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Refractive Indices and Molar Refractivities of Molten Rare-Earth Trichlorides and Their Mixtures with Alkali Chlorides

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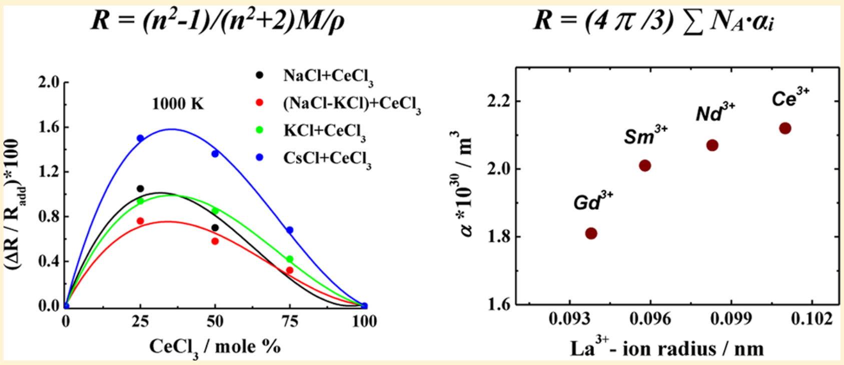
S *Supporting Information*



ABSTRACT: New experimental data on the refractive indices and molar refractivities of molten cerium, neodymium, samarium, and gadolinium trichlorides and $CeCl_3$−ACl, $SmCl_3$−ACl, Gd_3Cl−ACl (A = Na, 0.5Na−0.5K, K, and Cs) mixtures depending on the temperature and composition are reported. It is shown that the relative deviations of the molar refractivity of mixtures from their magnitudes inherent to the hypothetic ideal solutions increase as the radii of alkali metal cations rises. The difference in variation of the Ln^{3+}-ions electron polarizability with the atomic number or ionic radius is revealed for cerium and yttrium subgroups of the lanthanide row.

■ INTRODUCTION

The refractive index is one of the most informative optical properties that describe sufficiently the interaction of ions in the salt melts. The temperature and concentration dependencies of refractive index and molar refractivity of molten salt mixtures are necessary to understand the complexing phenomenon in ionic liquids at high temperatures[1,2] as well as to estimate the radiation contribution to the experimental values of thermal conductivity of "semitransparent" salt melts.[3−5] The electronic polarizability of ions calculated from the experimental values of refractive indices characterizes the degree of deformability of the outer electron shells of particles under the action of the effective local electric field. Thus, it is one of the basic fundamental characteristics in the evaluation of realistic intraionic interaction potentials for the computer simulation of the condensed substances structure by the method of molecular dynamics.[6] The electric polarizability of ions gives new insight into the complexing phenomenon of the molten salt. The refractive indices and molar refractivities of molten alkali halides and their mixtures were measured and discussed adequately in our earlier works.[7−11] A great body of information on the refractivity of salt melts containing rare-earth trichlorides was obtained by Japanese researchers,[12−17] although there are discrepancies between the data presented in aforementioned publications.

We have undertaken thorough systematic experimental studies of the refractive indices, molar refractivities, and electron polarizabilities of molten $NdCl_3$ and $LnCl_3$−ACl mixtures in which Ln = Ce, Sm, Gd and A = Na, (0.5Na−0.5K), K, Cs depending on the temperature and ionic composition to obtain new information on complexing in these unsymmetrical salt systems.

■ EXPERIMENTAL SECTION

Synthesis and Purification of the Salts. The molten mixtures of alkali and rare-earth chlorides are very sensitive to the action of water- and oxygen-containing atmosphere, which causes formation of unwanted impurities. Therefore, we concentrated our attention to prevent the occurrence of rare earth oxides and oxychlorides at all working stages.

Chemically pure sodium, potassium, and cesium chlorides (commercially produced) were carefully dried under vacuum at slow heating from 300 to 600 K and then were melted. These salts were subjected to a double zone recrystallization, after which they were cooled. The salts so prepared were stored in desiccators. An equimolar mixture of sodium and potassium chlorides was obtained in advance by fusing a needed quantity of components.

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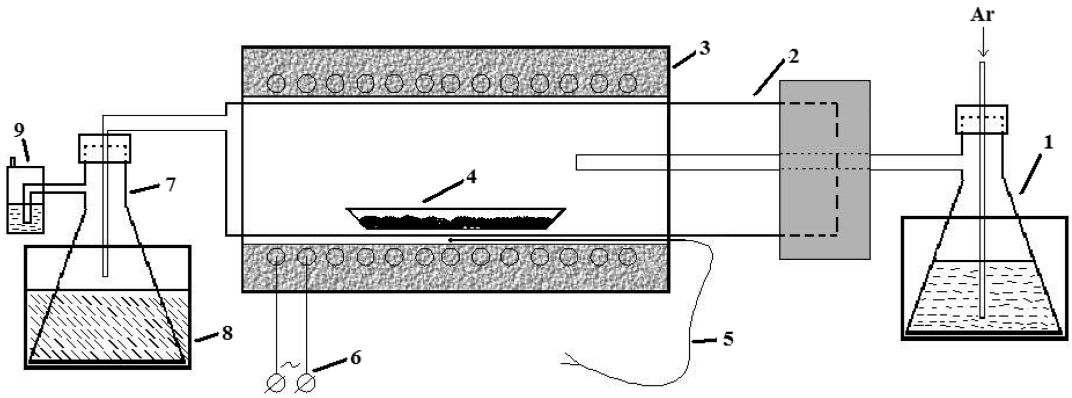

Figure 1. Reactor for synthesis of anhydrous rare-earth trichlorides: 1, vaporizer with CCl_4; 2, quartz tube; 3, electrical oven; 4, quartz boat with Ln_2O_3 or $LnCl_3{\cdot}nH_2O$; 5, thermocouple; 6, power source; 7, receiving vessel; 8, water cooler; 9, liquid seal.

Anhydrous rare earth trichlorides were synthesized through chlorination of lanthanide oxides (Ln_2O_3) or dehydration of hydrated lanthanide chlorides ($LnCl_3{\cdot}nH_2O$) prepared beforehand by the vapors of carbon tetrachloride (CCl_4) in a flow of dry high-purity argon.

