Rare earth (RE) elements have peculiar physicochemical properties and are indispensable for abrasives, catalysts, fluorescent materials and permanent magnets. In particular, Nd-Fe-B permanent magnets have high ferromagnetic performance and it has been used for a variety of high-tech products, such as voice coil motors in hard disk drives, magnetic field sources for magnetic resonance imaging, driving motors for hybrid-type electric vehicles etc.

From the standpoint of energy conservation, the development of a recovery process for RE metals with reduced energy consumption is desired. In previous investigations, we demonstrated the recovery of Nd metal using low-temperature molten salts (LTMSs), because an LTMS has many useful physicochemical properties such as a wide electrochemical window, low liquid-phase temperature, and high ionic conductivity. From an environmental point of view, LTMSs are stable during production cycles and be applied repeatedly as an electrolytic bath.

Coordinated states of Nd(II) and Nd(III) complexes in potassium bis(trifluoromethyl-sulfonyl)amide; K[TFSA] melts.

The coordination states of the multivalent neodymium complexes in potassium bis(trifluoromethyl-sulfonyl)amide; K[TFSA] melts were investigated by Raman spectroscopy. The concentration dependences of deconvoluted Raman spectra were investigated for 0.23–0.45 mol kg⁻¹ Nd(III), and mixed sample of Nd(II)/Nd(III) = 1/3 at the molar ratio in [TFSA]. According to the conventional analysis, the solvation number; n of neodymium complexes were determined to be n = 4.06 for Nd(II), 5.02 for Nd(III). Moreover, thermodynamic properties such as ΔHiso, ΔSiso, and ΔGiso for the isomerism of [TFSA]⁻ from trans- to cis-coordinated isomers were evaluated from temperature dependence of Raman bands. In the first solvation sphere of Nd³⁺ cation, ΔHiso(Nd) became remarkably negative, suggesting cis-[TFSA]⁻ isomers were stabilized by enthalpic contributions. Then, ΔGiso(Nd) contributed to the remarkable decrease in ΔGiso(Nd), and this result clearly indicates cis-[TFSA]⁻ conformers bound to Nd³⁺ cations are preferred coordination state of [Nd³⁺(cis-[TFSA]₂)₅]²⁻. Furthermore, the electrochemical analysis revealed the reduction process proceeded in two steps; [Nd³⁺(TFSA)₅]²⁻ + e⁻ → [Nd²⁺(TFSA)₅]²⁻ + [TFSA]⁻ and [Nd²⁺(TFSA)₅]²⁻ + 3e⁻ → Nd(0) + 5[TFSA]⁻. The diffusion coefficient of [Nd³⁺(TFSA)₅]²⁻ was larger than that of [Nd²⁺(TFSA)₅]²⁻ on the range of whole temperature. The activation energies of [Nd³⁺(TFSA)₅]²⁻ and [Nd²⁺(TFSA)₅]²⁻ were 29.5 kJ mol⁻¹ and 49.8 kJ mol⁻¹, respectively.

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**Experimental**

**Raman spectroscopy.**—Nd(TFSA)₃ salt was synthesized by a neutralization reaction between Nd₂O₃ (Wako Pure Chemical Industries Ltd, 99.9 %) and Li₁₁₁₁-trifluoro-o-(trifluoromethyl)sulfonyl) methanesulfonamide ([HTFSA], Kanto Chemical Co., Inc., > 99.8 %) in aqueous solution. The unreacted acid and water components in the resulting products were removed by evaporation at 393 K. Nd(TFSA)₃ was obtained as a purplish fine powder and dried in vacuo < 0.1 MPa at 393 K for 24 h. The yield of the synthesized Nd(TFSA)₃ was > 92.0 %. [K(TFSA)]⁻ (Kanto Chemical Co., Inc., > 99.5 %), used as an electrolyte, was dried under vacuum (< 0.1 MPa) at 373 K for 24 h before measurement. The suspension was clearly transformed to the transparent purple solution after the reaction between the metallic Nd components and the amide acid. The solution was evaporated at 423 K in order to remove the unreacted acid components.

