Spectrophotometric Study of Nd^{2+} Ions in LiCl-KCl Eutectic Melt

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A UV and visible spectrophotometric study was made in order to prove the existence of Nd^{2+} and clarify the equilibrium among Nd metal, Nd^{2+}, and Nd^{3+} in LiCl-KCl eutectic melt. Spectra assigned to Nd^{2+} were observed for $NdCl_2$ in $(LiCl\text{-}KCl)_{eut.}$ and Nd- $NdCl_3$ in $(LiCl\text{-}KCl)_{eut.}$ melts. Black corrosion products were observed on the surface of the glass cells used for the measurements, where the spectra assigned to Nd^{2+} were observed. X-ray diffraction measurements and electron-probe micro-analyses of the corroded glass cells revealed that the corrosion products contained NdOCl.

Key words: Disproportionation; Neodymium Dichloride; Neodymium Trichloride; Molten Salts; Spectrophotometry.

1. Introduction

Electrowinning processes in molten salt baths have been applied for the production of reactive metals such as lanthanides [1, 2]. The production of neodymium metal is known as a troublesome case because of the low current efficiency. It has been pointed out that the reaction of produced Nd metal with Nd^{3+} ions in the melt causes the low current efficiency [2 – 5]. Formation of Nd^{2+} in the molten salt bath has been suspected. Studies on the equilibrium between Nd metal, Nd^{2+}, and Nd^{3+} ions in molten salt baths are necessary for improving the electrowining process of neodymium metal. They are also useful for developing the pyrochemical reprocessing of spent nuclear fuels, where Nd and other lanthanides have to be removed from actinides. However, there have been no clear evidences for the existence of Nd^{2+} in molten salt baths. Furthermore, spectra of Nd^{2+} ions have only been reported of some solid compounds [6] and in organic solvents [7, 8], until those of $NdCl_2$-$NdCl_3$-$(LiCl\text{-}KCl)_{eut.}$ [9] were reported.

In the present study, the existence of Nd^{2+} ions and the equilibrium among Nd metal, Nd^{2+}, and Nd^{3+} in LiCl-KCl eutectic melt were investigated with UV and visible spectrophotometry. In addition, corrosion of the glass materials by the LiCl-KCl eutectic melt containing Nd^{2+} ions was investigated.

2. Experimental

LiCl-KCl mixed salts of eutectic composition (99.99% certified purity) were used as purchased from Anderson Physical Laboratory Engineered Materials. $NdCl_3 \cdot 6H_2O$ (> 99.5%) purchased from Wako Chem. Ind. Ltd. was dried at 473 K under vacuum for 72 hours, decomposed and purified by distillation in vacuum (10^{-3} Pa) at 1273 K to obtain anhydrous $NdCl_3$. Nd metal (99%) was used as purchased from Nilaco Corp. The procedure for preparing $NdCl_2$ was similar to that described in [10]. $NdCl_3$ powder and Nd metal filings were mixed and compressed to a pellet in an argon atmosphere glove box with $H_2O < 5$ ppm and $O_2 < 10$ ppm. The pellet, covered with molybdenum foil, was sealed into a quartz tube under vacuum of 10^{-3} Pa and heated at 796 K for 424 hours. The product was ground and again pressed to a pellet, then heated at 898 K for 184 hours.

Spectrophotometric cells were made from quartz or Pyrex glass tubes having (1.74 ± 0.01) cm of inner diameter. The cells were charged with the samples (about 10 g) in an argon atmosphere glove box with $H_2O < 4$ ppm and $O_2 < 2$ ppm, and filled with argon gas of the glove box atmosphere at about 80 kPa using a gas-tight cap. UV/visible absorption spectra were measured with a Shimadzu Corp. SPG-100ST spectrophotometer. The radiation source was a xenon lamp

Table 1. Composition of the samples and the material of the cell used in this study. Samples are $NdCl_3$ (A-1∼A-8), $NdCl_2$ (B-1∼B-5), $NdCl_3$ coexistent with Nd metal (C-1∼C-7), and Nd metal (D-1∼D-3) in LiCl-KCl eutectic melt.

