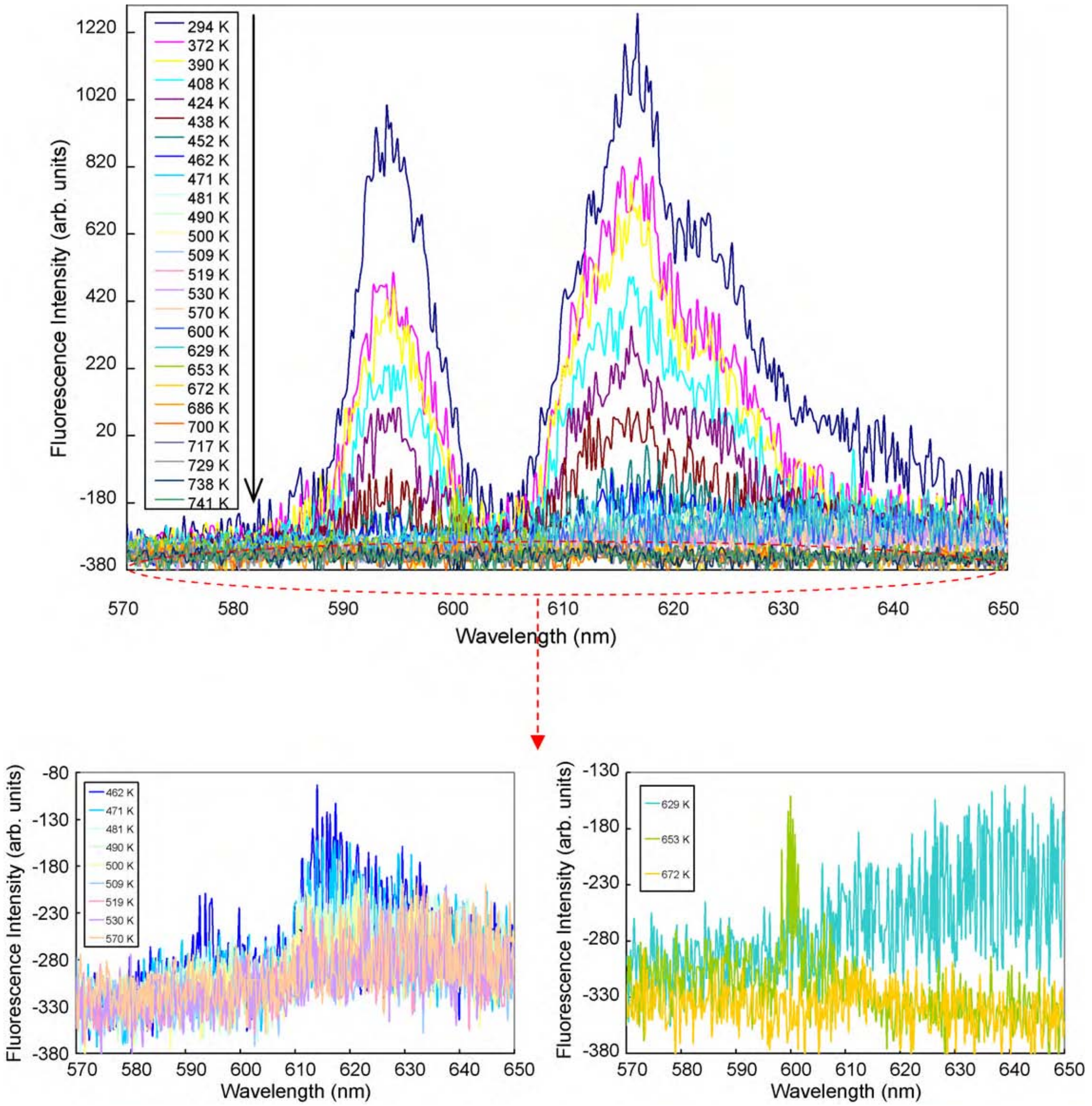

Fig. 4. Fluorescence spectra of $EuCl_3$ in LiCl–KCl molten salt measured in the range of room temperature to 741 K focused on Eu^{3+} fluorescence area (when increase the temperature) ($\lambda_{exc} = 337$ nm).

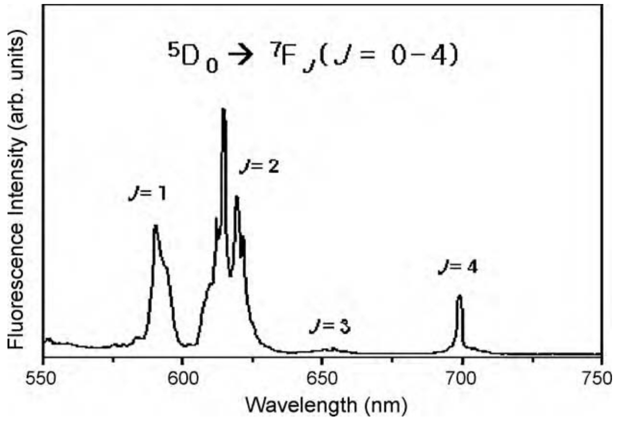

Fig. 5. Fluorescence spectrum of $EuCl_3$ in LiCl–KCl molten salt measured at room temperature using Cd–He laser source ($\lambda_{exc} = 325$ nm) focused on Eu^{3+} fluorescence area (adapted from Ref. [11]).

even the crystal of the complex for the XRD measurement could not obtained.

