Refractive Indices and Polarizabilities of Several Molten Rare Earth Chlorides

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Refractive indices of molten $LaCl_3$, $PrCl_3$, $NdCl_3$, $DyCl_3$, and YCl_3 were measured by the cylindrical lens method. The measurements were carried out with the lights of four wavelengths, and the refractive indices so obtained were represented by empirical equations as linear functions of temperature. From the data molar refractivities were calculated. The refractive indices at infinite wavelength were calculated by use of Cauchy's relation for dispersion, and electronic polarizabilities were obtained for the salt molecules in molten state, and also the electronic polarizabilities of La^{3+}, Pr^{3+}, Dy^{3+}, and Y^{3+} ions in the melts were obtained.

The refractive indices of molten salts are related to the polarizabilities, and especially the values extrapolated to infinite wavelength are directly related to the electronic polarizabilities of molecules or ions in the melts. But there are only a few available data of refractive indices for molten salts, because the experimental difficulties exist in such measurements. Zarzycki and Naudin[1] have reported the refractive indices of some alkali halides and alkali nitrates in molten states for the light of 546.1 nm, and Bloom *et al.* have reported the refractive indices[2] and other experimental data[3] of some nitrites, nitrates, chlorides, and binary chloride systems in molten states for the light of 589.3 nm, using the bent stick method. Marcoux[4,5] has measured the refractive indices of some gases in liquid and solid states and some molten ionic salts by the cylindrical lens method. Nakamura and Tanemoto[6] have also reported the refractive index of molten KCl measured by a He-Ne laser (632.8 nm).

In the present experiment, the refractive indices of molten $LaCl_3$, $PrCl_3$, $NdCl_3$, $DyCl_3$, and YCl_3 were measured by the cylindrical lens method with the lights of wavelengths, 656.3, 589.3, 486.2, and 434.1 nm.

Experimental

Preparations of $LaCl_3$, $PrCl_3$, $NdCl_3$, $DyCl_3$, and YCl_3. These rare earth chlorides were prepared by heating the mixtures of respective rare earth oxide and NH_4Cl according to the similar procedure in the previous paper.[7] Then, the crude chlorides were purified by sublimation, and their purities are shown in Table 1. The YCl_3 crystal had the similar purity as in the previous paper.[7]

Measurements of Refractive Indices. The apparatus used is based on that reported by Marcoux,[5] which measures the position of a focal point with a cylindrical lens. The schematic diagram of the apparatus is shown in Fig. 1, in which D is a transparent quartz cylinder tube of about 7 mm diameter. The distance between the center of the quartz tube and the position of the focal point depends on the refractive index of a liquid in the quartz tube. The distances were measured with a microscope by the precision of 1/100 mm for the several reference liquid materials of known refractive indices. The refractive index of a molten salt, therefore, can be obtained from the calibration curves in which the refractive indices of the reference materials were plotted against the measured distances. The calibration curves were drawn from the observed values at room temperature for CH_2I_2, $C_{10}H_7Br$, and CS_2 as the reference liquid materials, because the coefficient of expansion of quartz is very small (5.5×10^{-7}/deg). As the light source, a monochromator of UV-VIS spectrophotometer(HITACHI 139) was used, and the wavelengths

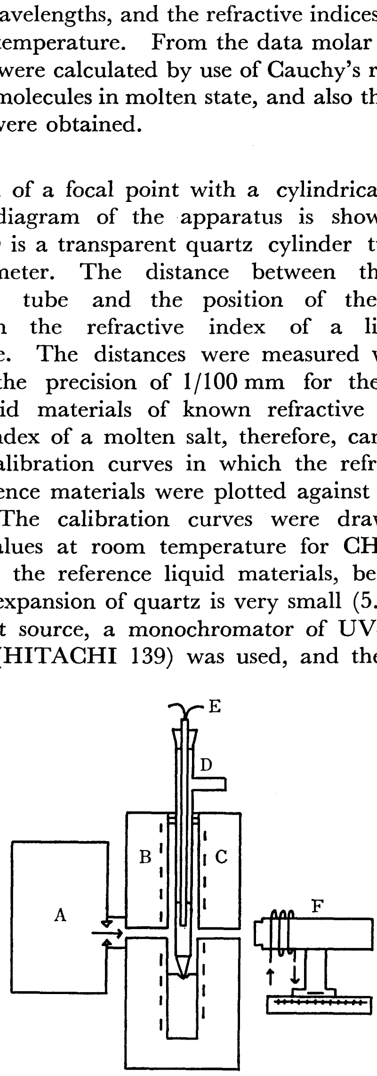

Fig. 1. Apparatus for measuring the refractive index of molten salts.
A: monochromator, B: electric furnace, C: Kanthal wire, D: quartz cell, E: C. A. thermocouple, F: microscope.