RUN No.	Concentration (mol%) in LiCl-KCl eutectic melt			molar ratio	
	$NdCl_2$	$NdCl_3$	Nd	Nd/$NdCl_3$	cell material
A-1		0.042			Pyrex
A-2		0.049			Pyrex
A-3		0.074			Pyrex
A-4		0.154			Pyrex
A-5		0.168			quartz
A-6		0.233			Pyrex
A-7		0.292			Pyrex
A-8		0.315			Pyrex
B-1	0.156				Pyrex
B-2	0.106				quartz
B-3	0.009				quartz
B-4	0.037				quartz
B-5	0.029				quartz
C-1		0.315	0.333 (powder)	1.058	Pyrex
C-2		0.049	0.056 (powder)	1.148	Pyrex
C-3		0.042	0.025 (grain)	0.608	Pyrex
C-4		0.151	0.097 (grain)	0.642	quartz
C-5		0.172	0.121 (grain)	0.704	quartz
C-6		0.170	0.074 (grain)	0.437	quartz
C-7		0.168	0.101 (grain)	0.601	quartz
D-1			0.426 (powder)		Pyrex
D-2			0.041 (grain)		quartz
D-3			0.051 (powder)		quartz

unit. The intensity of the transmitted light was measured in the range of 200 – 900 nm in wavelengths with a sweep rate of 100 nm/min. The incident and transmitted light were cut by slits of 5 mm width parallel to the cell tube axis. LiCl-KCl eutectic melt was chosen as a reference sample. Baseline corrections of the spectra were made in order to remove the spectra due to the corroded glass cells, if necessary. The baselines were given as functions of the wavelength (λ/nm), $a\lambda^2 + b\lambda + c$, where a, b, and c were fitted to the baseline of the obtained spectra. Table 1 summarizes the composition of the samples and cell materials used in this study.

The corroded glass cell wall was examined with X-ray diffraction (XRD) and electron-probe microanalyses (EPMA). A small piece of the corroded glass taken from the spectrophotometric cell was mounted on the aluminum sample holder for XRD measurements. Some samples were sealed in a polyethylene bag in the Ar atmosphere glove box to prevent it from absorbing moisture. The corrosion product that had been scraped from the cell and washed with water was mounted on a glass sample holder. XRD measurements were carried out with a conventional X-ray diffractometer using Cu K_α radiation. EPMA's were carried out on their surface and cross section to detect Nd, Cl, K, Si and Al with the acceleration voltage ranging from 15 to 25 kV.

3. Results and Disscusion

3.1. UV/visible Spectrophotometry

(a) $NdCl_3$ in LiCl-KCl eutectic melt

Figure 1 shows typical spectra of $NdCl_3$ in LiCl-KCl eutectic melt with various concentrations at 673 K and the concentration dependencies of the peak heights. The strongest peak at 589 nm is due to $^4G_{5/2} \leftarrow {}^4I_{9/2}$ of the f-f transition [11 – 13], which is a hypersensitive transition peak of Nd^{3+} ions. The bulk concentrations in mol/L were calculated using the density of the LiCl-KCl eutectic melt [14, 15]. The relationship between the absorption peak height at 589 nm (A) and the bulk concentration of $NdCl_3$ (C (mol/L)) was expressed by $A = (16.2 \pm 0.3)C$, as seen in the inset of Figure 1. The molar absorption coefficient is calculated to be 9.3 $\mathrm{Lmol^{-1}cm^{-1}}$. This value agrees reasonably with the literature values of similar systems: 11.9 $\mathrm{Lmol^{-1}cm^{-1}}$ for NdF_3-$(LiCl\text{-}KCl)_{eut.}$ at 673 K [12], 11 $\mathrm{Lmol^{-1}cm^{-1}}$ for molten $NdCl_3$ at 1103 K [13], and 10 $\mathrm{Lmol^{-1}cm^{-1}}$ for molten $Cs_2NaNdCl_6$ at 973 K [13]. Other peaks have been also reported in [12, 13], and their intensities are proportional to the concentration of $NdCl_3$, as shown in Figure 1.

(b) $NdCl_2$ in LiCl-KCl eutectic melt

The prepared $NdCl_2$ sample had a tint of green and was identified as pure $NdCl_2$ by X-ray diffraction analysis. Heating an $NdCl_2$ grain immersed in the LiCl-KCl eutectic salt up to 653 K gave a dark red melt. The glass cell was corroded to show a dark color on the surface; it became darker with time in the beginning of the experiments. The baseline of the spectra showed a slope, which rose with time as the color of the glass cell became darker. The baseline is considered to be due to the black corroded glass. The measurements were repeated until the spectra became constant; occasionally the sample cell was shaken to make the melt homogeneous before the measurement.