Four samples containing Nd(TFSA)₃ salts were prepared for the analysis of solvation number. Appropriate amounts of Nd(TFSA)₃ salts were dissolved in K[TFSA] at concentrations of 0.23, 0.30, 0.38, and 0.60 mol L⁻¹. The Nd(TFSA)₃, K[TFSA] and K(TFSA) salts were dried in vacuo before measurement.

**Figure 1.** The structure of metallic bis(trifluoromethyl-sulfonyl)amide; M(TFSA)ₓ = Li, Na and K.
and 0.45 mol kg\(^{-1}\), respectively. The samples containing each Nd(III) concentration were heated at 473 K before Raman spectroscopic measurement and the homogeneous liquid phase at 473 K was quenched into the quartz tube. The silver substrate with the hole on the center was used for Raman spectroscopic measurement with heating system. It is appropriate to use the silver substrate, because the thermal conductivity of silver was extremely high. The quenched Nd(III) sample was recovered and set on the center of the silver substrate in the glove box (H\(_2\)O and O\(_2\)<10 ppm). The heating system (LKM-10033, Japan High Tech Co., Ltd.) was based on Proportional-integral-derivative (PID) control method in this study. The temperature monitoring system was used for non-contact infrared radiation thermometer. Raman spectra (NRS-4100, JUSCO Corp.) were measured at elevated temperatures using a 532-nm laser for Nd. The calibration on a Raman spectroscopic measurement was confirmed for standard Si sample each time. The focusing of a laser beam was confirmed by the position which is inside approximately 5 \(\mu\)m from the edge of silver substrate. The appropriate gratings for the collection of the Raman spectra were 1800 mm\(^{-1}\) for Nd. These conditions were adopted to prevent fluorescence of the Nd ions, and the selection of the gratings is based on the results of our recent investigations.\(^{19,20}\) In order to analyze the solvation number of the Nd ions, and the selection of the gratings was therefore based on the results of our recent investigations.\(^{19,20}\)

**Electrochemical measurement.**—The K[TfSA] melts including Nd(III) (molar fraction: \(x_{Nd^3+}\) = 0.1) were applied as the electrolyte for the electrochemical experiment and this solution was dried at 373 K in a vacuum chamber (\(<0.1\) MPa) for 24 h. The water content of the electrolyte was measured at elevated temperatures, 473, 478, 483, 488 and 493 K. All of Raman spectra were accumulated 512 times in order to keep a sufficiently high S/N ratio. The overlapping Raman bands were deconvoluted into single component with a pseudo-Voigt function. Raman spectra were deconvoluted to extract single Raman bands. A single Raman band is evaluated according to

\[
\int_{-\infty}^{\infty} f_{\gamma}(v) \, dv = \int_{-\infty}^{\infty} f_{\mu}(v) \, dv + \int_{-\infty}^{\infty} f_{\sigma}(v) \, dv
\]

(1 – \(\gamma\)) is the fraction of the Lorentzian component. The intensity \(I\) of a single Raman band is evaluated according to

\[
I = I_L \cdot (1 – \gamma) + I_G \cdot \gamma
\]

where \(I_L\) and \(I_G\) denote integrated intensities of the Lorentzian and Gaussian components, respectively, and the parameter \(\gamma (0 < \gamma < 1)\) is the fraction of the Lorentzian component. The intensity \(I\) of a single Raman band is evaluated according to

\[
I = I_L \cdot (1 – \gamma) + I_G \cdot \gamma
\]

where \(I_L\) and \(I_G\) denote integrated intensities of the Lorentzian and Gaussian components, respectively. A nonlinear least square curve-fitting program was applied in this study.

**Results and Discussion**

**Analysis of the solvation number.**—Theoretical Raman spectrum (red line) for the optimized geometry of [TfSA\(^{-}\)] by DFT calculation and raw data (blue line) of Raman spectrum for Nd(III) sample at 478 K.

