— Technical Paper —

Complexation and Ionic Arrangement in Na_3ErCl_6 and K_3ErCl_6 Melts Analyzed by X-ray Diffraction

Yasuhiko IWADATE,*^a Kazuko FUKUSHIMA,^a Ryuzo TAKAGI,^b
and Marcelle GAUNE-ESCARD^c

^aDepartment of Materials Technology, Faculty of Engineering, Chiba University (Yayoi-cho 1-33, Inage-ku, Chiba 263-8522, Japan)

^bResearch Laboratory for Nuclear Reactors, Tokyo Institute of Technology (Ookayama 2-12-1, Meguro-ku, Tokyo 152-8550, Japan)

^cInstitut Universitaire des Systèmes Thermiques Industriels, Université de Provence (Technopôle Chateau-Gombert, 5 rue Enrico Fermi, 13453 Marseille Cédex 13, France)

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The short range structure of Na_3ErCl_6 melt at 973 K and K_3ErCl_6 melt at 1053 K was investigated by X-ray diffraction. The nearest neighbor distance of $\text{Er}^{3+}\text{-Cl}^-$ and the coordination number of Cl^- around Er^{3+} in Na_3ErCl_6 melt, for instance, were estimated to be 2.61 Å and 5.7, respectively, and the $\text{Er}^{3+}\text{-Er}^{3+}$ and $\text{Cl}^-\text{-Cl}^-$ distances 5.15 Å and 3.90 Å, respectively. The ratio of the anion-anion pair distance to the cation-anion pair distance (r_{--}/r_{+-}) was, therefore, 1.49, being close to 1.41, characteristic of octahedral geometry. These results indicate that the stable ErCl_6^{3-} octahedra exist in Na_3ErCl_6 and K_3ErCl_6 melts. Probably, complex ions such as $\text{Er}_2\text{Cl}_{10}^{4-}$ and $\text{Er}_2\text{Cl}_{11}^{5-}$ expected to be in the pure ErCl_3 melt are little formed at these compositions according to the geometrical calculations of bond lengths and bond angles.

Key Words: X-ray Diffraction, Short Range Structure, Erbium Chloride, Octahedron

1 Introduction

Pioneering high temperature Raman spectroscopic studies have been made on rare earth chloride systems in the liquid and solid states in the middle of 1970's.¹⁻³⁾ After some intermissions of the work, structural analyses have been restarted by using both X-ray diffraction and Raman spectroscopy on pure lanthanide trichlorides^{4,5)} with UCl_3 -type crystal structure (hexagonal). Those results indicated that the nearest neighbour chloride coordination number of a lanthanide ion changed from 9 in the crystal to 6 in the melt, allowing for octahedral geometry around the lanthanide ions. The structural studies on melts of lanthanide trichlorides with AlCl_3 -type crystal structure (monoclinic; six-fold coordination) have been carried out for YCl_3 ⁶⁾ and ErCl_3 .⁷⁾ The melting behavior of ErCl_3 has been confirmed to be similar to that of YCl_3 , having the same crystal structure. In recent years, structural correlations in molten trivalent metal chlorides have been estimated as functions of the metal ion size for LaCl_3 and AlCl_3 -type lanthanide trichlorides, using a charged soft-sphere model and the hypernetted chain approximation.⁸⁾ Furthermore, Erbölükbas *et al.*⁹⁾ have analyzed the available data on bond lengths and Raman frequencies by treating an isolated octahedral complex

ion within a model which adopts charged soft-sphere interionic potentials, supplemented by taking ionic polarization into account.

In the present work, the short range structure of Na_3ErCl_6 and K_3ErCl_6 melts was studied by X-ray diffraction since little is known on the melt structure of lanthanide trichlorides with alkali chlorides. Possible anionic species and ionic arrangements are discussed in view of interatomic distances and bond angles.

2 Experimental

ErCl_3 was prepared by heating a mixture of analytical grade Er_2O_3 and 2.5 times the theoretical amount of NH_4Cl at 623 K for 3 hours. Excess NH_4Cl was removed by heating at 1173 K. The chlorination reaction is

ErCl_3 thus obtained was purified by ErCl_3 vapor deposition onto the surface of a quartz tube cooled with water under reduced pressure down to 10^{-2} Pa for 12 hours. The vapour source was heated at 1253 K, so as to remove small amounts of water, oxychloride, unreacted NH_4Cl and oxide. Two intermediate compounds Na_3ErCl_6 and K_3ErCl_6 were prepared by

accurately weighing each ErCl_3 , NaCl , and KCl and premelting in the fused silica vessel. The molar volumes measured dilatometrically were taken from the literature¹⁰⁾ in order to estimate the atomic number density of the melts.

In the X-ray scattering measurements, the purified sample was sealed in a thin quartz tube cell to prevent its spoilage. The X-ray diffractometer, having a θ - θ type reflection geometry (Rigaku Corporation, Tokyo, Japan), was employed with $\text{MoK}\alpha$ radiation, and the diffracted beam was monochromatized with curved graphite. The Q -range, $0.93 \leq Q / \text{\AA}^{-1} \leq 12.5$, was explored with two pairs of divergence and scattering slits $[1 / 2^\circ - 1 / 2^\circ]$ when $2.5^\circ \leq \theta \leq 15^\circ$, and $[1^\circ - 1^\circ]$ when $13^\circ \leq \theta \leq 45^\circ$ (2θ = scattering angle and $Q = 4\pi \sin \theta / \lambda$ with λ being the wavelength of the radiation $0.71069 \text{\AA}$; $1 \text{\AA} = 10^{-10} \text{ m}$). The receiving slit was 0.6 mm throughout this work. The scattered X-ray intensities so obtained were corrected for background, polarization, absorption and Compton scattering, and normalized to the coherent scattering intensity of the stoichiometric unit, in accordance with the usual procedure.¹¹⁾ Atomic scattering factors and Compton scattering factors were taken from the literature.^{12,13)} Thus, experimental structure factors and radial distribution functions were obtained.