For the conversion of Eu^{2+} from Eu^{3+} of $EuCl_3$ in eutectic melts, a similar fluorescence spectrum of both ions' existence from $EuCl_3$ in KCl at high temperature has been reported [15]. $EuCl_3$ is more likely to be stable in aqueous solution as Eu^{3+}(aq), and most Ln^{2+} are not stable in the solution but could be stabilized by the use of nonaqueous solvents such as HMPA and THF, and by electrolytic reduction. However, dihalides like $EuCl_2$ are most common for metals with a stable (+2) state [9], and it was also reported in the Merck Index [16] that $EuCl_3$ is reduced to $EuCl_2$ with hydrogen at 873 K.

The fluorescence-trend of the europium changed when the sample was solidified from the melt or vice versa. Fig. 6 shows the photos of $EuCl_3$ in the LiCl–KCl molten salt taken in the range of room temperature to 738 K. The photo was taken through the quartz window of the temperature-controlled furnace, and the melting tendency of molten salts could be observed. The fluorescence of the europium ions was decreased possibly by the quenching (thermal or dynamic) of the f-elements in the LiCl–KCl molten salt at a high temperature. The decrease of fluorescence in the molten salt according to the temperature increase was explained by Dr. Carnall et al. by using the life times of Tb^{3+}

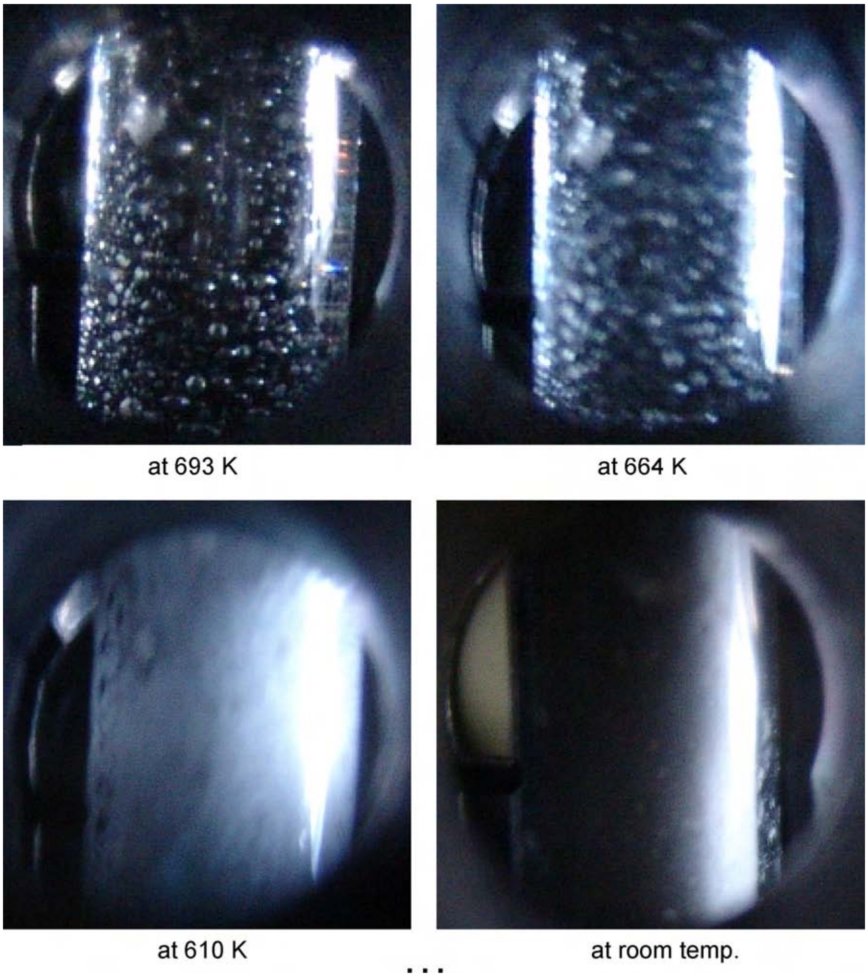

Fig. 6. Photos of $EuCl_3$ in the LiCl–KCl molten salt taken in the range of room temperature to 738 K.

