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Letter

Electronic absorption spectra of lanthanides in a molten chloride II. Absorption characteristics of neodymium(III) in various molten chlorides

Toshiyuki Fujii[a,*], Takayuki Nagai[b], Nobuaki Sato[c], Osamu Shirai[a], Hajimu Yamana[a]

[a] Research Reactor Institute, Kyoto University 2-1010, Asashiro Nishi, Kumatori, Sennan, Osaka 590-0494, Japan
[b] Japan Nuclear Cycle Development Institute, 4-33, Muramatsu, Tokai, Ibaraki 319-1194, Japan
[c] Institute for Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1, Katahira, Sendai 980-8577, Japan

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Abstract

Electronic absorption spectra of trivalent neodymium in LiCl–KCl eutectic, NaCl–2CsCl eutectic, $CaCl_2$, LiCl, CsCl and mixtures of these at various temperatures were measured, and the variation of the absorption bands, $^4G_{5/2}$, $^2G_{7/2} \leftarrow {}^4I_{9/2}$, were carefully analyzed. The dependence of their molar absorptivity, oscillator strength, and the degree of the energy splitting on temperature and melt composition were determined. As a result, it was suggested that the $NdCl_6^{3-}$ complex keeps its octahedral symmetry in the NaCl–2CsCl eutectic, while this symmetry is more distorted in LiCl and $CaCl_2$. Based on these data, the chemical status of $NdCl_6^{3-}$ complex in molten chlorides was discussed.

Keywords: Molten salt; Neodymium; Electronic absorption spectrometry; Oscillator strength; Molar absorptivity

1. Introduction

The pyrochemical reprocessing technique using molten salts is considered to be one candidate for the future reprocessing technique of spent nuclear fuels. The chemical characteristics of fission products, including lanthanides and actinides, in molten salts are important information for understanding the pyrochemical reprocessing system. UV–vis spectrophotometry is a strong analytical technique for characterizing chemical species and their behavior in molten salts. As the first step of our spectrophotometric study of trivalent lanthanides with molten salts, we have measured electronic absorption spectra of neodymium in a LiCl–KCl eutectic mixture at 873 K, and have determined molar absorptivities of its detectable absorption bands in the visible region [1].

From a technological viewpoint of pyrochemical reprocessing, three different chloride melts have attracted attention. A LiCl–KCl eutectic mixture (mole ratio of lithium to potassium = 59/41) has been considered for metallic fuel reprocessing, and a NaCl–2CsCl eutectic mixture (mole ratio of sodium to cesium = 1/2) for oxide fuel reprocessing. Recently, $CaCl_2$ has attracted a particular interest for the electrolytic reduction of actinide dioxide fuels into metal. Since the thermochemical stabilities of lanthanides and actinides in melts greatly influence the performance of the reprocessing process, and since their differences are the results of the individual chemical status of their chloride complexes in different melts and other conditions, the analyses of the species in the melts is an important subject for research of molten salt system. Absorption spectrophotometry, which provides information about the change of the chemical status of complexes through the change in electronic absorption spectrum is an adequate technique for this subject. In this paper, we present the variation of the electronic absorption spectra of Nd(III) in various molten chlorides at various temperatures. The change of the coordination circumstance of Nd(III) will also be discussed.

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[*] Corresponding author.
E-mail address: tosiyuki@hl.rri.kyoto-u.ac.jp (T. Fujii).

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2. Experimental details

Anhydrous neodymium trichloride was synthesized from the reaction of neodymium sesquioxide, Nd_2O_3, with carbon tetrachloride under an inert atmosphere. Nd_2O_3 was obtained from Nihon Yttrium Co. Ltd. (99.99% purity), and CCl_4 from Wako Pure Chem. Ind. Ltd. (99% purity). Nitrogen gas of 99.99% was purchased from Nippon Sanso Co. Ltd. Nd_2O_3 powder in a quartz boat was set in a quartz reaction tube of a horizontal electric furnace. Under N_2 atmosphere, the CCl_4/N_2 mixed gas was introduced to the reaction tube for 6 h at 773 K. Subsequently, for the growth of granules, the temperature of the furnace was raised to 973 K and kept for 9 h with a N_2 flow. The product identified as $NdCl_3$ by XRD analysis was supplied to the present study.

