

Fluorescence Resonance Energy Transfer of the Tb(III)-Nd(III) Binary System in Molten LiCl-KCl Eutectic Salt

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1. Introduction

The molten chloride salt is used in the pyrochemical process as an ionic liquid solvent. In the electro-winning process, the lanthanides can be co-extracted in liquid cadmium electrode due to their similar reduction potential of TRU elements. The lanthanides act as a neutron poison in nuclear reactor with large neutron absorption cross section. For that reason, very low amount of lanthanides is required in the recovered U/TRU ingot product from pyrochemical process. In view of that, the investigation of thermodynamic properties and chemical behaviors of lanthanides in molten chloride salt are necessary to estimate the performance efficiency of pyrochemical process. However, there are uncertainties about knowledge and understanding of basic mechanisms in pyrochemical process, such as chemical speciation and redox behaviors due to the lack of *in-situ* monitoring methods for high temperature molten salt. The spectroscopic analysis is one of the probable techniques for *in-situ* qualitative and quantitative analysis. Recently, a few fluorescence spectroscopic measurements on single lanthanide element in molten LiCl-KCl eutectic have been investigated [1-5]. However, lanthanide and actinide elements co-exist in spent nuclear fuel and there have no adequate experimental evidences to prove chemical structure of a mixture of lanthanides in high temperature molten salts.

In this study, the chemical behaviors of Tb(III)-Nd(III) binary system in high temperature molten LiCl-KCl eutectic have been characterized using fluorescence resonance energy transfer (FRET). The fluorescence energy transfer mechanism of the Tb(III)-Nd(III) binary system were investigated in molten LiCl-KCl eutectic, and the Förster distance between the Tb(III) and Nd(III) ions were calculated. Moreover, the structural change of LnCl_6^{3-} and the complexation between metal ions in the binary system were examined under the experimental conditions.

2. Experimental

The molten salt experiments were performed in a glove box under high-purity argon gas atmosphere (99.9999 % Ar, H_2O and $\text{O}_2 < 1\text{ppm}$) to avoid unintentional oxidation and hydration of elements. The polarographic-grade anhydrous LiCl-KCl eutectic salt (Sigma-Aldrich, 99.99 % purity, 44 wt.% LiCl) was

melted in the furnace, and the concentration of Ln(III) (Ln = Nd, Tb) in the anhydrous chloride form (Sigma-Aldrich, 99.99 %, powder) varied by dissolution in LiCl-KCl eutectic salt. The concentration of Ln(III) was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES). For time-resolved laser fluorescence spectroscopy (TRLFS), the wavelength-tunable OPO (optical parametric oscillator) laser system (OPOTEK Inc., Vibrant 355) was used to analyze the energy transfer process of the binary system in molten LiCl-KCl eutectic with a selective excitation wavelength.

3. Results

3.1 Energy transfer mechanism

The resonance energy transfer is explained as the transfer of an excited donor to an acceptor. This process occurs when the sufficient spectral overlap between the emission of donor and the absorption of acceptor exist. As a result, the excited state lifetime of donor decreases, while the fluorescence of the acceptor is sensitized [6].

The resonance energy transfer is classified as collisional quenching following the Stern-Volmer equation (Eq. 1) [7,8].

$$\frac{F_0}{F} = 1 + k_q \tau_0 [Q] = 1 + K_D = \frac{\tau_0}{\tau} \quad (1)$$

where F_0 (τ_0) and F (τ) are fluorescence intensities (fluorescence lifetimes) in the absence and presence of quencher, respectively. k_q is the biomolecular quenching rate constant, Q is the concentration of quencher, and $K_D = k_q \tau_0$ is the Stern-Volmer quenching constant.

The rate of energy transfer is given by [6-11]:

$$k_T(r) = \frac{Q_D \kappa^2}{\tau_D r^6} \left(\frac{9000(\ln 10)}{128\pi^5 N n^4} \right) \int_0^\infty F_D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda \quad (2)$$

where Q_D is the quantum yield of the donor in the absence of the acceptor, τ_D is the fluorescence lifetime in the absence of the acceptor, r is the distance between donor ions and acceptor ions, n is the refractive index, N is the Avogadro's number, $F_D(\lambda)$ is the corrected fluorescence intensity of the donor in the wavelength range of overlap region which is normalized such that