$CeCl_3$ and $SmCl_3$ free of oxide and oxychlorides impurities were prepared in the following way: the $CeCl_3{\cdot}nH_2O$ and $SmCl_3{\cdot}nH_2O$ (n = 4−6) crystal hydrates were initially synthesized by dissolving high-purity CeO_2 and Sm_2O_3 commercially produced in hydrochloric acid with a subsequent evaporation of solution until solid substances formed which were put into a chlorination reactor as shown in Figure 1. These substances were dried in a flow of (CCl_4 + Ar) mixture at a slowly increasing temperature to 980 K ($CeCl_3$) or 850 K ($SmCl_3$). The synthesis cycle continued from 24 to 36 h.

Gadolinium and neodymium trichlorides were prepared using the direct chlorination of GdO-G grade Gd_2O_3 and NdO-E grade Nd_2O_3 by vapors of high-purity carbon tetrachloride in a flow of dry high-purity argon in the same reactor. In all cases the synthesis cycles continued from 24 to 36 h.

The purity of the $LnCl_3$ synthesized was controlled by IR and Raman spectroscopy, and thermal analysis, as well as dissolving the salts in distilled water. The refractive index measurements were performed using only the samples which did not show any vibrational bands attached to rare-earth oxychlorides,[18] suspended and precipitated particles in water solutions. The molten points of synthesized salts determined with the STA 449C Jupiter synchronous thermal analyzer (NETZSCH, Germany) agree with the most reliable literature data[19] within the experimental error (±2 K).

The rare-earth trichlorides so prepared were stored in desiccators. All subsequent operations were performed in a sealed glovebox under the atmosphere of pure dry nitrogen.

The absence of any possible traces of moisture and hydrolysis products was monitored before and after the experiment. Their IR spectra were recorded using the Tensor 27 FTIR spectrometer.

Method of Measuring Refractive Index. Different ways of the refractive index measurement were used to study chloride melts including the bent stick (cross-wires),[1,20] hollow prism,[12−17,21−24] liquid metal window reflection,[7−11] and interferometry[25−27] methods. In our work, the refractive indices of molten rare-earth trichlorides and their mixtures with alkali chlorides were measured by the ellipsometry method described thoroughly in refs 28 and 29. The measurements were carried out with the ellipsometer LEF - 3 M using the optical cell placed into the high-temperature sealed stainless steel chamber shown in Figure 2. The apparatus design was similar to that described earlier.[30] The measuring procedure was the same. The helium−neon laser with a wavelength of 632.8 nm served as a working monochromatic light source. During the measurements the temperature of the melt was constant within the limits of ±2 K. It was controlled with the Pt/Pt−Rh thermocouple located near the melt surface. The melts under study were housed in a crucible made from glassy carbon, which does not interact with the chloride melts in a wide temperature range. All measurements were conducted under a gaseous atmosphere of dried high-purity argon. The results of postexperimental chemical analysis showed that the mixture composition remained constant during measurements.

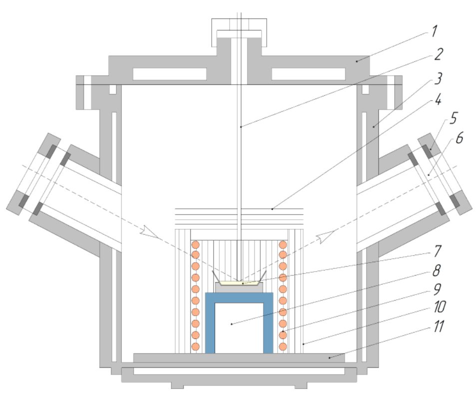

Figure 2. Sealed chamber for high-temperature optical research: 1, chamber cover; 2, thermocouple; 3, heat-resistant steel chamber body; 4, nickel heat shields; 5, annular vacuum gasket; 6, fused quartz window; 7, molten salt; 8, metal or quartz support; 9, nichrome heater; 10, ring-shaped nickel heat shields; 11, ceramic plate.

■ RESULTS AND DISCUSSION

Refractive Indices. The refractive indices n of the molten $NdCl_3$ and $CeCl_3$−ACl, $SmCl_3$−ACl, and $GdCl_3$−ACl mixtures were measured, dependent on the temperature and composition. The increase in temperature resulted in the decrease in the refractive indices according to the linear equation: $n = n_0 - aT$. The n_0 and a coefficients as well as the dispersion of the experimental values ($\pm\Delta n$) are listed in Table 1.

Figure 3 illustrates the refractive indices of molten alkali chlorides as a function of temperature. The correlation between

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Table 1. Refractive Indices of Molten Rare-Earth Trichlorides ($LnCl_3$) and Their Mixtures with Alkali Chlorides ($LnCl_3$−ACl, where A = Na, 0.5Na−0.5K, K, and Cs) as a Function of Temperature ($n = n_0 - aT$); Molar Refractivities (R) at 1100 K, and Their Relative Deviations from Additive Values ($\Delta R/R$)