The evolution of the spectra of 0.029 mol% $NdCl_2$ in LiCl-KCl eutectic melt (RUN No. B-5) after the

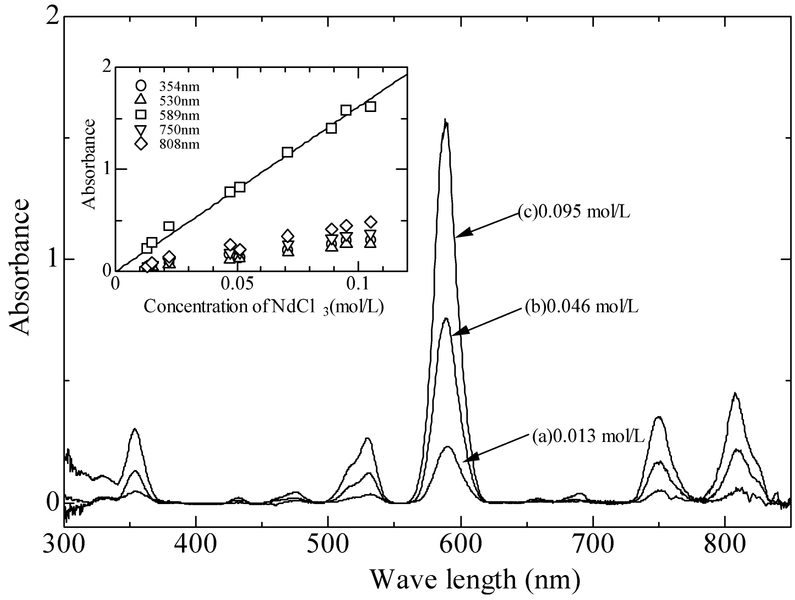

Fig. 1. UV/vis- Spectra of Nd^{3+} in LiCl-KCl eutectic melt at 673 K and the concentration dependencies of the peak intensities. Bulk concentrations of $NdCl_3$ are (a) 0.095, (b) 0.046, and (c) 0.013 mol/L.

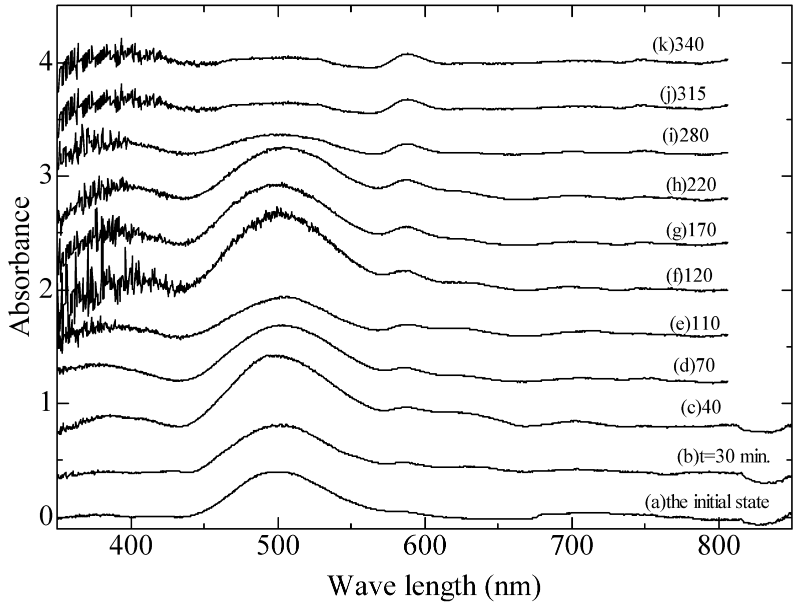

Fig. 2. UV/vis-spectra of 0.029 mol% $NdCl_2$ in LiCl-KCl eutectic melt at 653 K after the baseline correction, (a) the initial state, (b) 30, (c) 40, (d) 70, (e) 110, (f) 120, (g) 170, (h) 220, (i) 280, (j) 315, and (k) 340 minutes later. The sample cell was shaken before the measurements of the spectra (c) and (f). Each spectrum is shifted vertically.