Anhydrous alkaline chloride samples used, LiCl–KCl eutectic mixture (mole ratio of lithium to cesium = 59/41), NaCl–2CsCl eutectic mixture (mole ratio of sodium to cesium = 1/2), $CaCl_2$, LiCl, and CsCl were products of Anderson Physics Laboratory Engineered Materials.

All the experiments were carried out in a glove box system filled with dry Ar continuously purified to remove oxygen and humidity. The content of impurity O_2 and H_2O in the inside atmosphere was continuously maintained less than 1 ppm. Absorbance measurements were performed with various molten chlorides containing ca. 0.07 mol dm^{-3} (M) $NdCl_3$. The details of our experimental apparatus and the procedure for absorbance measurements can be seen elsewhere [1,2]. The temperature of the sample during the experiment was controlled to the desired value within ±3°.

3. Results and discussion

The electric dipole transition between f-orbitals that show abnormal variations in intensity are classified as hypersensitive transitions. These variations are attributed to the action of an inhomogeneous electromagnetic field from the surrounding medium. In the case of neodymium, transitions from the ground level $^4I_{9/2}$ to excited levels of $^2G_{7/2}$ and $^4G_{5/2}$, which are abbreviated as $^4G_{5/2},{}^2G_{7/2} \leftarrow {}^4I_{9/2}$, are sensitive to the coordination circumstances, and they are commonly used to examine the coordination of Nd^{3+} [3]. The transition $^4G_{5/2} \leftarrow {}^4I_{9/2}$ is known as the hypersensitive transition, which is accompanied by and overlapped with a less intensive non-hypersensitive transition to the level $^2G_{7/2}$. Figs. 1 and 2, which are given in units of molar absorptivity, show the observed absorption bands over the wavelength region from 562 to 625 nm, which corresponds to these two transitions of neodymium in various molten chlorides. These absorption bands are composed of several transitions between degenerate terms of the ground and excited levels. These transitions have been explained in the literature [4], as schematically shown in Fig. 3, and the observed absorption peaks in Figs. 1 and 2 are attributable to transitions (I)–(V) of Fig. 3.

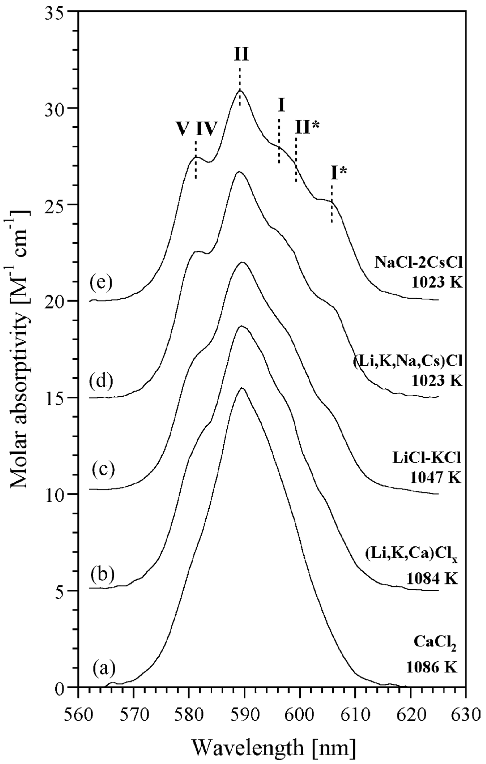

Fig. 1. Electronic absorption spectra of Nd(III) in molten chlorides: (a) $CaCl_2$ at 1086 K, (b) mixture of 72 mol% LiCl–KCl and 28 mol% $CaCl_2$ at 1084 K, (c) LiCl–KCl eutectic at 1047 K, (d) mixture of 50 mol% LiCl–KCl and 50 mol% NaCl–2CsCl at 1023 K, and (e) NaCl–2CsCl eutectic at 1023 K.