**Calculation methods.**—DFT calculation of the anion components of the K[TfSA\(^{-}\)] was carried out using the Gaussian09 program.\(^{25}\) The calculation on model of [trans-TfSA\(^{-}\)] and [cis-TfSA\(^{-}\)] ions were performed at the B3LYP/6-311G(d,p) level. Subsequently, frequency analysis was carried out on the optimized geometry. The hybrid functional B3LYP, which includes a mixture of Hartree-Fock exchange and DFT exchange-correlation, is the three-parameter hybrid method(B3)\(^{26}\) with non-local correlation provided by the Lee, Yang, and Parr (LYP) functional.\(^{27}\)

**Figure 2.** Theoretical Raman spectrum (red line) for the optimized geometry of [TfSA\(^{-}\)] by DFT calculation and raw data (blue line) of Raman spectrum for Nd(III) sample at 478 K.

**Figure 3.** The raw and deconvoluted bands of Raman spectrum for Nd(III) sample at 478 K. Solid line: raw data, dotted line: deconvoluted data at 740 cm\(^{-1}\), chain line: deconvoluted data at 750 cm\(^{-1}\).
respectively. The Raman spectra in this range were separated into two components at approximately 740 cm\(^{-1}\) and 751 cm\(^{-1}\). These two bands at 740 cm\(^{-1}\) and 751 cm\(^{-1}\) are caused by the free [TFSA]\(^{-}\) anion and the [TFSA]\(^{-}\) anion bound to Nd\(^{3+}\) ion, respectively. As can be seen from Fig. 4, a new band at 751 cm\(^{-1}\) was observed as a shoulder of the band at 740 cm\(^{-1}\). This new band intensified with increasing the concentration of Nd(III) in K[TFSA].

The solvation number of Nd(II) in K[TFSA] was evaluated using the similar analysis method suggested by Uemabayashi et al.\(^{13,14}\) The intensity of the deconvoluted Raman band of free [TFSA]\(^{-}\) anions in the bulk K[TFSA] was represented as \(I_f = I_f(c_T - c_M)\), where \(I_f\) and \(c_T\) were the molar Raman scattering coefficient and the concentration of free [TFSA]\(^{-}\) anions in the bulk, respectively. The \(c_T\) value was represented as \(c_T = c_T - c_b = c_T - n_cM\), where \(c_T\), \(c_b\), \(c_M\), and \(n\) expressed for the concentration of total [TFSA]\(^{-}\) anions, that of bound [TFSA]\(^{-}\) anions (solvated to the metal ion), that of metal ion, and the solvation number of the metal ion, respectively. By inserting \(c_f = c_T - c_b = c_T - n_cM\) into \(I_f = I_f(c_T - c_M)\), the following equation was obtained:

\[
I_f/c_M = I_f(c_T/c_M - n) \tag{1}
\]

The plot of \(I_f/c_M\) against \(c_T/c_M\) leads a straight line if the solvation number of the Nd cation in K[TFSA] is constant. Thus, the value of \(n\) is obtained using \(n = -\beta/\alpha\) from a slope of \(\alpha = I_f\) and an intercept of \(\beta = -I_fn\). The plots of \(I_f/c_M\) against \(c_T/c_M\) for K[TFSA] melts containing 0.23–0.45 mol kg\(^{-1}\) Nd(III) and Nd(II)/Nd(III) mixed samples, were represented in Figs. 5a and 5b, respectively. As shown in these plots, the strong linear relationship indicated that the number of the [TFSA]\(^{-}\) anion solvated to the Nd(II) and Nd(III) was maintained unchanged under the examined experimental conditions. Hence, the estimated \(n\) values of Nd(III) and Nd(II)/Nd(III) mixed sample were evaluated as \(n_{Nd(III)} = 5.02\) and \(n_{Nd(II)/Nd(III)} = 4.68\), respectively. This result suggested that the centered [Nd\(^{3+}\)] cation in K[TFSA] was solvated by five [TFSA]\(^{-}\) anions and the complexation of [Nd\(^{3+}\)(TFSA)]\(^{2+}\)-cluster existed in this system. In addition, considering that the molar ratio of mixed samples, Nd(II)/Nd(III) is 1/3, the result of \(n_{Nd(II)/Nd(III)} = 4.68\) allowed us to conclude that the solvation number of Nd(II) in K[TFSA] was \(n_{Nd(II)} = 4.06\). Therefore, the centered Nd\(^{3+}\) cation was found to be existed as the complex state of [Nd\(^{3+}\)(TFSA)]\(^{2+}\)-cluster in K[TFSA]. It was found that the solvation number of [TFSA]\(^{-}\) anion on the centered Nd\(^{3+}\) cation was smaller than that on the centered Nd\(^{3+}\) cation. This decrease in the solvation number would be due to the difference in ionic valence of the centered cation metals. This result was also consistent with the previous result using ILs that the diffusion coefficient\(^{20}\) of Dy(II) was larger than that of Dy(III) in [P\(_2\)C\(_5\)][TFSA]. Thus, the definite difference of the diffusion coefficient between Dy(II) and Dy(III) clusters would be due to the difference of electrostatic interaction between the centered metal ion and the surrounding [TFSA]\(^{-}\) anion by the solvation structure in [TFSA]-based ILs.