$LnCl_3$ mole %	ΔT/K	n_0	$a \cdot 10^3$/K^{-1}	$\pm \Delta n \cdot 10^3$	$R_{(1100\ K)} \cdot 10^6$/m^3	$\Delta R/R_{add} \cdot 100$
			$NdCl_3$			
100	1053−1213	1.864	0.152	0.4	29.18	0
			NaCl−$CeCl_3$			
0	1083−1193	1.533	0.114	0.1	9.44	0
25	1073−1173	1.678	0.153	0.5	14.56	1.05
50	1073−1193	1.758	0.152	0.5	19.51	0.70
75	1073−1223	1.840	0.172	0.3	24.42	0.32
100	1103−1233	1.885	0.171	0.4	29.31	0
			(0.5Na−0.5K)Cl−$CeCl_3$			
0	953−1173	1.561	0.148	0.3	10.66	0
25	1043−1173	1.669	0.160	0.1	15.43	0.76
50	1073−1193	1.758	0.161	0.1	20.11	0.58
75	1073−1223	1.828	0.171	0.5	24.73	0.32
			KCl−$CeCl_3$			
0	1073−1193	1.568	0.163	0.1	11.78	0
25	1073−1193	1.645	0.155	0.7	16.32	0.94
50	1073−1203	1.731	0.159	0.5	20.71	0.85
75	1073−1173	1.744	0.142	1.8	25.03	0.42
			CsCl−$CeCl_3$			
0	1023−1173	1.633	0.189	0.7	16.55	0
25	1073−1173	1.667	0.162	0.1	20.36	1.5
50	1073−1213	1.729	0.164	0.4	23.24	1.36
75	1073−1223	1.811	0.170	1.5	26.30	0.68
			NaCl−$SmCl_3$			
25	973−1193	1.644	0.273	0.4	14.46	0.85
50	973−1173	1.783	0.315	0.6	19.35	0.60
75	973−1173	1.835	0.242	0.3	24.21	0.32
100	973−1173	1.917	0.211	0.4	29.03	0
			KCl−$SmCl_3$			
25	1073−1203	1.801	0.303	0.3	16.23	0.89
50	973−1203	1.893	0.316	0.2	20.56	0.82
75	973−1203	1.925	0.273	0.3	24.81	0.41
			CsCl−$SmCl_3$			
15	1023−1173	1.703	0.218	0.3	18.64	1.18
50	973−1203	1.740	0.179	0.1	23.08	1.27
75	973−1203	1.834	0.167	0.2	27.26	0.55
			NaCl−$GdCl_3$			
25	923−1173	1.662	0.147	0.1	14.36	1.04
50	923−1173	1.750	0.176	0.2	19.12	0.72
75	923−1173	1.753	0.175	0.3	23.84	0.35
100	923−1173	1.832	0.147	0.3	28.53	0
			KCl−$GdCl_3$			
25	1023−1173	1,638	0.153	0.4	16.08	0.91
50	923−1173	1.661	0.113	0.3	20.32	0.83
75	923−1173	1.937	0.293	0.3	24.44	0.41
			CsCl−$GdCl_3$			
15	1073−1173	1.707	0.230	0.4	18.54	1.12
50	923−1173	1.723	0.168	0.4	22.95	1.81
75	923−1173	1.751	0.133	1.0	25.68	0.98

their values found at 1173 K and the literature data[1,14,15,31] are presented in Figure 4. A good agreement is observed only for potassium and cesium chlorides, whereas the NaCl refractive indices reported by Bloom[1] and Japan researches[15,31] disagree with those determined in our experiments. The refractive indices of the molten equimolar NaCl−KCl mixture have been measured for the first time. In the temperature range of 1073 to 1173 K they are ∼1.0% above the values calculated using the refractive indices of components by the additivity law.

The measured refractive indices of molten cerium, neodymium, samarium, and gadolinium trichlorides are depicted in Figure 5 together with the data of Sasaki et al.[13] and Iwadate et al.[14,17] for $GdCl_3$ and $SmCl_3$ adapted to our working wavelength (632.8 nm). A gap between our data and the earlier data is likely due to some uncertainty of the empiric

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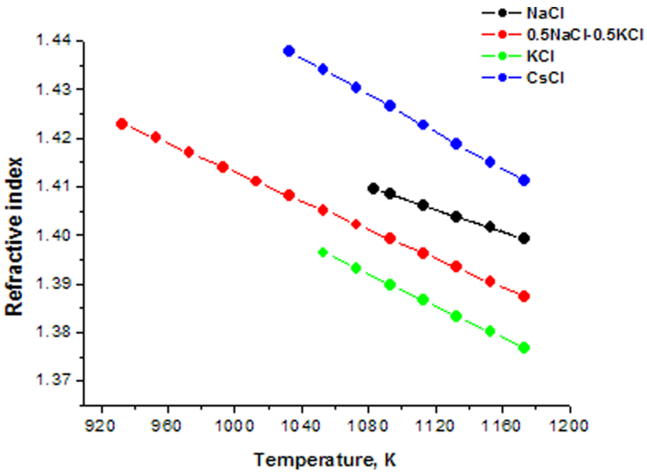

Figure 3. Temperature dependence of the molten alkali chlorides refractive indices.

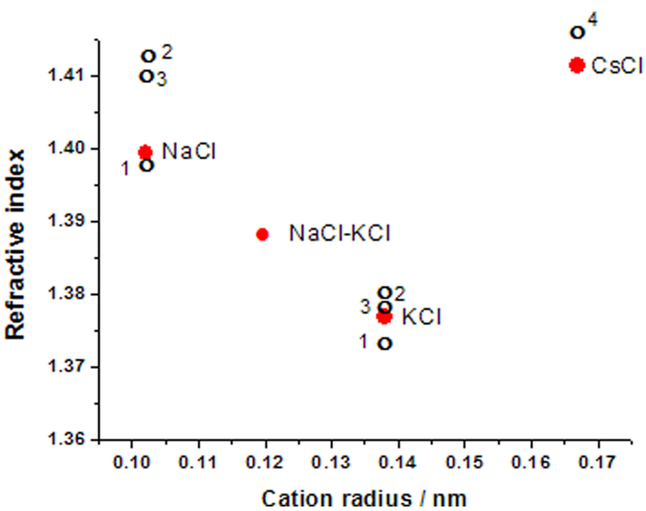

Figure 4. Relation between alkali chlorides refractive index and cation radius[32] at 1173 K. Red points 1,[1] 2,[15] 3,[31] 4,[14] our data.

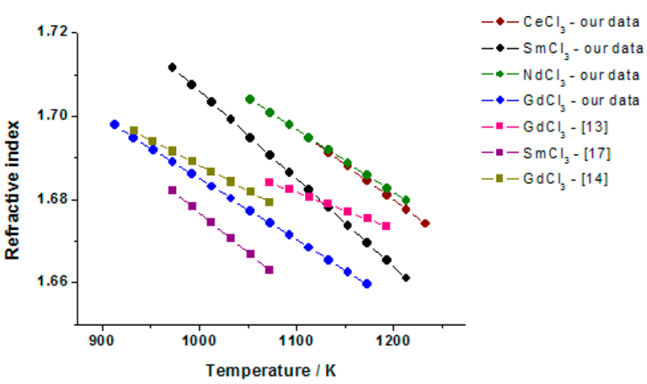

Figure 5. Temperature dependence of the molten rare-earth trichlorides refractive indices.

coefficients in the Cauchy dispersion equations presented in these publications.

The experimental values of the refractive indices for all studied melts identically change with temperature and composition. We refer to the temperature and concentration dependences of the refractive indices for ACl−$GdCl_3$ (A = Na, K, Cs) mixtures shown in Figures 6 and 7 for a typical example.