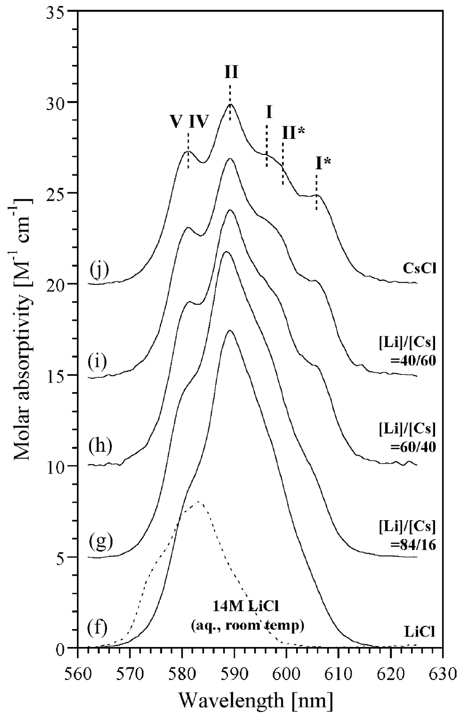

Fig. 2. Electronic absorption spectra of Nd(III) in LiCl, CsCl, and these mixtures at 973 K. Dotted spectrum is obtained for Nd(III) in 14 M LiCl at room temperature (~298 K).

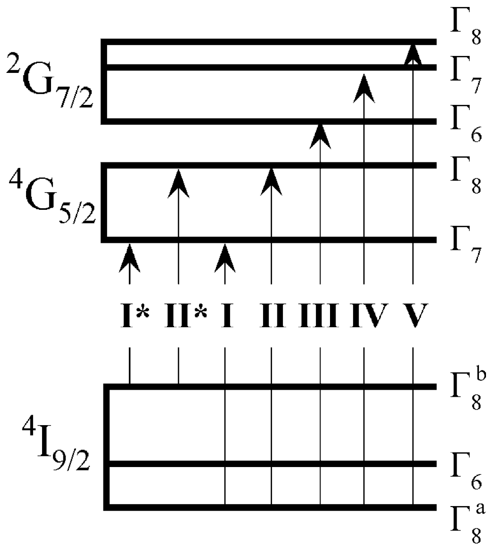

Fig. 3. Diagram of hypersensitive transitions of $NdCl_6^{3-}$.

A neodymium compound $Cs_2NaNdCl_6$, which is one kind of elpasolite, is known to provide highly symmetric octahedral coordination to Nd(III) in its crystal matrix [4], and the absorption spectrum of Nd(III) in elpasolite is regarded as a reference for spectral identification of octahedral symmetry of f-elements. In Fig. 1, spectrum (e) shows four peaks, which include transitions (I*), (I, II*), (II), and (IV, V), and this is quite similar to the spectrum of Nd(III) in molten elpasolite [4]. Molten elpasolite is considered to maintain the high symmetry of octahedral coordination of Nd as in solid elpasolite, and the four peaks are thus considered to indicate the result of the degeneracy of energy levels $^4G_{5/2}$ and $^4I_{9/2}$, under the ligand field by the highly symmetric octahedral coordination. The similarity of the four peaks observed in the NaCl–2CsCl melt to that in molten elpasolite suggests that Nd^{3+} has a similar highly symmetric octahedral coordination as in molten elpasolite.

The result for the LiCl–KCl eutectic (spectrum (c)) shows a sharper spectrum than that of the NaCl–2CsCl eutectic. This suggests that the degree of the symmetric ligand field effect is lower in LiCl–KCl, while also suggesting a lower symmetry of the $NdCl_6^{3-}$ complex in the LiCl–KCl eutectic than in the NaCl–2CsCl eutectic. The results obtained for the mixture of LiCl–KCl and NaCl–2CsCl (spectrum (d)) show intermediate properties between spectra (c) and (e). It is reasonably understood that the octahedral symmetry of $NdCl_6^{3-}$ in mixture (d) is distorted more than that in the NaCl–2CsCl eutectic, but the degree of distortion is smaller than in the case of the LiCl–KCl eutectic. The same trend can be seen in the comparison of spectra (a)–(c). Spectrum (a) for pure $CaCl_2$ is the sharpest, suggesting that, the $NdCl_6^{3-}$ complex has the highest distortion in the various melts tested. The mixture of $CaCl_2$ and LiCl–KCl seems to have intermediate property between the systems (a) and (c).