$\int_0^\infty F_D(\lambda) d\lambda = 1$, and ε_A is the acceptor absorption spectrum expressed in molar absorptivity ($M^{-1}cm^{-1}$). κ^2 is an orientation factor in space of the transition dipoles of the donor and the acceptor, and is usually assumed to be equal to $2/3$, which is appropriate for dynamic random averaging of the donor and the acceptor [8]. The overlap integral, $J(\lambda)$, describes the extent of spectral overlap between donor emission and acceptor absorption defined as:

$$J(\lambda) = \int_0^\infty F_D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda \quad (3)$$

The Förster distance R_0 is the characteristic distance at which the FRET efficiency is 50% when the distance between the donor and the acceptor is equal to R_0 .

$$R_0^6 = \frac{9000(\ln 10)\kappa^2 Q_D}{128\pi^5 N n^4} \int_0^\infty F_D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda \quad (4)$$

Eq. 2 is rearranged to:

$$k_T(r) = \frac{1}{\tau_D} \left(\frac{R_0}{r} \right)^6 \quad (5)$$

The energy transfer efficiency, E , is defined as the fraction of excited photons of the donor undergoing energy transfer to the acceptor, and it is expressed in terms of the rate of energy transfer:

$$E = \frac{k_T(r)}{k_T(r) + \tau_D^{-1}} \quad (6)$$

Eq. 6 is rearranged by recalling Eq. 5.

$$E = \frac{R_0^6}{R_0^6 + r^6} = 1 - \frac{F_{D,A}}{F_D} = 1 - \frac{\tau_{D,A}}{\tau_D} \quad (7)$$

where $F_{D,A}$ and $\tau_{D,A}$ are the fluorescence intensity and the fluorescence lifetime in the presence of acceptor ions, respectively and F_D is the fluorescence intensity in the absence of acceptor ions, and τ_D is the lifetime in the absence of acceptor ions.

3.2 Energy transfer of Tb(III)-Nd(III) binary system

In the Tb(III)-Nd(III) binary system, Tb(III) and Nd(III) were used as a donor and acceptor, respectively. The emission of the Tb(III) donor ($^5D_4 \rightarrow ^7F_4$) and the absorption of the Nd(III) acceptor ($^4G_{5/2} \leftarrow ^4I_{9/2}$) exhibited a significant extent of spectral overlap (Fig. 1). The fluorescence spectrum was measured using 490 nm of an excitation source in order to exclude a phenomenon of the increase in fluorescence intensity of the 5D_4 transition by the cross relaxation from the 5D_3 transition.

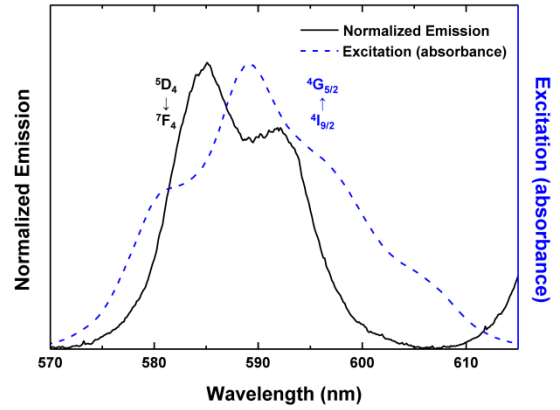


Fig. 1. Spectral overlap between the emission of Tb(III) and the absorption of Nd(III) in molten LiCl-KCl eutectic at 500 °C.

