The Near-infrared Absorption Spectra of Lanthanide Chlorides Dissolved in Molten LiCl-NaCl-KCl Eutectic

By Masato MAMIYA

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The observation of the absorption spectra of fused metal salt with[1-12] or without[13-15] the addition of a diluent has recently become a powerful means for analyzing or identifying the metallic constituents of the salts.

This investigation is concerned with the determination of molar absorptivities for significant absorption bands from the near-infrared absorption spectra of lanthanide chlorides dissolved in molten alkali chloride eutectic solvents.

A previous report on the spectra of several lanthanide chlorides in a fused LiCl-KCl eutectic solution was limited to the visible and ultraviolet regions.[7] Similar studies in the visible region have been carried out in molten LiF-KF[5,6] and in $LiNO_3$-KNO_3 eutectics.[2] Recently, the near-infrared absorption spectra of lanthanides in molten $LiNO_3$-KNO_3 eutectic and in a deuterium perchloric acid solution have been observed by Carnall and his associates.[9]

There are, of course, many different fused salt systems in which a spectrophotometric study could be made; most of the work has thus far been done in alkali fluorides, chlorides, nitrates and sulfates. In this paper, the fused LiCl-NaCl-KCl eutectic was used because of the advantage of its optical transparency in the near-infrared region and its relatively low melting point (about 333°C).

Several characteristic absorption bands of praseodymium, neodymium, samarium, dysprosium holmium, erbium, thulium and ytterbium in this medium were observed in the region from 0.8 to 2.6 μ. These near-infrared data will be compared with similar results which have been obtained in molten nitrate[9] and deuterium oxide solutions.[16]

Experimental

Apparatus. — The spectral measurements were made using a Cary recording spectrophotometer, Model 14M, equipped with the high-temperature cell assembly described in a previous report by the present author.[12] The furnace was designed for high temperature investigation in the near-infrared region. Temperature control to ±2°C at 400°C was achieved with an electronic thermocouple control unit on a Chino automatic thermometer, Modell 600, and temperatures were measured with a platinum-platinum rhodium thermocouple (0°C cold junction) placed near the sample. The optical absorption cells used were fused quartz cells with 10.0 and 2.0 mm. light paths.

Alkali Chlorides Eutectic. — In most of the reported spectrophotometric studies of solutions of several chloride salts, a LiCl-KCl mixture with a composition close to that of eutectic (about 59 mol.% LiCl m. p. 350°C) has been used. The solvent used in this study was a eutectic mixture of LiCl-NaCl-KCl (49.0 - 17.3 - 33.7 mol.%, m. p. 333°C) which melts at a lower temperature than the above binary mixture.

In order to obtain clear sample solutions, free of oxidation and precipitation products, the eutectic had to be anhydrous. Since water has an appreciable solubility in the eutectic, even at 500°C, it is very difficult to achieve complete dehydration by vacuum fusion alone. Various techniques have been described for preparing anhydrous melts, techniques which involve treatment while dry hydrogen chloride gas is blown in to the molten salts.[3,17] The pure alkali chlorides eutectic pellets were dehydrated and purified by the bubbling method proposed by Gruen and McBeth.[2]

Sample Preparation.—The lanthanides used were obtained commercially in the form of oxides with a stated purity higher than 99.0%. The dried

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[1] D. M. Gruen, *Nature*, **178**, 1181 (1956).

[2] D. M. Gruen, *J. Inorg. & Nucl. Chem.*, **4**, 74 (1957).

[3] C. R. Boston and G. P. Smith, *J. Phys. Chem.*, **62**, 409 (1958).

[4] D. M. Gruen and R. L. McBeth, *J. Inorg. & Nucl. Chem.*, **9**, 290 (1959).

[5] J. P. Young and J. C. White, *Anal. Chem.*, **31**, 1658 (1959).

[6] J. P. Young and J. C. White, ibid., **32**, 799 (1960).

[7] C. V. Banks, M. R. Heusinkveld and J. W. O'Langhlin, ibid., **33**, 1235 (1961).

[8] D. M. Gruen and R. L. McBeth, *J. Phys. Chem.*, **66**, 57 (1962).