in $LiNO_3$–KNO_3 eutectic [17]. According to their explanation, the decrease in the lifetime of $^5D_0$ at a certain temperature of the molten salts, especially for which no solid was observed to precipitate, was solely due to a nonradiative temperature-dependent mechanism and not a change in the radiative transition rate. The temperature dependence of the lifetime suggested the fluorescence decrease according to the temperature increase and the very steep decreasing speed from fluidic molten salt than from the solid molten salt from the boundary of the melting point of the molten salt [17]. As mentioned earlier in this paper, a similar tendency was observed in the plot of fluorescence intensities vs. temperature as shown in Fig. 7 in the system of the europium ions in LiCl–KCl molten salt. Dr. Carnall et al. could explain energy transfer from the $^5D_0$ to the upper $^5D_1$ state of Eu^{3+} via thermally

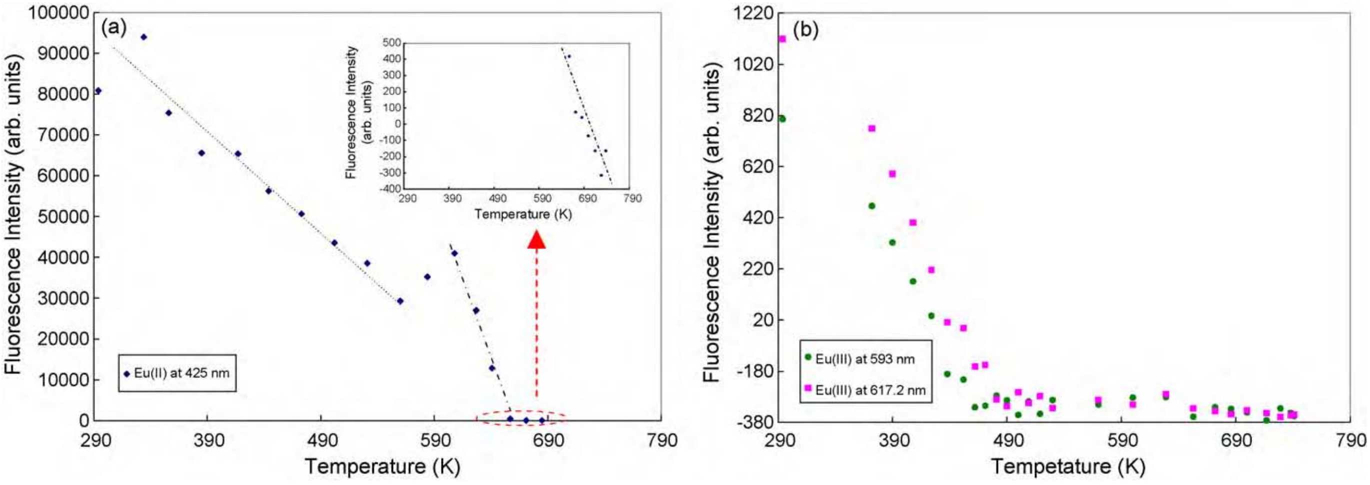

Fig. 7. Plot of fluorescence intensities of (a) Eu^{2+} from Fig. 3 and (b) Eu^{3+} from Fig. 4 in LiCl–KCl molten salt as a function of temperature (λ_{exc} = 337 nm).

induced activation. It caused the depopulation of the $^5D_0$ for fluorescence, and the subsequent decay by nonradiative deexcitation of the $^5D_1$ state was observed by Kropp and Dawson [18]. This can also explain the fluorescence decrease according to the temperature increase observed in the current KCl–LiCl molten-salt experiments.

4. Conclusion

The fluorescence of the europium ions in LiCl–KCl molten salt generally decreased when the temperature increased. Moreover, the fluorescence intensities of the europium ions suddenly changed when the sample melted from the solidified one or vice versa. At the high temperature of the molten-salt media, the reduced fluorescence of the europium ions was considered to possibly be from a high probability of nonradiation transition and other processes, e.g. thermal and dynamic quenching and so on.

With a spectroscopic study in molten salts according to temperature changes: chemical species could be monitored, the approximate chemical structure of lanthanide ions in molten salt estimated, energy levels understood, valence states identified, and *in situ* reaction processes observed. The fluorescence measurement, especially, could be a supplementary tool for better understanding the change of the chemical properties of solutes in the molten salts. As an example, the absorption spectra of Eu^{2+} and Eu^{3+} of $EuCl_3$ in LiCl–KCl eutectic melts could not provide the exact coexistence of these ions in molten salt due to the similar peak shape and absorption area although the transitions are different as f–d transition and f–f transition [10]. The advantages of the conventional fluorescence technique can include high sensitivity, nearly simultaneous non-destructive identification and determination of multiple species, and rapid analysis time. More practically, it would be beneficial to monitor the lanthanide or actinide species and concentrations in the molten salts so that it can be determined at what time the salt should be treated to remove these species during pyrochemical processing.

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