TABLE 1. IMPURITIES IN $LaCl_3$, $PrCl_3$, $NdCl_3$, AND $DyCl_3$

$LaCl_3$[a)]		$PrCl_3$[b)]		$NdCl_3$[b)]		$DyCl_3$[a)]	
Element	Content (ppm)	Element	Content (ppm)	Element	Content (ppm)	Element	Content (ppm)
Ce	<30	La	<30	La	<60	Y	60
Pr	110	Ce	<20	Ce	<60	Tb	<15
		Nd	<15	Pr	<20	Ho	<15
		Sm	<15	Sm	<15	Er	<15
				Eu	<20		

a) Emission spectrographic analysis. b) Fluorescence X-ray analysis.

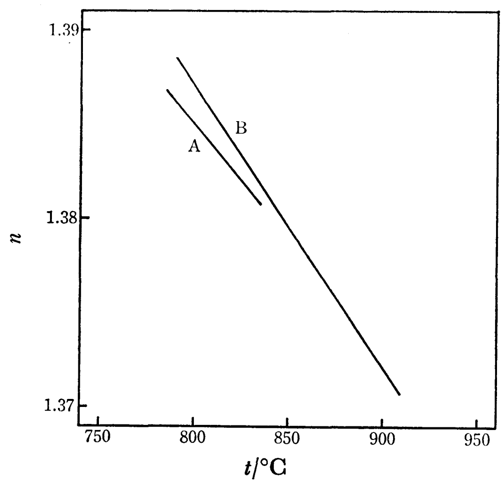

Fig. 2. Refractive indices of molten KCl (589.3 nm). A: Literature,[2] $n=1.481-1.2\times10^{-4}\,t$, (785—835 °C), B: this work, $n=1.507-1.5\times10^{-4}\,t$, (790—909 °C).

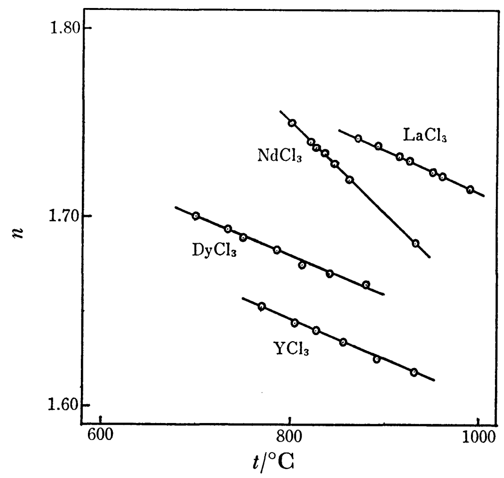

Fig. 3. Refractive indices of $LaCl_3$, $NdCl_3$, $DyCl_3$, and YCl_3 melts at 486.2 nm.

of lights used in this measurements were C(656.3 nm), D (589.3 nm), F(486.2 nm), and G(434.1 nm) lines. The refractive indices of the molten KCl observed in this apparatus were in fair agreement with the values in literature[2] as shown in Fig. 2.

Results and Discussion

As $PrCl_3$ and $NdCl_3$ melts have the absorption bands in the measured wavelengths, the refractive indices of $PrCl_3$ melt were measured at 656.3, 589.3, and 434.1 nm, and those of $NdCl_3$ melt at 486.2 nm only. The temperature dependence of refractive indices for these molten rare earth chlorides were linear at respective wavelength in the measured range of temperature. The results obtained at 486.2 nm are shown in Fig. 3. From the measured data, the refractive indices were represented by use of the method of least-squares as functions of temperature. The results are given in Table 2. In Table 2, σ is the standard error of estimate in refractive index equation. The relations of the refractive indices of $LaCl_3$, $PrCl_3$, $DyCl_3$, and YCl_3 melts *vs.* wavelength are shown in Fig. 4, in which the refractive indices slightly decrease in longer wavelength region, whereas in shorter wavelength region the dispersions of the refractive indices for $LaCl_3$, $PrCl_3$, and YCl_3 melts are observed.