**Thermodynamic stability for [TFSA]\(^{-}\) isomerism.**—The temperature dependence of Raman spectra for Nd(III) in K[TFSA] \((\omega = 0.000, 0.033, 0.055\) and 0.075) was measured in order to evaluate the thermodynamic stability for [TFSA]\(^{-}\) isomerism. Temperature dependences of the deconvoluted Raman spectra for (a) neat K[TFSA], (b) Nd(II) in K[TFSA] \((\omega_{Nd(II)} = 0.033)\) in the frequency range of 370–440 cm\(^{-1}\) were shown in Figs. 6a and 6b, respectively. However, these peaks appeared in this figure were suitable for analysis of the [TFSA]\(^{-}\) isomer and these theoretical spectra for the optimized geometries of trans-[TFSA]\(^{-}\) and cis-[TFSA]\(^{-}\) were calculated by DFT method. The bands of trans-[TFSA]\(^{-}\) and cis-[TFSA]\(^{-}\) were assigned at 370 cm\(^{-1}\) and 380 cm\(^{-1}\), respectively. Therefore, Raman bands of 396 cm\(^{-1}\) and 403 cm\(^{-1}\) shown in Fig. 6 were corresponding to the trans-[TFSA]\(^{-}\) and cis-[TFSA]\(^{-}\) isomers, respectively. As for the temperature dependence of neat K[TFSA], the decreasing degree of the Raman intensity of trans-[TFSA]\(^{-}\) was larger than that of cis-[TFSA]\(^{-}\). This result revealed that the trans-[TFSA]\(^{-}\) isomers was enthalpically stable compared to cis-[TFSA]\(^{-}\) isomers. With regard to the Raman band of Nd(III) in K[TFSA] at \(\omega_{Nd(III)} = 0.033\), the peak area of the cis-isomers increased clearly in comparison with the band of neat K[TFSA]. This result indicated that the [TFSA]\(^{-}\) anion solvated in Nd(III) would be coordinated as the cis-isomers anion dominantly. That is to say, when [TFSA]\(^{-}\) bound to the Nd(III) in
K[TFSAs], the cis-[TFSAs]− isomers was more stable than the trans-[TFSAs]− isomers.

In order to perform a quantitative evaluation based on thermodynamics about [TFSAs]− isomers, the apparent thermodynamic quantities; ΔisoG, ΔisoH and ΔisoS were determined from van’t Hoff plots analysis.12 The parameters of ΔisoG, ΔisoH and ΔisoS from the trans-[TFSAs]− to cis-[TFSAs]− as a function of $x_{\text{Nd}}$ can be defined as follows. The first step, the apparent equilibrium constant, $K_{\text{ISO}}$ for the [TFSAs]− conformational isomerism from the trans-[TFSAs]− to cis-[TFSAs]− as a function $x_{\text{Nd}}$ was defined as $K_{\text{ISO}} = \frac{c_{\text{cis}}}{c_{\text{trans}}}$ Using this equilibrium constant, $K_{\text{ISO}}$, ΔisoG was represented as follows.