baseline correction is shown in Figure 2. A broad peak exists around 500 nm; its position is similar to that of the broad peak reported for Nd^{2+} in THF solutions [7, 8] and $NdCl_2$-$NdCl_3$-$(LiCl\text{-}KCl)_{eut.}$ with 1 to 3 mol% of $NdCl_2$ [9]. The peak has been assigned to the f-d transition, because it is broad and has a large molar absorption coefficient [7–9]. The observed red color of $NdCl_2$ – $(LiCl\text{-}KCl)_{eut.}$ is also similar to the color of Nd^{2+} in THF solution (cherry red) [8]. As seen on the spectra (c) and (f) in Fig. 2, shaking the sample cell before the measurements made the Nd^{2+} peak larger by dissolving the $NdCl_2$ sample into the melt. After the rise of the baseline terminated, later than 220 minutes from the first measurement, the peak around 500 nm began to fall significantly. The peak at 589 nm, which rose with time, is assigned to Nd^{3+} ions. The behavior of the peaks assigned to Nd^{2+} and Nd^{3+} will be discussed later.

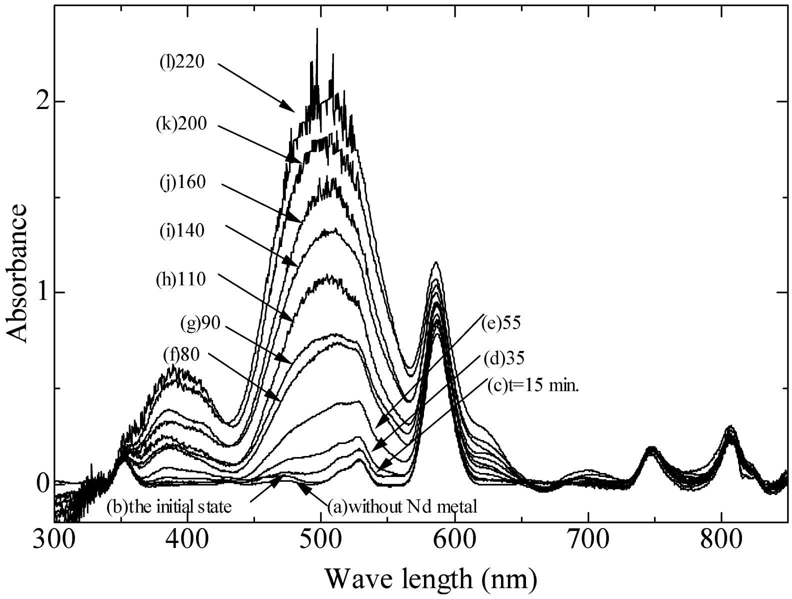

Fig. 3. UV/vis-spectra of 0.168 mol% $NdCl_3$ with Nd metal grain (molar ratio: $Nd/NdCl_3 = 0.601$) in LiCl-KCl eutectic melt at 653 K after the baseline correction, (a) without Nd metal, (b) initial state with the Nd metal grain, (c) 15, (d) 35, (e) 55, (f) 80, (g) 90, (h) 110, (i) 140, (j) 160, (k) 200, and (l) 220 minutes later. The sample cell was shaken before the measurement of the spectrum (c).

(c) Nd metal coexistent with $NdCl_3$ in LiCl-KCl eutectic melt

A mixture of $NdCl_3$ and LiCl-KCl eutectic salt was first heated to make the melt homogenous. After cooling, Nd metal was placed on the solidified salt in the Ar atmosphere glove box; the sample was then heated up to 653 K again. The color of the melt soon became violet, which can be explained by the coexistence of violet-blue Nd^{3+} [16] and red Nd^{2+}, and is similar to that reported in literature [17, 18]. The glass wall of the cell was corroded and darkend.