Molar refractivity is one of the characteristic properties and is given by the following equation,

$$R_\lambda = \{(n_\lambda^2-1)/(n_\lambda^2+2)\}\times V_m,$$

where R_λ is the molar refractivity of the molten salt in cm^3, n_λ the refractive index of the molten salt for the light of wavelength λ, V_m the molar volume of the molten salt at the measured temperature, and λ represents C, D, F, or G line. The molar refractivities calculated are shown in Table 3. The molar refractivities are almost independent of temperature, and therefore the results in Table 3 are the averaged values over the measured temperature range.

The refractive indices at infinite wavelength can be calculated by Cauchy's approximate relation,

$$n_\lambda = A + B/\lambda^2,$$

where n_λ is the refractive index, A and B the constants for respective melt, and λ the wavelength. The electronic polarizabilities of molecules in a melt are given by the following equation,

$$\alpha_\infty^m = \{3/(4\pi N)\}\{(n_\infty^2-1)/(n_\infty^2+2)\}V_m,$$

where α_∞^m is the electronic polarizability of molecule in the melt, N Avogadro number, V_m the molar volume of the melt, and n_∞ the value of n_λ at $\lambda=\infty$. The obtained values of n_∞ and α_∞^m are shown in Table 4, in which n_∞ were calculated by the method of least-squares. As shown in Table 4, the order of magnitude in the electronic polarizabilities for the molten rare earth chlorides is in agreement with the order of the radii of cations contained in the molecules, and this fact satisfies the result of lanthanide contraction. The

Table 2. Refractive index equations ($n=a+b\times10^{-3}\,t$, t: °C)

	Wavelength (nm)	a	b	Temp range (°C)	σ ($\times10^{-2}$)
$LaCl_3$	434.1	2.1858	−0.4701	870—989	0.57
	486.2	1.9446	−0.2320	870—990	0.32
	589.3	1.8916	−0.1843	915—993	0.40
	656.3	1.9554	−0.2521	875—990	0.36
$PrCl_3$	434.1	2.0629	−0.3687	789—933	0.27
	589.3	2.0180	−0.3384	808—934	0.26
	656.3	1.9951	−0.3313	806—928	0.15
$NdCl_3$	486.2	2.1433	−0.4909	800—932	0.20
$DyCl_3$	434.1	1.9360	−0.3241	704—795	0.27
	486.2	1.8655	−0.2339	702—880	0.21
	589.3	1.8396	−0.2159	662—880	0.18
	656.3	1.8100	−0.1870	750—890	0.22
YCl_3	434.1	1.7685	−0.1339	721—934	0.10
	486.2	1.8137	−0.2099	768—932	0.14
	589.3	1.7788	−0.1804	768—928	0.11
	656.3	1.7667	−0.1585	788—925	0.19

Table 3. Molar refractivities (cm^3)

	R_G	R_F	R_D	R_C	Temp range (°C)
$LaCl_3$	31.7	31.2	30.9	30.9	900—980
$PrCl_3$	30.8	—	30.2	29.7	800—920
$NdCl_3$	—	30.0	—	—	800—920
$DyCl_3$	28.7[a]	28.6	28.2	28.0	700—880
YCl_3	28.3	27.6	27.3	27.3	740—780

a) 720—780 (°C).