[9] W. T. Carnall, *Anal. Chem.*, **34**, 786 (1962).

[10] W. T. Carnall, D. M. Gruen and R. L. McBeth, *J. Phys. Chem.*, **66**, 2159 (1962).

[11] W. T. Carnall, ibid., **67**, 1206 (1963).

[12] M. Mamiya, *J. Chem. Soc. Japan, Ind. Chem. Sec. (Kogyo Kagaku Zasshi)*, **66**, 1625 (1963).

[13] E. Rhodes and A. R. Ubbelohde, *Proc. Faraday Soc.*, **A251**, 156, (1959).

[14] G. P. Smith and C. R. Boston, *Discussions Faraday Soc.*, **32**, 14 (1961).

[15] B. Cleaver, E. Rhodes and A. R. Ubbelohd, ibid., **32**, 22 (1961).

[16] M. Mamiya, *Molecular Structure and Spectroscopy*, **A**, **402**, Tokyo (1962); *Japan Analyst (Bunseki Kagaku)*, **11**, 1262 (1962).

[17] B. R. Sundheim and J. Greenberg, *J. Chem. Phys.*, **66**, 1056 (1958).

lanthanide oxides were weighed and then dissolved in a minimum of hydrochloric acid. These solutions were evaporated to dryness by heating them at 200°C for two hours under an atmosphere of flowing nitrogen gas. A weighed amount of the appropriate lanthanide chloride was placed in the spectrophotometer cell with the desired amount of the purified eutectic pellets, and the cell was heated to 400°C under the above conditions.

The lanthanide dissolved when the molten eutectic solution was stirred with bubbles of dry nitrogen gas from a tube inserted in the cell. If water and oxygen remain in the eutectic solvent, lanthanide chloride reacts with these, water, and oxygen to form lanthanide oxychloride, which is not soluble in the molten salt solution. This insoluble matter may, however, be brought into the solution by the addition of a few grams of ammonium chloride. This salt acts as an acid in the chloride melt and dissolves the insoluble lanthanide compound when nitrogen is bubbled at 450°C for 1 to 2 hr.

Figure 1 shows the absorption characteristics of the pure LiCl-NaCl-KCl eutectic melt in a 10.0 mm. fused quartz cell for the range between 0.8 and 2.6 μ at 350°C, together with the absorption characteristics of water, deuterium oxide, and $LiNO_3$-KNO_3 eutectic in this range. The pure alkali chloride eutectic mixture has no absorption band, and other solvents absorb strongly in the near-infrared region, but the deuterium oxide and molten alkali nitrate solvents were seen to have a wide range of transparency. The absorption increase in alkali chloride eutectic (shown in Fig. 2) at wavelengths shorter than 1.0 μ arises from the optical cell etching caused by the impurity in the eutectic salts at temperatures above 600°C, but below 550°C the polished quartz cell was not etched, even after repeated measurements. The effect of temperature on a blank run is not observed at temperatures below 500°C, but at high temperatures, above 550°C the polychromatic radiation from an emitting eutectic medium and furnace is accepted by the signal amplifier, resulting in increased transmittance signals.

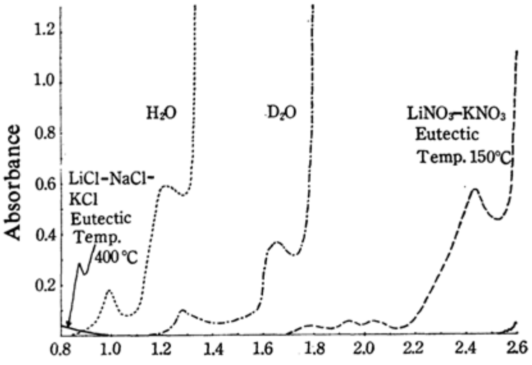

Fig. 1. Absorption characteristics of water, deuterium oxide, $LiNO_3$-KNO_3 and LiCl-NaCl-KCl in the near infrared region using quartz cell with 10.0 mm. path length.