Figure 3 shows the evolution of the spectra of Nd metal coexistent with 0.168 mol% $NdCl_3$ (molar ratio: $Nd/NdCl_3 = 0.601$) in LiCl-KCl eutectic melt after the baseline correction for the corrosion of the glass cell. Reliable measurements became impossible later than 220 minutes after the first measurement, because the transmitted light through the corroded glass cell decreased with time. The broad Nd^{2+} peak around 500 nm rose with time and the peaks assigned to Nd^{3+} remained. The results suggest that the reaction

$$2Nd^{3+} + Nd\,(solid) = 3Nd^{2+} \qquad (1)$$

occurred. With this reaction, the concentration of Nd^{3+} should decrease, though this was not observed clearly. The experimental results can be explained by the difference between the molar absorption coefficients of Nd^{2+} and Nd^{3+}. The molar absorption coefficient of Nd^{2+} (f-d transition), which has not been reported in molten salts, is expected to be much bigger than that of Nd^{3+} (f-f transition). Reported molar absorption coefficients were 450 ($Lmol^{-1}cm^{-1}$) for Nd^{2+} in THF at 500 nm [7, 8] and 0.7 ($Lmol^{-1}cm^{-1}$) for Nd^{3+} in aqueous solution at 589 nm [13]. If only 1% of Nd^{3+} ions (which is smaller than the detection limit of our instruments) are converted to Nd^{2+} by the reaction in our measurement, the peak of Nd^{2+} at 500 nm should be about 10 times larger than that of Nd^{3+} at 589 nm calculated with the molar absorbance coefficients above. The observed ratios of these peaks were smaller than the calculated one. This fact supports that the ratio $[Nd^{2+}]/[Nd^{3+}]$ is smaller than 0.01 as reported by Yamamura et al. [17]. The spectra also show small peaks around 400 nm, and 630 nm, which are not assigned in this study and are due to neither Nd^{2+} nor Nd^{3+} ions.

(d) Nd metal in LiCl-KCl eutectic melt

To clarify the corrosion behavior of glass cells, Nd metal immersed in LiCl-KCl eutectic melt was heated up to 653 K. The Nd metal samples were either in powder or in grain form. With Nd metal powder almost all parts of the glass surface touching the melt were corroded to show a dark appearance. The color was darker at the bottom of the cell. The spectra show a sloped baseline without any appreciable peaks. With the Nd metal grains, the melt showed a pale yellow color; only the spot where the grain touched the glass wall became

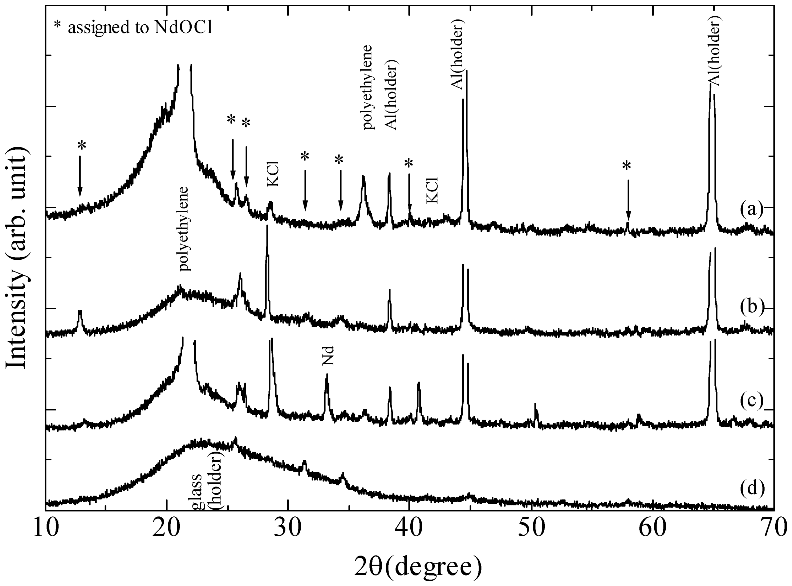

Fig. 4. X-ray diffraction patterns of the corrosion products. (a) A pyrex glass cell used for $NdCl_3$-$(LiCl$-$KCl)_{eut.}$-Nd sample. (b) the same as (a) without a polyethylene bag. (c) A quartz glass cell used for $(LiCl$-$KCl)_{eut.}$-Nd sample. (d) Corrosion products scraped from the quartz glass cell used for $NdCl_3$-$(LiCl$-$KCl)_{eut.}$-Nd sample.

black. The spectra of the melt show small peaks around 400 nm and 630 nm, which are also seen on the spectra of $NdCl_3$-$(LiCl$-$KCl)_{eut.}$-Nd in Fig. 3, without a sloped baseline.