Fig. 2 shows the electronic absorption spectra of Nd(III) in LiCl, CsCl, and their mixtures at 973 K. Spectra (f) through (i) indicate the effect of the addition of CsCl to pure LiCl. Peak splitting in (h)–(j) is clear, but it is not clear in (f) and (g). This suggests that there is possibly a sharp change in the coordination circumstance during the process from (f) through (h), and this changing point corresponds to a CsCl content around 40%. The spectrum of the CsCl system is similar to that of the NaCl–2CsCl system shown in Fig. 1, spectrum (e). This convinces us that Nd(III) in pure CsCl may have a coordination similar to that in the NaCl–2CsCl. Consequently, we suggest that Nd(III) in systems containing more CsCl than 40% has quite a highly symmetric coordination, similar to that in molten elpasolite. In other words, the addition of LiCl over 60% makes it lose the symmetry to a certain distorted octahedral symmetry.

Table 1
Sum of splittings of electronic energy levels, molar absorptivity at 589 nm, and oscillator strength of hypersensitive transitions

Spectrum	Medium	Temperature (K)	ε_{589} (M^{-1} cm^{-1})	f ($\times 10^6$)	$\sum(\Delta E)$[a] (cm^{-1})
(a)	$CaCl_2$	1086	15.3	25.2	419
(b)	(Li, K, Ca)Cl_x[b]	1084	13.6	27.1	440
(c)	LiCl–KCl	1047	11.9	25.5	457
(d)	(Li, K, Na, Cs)Cl[c]	1023	11.7	24.9	465
(e)	NaCl–2CsCl	1023	10.9	24.4	470

[a] $\Delta E(^4I_{9/2}) + \Delta E(^4G_{5/2})$. Peak positions were analyzed by dividing the raw spectrum into four simple Gaussian functions.
[b] Mixture of 72 mol% LiCl–KCl and 28 mol% $CaCl_2$.
[c] Mixture of 50 mol% LiCl–KCl and 50 mol% NaCl–2CsCl.

Table 2
Sum of splittings of electronic energy levels, molar absorptivity at 589 nm, and oscillator strength of hypersensitive transitions

Spectrum	Medium	Temperature (K)	ε_{589} (M^{-1} cm^{-1})	f ($\times 10^6$)	$\sum(\Delta E)$ (cm^{-1})
(f)	LiCl	973	17.4	30.6	424
(g)	LiCl–CsCl, [Li]/[Cs] = 84/16	973	16.7	31.6	441
(h)	LiCl–CsCl, [Li]/[Cs] = 60/40	973	14.0	28.9	466
(i)	LiCl–CsCl, [Li]/[Cs] = 40/60	973	11.9	25.2	463
(j)	CsCl	973	9.9	22.4	478

In order to know the coordination circumstance change of molten chlorides in terms of the absorption transition probability, we evaluated the oscillator strength for our results shown in Figs. 1 and 2. The oscillator strength can be defined as,

$$f = 4.319 \times 10^{-9} \frac{9n}{(n^2+2)^2} \int \varepsilon(\nu)\mathrm{d}\nu \qquad (1)$$

where $\varepsilon(\nu)$ is the molar absorptivity at energy ν (cm^{-1}) and n is the refractive index of the solvent medium. Data for n are available for molten LiCl [5], KCl [5], NaCl [5], CsCl [5], and $CaCl_2$ [6]. For the mixed molten chlorides, the refractive indexes were estimated by a linear interpolation between the values of pure component melts [7]. Tables 1 and 2 show the calculated oscillator strengths. The molar absorptivities at 589 nm are shown together.