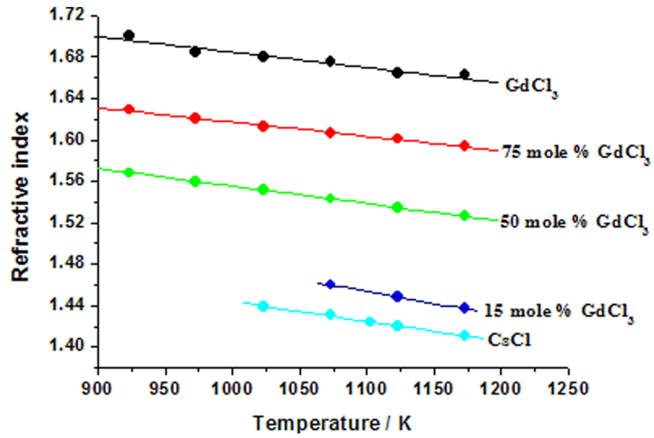

Figure 6. Temperature dependence of the refractive indices of molten CsCl−$GdCl_3$ mixtures.

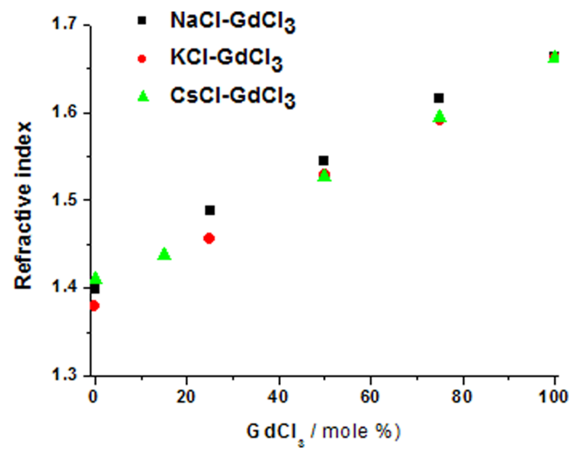

Figure 7. Concentration dependence of the refractive index of molten ACl−$GdCl_3$ mixtures at 1173 K.

It is evident from Figure 7 that the refractive indices of the binary ACl−$GdCl_3$ mixtures is closely proportional to the concentration of components.

Molar Refractivities. The experimental values of refractive indices n of the molten mixtures were used to calculate the molar refractivity

$$R = [(n^2 - 1)/(n^2 + 2)]\cdot(M/\rho) \quad (1)$$

where M and ρ are the molecular mass and density of substance, respectively. The calculations were performed with the density data published in refs 33 and 34. The molar refractivities of the molten salt mixtures under study, like the refractive indices, vary linearly with temperature in the manner indicated in Figure 8. Figure 8 illustrates where the data for KCl−$CeCl_3$ melts as a typical example. It is worthy of note that the molar refractivities of all molten salt compositions studied are slightly sensitive to the changes in temperature.

The molar refractivity is measure of average polarizability of one mole of substance. It is connected with the polarizability α_i of its constituent particles (molecules, atoms, ions) by the expression

$$R = (4\pi/3) \sum N_A \alpha_i \quad (2)$$

where N_A is the Avogadro's number. Its values at 1173 K are presented in Table 1.

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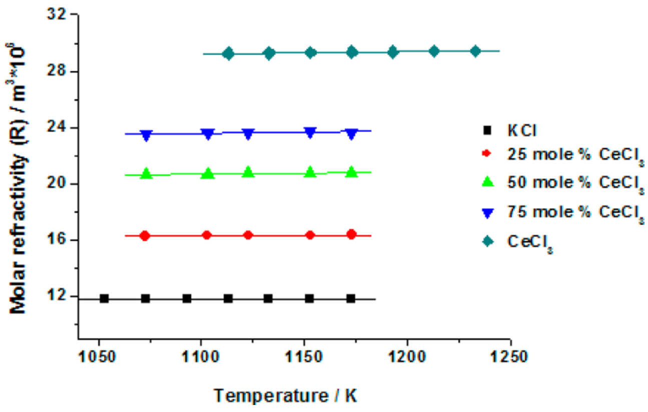

Figure 8. Temperature dependence of the molar refractivity of the molten KCl−$CeCl_3$ mixtures.

The molar refractivity dependence on the salt mixture composition appears to be the additive concentration function ($R = \sum X_i{\cdot}R_i$), if the polarizability of components does not undergo changes at mixing. The deviations of experimental molar refractivity values from those calculated by the additivity law indicate the presence of the components interaction which leads to a complex formation that is also revealed by other structure-sensitive methods.[35−41] Figure 9 demonstrates the molar refractivity variations with composition by the example of molten ACl−$GdCl_3$ mixtures. One can see that the salt mixtures molar refractivities deviate slightly from their ideal values calculated using the component refractivities by the additivity law, though the tendency in increasing departures manifests itself as alkali cation radius growths.

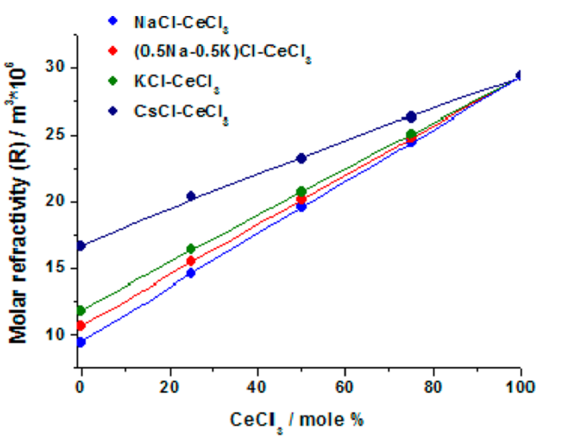

Figure 9. Concentration dependence of the molar refractivity of molten ACl−$CeCl_3$ mixtures at 1173 K.