3.2. Corrosion of the Glass Cells

XRD patterns of the corroded Pyrex glass cell used for $NdCl_3$-$(LiCl$-$KCl)_{eut.}$-Nd (RUN No. C-1) are shown in Figure 4. An XRD pattern of the corroded quartz glass cell and that of the black product scraped from the surface of the glass wall used for $(LiCl$-$KCl)_{eut.}$-Nd (RUN No. C-4) are also shown in Figure 4. Peaks assigned to NdOCl were observed in all the XRD patterns.

With EPMA, Nd, K, and Cl were found on the surface of the Pyrex glass wall used for $NdCl_3$-$(LiCl$-$KCl)_{eut.}$-Nd (RUN No. C-1) or Nd metal powder immersed in LiCl-KCl eutectic melt (RUN No. D-1). The thickness of the layer with Nd, K, and Cl was less than 1 μm, which is around the resolution limit of the apparatus. Exchange of K^+ ions in the molten salts with other cations contained in the Pyrex glass [19] was also observed, with the formation of a K containing layer of 5 µm depth.

The formation of NdOCl on the glass surface suggests that Nd metal, which existed initially or was produced by disproportionation of $NdCl_2$, reacted with the glass components and LiCl-KCl eutectic melt. The reactions producing NdOCl, such as

Table 2. The final concentrations of Nd^{3+} at 653 K, obtained from the absorbance at 589 nm with those expected from the initial concentrations of Nd^{2+}.

RUN No.	Absorbance at 589 nm	$[Nd^{3+}]_{final}^{(spec.)}$ $(10^{-3}M)$	$[Nd^{3+}]_{final}^{(initial\ conc.)}$ $(10^{-3}M)$
B-3	0.04	2.5	1.9
B-4	0.13	8.3	7.6
B-5	0.10	6.4	5.9

$$Nd + ACl + 1/2\ SiO_2 = NdOCl + A + 1/2\ Si \quad (2)$$
$$(A = \text{alkali metal (Li, K)}),$$

propably occurred as reported for Nd metal coexistent with molten alkali chlorides [20]. The calculated free energy changes of the reactions (2), using thermochemical data [21], support the formation of NdOCl even at 298.15 K. The free energy change of the reactions at 298.15 K are -131 kJ/mol for A = Li, and -106 kJ/mol for A = K. The formed elemental Si in (2) is considered to be the origin of the dark color of the glass surface. Other reactions, such as $2/3Nd + 1/3NdCl_3 + 1/2SiO_2 = NdOCl + 1/2Si\,(\Delta G^{298.15} = -193$ kJ/mol [21]) can also give NdOCl, as reported for the Ce-$CeCl_3$ system [22].

For $NdCl_2$-$(LiCl$-$KCl)_{eut.}$ samples, the corrosion was seen on the whole surface of the glass touching the melt. The fact supports that Nd metal produced by (1) is dispersed in the melt as a metal fog. The concentrations of Nd^{3+} increased as Nd was removed from the system by the corrosion. At the final stage of the experiments, Nd^{3+} existed with a negligible amount of Nd^{2+}. The concentrations of Nd^{3+} were calculated from the peak height at 589 nm (A) with the relation $C = A/16.2$. Table 2 shows the obtained concentrations $[Nd^{3+}]_{\text{final}}$ and those expected from the initial concentration of Nd^{2+}, which was calculated from the relation $[Nd^{2+}]_{\text{initial}}/[Nd^{3+}]_{\text{final}} = 3/2$ derived from (1). They agree fairly well for all samples. The result supports that the main corrosion mechanism does not consume Nd^{3+} ions and can be expressed by (2). The experimental results on $NdCl_2$-$(LiCl\text{-}KCl)_{\text{eut.}}$ suggest that the disproportionation equilibrium (1) exists and the solid Nd metal was gradually removed by corrosion of the glass cells.

4. Conclusion

The existence of Nd^{2+} ions in the LiCl-KCl eutectic melt at 653 K was confirmed spectrophotometrically. Melts containing Nd^{2+} ions were prepared by dissolution of $NdCl_2$ or by the reaction of Nd^{3+} with Nd metal in the melt. The existence of the disproportionation equilibrium $2Nd^{3+}$ + Nd (solid) = $3Nd^{2+}$ in the LiCl-KCl eutectic melt is confirmed. Corrosion of the glass cells by Nd metal fog, which is produced by the disproportionation of Nd^{2+} ions, was observed. The corrosion products contain NdOCl.

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