As shown in Fig. 3, the energy difference between transitions (I) and (I*), as well as that between transitions (II) and (II*), is equal to the energy difference between two levels as a result of the splitting of the ground level, $\Delta E(^4I_{9/2})$. In a similar manner, the energy difference between transitions (I) and (II), as well as that between transitions (I*) and (II*), is equal to the splitting of the excited level, $\Delta E(^4G_{5/2})$. The electric field given by the octahedral coordination of Cl^- promotes the splitting of these terms, and thus the change on ΔE can be used as a probe for the change of the coordination symmetry of $NdCl_6{}^{3-}$. Although some have studied ΔE values of $NdCl_6{}^{3-}$ for some molten chlorides [4,8], it was difficult in this study to isolate the peaks of transitions (I) and (II*) due to limited resolution of the spectrum. However, since the peak positions of the transition (I*) and (II) were detectable, we discuss the trend of the sum of $\Delta E(^4I_{9/2})$ and $\Delta E(^4G_{5/2})$, which is defined by $\sum(\Delta E) = \Delta E(^4I_{9/2}) + \Delta E(^4G_{5/2})$. This value can be obtained as the difference between transitions (I*) and (II) listed in Tables 1 and 2.

As shown in Table 1, $\sum(\Delta E)$ decreases from spectrum (e) to (a). This means that the octahedral symmetry of $NdCl_6{}^{3-}$ gradually gets distorted in this order. The *f*-values increased in this order (except (a)), meaning that the transition probability increased along with the increasing distortion of the symmetry, in compliance with the Judd–Ofelt Theory. These two observations agree in supporting the increasing distortions of the octahedral symmetry along with the variation of the melt from NaCl–2CsCl to $CaCl_2$. The exception of (a) may be due to the strong polarizing power of Ca^{2+} surrounding $NdCl_6{}^{3-}$, which is likely to make the electron-donating ability of Cl^- weaker, resulting in a decrease of oscillator strength.

As shown in Table 2, for spectra (h)–(j), $\sum(\Delta E)$ values are similar, but f increases by adding LiCl. This suggests that the octahedral symmetry of $NdCl_6{}^{3-}$ is retained, but the electron-donating ability of Cl^- may increase with the increasing LiCl content. On the other hand, $\sum(\Delta E)$-value of spectrum (f) through (h) shows a sharp increase. This supports the above-mentioned suggestion of a significant change of the coordination circumstance of Nd(III) in LiCl–CsCl mixture possibly occurs in the [Li]/[Cs] region from 60/40 to 100/0. Structure of the molten LiCl–CsCl, which possibly influences the coordination status of dissolved Nd(III), have been studied by neutron diffraction analysis [9] and Raman spectroscopic analysis [10]. A difference in the melt structure has been pointed out between the Cs^+-rich mixture and the Li^+-rich mixture [10]. This structure change of the melt may influence the symmetry of the Nd(III) complex, causing the sharp change of Nd(III) spectrum, but further investigation is required for clarifying this correlation.

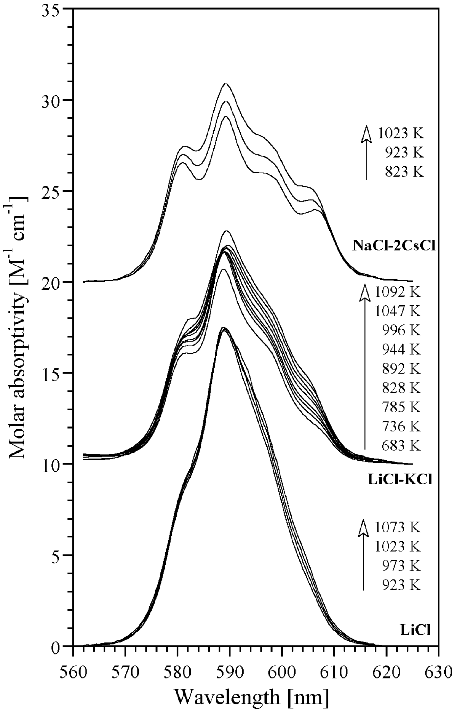

Fig. 4. Temperature dependence of molar absorptivity of Nd(III) in LiCl, LiCl–KCl eutectic, or NaCl–2CsCl eutectic.