$$\Delta_{\text{ISO}}G = -RT \ln K_{\text{ISO}} = -RT \ln \left(\frac{c_{\text{cis}}}{c_{\text{trans}}}\right)$$

where $R$ and $T$ were a gas constant and an absolute temperature, respectively. In addition, ΔisoG can be expressed as ΔisoG = ΔisoH = ΔTisoS. Using the above van’t Hoff equation12 was obtained.

$$-RT \ln \left(\frac{c_{\text{cis}}}{c_{\text{trans}}}\right) = \Delta_{\text{ISO}}H/T - \Delta_{\text{ISO}}S - R \ln \left(\frac{c_{\text{cis}}}{c_{\text{trans}}}\right)$$

where $I_{\text{cis}}$ and $I_{\text{trans}}$ are the Raman intensity of cis-[TFSAs]− and trans-[TFSAs]−, respectively. $J_{\text{cis}}$ and $J_{\text{trans}}$ stand for the Raman scattering coefficients for the cis-[TFSAs]− and trans-[TFSAs]− isomers. The similar measurements were performed for the samples varied in $x_{\text{Nd}(III)}$ ($x_{\text{Nd}(III)} = 0.000, 0.033, 0.055, 0.075$). The van’t Hoff plot showed a good linear relation in all $x_{\text{Nd}(III)}$ concentrations and the concentration dependence was confirmed in the slopes clearly. Thus, it was suggested that the slopes, in other words, a value of $x_{\text{Nd}}$ was estimated by means of the relationship of $x_{\text{Nd}(III)} = 0$ and 0.33 are $x_{\text{Nd}(III)}$ (bulk) and $x_{\text{Nd}(III)}$ (Nd), respectively, as shown with the broken lines in Fig. 7. Thermodynamic quantities for [TFSAs]− of the bulk and the first solvation sphere of Nd(III) were listed in Table I. In the first solvation sphere of Nd(III), the value of ΔisoH(Nd) (−47.42 kJ mol$^{-1}$) increased to the negative value remarkably and implied that the cis-[TFSAs]− isomers were stabilized for enthalpy. This value of ΔisoH(Nd) contributed to the remarkable decrease in the value of ΔisoG(Nd) which greatly changed into the negative direction (−12.86 kJ mol$^{-1}$) compared with the ΔisoG(Nd). This result clearly showed that the cis-[TFSAs]− bound to the Nd(III) cation was preferred and the coordination state of [Nd(III)(cis-TFSAs)$_{\text{5}}$]$^{2-}$ was stable in K[TFSAs]. This stabilization of the cis-[TFSAs]− bound to the centered Nd(III) cation would be resulted from a charge-dipole interaction between the Nd(III) cation and cis-[TFSAs]− anion. The dipole moment of trans-[TFSAs]− and cis-[TFSAs]− estimated from DFT calculations at B3LYP/6-31+G(d,p) were 0.29 and 4.07, respectively. It was supposed that cis-[TFSAs]− isomer form a relatively large electric charge-dipole interaction to dysprosium ion, and form a more stable solvation structure, because the dipole moment of cis-[TFSAs]− was larger than that of trans-[TFSAs]−.

**Table I. Thermodynamic properties for the isomerism of [TFSAs]− from the trans- to cis-isomer in bulk and the first solvation sphere of Nd(III) in K[TFSAs] at 473 K.**

| Thermodynamic properties | bulk | Nd$^{3+}$ first solvation sphere |
|--------------------------|------|-------------------------------|
| ΔisoG [kJ mol$^{-1}$]    | −1.09| −12.86                        |
| ΔisoH [kJ mol$^{-1}$]    | 6.92 | −47.42                        |
| TΔisoS [kJ mol$^{-1}$]   | 8.04 | −34.56                        |

**Figure 7.** Apparent thermodynamic properties for the conformational isomerism of [TFSAs]− from the trans- to cis-isomer as a function of $x_{\text{Nd}}$ at 478 K.