As is evident from Figure 10, where the data for ACl−$SmCl_3$ (A = Na, K, Cs) are shown as a typical example, this regularity is the most conspicuous in the relative deviations of the molar refractivity $(R_{exp} - R_{add})/R_{add} = \Delta R/R_{add}$. As this takes place, the relation between the $\Delta R/R_{add}$ values and concentration is sharply defined. Moreover, the maximum relative deviations observed in the concentration range from 30 to 40 mol % of rare-earth trichloride rise as alkali cation radius increases (Figure 11) as well as the relative deviations of other molten salt mixtures molar properties (molar volume, enthalpy of mixing, heat capacity, electrical conductivity, viscosity, *etc.*) from their "ideal" values.[42−46] These data clearly demonstrate

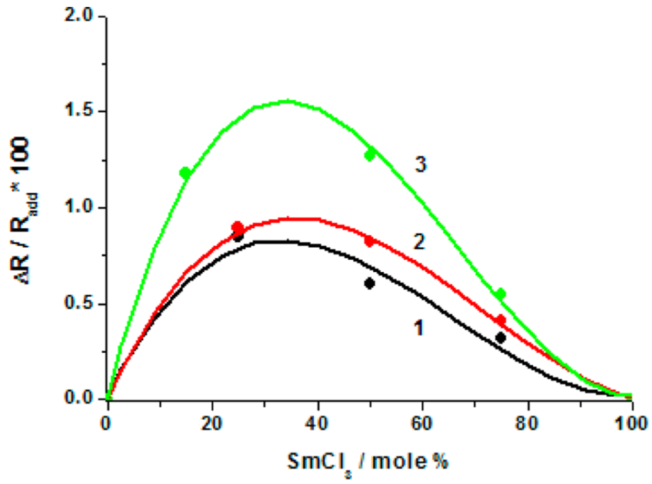

Figure 10. Relative deviation of molar refractivity from additive values for molten NaCl-$SmCl_3$ (1), KCl−$SmCl_3$ (2), and CsCl-$SmCl_3$ (3) at 1100 K.

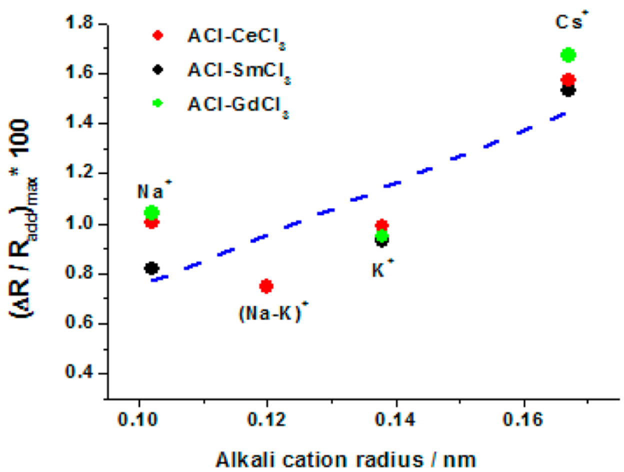

Figure 11. Maximum relative deviations of ACl−$LnCl_3$ melts molar refractivity from additive values at 1100 K as a function of alkali cation radius.

the occurrence of the $LnCl_n^{(n-3)-}$ complex particles in such salt mixtures. An octahedral coordination $(LnCl_6)^{3-}$ in molten salt systems containing lanthanide trichlorides follows from a large body of direct data on the diffraction and optical properties and structure modeling. Using molten $LaCl_3$−ACl (A = Li, Na, K, Cs) mixtures as an example, Rollet and Salanne[47] have noted the following trends deduced from model calculation and NMR data: (1) isolated species $LaCl_6^{3-}$ are obtained upon dilution in ACl; (2) the bigger is the alkaline ion, the stronger is the decrease of the first coordination number (La^{3+}−Cl^-). In addition to the above, the alterations of Raman and electron absorption spectra in $NdCl_3$−ACl melts with changing $NdCl_3$ concentration and alkali ions local environment reinforce essentially these trends. Indeed, the octahedral symmetry is distorted both with increasing $NdCl_3$ content[48] and with decreasing alkali ion radius in going from the $NdCl_3$−CsCl system to the $NdCl_3$−LiCl one.[49] In our case these results show up in elevating values of the relative deviation of molar refractivity from additivity and a slight displacement of the maximum deviation position in the direction of decreasing $LnCl_3$ concentration with increasing alkali metal ionic radius.

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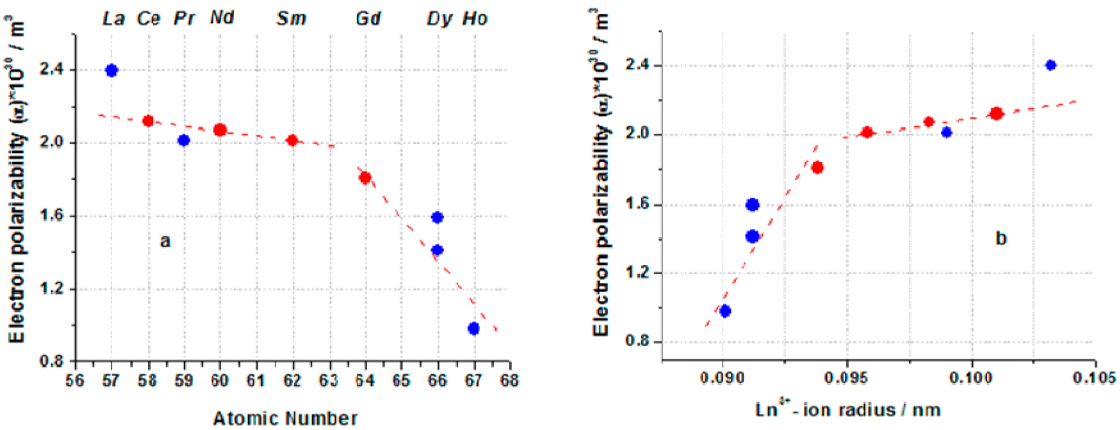

Figure 12. Ln^{3+} electron polarizability versus atomic number (a) and Ln^{3+} radius (b) at 1100 K. Red points, our data; blue points, literature data (see Table 2).