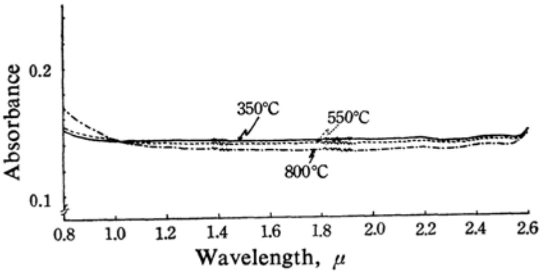

Fig. 2. Absorption base lines of LiCl-NaCl-KCl eutectic at several temperatures.

A correction for emission becomes necessary for wavelengths above approximately 1.0 μ.

The ratio of the energy emitted by the furnace and the sample to that emitted by the light source is given in Plank's equation:

$$E_{\lambda T_1}/E_{\lambda T_2}=(e^{1.43/\lambda T_2}-1)/(e^{1.43/\lambda T_1}-1)$$

where λ is the wavelength, T_1 the temperature of the light source, and T_2 the temperature of the furnace and the sample. This calculated value is not the same as the experimentally determined value.[8] The discrepancy undoubtedly is due to the fact that the assumption of equal emitting values made in Plank's equation is inadequate for this particular experiment.

The correction for radiation from the molten salts solution, cell and furnace at a high temperature was made by the base line method.[2]

The experimental results are plotted in terms of molar absorptivity, $\varepsilon=\log(I_0/I)cd$, where I_0/I is the intensity ratio of the incident to the transmitted light beam, c the molar concentration, and d the light path length. Molar concentrations were calculated from density values of Van Artsdalen and Yaffe who have determined the values for the LiCl, NaCl, KCl and LiCl-KCl eutectics. Their value of 1.69 g. per cubic centimeter at 400°C was used in calculating the molarity of each molten LiCl-NaCl-KCl eutectic.

In each case, the absorption bands of lanthanide in the alkali chloride eutectic was determined by a comparison of the spectra of the sample and of the solvent. Thus, the blank run was measured by recording first the characteristic spectrum of a cell containing the pure eutectic solution vs. air as the reference, and then sample spectra were measured by running the same cell containing the desired concentration of the lanthanide vs. air. All the absorption bands were scanned at speeds commensurate with their sharpness to obtain a reliable value at the position of the absorbance maximum.

Results and Discussion

The absorption spectra of fourteen lanthanide chlorides, from lanthanum to lutetium (except. promethium), in the molten LiCl-NaCl-KCl eutectic media have been measured at temperatures 400±2°C in the range from 0.8 to 2.6 μ.

Of these, it was found that praseodymium, neodymium, samarium, dysprosium, holmium, thulium and ytterbium each have a characteristic absorption band, as is shown in Figs. 3 to 5. Near-infrared absorption bands of lanthanide ions arise from electronic transitions within the inner shell 4f-configurations, as is the case with their visible and ultraviolet absorption bands, with few exceptions.

Lanthanum and lutetium lie at the extremes of the lanthanide group, the former with no 4f-electrons and the latter with a completed 4f-electron shell. Trivalent ions of neither element showed any characteristic absorption band in the 0.8 to 2.6 μ range.

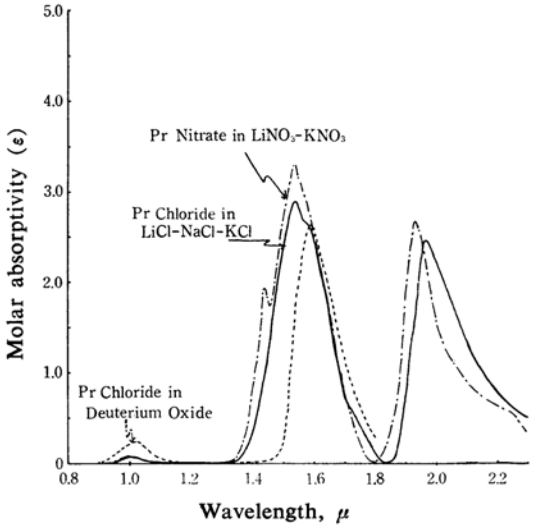

Fig. 3. Absorption spectra of praseodymium in the near-infrared region.