**Figure 8.** Cyclic voltammogram of [Nd(III)[TFSAs]$_{\text{5}}$]$^{2-}$ ($x_{\text{Nd}} = 0.10$) in K[TFSAs] melts at 493 K using Pt electrode with different scan rates, 0.02 V s$^{-1}$ (chain line), 0.05 V s$^{-1}$ (dotted line) and 0.10 V s$^{-1}$ (solid line).
the reduction of Nd(III) was an irreversible process. As Raman spectroscopic analysis, [Nd(III)(TFSA)5]2− complex has five large [TFSA]− ligands and the reduction process would relatively slowly proceed by steric hindrance of such large ligands. Otherwise, the standard rate constant of Nd(III)/Nd(0) would be extremely small in this system. Londermeyer et al.30 also observed that no oxidation peak of Dy(0) in DMF and DMPT. The report concluded that the reduction process of Dy(III) was an irreversible system by electrochemical quartz crystal microbalance (EQQCM) analysis. As seen from Fig. 8, there were two reduction peaks around +1.0 V and +2.3 V in voltammogram. The reduction peak (A) around +2.3 V and the reduction peak (B) around +1.0 V would be based on the following two step reactions.

\[
[\text{Nd}^{3+} \text{(TFSA)5}^- \rightarrow [\text{Nd}^{2+} \text{(TFSA)5}^-] + \text{TFSA}^-] \quad [\text{peak (A)}] \tag{5}
\]

\[
[\text{Nd}^{2+} \text{(TFSA)5}^- + 3\text{e}^- \rightarrow \text{Nd} \text{(0)} + 5\text{[TFSA]^-}] \quad [\text{peak (B)}] \tag{6}
\]

Regarding each peak based on the cathodic Reactions 5 and 6, it was confirmed that the plot of the cathodic peak of the current density, \(i_t\) vs. the square root of the scan rate; \(v^{1/2}\) showed a good linear relations. This result indicated that both of two reduction reactions were controlled by the diffusion process; the mass transport under semi-infinite linear diffusion conditions. Elucidation of the diffusion behavior of [Nd(III)(TFSA)5]2− in K[TFSA] melts as well as the reduction behavior is necessary in order to perform the electrodeposition of Nd metal; thus, we evaluated the diffusion coefficients of [Nd(III)(TFSA)5]2− in K[TFSA] melts. The diffusion coefficients were analyzed by SI and SD methods. Initially, the SI curve (solid line) was obtained from convolutional voltammogram for [Nd(III)(TFSA)5]2− (\(\theta_{\text{cd}} = 0.1\)) in K[TFSA] melts as shown in Fig. 9. The diffusion coefficients were calculated from the limiting current, \(m^*\) according to the following equation.31

\[
m^* = nFAD_0^{1/2}C_0 \tag{7}
\]

where \(n\) is the number of electrons involved in the charge transfer reaction, \(F\) is the Faraday constant, \(A\) is the electrode surface area, and \(C_0\) is the bulk concentration of the electroactive species. As seen from Fig. 9, SD curve (chain line) was also obtained from the voltammogram by SD method. The value of \(W_p\); the width of a derivative neopolarographic peak at half its height, and \(e_p\); the current semi-derivative at the peak of the derivative neopolarogram, were determined from the SD curve. The diffusion coefficients were calculated using the following equations32 that were established in the case of the irreversible reaction:

\[
W_p = 2.94RT/an F \tag{8}
\]

\[
e_p = an^2F^2AV_o D_0^{1/2}/3.367RT \tag{9}
\]

The obtained diffusion coefficients by SD analysis were relatively close to the value derived from SI analysis. This congruence suggests high reliability of the calculated diffusion coefficients of [Nd(III)(TFSA)5]2− in K[TFSA] melts derived from SI and SD analyses.