Electron Polarizabilities. Taking into account a complicated actual ionic composition of ACl−$LnCl_3$ melts, there is no way of adequate evaluation of the electron polarizability of each ion owing to the stubborn problem of a suitable reference system choice. Therefore, we restricted ourselves to the calculation of the Ln^{3+}−ions electron polarizability in molten rare-earth trichlorides at 1100 K using eq 2 and the rule of summing ion polarizabilities in a molecule: $\alpha(LnCl_3) = \alpha(Ln^{3+}) + 3\alpha(Cl^-)$. The value of $3.17 \cdot 10^{-30}$ m^3 recommended by Shirao et al.[21] was taken as the Cl^--ion electron polarizability. The calculated Ce^{3+}, Nd^{3+}, Sm^{3+}, and Gd^{3+} electron polarizabilities are shown as functions of the lanthanide atomic number and ion radius in Figure 12. These values correlate satisfactorily with the La^{3+}, Pr^{3+}, Dy^{3+}, and Ho^{3+} electron polarizabilities.[12,31,50] Indeed, the polarizability of these triple-charge ions are $2.40 \cdot 10^{-30}$,[12] $2.01 \cdot 10^{-30}$,[12] $1.41 \cdot 10^{-30}$[12] ($1.59 \cdot 10^{-30}$[31]), and $0.98 \cdot 10^{-30}$[50] m^3, respectively. When considering all assembly of the data presented, one can note the different character of the changing electron polarizability of the lanthanide triple-charge ions in the cerium and yttrium series showing a manifestation of the secondary periodicity and lanthanide contraction inherent to this group of chemical elements.

Moreover, the correlations are observed between the rare-earth ions polarizability and short-range structure parameters of molten $LnCl_3$, such as Ln^{3+}−Cl^- distances (a) and coordination numbers of chloride ions around the lanthanide ion (n) determined with the various X-ray and neutron diffraction methods.[51−55] Table 2 presents the relation between the electron polarizability of Ln^{3+}-ions and structural parameters of molten $LnCl_3$. From these data it is possible to make tentative estimates of both optical and structural characteristics of molten rare-earth trichlorides, which still require a further thorough examination.

The regularities observed show that the lanthanide contraction increases as the rare-earth metal atomic number rises, which results in a decrease of the lanthanide-ion electron polarizability.

■ CONCLUSION

The experimental data on the refractive indices of molten cerium, neodymium, samarium, and gadolinium trichlorides and $CeCl_3$−ACl, $SmCl_3$−ACl, Gd_3Cl−ACl (A = Na, 0.5Na−0.5K, K, and Cs) mixtures obtained with the ellipsometric method were used to calculate the molar refraction depending on temperature and composition. It is shown that the relative deviations of molar refractivity of mixtures from their magnitudes inherent to the hypothetic ideal solutions increase as the alkali metal ion radii rise. The Ln^{3+}-ions electron polarizability in molten lanthanide chlorides is constant in the temperature ranges studied: $CeCl_3$ (1113−1233 K), $NdCl_3$ (1053−1213 K), $SmCl_3$ (973−1213 K), and $GdCl_3$ (913−1173 K). The difference in their variations with atomic number or ionic radius is revealed for cerium and yttrium subgroups of the lanthanide row.

Table 2. Relation between the Ln^{3+}-ions Electron Polarizability and Parameters of Molten Rare-Earth Trichlorides ($LnCl_3$) Local Structure

$LnCl_3$	$r(Ln^{3+})$/nm[32]	$\alpha(Ln^{3+}) \cdot 10^{30}$/$nm^3$	$a(Ln^{3+}-Cl^-)$/nm	n
$LaCl_3$	0.1032	2.40[12]	0.289[54]	7.4
$CeCl_3$	0.1010	2.12 (our data)	0.281[55]	6.52
$NdCl_3$	0.0983	2.07 (our data)	0.277[56]	5.5
$PrCl_3$	0.0990	2.01[12]		
$SmCl_3$	0.0958	2.01 (our data)		
$GdCl_3$	0.0938	1.81 (our data)		
$TbCl_3$	0.0923		0.272,[54] 0.268[59]	6.3 5.7
$DyCl_3$	0.0912	1.41[12] 1.59[31]	0.265[58]	5.99
$HoCl_3$	0.0901	0.98[50]	0.276[54]	6.4
$ErCl_3$	0.0890		0.263[57]	5.8

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jced.6b00362.

Information on salt samples and the experimental data on the refractive indices of molten salt compositions studied(PDF)

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Notes

The authors declare no competing financial interest.