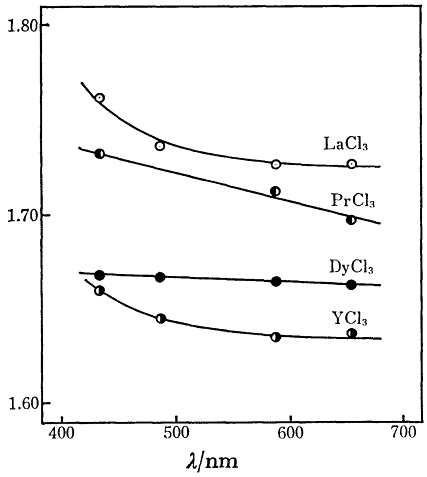

Fig. 4. Variation of the refractive index with wavelength.
○: $LaCl_3$ at 900 °C, ◐: $PrCl_3$ at 900 °C, ●: $DyCl_3$ at 800 °C, ◑: YCl_3 at 800 °C.

differences in electronic polarizabilities of molecules, therefore, are equal to those of cations, because the rare earth chloride molecules have chloride ion as a common anion. The values of polarizabilities for chloride ion in crystal at λ=589.3 nm(D-line) were reported by Tessman *et al.*[8] and by Kordes[9] to be 2.96 and 2.72 ($\times 10^{-24}$ cm^3), respectively, while that reported by Böttcher[10] for the same ion and wavelength in aqueous solution was 3.00×10^{-24} cm^3. The polarizabilities (α_D) of the rare earth cations in molten state calculated approximately using the above polarizabilities of chloride ion are shown in Table 5. Tessman *et al.*[8] have reported that the electronic polarizability was 2.97 ($\times10^{-24}$ cm^3) for chloride ion in crystal, and Böttcher[11] reported the value 2.60 ($\times$ 10^{-24} cm^3) for chloride ion in aqueous solution. The electronic polarizabilities (α_∞) of the rare earth cations in molten state approximately calculated using these values are shown in Table 6. The values in Tables 5 and 6 were calculated by the following equation,

$$(n_\lambda^2-1)/(n_\lambda^2+2) = (4\pi/3)\sum N_i\alpha_{\lambda,i},$$

where N_i is the number of i-th ion per unit volume, and $\alpha_{\lambda,i}$ the polarizability of i-th ion at wavelength λ. According to Cauchy's relation, the longer the wavelength of light used in measurement is, the less polarizability of ion is obtained. The values of chloride ion in aqueous solution reported by Böttcher[10,11] are not appropriate for the estimation in molten state.

Table 4. n_∞ and α_∞^m of the rare earth chlorides in molten state

	Temp (°C)	Refractive index at $\lambda=\infty$ n_∞	Electronic polarizability of molecule α_∞^m ($\times10^{-24}$ cm^3)
$LaCl_3$	920	1.696	11.91
	980	1.695	12.05
$PrCl_3$	820	1.702	11.52
	920	1.672	11.51
$DyCl_3$	720	1.663	10.92
	880	1.628	10.85
YCl_3	800	1.617	10.59
	920	1.594	10.50

Table 5. Polarizabilities of rare earth cations in molten state (α_D) calculated from data of chloride ion in literatures ($\times10^{-24}$ cm^3)

Rare earth cation	Polarizability (α_D)[a] calculated from		
	Tessman's value	Kordes' value	Böttcher's value
La^{3+}	3.38	4.10	3.26
Pr^{3+}	3.10	3.82	2.98
Dy^{3+}	2.31	3.03	2.19
Y^{3+}	1.95	2.67	1.83

a) The temperature ranges are the same as those in Table 3.

Table 6. Electronic polarizabilities of rare earth cations in molten state (α_∞) calculated from data of chloride ion in literatures ($\times10^{-24}$ cm^3)

Rare earth cation	Electronic polarizability (α_∞) calculated from		Temp (°C)
	Tessman's value	Böttcher's value	
La^{3+}	3.00	4.11	920
Pr^{3+}	2.60	3.71	920
Dy^{3+}	1.94	3.05	880
Y^{3+}	1.59	2.70	920

The electronic polarizabilities of rare earth ions in molten state seem to be close to the values estimated from the chloride ion polarizability by Tessman *et al.*[8] *viz.* 2.97×10^{-24} cm^3. The estimations seem to yield good approximate polarizabilities of rare earth cations in molten state, though the chloride ion polarizabilities in different conditions were used.

Since the cylindrical lens method tends to give an error in the measurement of the focal distance for a substance with a large refractive index, it is desirable that the goniometry method reported by Nakamura and Tanemoto[6] is used.

Calculations were carried out with the computers in the University of Tokyo and Chiba University.

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