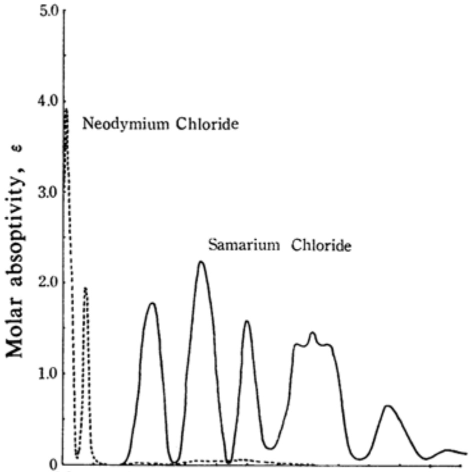

Fig. 4. Absorption spectra of neodymium and samarium chlorides in LiCl-NaCl-KCl eutectic.

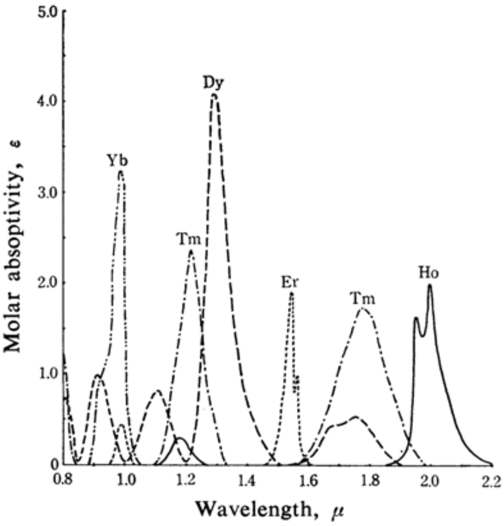

Fig. 5. Absorption spectra of dysprosium, holmium, erbium, thulium and ytterbium in LiCl-NaCl-KCl eutectic.

Trivalent cerium and gadolinium, whose absorption bands are observed only in the ultraviolet[7] and/or infrared regions,[19] have no bands in the wavelength range investigated in this study.

Promethium was excepted from the present experiment because this element is non-existent in natural lanthanide, and the absence of an absorption band in the near-infrared region in molten nitrate and deuterium oxide solutions has been indicated by Carnall[9] and Gruber.[20]

Praseodymium Chloride. — The absorption spectra in the near-infrared region of praseodymium chloride in fused LiCl-NaCl-KCl eutectic and of praseodymium ions at 400°C in the alkali chloride eutectic solution resemble the spectra at 150°C in molten nitrate media, in spite of the large differences in temperature and solvent effects. An absorption peak occurring at 1.445 μ in fused nitrate eutectic has been reported. This peak, however, has not been observed in alkali chloride eutectic and in a deuterium oxide solution. On the basis of these data, it seemed reasonable to assume that this absorption band is the O–H overtone of the water remaining in molten nitrate media as a result of incomplete dehydration.

Neodymium Chloride. — The trivalent neodymium ion in the LiCl-NaCl-KCl eutectic has only two absorption maxima, at 0.810 and 0.876 μ, in the near-infrared region. These absorption maxima are quite comparable to

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[19] R. J. Lang, *Can. J. Res.*, **14**, 127 (1936).

[20] J. B. Gruber and J. G. Conway, *J. Inorg. & Nucl. Chem.*, **14**, 303 (1960).

the absorption maxima of neodymium in LiCl-KCl eutectic, at 0.810 and 0.885 μ, which have been reported by Sundheim and Harrington.[21] The effect of different solvents on these absorption bands is small; namely, the similar spectra are obtained in molten nitrate media[9] and in other solvents.[5]

Samarium Chloride. — The spectrum of samarium chloride in fused LiCl-NaCl-KCl eutectic is presented in Fig. 4. The wavelengths of the absorption bands below the 1.4 μ range obtained by the author in aqueous solution are almost the same as those reported by Carnall[9] in alkali nitrates eutectic. The absorption maxima beyond the 1.40 μ range were found to be located at different wavelengths due to the solvent effect. These absorption bands showed the formation of different species of the complex in each solvent.