REFERENCES

(1) Bloom, H.; Peryer, B. M. Molten salt mixtures. VIII. The refractive index of molten salt mixtures and their molar refractivities. *Aust. J. Chem.* **1965**, *18*, 777−782.
(2) *Molten Salt Chemistry. An Introduction and Selected Applications*; Mamantov, G., Marassi, R., Eds.; D. Reidel Publishing Company: Dordrecht, Holland, 1987.
(3) Gardon, R. A review of radiant heat transfer in glass. *J. Am. Ceram. Soc.* **1961**, *44*, 305−312.
(4) Siegel, R.; Howell, J. *Thermal Radiation Heat Transfer*; Academic Press: New York, 1972.
(5) Firoz, S. H.; Sakamaki, T.; Endo, R. K.; Susa, M. Refractive index measurements of CaF_2 single crystal and melt by ellipsometry. *High Temp.-High Press.* **2008**, *37*, 163−173.
(6) Salanne, R. M.; Madden, P. A. Polarization effects in ionic solids and melts. *Mol. Phys.* **2011**, *109*, 2299−2315.
(7) Kochedykov, V. A.; Smirnov, M. V.; Khaymenov, A. P. Molar refractivities of molten alkali halides and their mixtures. Physical chemistry of salt melts and solid electrolytes. Trans.(Trudy) Inst. Electrochem. *Ural Centre, USSR Acad. Sci.* **1978**, *26*, 3−5 (in Russian).
(8) Kochedykov, V. A.; Khokhlov, V. A. Polarisability of ions in molten alkali halides and their mixtures. Euchem Conf. on Molten Salts. (Bad Herrenalb, Germany, August 21−26, 1994). *Abstracts* **1994**, B−25.
(9) Kochedykov, V. A.; Khokhlov, V. A. Polarizability of ions in molten alkali chlorides and their mixtures. *Melts (Rasplavy)* **1994**, *5*, 38−43 (in Russian).
(10) Kochedykov, V. A.; Khokhlov, V. A. Refractive indices and polarizability of alkali fluorides and their mixtures. *Melts (Rasplavy)* **2000**, *6*, 22−26 (in Russian).
(11) Kochedykov, V. A.; Khokhlov, V. A. Refractive indices and molar refractivities of lithium, sodium, potassium fluorides and their eutectic mixture. *Abstracts of the XI Conference on Physical Chemistry and Electrochemistry of Molten and Solid Electrolytes* **1998**, *1*, 28 (in Russian).
(12) Mochinaga, J.; Igarashi, K.; Aoki, T.; Iwadate, Y. Refractive Indices and Polarizability of Several Molten Rare Earth Chlorides. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3107−3110.
(13) Sasaki, Y.; Igarashi, K.; Mochinaga, J. Refractive index and molar volume of molten binary $GdCl_3$-NaCl and $GdCl_3$-KCl systems. *Denki Kagaku* **1982**, *50*, 226−231 (in Japanese).
(14) Iwadate, Y.; Mochinaga, J.; Kawamura, K. Refractive Indexes of Ionic Melts. *J. Phys. Chem.* **1981**, *85*, 3708−3712.
(15) Iwadate, Y.; Kikuchi, K.; Igarashi, K.; Mochinaga, J. Refractive Index of Molten $PrCl_3$-NaCl and $PrCl_3$-KCl Mixtures. *Z. Naturforsch., A: Phys. Sci.* **1982**, *37*, 1284−1288.
(16) Igarashi, K.; Iwadate, Y.; Mochinaga, J.; Kawamura, K. Refractive Index of Molten $LaCl_3$-KCl, $LaCl_3$- NaCl, and $LaCl_3$-$CaCl_2$ Mixtures. *Z. Naturforsch., A: Phys. Sci.* **1984**, *39*, 754−758.
(17) Iwadate, Y.; Shirao, K.; Fukushima, K. Electronic polarizability of a Sm^{3+} ion estimated from refractive indexes and molar volumes of molten $SmCl_3$. *J. Alloys Compd.* **1999**, *284*, 89−91.
(18) Hase, Y.; Dunstan, P.; Temperini, M. Raman Active Normal Vibrations of Lanthanide Oxychlorides. *Spectrochim. Acta. Part A* **1981**, *37*, 597−599.
(19) Laptev, D. M. *Physicochemical Properties of Lanthanide Chlorides and Their Interaction in the $LnCl_3$−$LnCl_2$ Systems*; D. Sci. (Phys._Math.) Dis.; Sibirian State Mining-Metallurg. Acad.: Novokuznetsk, 1996 (in Russian).
(20) Bloom, H.; Rhodes, D. C. Molten Salt Mixtures. Part 2. The Refractive Index of Molten Nitrate Mixtures and Their Molar Refractivities. *J. Phys. Chem.* **1956**, *60*, 791−793.
(21) Fukushima, K.; Iwadate, Y. Refractive indexes of molten $LaBr_3$ measured by goniometry. *J. Alloys Compd.* **1996**, *238*, L1−L3.
(22) Mochinaga, J.; Irisawa, K. Phase Diagrams of YCl_3-KCl, YCl_3-KCl, and YCl_3-KCl Systems, and Densities of Their Molten Mixtures. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 364−367.
(23) Shirao, K.; Fujii, Y.; Tominaga, J.; Fukushima, K.; Iwadate, Y. Electronic polarizabilities of Sr^{2+} and Ba^{2+} estimated from refractive indexes and molar volumes of molten $SrCl_2$ and $BaCl_2$. *J. Alloys Compd.* **2002**, *339*, 309−316.
(24) Mochinaga, J.; Sasaki, Y.; Igarashi, K.; Suda, T. Molar Volumes and Refractive Indices of Alkali Thiocyanates (RSCN, R = Li, Na, K, Rb, and Cs) in the Molten State. *Nippon Kagaku Kaishi* **1982**, *6*, 947−952 (in Japan)..
(25) Wendelöv, L. W.; Wallin, L.-E.; Gustafsson, S. E. Refractive Index Measurements of Molten Salts with Wave-front-shearing Interferometry I. Test of Apparatus and Procedure /. *Z. Naturforsch., A: Phys. Sci.* **1967**, *22*, 1180−1184.
(26) Karawacki, E.; Gustafsson, S. E. Refractive Index Measurements on Fused $LiNO_3$, $RbNO_3$, and $CsNO_3$ with a Modified Thermooptic Technique. *Z. Naturforsch., A: Phys. Sci.* **1976**, *31*, 956−959.
(27) Uchiyama, Y.; Karawacki, E. Refractivity of Molten Nitrates and Chlorides: Binary Mixtures Containing Cesium Ions. *Z. Naturforsch., A: Phys. Sci.* **1981**, *36*, 467−472.
(28) Azzam, M. A.; Bashara, N. M. *Ellipsometry and Polarized Light*; North-Holland Pub. Co.: Amsterdam, 1987.
(29) *Handbook of ellipsometry*; Tompkins, H. G., Irene, E. A., Eds.; William Andrew Publishing - Springer-Verlag GmbH & Co. KG.: Norwich- Heidelberg, 2005.
(30) Akashev, L. A.; Kononenko, V. I.; Kochedykov, V. A. Optical properties of liquid lanthanum. *Melts* **1988**, *2*, 313−317.
(31) Mochinaga, J.; Iwadate, Y. Refractive Indices, Molar Refractivities, and Electronic Polarizabilities of YCl_3-NaCl and $DyCl_3$-NaCl Mixture Systems in the Molten State. *Denki Kagaku* **1979**, *47*, 345−354.
(32) Shannon, R. D. Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1976**, *32*, 751−767.
(33) Potapov, A. M. Approximate evaluation of density of the fused mixtures of rare earth chlorides with alkali metal chlorides. *Melts (Rasplavy)* **2001**, *5*, 25−32 (in Russian)..
(34) Potapov, A. M. *Molten Salts−Data Organizer*, version 1.0; RU 2007613125; Informer Technologies, 2007.
(35) Mochinaga, J.; Ikeda, M.; Igarashi, K.; Fukushima, K.; Iwadate, Y. X-ray diffraction and Raman spectroscopic study on the short-range structure of molten $CeCl_3$. *J. Alloys Compd.* **1993**, *193*, 36−37.
(36) Photiadis, G. M.; Borresen, B.; Papatheodorou, G. N. Vibrational modes and structures of lanthanide halide−alkali halide binary melts $LnBr_3$-KBr (Ln = La, Nd, Gd) and $NdCl_3$- ACl (A = Li, Na, K, Cs). *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 2605−2613.
(37) Wasse, J. C.; Salmon, Ph. S. Structure of molten lanthanum and cerium tri-halides by the method of isomorphic substitution in neutron diffraction. *J. Phys.: Condens. Matter* **1999**, *11*, 1381−1396.
(38) Chrissanthopoulos, A.; Papatheodorou, G. N. Probing the structure of $GdCl_3$−KCl melt mixtures by electronic absorption spectroscopy of the hypersensitive f←f transitions of $Ho^{3+}$and by Raman spectroscopy. *Phys. Chem. Chem. Phys.* **2000**, *2*, 3709−3714.
(39) Uda, T.; Fujii, T.; Iwadate, Y.; Uehara, A.; Yamana, H. Raman spectroscopic study of rare earth chlorides in alkali chloride eutectic melts. *Z. Anorg. Allg. Chem.* **2013**, *639*, 765−769.
(40) Zakir'yanova, I. D.; Salyulev, A. B.; Khokhlov, V. A. Raman spectroscopy study of the phase transitions in rare-earth metal trichlorides. *Russ. Metall.* **2011**, *2011*, 754−759.
(41) Kalampounias, A. G. Picosecond dynamics from lanthanide chloride melts. *J. Mol. Struct.* **2012**, *103*, 125−130.
(42) Bloom, H. *The Chemistry of Molten Salts*; W.A. Benjamin, Inc.: New York, 1967.
(43) Danek, V. *Physico-chemical analysis of molten electrolytes*; Elsevier B.V.: Amsterdam, 2006.
(44) Minchenko, V. I.; Stepanov, V. P. *Ionic Melts. Elastic and Caloric Properties*; Ekaterinburg, UB RAS, 2008 (in Russian).