Then, we evaluated the activation energy for diffusion, \(E_{a,D}\), using the diffusion coefficients with temperature dependence. The transfer of the metallic cations in the electrolysis was generally affected by the electrostatic interaction of the ion constituting metal complexes. Therefore, the diffusion of the metallic cations in K[TFSA] melts needs the activation energy more than the dissociation energy with surrounding anions constituting the metal complexes. The value of \(E_{a,D}\) is derived from the following Arrhenius rule:

\[
D = A^* \exp \left(-E_{a,D}/RT \right) \tag{10}
\]

where \(A^*\) is the frequency factor, \(R\) the gas constant, and \(T\) the absolute temperature. Arrhenius plot of the diffusion coefficient for [Nd(III)(TFSA)5]2− and [Nd(III)(TFSA)3]2− was shown in Fig. 10. The \(E_{a,D}\) values for [Nd(III)(TFSA)5]2− and [Nd(III)(TFSA)3]2− in K[TFSA] melts were 29.5 kJ mol\(^{-1}\)and 49.8 kJ mol\(^{-1}\), respectively. Thus, the \(E_{a,D}\) value of [Nd(III)(TFSA)5]2− was smaller than that of [Nd(III)(TFSA)3]2−. This result was consistent with the tendency of the diffusion coefficient estimated from the SI analysis. This result indicated that the electrostatic interaction with [TFSA]− anions of [Nd(III)(TFSA)5]2− was weaker than that of [Nd(III)(TFSA)3]2− due to smaller coulombic interactions and total electrowinning energy of Nd metal would lead to smaller consumption.

**Conclusions**

The solvation structures of the divalent and trivalent neodymium complexes in K[TFSA] were investigated by Raman spectroscopic analysis. From the analysis of Raman intensity range of 740–751 cm\(^{-1}\)for Nd(II)/Nd(III), the number of [TFSA]− anions solvated to Nd\(^{2+}\) was evaluated to be 4.06, therefore, Nd\(^{2+}\) cation existed as the state of \([\text{Nd}^{2+} \text{(TFSA)4}^2-]\) in K[TFSA] melts. According to the conventional analysis, the solvation number of Nd(III) in K[TFSA] was determined to be 5.02, therefore, Nd\(^{3+}\) cation existed as the state of \([\text{Nd}^{3+} \text{(TFSA)5}^2-]\) in K[TFSA] melts.

Moreover, the thermodynamic stability for [TFSA]− isomerism was evaluated from the van’t Hoff plots from the temperature dependence of the Raman spectra. The thermodynamic properties such as \(\Delta_{\text{iso}}G\), \(\Delta_{\text{iso}}H\) and \(\Delta_{\text{iso}}S\) for the isomerism of [TFSA]− from...
trans- to cis-isomer in bulk and the first solvation sphere of the centered Nd³⁺ cation in K[TfSA] were calculated in the range of 298–398 K. In the first solvation sphere of Nd³⁺ cation, ∆H(Nd) increased to the negative value (−47.42 kJ mol⁻¹) remarkably and revealed that the cis-[TfSA]⁻ isomers were stabilized for enthalpy. ∆H(Nd) contributed to the remarkable decrease in the ΔH(G(Nd)) and this result indicated that the cis-[TfSA]⁻ bound to Nd³⁺ cation was preferentially stabilized and the coordination state of [Nd(III)(cis-TfSA)₅]²⁻ became steady in K[TfSA] melts.

Furthermore, the diffusion behaviors of [Nd(II)(TfSA)₄]²⁻ and [Nd(III)(TfSA)₅]²⁻ complexes in K[TfSA] melts investigated by cyclic voltammogram. The result expressed that the reduction process of [Nd(III)(TfSA)₅]²⁻ proceeded in two steps by way of [Nd(II)(TfSA)₄]²⁻ in K[TfSA] melts. The semi-integral analysis was applied for the estimation of the diffusion coefficients and the activation energies for diffusion of [Nd(III)(TfSA)₅]²⁻ and [Nd(II)(TfSA)₄]²⁻. The diffusion coefficients of [Nd(II)(TfSA)₄]²⁻ were larger than those of [Nd(III)(TfSA)₅]²⁻ at all measurement temperatures and the activation energies for diffusion of [Nd(III)(TfSA)₅]²⁻ and [Nd(II)(TfSA)₄]²⁻ were 29.5 kJ mol⁻¹ and 49.8 kJ mol⁻¹, respectively. According to these results, the coordination number of [TfSA]⁻ anions around the centered Nd³⁺ ion for [Nd(II)(TfSA)₄]²⁻ would be smaller than for [Nd(III)(TfSA)₅]²⁻ due to the electrostatic interaction.