Europium Chloride.—The europium chloride in molten LiCl-NaCl-KCl eutectic has no absorption peaks in the near-infrared range, and also no absorption band structure is reported in the visible range for europium chloride in fused LiCl-KCl eutectic.[7] However, the characteristic absorption bands of europium in molten nitrate media have been reported; the maximum absorbance was observed at 0.395, 0.465, 2.05 and 2.165 μ in the visible and near-infrared ranges by Carnall.[9]

In the visible range, the spectra of europium chloride in molten alkali chloride eutectic are similar to the spectra of Eu^{2+} in an aqueous solution.[22] It is reported that $EuCl_2$ can be formed from $EuCl_3$ at about 270°C under an atmosphere of flowing hydrogen gas,[23] since the absorption spectrum obtained in the LiCl-NaCl-KCl eutectic melt may be due at least in part to $EuCl_2$ formed by the practical thermal decomposition of $EuCl_3$ or by reducing matter in the eutectic media. The difference between near-infrared absorption spectra in molten chloride and nitrate solutions is due to the existence of different valency ions and complex species in each solution.

Terbium Chloride.—The terbium chloride in fused LiCl-NaCl-KCl eutectic media has no absorption band in the range from 0.8 to 2.6 μ. However, the characteristic absorption bands of terbium in molten nitrate media have been reported; maximum absorbance was observed at 1.837, 1.938 and 2.275 μ in the near-infrared region by Carnall.[9] The difference between the absorption spectra in the two molten salts solutions is due to the presence of different complex species in each solvent.

Holmium Chloride. — The near-infrared absorption spectrum of holmium chloride in the molten alkali chloride eutectic is presented in Fig. 5. The absorption band at 1.18 μ is identified in various fused salt media and in an aqueous solution. However, the absorption band at about 1.95 μ was found to be different in molten nitrate and chloride eutectic solvents; thus, the absorption bands have been determined to be located at 1.922 μ in $LiNO_3$-KNO_3 eutectic,[9] whereas, for holmium in LiCl-NaCl-KCl eutectic media, its two absorption peaks occur at 1.959 and 1.996 μ. This discrepancy is due to the different species of complexes in the different molten salts solutions.

Other Lanthanide Chlorides.—The near-infrared absorption spectra of dysprosium, erbium, thulium and ytterbium chlorides in fused LiCl-NaCl-KCl eutectic media are presented in Fig. 5. The wavelengths of the maximum absorbances of these lanthanide chlorides in molten alkali chloride eutectic media at 400°C, in fused nitrate media at 150°C and in deuterium oxide solution[16] are substantialy comparable, considering the great differences in measurement conditions.

Solvent Effect. — A number of studies have been made concerning chlorocomplexes of metal ions in nitrate melts to which excess chloride ions have been added.[4] This method was here applied to lanthanide, that is, lithium chloride was added to the fused $LiNO_3$-KNO_3 eutectic lanthanide nitrates solution until the solution was saturated with the chloride ions. As a result, the author observed only an absorbance decrease on the characteristic absorption band of lanthanide nitrate in the wavelength range investigated. Most of the lanthanide complexes in fused nitrate media react with the chloride ions and water in

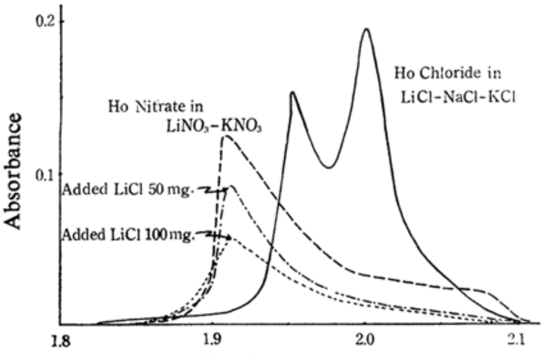

Fig. 6. The change of absorption spectra of holmium ion in $LiNO_3$-KNO_3 eutectic at 160°C by addition of several amounts of lithium chloride.

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[21] B. R. Sundheim and G. Harrington, *U. S. Atomic Energy Comm., Report* NYO-7742, March 9, 1959.