DOI: 10.1021/acs.jced.6b00362
J. Chem. Eng. Data XXXX, XXX, XXX−XXX

(45) Potapov, A.; Khokhlov, V.; Korosteleva, N. The Molar Volume of Molten Mixtures of MCl-$LnCl_2$ (M = Alkali Metals, Ln = Lanthanoides). *Z. Naturforsch., A: Phys. Sci.* **2008**, *63a*, 203−209.
(46) Gaune-Escard, M.; Bogacz, A.; Rycerz, L.; Szczepaniak, W.; Chemla, M.; Devilliers, D.; Vogler, M. Neodymium Chloride and Alkali Chlorides Mixtures: Calorimetric Investigation and Modeling. In Molten Salt Chemistry and Technology /. *Mater. Sci. Forum* **1991**, *73-75*, 61−70.
(47) Rollet, A.-L.; Salanne, M. Studies of the local structures of molten metal halides. *Annu. Rep. Prog. Chem., Sect. C: Phys. Chem.* **2011**, *107*, 88−123.
(48) Photiadis, G. M.; Brresen, B.; Papatheodorou, G. N. Vibrational modes and structures of lanthanide halide−alkali halide binary melts $LnBr_3$−KBr (Ln = La, Nd, Gd) and $NdCl_3$−ACl (A = Li, Na, K, Cs). *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 2605−2613.
(49) Fujii, T.; Nagai, T.; Sato, N.; Shirai, O.; Yamana, H. Electronic absorption spectra of lanthanides in a molten chloride: II. Absorption characteristics of neodymium(III) in various molten chlorides. *J. Alloys Compd.* **2005**, *393*, L1−L5.
(50) Shirao, K.; Iida, T.; Fukushima, K.; Iwadate, Y. Refractive indexes and electronic polarizabilities of molten $HoCl_3$−NaCl and $HoCl_3$−KCl mixtures. *J. Alloys Compd.* **1998**, *281*, 163−168.
(51) Wasse, J. C.; Salmon, P. S. Structure of molten trivalent metal chlorides. *Phys. B* **1998**, *241−243*, 967−969.
(52) Wasse, J. C.; Salmon, P. S. Structure of molten lanthanum and cerium tri-halides by the method of isomorphic substitution in neutron diffraction. *J. Phys.: Condens. Matter* **1999**, *11*, 1381−1396.
(53) Wasse, J. C.; Salmon, P. S. Structure of molten trivalent metal chlorides studied by using neutron diffraction: the systems $TbCl_3$, YCl_3, $HoCl_3$ and $ErCl_3$. *J. Phys.: Condens. Matter* **1999**, *11*, 9293−9302.
(54) Okamoto, Y.; Shiwaku, H.; Yaita, T.; Narita, H.; Tanida, H. Local structure of molten $LaCl_3$ by K-absorption edge XAFS. *J. Mol. Struct.* **2002**, *641*, 71−76.
(55) Matsuura, H.; Watanabe, S.; Sakamoto, T.; Kanuma, T.; Naoi, K.; Hatcho, M.; Kitamura, N.; Akatsuka, H.; Adya, A. K.; Honma, T.; Uruga, T.; Umesaki, N. Short-range structure of molten $CeCl_3$ and $NdCl_3$ determined by XAFS. *J. Alloys Compd.* **2006**, *408−412*, 80−83.
(56) Igarashi, K.; Kosaka, M.; Ikeda, M.; Mochinaga, J. X-ray Diffraction Analysis of $NdCl_3$ Melt. *Z. Naturforsch., A: Phys. Sci.* **1990**, *45*, 623−626.
(57) Iwadate, Y.; Iida, T.; Fukushima, K.; Mochinaga, J.; Gaune-Escard, M. X-Ray Diffraction Study on the Local Structure of Molten $ErCl_3$. *Z. Naturforsch., A: Phys. Sci.* **1994**, *49*, 811−814.
(58) Neilson, G. W.; Adya, A. K.; Ansell, S. Neutron and X-ray diffraction studies on complex liquids. *Annu. Rep. Prog. Chem., Sect. C: Phys. Chem.* **2002**, *98*, 273−322.
(59) Martin, R. A.; Salmon, Ph. S.; Barnes, A. C.; Cuello, G. J. Structure of molten $TbCl_3$ measured by neutron diffraction. *J. Phys.: Condens. Matter* **2002**, *14*, L703−L707.

DOI: 10.1021/acs.jced.6b00362
J. Chem. Eng. Data XXXX, XXX, XXX−XXX