The energy transfer between the Tb(III) donor and the Nd(III) acceptor has been clearly observed and the formation of binary chloride complexes and the structural symmetry were characterized by addition of acceptor ions. The concentration of Tb(III) was sustained at 0.91 wt.%. The fluorescence intensity and lifetime were decreased by following the Eq. 1 and the linear relationship with almost $F_0/F = \tau_0/\tau$ was obtained undoubtedly, indicating the collisional quenching of Tb(III) and Nd(III). As a consequence, we may conclude that the structural change did not appear in the binary system under this experimental condition. The fluorescence lifetime of Nd(III) due to the electronic transitions from $^4F_{1/2}(l = 5,3)$ to $^4I_{9/2}$ was decreased from $81.4 \pm 2.5 \mu s$ to $35.9 \pm 0.1 \mu s$ in the Nd(III) concentration range of 0.11 - 0.79 wt.%. The fluorescence lifetime of Nd(III) steadily converged to the lifetime of pure Nd(III) with its increasing concentration in the binary system. The lifetime increase of Nd(III) in the binary system has been assumed as a sign of resonance energy transfer in molten LiCl-KCl salt. The rising time of fluorescence intensity of Nd(III) appeared due to the energy transfer, and it was shortened according to the decrease in the fluorescence lifetime of Tb(III) with increasing Nd(III) concentrations. The rising time of fluorescence intensity appeared as a result of the cross-relaxation by the interaction of excited Tb(III) ions in the 5D_4 state with unexcited Nd(III) ions, and thus the emission intensity and the lifetime of Tb(III) are simultaneously decreased. Finally, the linear relationship between the rising time of Nd(III) and the lifetime of Tb(III) was clearly deduced, indicating that the rising time was utterly caused by energy transfer. The most appropriate and direct results showing the energy transfer was depicted in Fig. 2. The fluorescence intensity of Nd(III) was enhanced after adding $TbCl_3$ to the binary molten salt system, and it represents that the emitted photons from Tb(III) were reabsorbed by the energy level of Nd(III) through energy transfer.

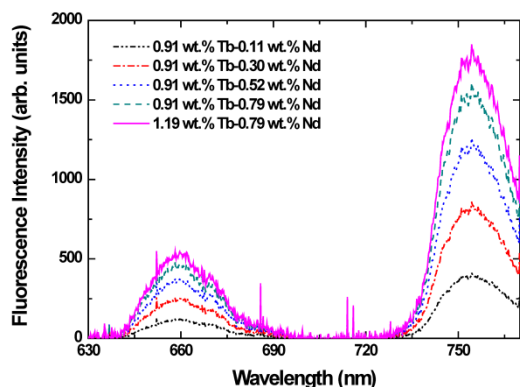


Fig. 2. Fluorescence spectra of Nd(III) in the Tb(III)-Nd(III) binary system in molten LiCl-KCl eutectic at 500 °C.

By applying the Förster energy transfer theory, the Förster distance (R_0) was evaluated based on the experimental results in molten LiCl-KCl salt at 500 °C by using Eq. 4. In Eq. 4, the information about the refractive index (n) and the quantum yield of Tb(III) in the absence of Nd(III) (Q_D) has not yet been analyzed in high temperature chloride salts. Therefore, the fluorescence quantum yield of Tb(III) has been assumed in the range of 0.1-1.0, and the refractive index (n) was estimated based on the literature work in pure LiCl and KCl media at various temperatures [12]. In this study, the experimental temperature (500 °C) was around 140 °C higher than the melting temperature of LiCl-KCl eutectic (357 °C, certified by Sigma-Aldrich), thereby the refractive index of LiCl-KCl at 500 °C was estimated based on the refractive indexes of LiCl at 735 °C (melting point = 605 °C) and KCl at 895 °C (melting point = 770 °C). The refractive indexes calculated according to the empirical formula [12] were determined to be $n_{LiCl,735} = 1.496$ and $n_{KCl,895} = 1.387$ at the wavelength of 490 nm. In order to compensate the error caused by assuming the values of Q_D and n , the Förster distance (R_0) was derived in the specific range of Q_D (0.1-1.0) and n (1.387-1.496) by Eq. 4. The results are summarized in Table 1. The center-to-center distance (r) between metal ions can be calculated based on the Förster distance and the measurement of energy transfer efficiency (Eq. 7).

Table I. The Förster distance of Tb(III)-Nd(III) in molten LiCl-KCl eutectic salt at 500 °C.

	$Q_D=0.1$ (Å)	$Q_D=1.0$ (Å)
$n = 1.387$	10.9	16.0
$n = 1.496$	10.4	15.2

4. Conclusions

The formation of binary chloride complexes and their structural change have been investigated in the Tb(III)-Nd(III) binary system by investigating the fluorescence resonance energy transfer. Tb(III) was used as a donor

and Nd(III) was used as an acceptor. The fluorescence intensity and the fluorescence lifetime of Tb(III) were decreased as increasing the concentration of Nd(III), demonstrating collisional quenching between donor ions and acceptor ions. The Förster distance (R_0) of Tb(III)-Nd(III) binary system in molten LiCl-KCl eutectic was determined in the specific range of Q_D (0.1-1.0) and n (1.387-1.496). However, the structural change of $LnCl_6^{3-}$ and the complexation between lanthanide chloride ions did not take place under the experimental condition.

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