[22] F. S. Butement, *Trans. Faraday Soc.*, **44**, 617 (1948).

[23] Y. Shibata, "Inorganic Chemistry (Mukikagaku Zensho)," IX-2, Maruzen, Tokyo (1948), p. 685.

solvent to form insoluble compounds, oxychlorides. Thus, the absorbance on characteristic bands of lanthanide nitrate is decreased.

For example, the change in the absorption bands of holmium nitrate in fused $LiNO_3$-KNO_3 eutectic media upon the addition of lithium chloride is presented in Fig. 6. Thus, the chlorocomplex of lanthanides in molten nitrate media was not observed by this method. However, several different absorption bands have been observed in various solvents, such as molten nitrate, chloride and deuterium oxide solutions. These solvent effects could be attributed to the presence of different complex species in the various solvents, for the ligand field affects the 4f-electronic energy levels of the lanthanide elements.

Temperature Effect. — Most of the peaks of the near-infrared absorption bands of lanthanide chloride in fused LiCl-NaCl-KCl eutectic are slightly shifted to longer wavelengths when the temperature is increased from 400 to 800°C, and at the same time their absorbances decrease. For example, the temperature effect of the absorption bands of holmium chloride in molten alkali chloride media is shown in Fig. 7.

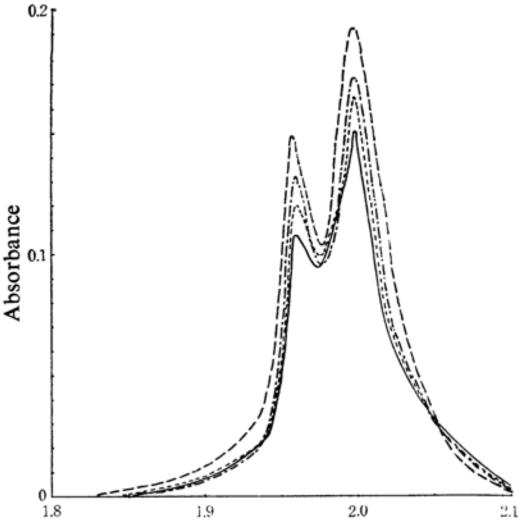

Fig. 7. Absorption spectra of holmium chloride in LiCl-NaCl-KCl eutectic at various temperatures.

Temp.		Temp.	
------	400°C	········	660°C
—·—·	530°C	———	800°C

This observation is not comparable with the fact that in the study of the molten salt spectra absorption peaks have been observed to change with the chang of temperature.[3,12,24] Because the shifts of the absorption peaks are too small for the absorption species to be distinguished, the concentration of the lanthanide ions changes as the fluid expands and contracts, and also the absorption bands are broadened at high temperatures. Thus, the temperature effect of lanthanide absorption bands is due to a single absorbing species, the concentration and peak intensity of which change as a function of the temperature. However, in the narrow temperature range of 400±2°C, the temperature effect on the characteristic lanthanide absorption band is negligibly small.

Analytically Principal Lanthanide Absorption Bands.—As can be seen from the spectra and