The temperature dependence of the electronic absorption spectrum of Nd(III) was studied for LiCl, the LiCl–KCl eutectic, and the NaCl–2CsCl eutectic. The spectra obtained are shown in Fig. 4. The f values and the $\sum(\Delta E)$ values are determined and are shown in Fig. 5. In all systems, oscillator strengths increase with temperature. This indicates that the distortion of the $NdCl_6{}^{3-}$ complex from octahedral symmetry grows with increasing temperature. Thermal motion of ions may have generated asymmetric vibrations of the $NdCl_6{}^{3-}$ complex. The electron-donating ability of Cl^-, which is another cause of the increase of the *f*-value and is likely to be influenced by coexisting alkaline cations, may have been influenced by the temperature increase.

For the LiCl–KCl and the NaCl–2CsCl eutectics, $\sum(\Delta E)$s decrease with increasing temperature. This suggests the reduction of the ligand field of octahedral symmetry of the $NdCl_6{}^{3-}$ complex, and thus it means an increased distortion of octahedral symmetry with increasing temperature. The increase of oscillator strength, which is also the result of the

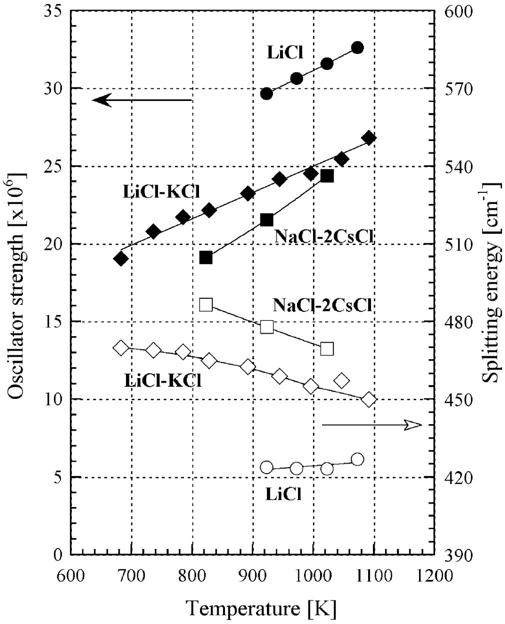

Fig. 5. Temperature dependence of oscillator strength and energy of splittings for Nd(III) hypersensitive transitions. *f*-values (solid marks), $\sum(\Delta E)$ values (open marks).

distortion of the octahedral symmetry, agrees with this result of for $\sum(\Delta E)$. In contrast, for the LiCl system, $\sum(\Delta E)$s did not show appreciable change with increasing temperature, while its oscillator strength showed an increase with increasing temperature similar to that of other melts. It is considered that the octahedral symmetry of the $NdCl_6{}^{3-}$ complex in LiCl is quite distorted, which is strongly supported by its higher oscillator strength than in other melts containing CsCl. Therefore, the ligand field effect by octahedral symmetry to Nd^{3+} in LiCl is considered to be so small that the degenerate levels are not resolved, and the low $\sum(\Delta E)$ observed for LiCl can be attributable to this effect. Increased temperature, which promotes the distortion in the case of other melts, does not overcome the sufficiently degenerate levels.

4. Conclusions

The characteristics of the hypersensitive absorption band of Nd^{3+} in various chloride melts were observed, and the state of the octahedral symmetry of $NdCl_6{}^{3-}$ complex in various molten chlorides was discussed. The observed characteristics of the oscillator strength and splitting of the hypersensitive transitions, $^4G_{5/2},^2G_{7/2} \leftarrow {}^4I_{9/2}$, suggested that $NdCl_6{}^{3-}$ complex in the NaCl–2CsCl eutectic and in molten CsCl have quite high octahedral symmetry, but that they are distorted in molten LiCl and $CaCl_2$. The observations for the mixture of LiCl, KCl, and CsCl were reasonably intermediate between the LiCl and CsCl observations. With increase of temperature, the oscillator strength increased and the peak splitting decreased. This indicates that the distortion of $NdCl_6{}^{3-}$ complex from octahedral symmetry proceeds with the increasing temperature.

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