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References

1. J. Yang, X. Li, J. Lang, L. Yang, M. Wei, M. Gao, X. Liu, H. Zhai, R. Wang, Y. Liu, and J. Cao, Mater. Sci. Semicond. Process., 14, 247 (2011).
2. R. P. Rao and D. J. Devine, J. Lumín., 87, 1260 (2000).
3. C. W. Thiel, T. Böttger, and R. L. Cone, J. Lumín., 131, 353 (2011).
4. D. Yuan and Y. Liu, Mater. Chem. Phys., 96, 79 (2006).
5. N. Ono, M. Sagawa, R. Kasada, H. Matsui, and A. Kimura, J. Magn. Magn. Mater., 323, 297 (2011).
6. K. Murakawa, M. Ishii, and K. Machida, J. Alloys Compd., 466, 228 (2008).
7. Y. Matsuura, J. Magn. Magn. Mater., 303, 344 (2006).
8. H. Ota, M. Matsuyama, T. Yamada, T. Fujita, and S. Kawakami, Sep. Purif. Technol., 170, 417 (2016).
9. A. Nishimura, M. Matsuyama, H. Ota, and S. Kawakami, Electrochem. Commun., 65, 23 (2016).
10. R. Hagiwara, K. Tamaki, K. Kubota, T. Goto, and T. Nohira, J. Chem. Eng. Data, 55, 355 (2010).
11. K. Kubota, K. Tamaki, T. Nohira, T. Goto, and R. Hagiwara, Electrochim. Acta, 55, 417 (2010).
12. M. Mestdeth, M. Smirnov, P. Johansson, M. Chami, J. Grondin, L. Servant, and J.-C. Lassegues, J. Raman Spectrosc., 36, 762 (2005).
13. Y. Umebayashi, S. Mori, K. Fujii, S. Tsuzuki, S. Seki, K. Hayamizu, and S. Ishiguro, J. Phys. Chem. B, 114, 6513 (2010).
14. Y. Umebayashi, T. Mitsugi, S. Fukuda, T. Fujimori, K. Fujii, R. Kanazi, M. Takeuchi, and S. Ishiguro, J. Phys. Chem. B, 111, 13028 (2007).
15. A. Shirai, K. Fujii, S. Seki, Y. Umebayashi, S. Ishiguro, and Y. Ikeda, Anal. Sci., 24, 1291 (2008).
16. J.-C. Lassegues, J. Grondin, C. Aupeit, and P. Johansson, J. Phys. Chem. A, 113, 305 (2009).
17. K. Fujii, T. Nonaka, Y. Akimoto, Y. Umebayashi, and S. Ishiguro, Anal. Sci., 24, 1377 (2008).
18. Y. Umebayashi, K. Matsumoto, Y. Mune, Y. Zhang, and S. Ishiguro, Phys. Chem. Chem. Phys., 5, 2552 (2003).
19. M. Matsuyama, Y. Kami, H. Kata, and K. Tsunashima, J. Mol. Struct., 1048, 59 (2013).
20. M. Matsuyama, Application of Ionic Liquids on Rare Earth Green Separation and Utilization, 117 (2016).
21. N. Tsuda, M. Matsuyama, K. Tsunashima, and S. Kodama, ECS Trans., 50, 539 (2012).
22. M. Furlani, A. Ferry, A. Franke, P. Jacobsson, and B.-E. Mellander, Solid State Ionics, 113–115, 129 (1998).
23. M. Matsuyama, R. Kazama, and K. Tsunashima, J. Mol. Liq., 215, 308 (2016).
24. R. Kazama, M. Matsuyama, N. Tsuda, and K. Tsunashima, Electrochim. Acta, 113, 269 (2013).
25. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L.Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, C. Raghavachari, J. V. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Vreven, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

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