TABLE I. MOLAR ABSORPTIVITIES OF PRINCIPAL LANTHANIDE ABSORPTION BANDS IN VARIOUS SOLVENTS IN THE NEAR-INFRARED REGION

D_2O or H_2O[16) 25°C		$LiNO_3$-KNO_3[9) 150°C		LiCl-NaCl-KCl 400°C	
μ	ε	μ	ε	μ	ε
		Pr			
0.800	5.60	0.81_0	3.8_5	0.810	3.89
0.862	2.90	0.87_0	0.9_5	0.866	1.88
—	—	1.445	1.83	—	—
1.590	2.58	1.538	3.17	1.535	2.81
		Nd			
0.803	5.42	0.798	3.80	0.810	3.89
0.868	2.57	0.87_0	0.9_5	0.876	1.88
		Sm			
1.095	2.00	1.088	1.51	1.087	1.54
1.250	2.19	1.246	2.10	1.241	2.61
1.385	0.55	1.385	1.32	1.390	1.67
1.530	0.62	1.500	1.87	1.550	1.33
—	—	1.557	1.87	1.615	1.47
		Dy			
0.810	1.50	0.80_5	0.7_0	0.803	0.69
0.911	2.04	0.910	1.16	0.910	0.99
1.102	1.83	1.108	1.06	1.110	0.81
1.300	1.24	1.290	4.20	1.290	4.07
1.670	0.85	1.691	1.05	1.670	0.42
—	—	—	—	1.750	0.52
		Ho			
1.145	0.80	—	—	—	—
1.197	0.76	1.17_5	0.7_0	1.180	0.34
—	—	1.922	1.14	1.959	1.46
—	—	—	—	1.996	1.56
		Er			
0.980	1.02	0.98_0	0.6_5	0.985	0.50
1.510	1.02	1.510	1.26	1.542	1.85
—	—	—	—	1.560	0.93
		Tm			
1.220	1.09	1.212	1.38	1.222	2.36
1.720	1.13	1.740	1.79	1.775	1.72
		Yb			
0.974	2.12	0.975	3.77	0.982	3.22

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24) J. R. Morrey, *J. Chem. Phys.*, **66**, 2169 (1962).

TABLE II. REPRODUCIBILTY OF SEVERAL ABSORPTION BANDS OF LANTHANIDE CHLORIDES DISSOLVED IN MOLTEN LiCl-NaCl-KCl EUTECTIC AT 400±2°C

Element	Absorption peak, μ	Mean. value	Concn. range mg./5 g.	No. of readings	Std. error, %
Pr	1.535	2.81±0.03	50—200	4	1.0
Sm	1.241	2.61±0.03	50—200	4	1.1
	1.615	1.47±0.04	50—200	4	2.7
Ho	1.939	1.46±0.02	50—150	3	1.4
	1.996	1.56±0.02	50—150	3	1.3

molar absorptivities, it would be practical to determine the concentrations of most of lanthanides dissolved in fused salts media by the use of the spectrophotometric technique. The wavelengths and molar absorptivities of the main absorption bands found in the spectra of eight of the lanthanide chlorides in fused LiCl-NaCl-KCl at 400±2°C are presented in Table I, along with the absorbance peaks which have been reported in a deuterium oxide solution and the lanthanide nitrates reported in molten $LiNO_3$-KNO_3 media. The reproducibility of all the absorption spectra of these lanthanide chlorides was good, with standard deviations below 3.0% (Table II), and the absorbances of these spectra obeyed Beer's law, indicating that these absorption bands could be used for the quantitative analysis of each lanthanide.

Summary

Using a high temperature cell for molten salts, a spectrophotometric investigation in the near-infrared region from 0.8 to 2.6 μ and at temperatures from 400 to 800°C has been carried out with fourteen lanthanide chlorides dissolved in a LiCl-NaCl-KCl mixture of eutectic composition (49.0 - 17.3 - 33.7 mol.%, m. p. 333°C). Praseodymium, neodymium, samarium, dysprosium, holmium, erbium, thulium and ytterbium have characteristic absorption bands in this region. Most of the near-infrared absorption bands of lanthanide chlorocomplexes have been compared to similar spectra obtained in molten nitrate media. However, the several absorption bands have been found to be different in molten nitrate and chloride eutectics. Thus, the absorption bands of europium and terbium have been observed in nitrate, wheras their bands have not been found in chloride, and the absorption bands of praseodymium, samarium and holmium beyond the 1.4 μ range have been found to be located at different wavelengths. These solvent effects can be attributed to the existence of a different lanthanide complex in each solvent, for the ligand field affects the 4f-electronic energy levels of the above elements.

The absorption peaks of lanthanide ions decrease as the temperature increases, partly due to the change in the concentration of the ions associated with the volume change. However, all the characteristic absorption bands of lanthanide in the near-infrared region have stable molar absorptivities at a constant temperature. These absorption bands can be used for the investigation of chemical constitution and electronic structure, for analysis and for other purposes.

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Goverment Chemical Industrial
Research Institute, Tokyo
Shibuya-ku, Tokyo