3 Results and Discussion

The interference function, $Q \cdot i(Q)$, the radial distribution function, $D(r)$, and the correlation function, $G(r)$, are defined by Equations (2), (3), and (4), respectively.

$$Q \cdot i(Q) = Q \cdot [I^{\text{coh}}(Q) - \sum_i f_i(Q)^2] / (\sum_i f_i(Q))^2 \quad (2)$$

$$D(r) = 4\pi r^2 \rho_0 + (2r / \pi) \int_0^{Q_{\text{max}}} Q \cdot i(Q) \sin(Qr) dQ \quad (3)$$

$$G(r) = 1 + (2\pi^2 r \rho_0)^{-1} \int_0^{Q_{\text{max}}} Q \cdot i(Q) \sin(Qr) dQ \quad (4)$$

where $I^{\text{coh}}(Q)$ is the total coherent intensity, $f_i(Q)$ the independent atomic scattering amplitude of the atom i , and ρ_0 the number of stoichiometric units per cubic $\text{\AA}$, and Q_{max} the maximum value of Q reached in the experiments. Summation for i is made over the stoichiometric unit. These functions were calculated

Table 1 Numerical parameters in the radial distribution analysis.

Melt system	Na_3ErCl_6	K_3ErCl_6
Temperature / K	973	1053
Density / g cm^{-3}	2.521	2.211
Number density / $\text{\AA}^{-3}$	3.381×10^{-3}	2.693×10^{-3}
$Q_{\text{max}} / \text{\AA}^{-1}$	12.5	12.5

with the parameters listed in Table 1 where details of the analytical procedure are described elsewhere.¹⁴⁾

3. 1 Evaluation of ErCl_3 in lanthanum series from molar volume change on melting

It is well known that the elements of lanthanide series as well as their compounds possess physico-chemical properties similar to one another, but the actual situation is not the case as shown below. The problem is where we should *place or rank* the individual elements or compounds in the whole lanthanide series.

Since ErCl_3 forms a monoclinic crystal,¹⁵⁾ the molar volume V_m in the crystalline state was calculated from the equation, $V_m = (N_A / Z) a b c \sin \beta$, so as to study the volume change on melting, where a , b , c , and β are the lattice constants, N_A and Z are Avogadro constant and the number of stoichiometric units contained in the unit cell, respectively. For the lanthanide trichlorides with hexagonal structure¹⁶⁾ the molar volume was calculated by $V_m = (\sqrt{3} / 2) a^2 c (N_A / Z)$. The molar volume of molten ErCl_3 has been measured and expressed as a linear function of temperature.¹⁰⁾ For comparison, the molar volumes of several lanthanide trichlorides are tabulated in Table 2. As can be seen from Table 2, the molar volume changes of UCl_3 -type (hexagonal) lanthanide trichlorides on melting are generally very large, but in striking contrast those of AlCl_3 -type (monoclinic) lanthanide trichlorides being quite small. Therefore, the nearest neighbor ordering in molten ErCl_3 appears to be similar to that in the solid state. In other words, the number of the nearest Cl^- ion around Er^{3+} ion is unchanged to be six even on melting, but for the hexagonal type crystal, that around lanthanide ion varies from nine to six on melting.¹⁷⁾ In this way, ErCl_3 behaves suspiciously on melting, being different from the usual ionic crystals. It is of much interest to add the typical ionic crystals NaCl and KCl to ErCl_3 and to study the Cl^- coordination around Er^{3+} on melting.

Table 2 Molar volume changes on melting.

System	T_m / K	$V_c / \text{cm}^3 \text{mol}^{-1}$	$V_m / \text{cm}^3 \text{mol}^{-1}$	$100(V_m - V_c) V_c^{-1} / \%$
LaCl_3	1150	63.90	76.30	19.1
CeCl_3	1095	62.42	76.06	21.9
PrCl_3	1059	61.40	74.30	21.0
NdCl_3	1029	60.47	73.65	21.8
SmCl_3	935	59.23	73.73	24.5
GdCl_3	875	58.03	73.34	26.4
DyCl_3	928	74.38	74.62	0.3
HoCl_3	993	73.02	74.00	1.3
ErCl_3	1046	72.11	75.65	4.9
YCl_3	987	74.83	75.17	0.5

T_m , V_c , and V_m refer to the melting point, the molar volumes of crystal and melt, respectively.

3. 2 Radial distribution analysis (*r* space)

The $G(r)$ curves of Na_3ErCl_6 and K_3ErCl_6 melts are shown in Fig. 1 and the $D(r)$ curves in Figs. 2 and 3, respectively. The center of the first peak in $G(r)$ appeared in the range of 2.60 Å to 2.65 Å. Considering the sum of individual ionic radii given by Shannon¹⁸⁾ with Er^{3+} and Cl^- being 0.89 Å and 1.81 Å, respectively, the first peak was assigned to the nearest neighbor correlation $\text{Er}^{3+}\text{-Cl}^-$ and the other correlations hardly contributed to this peak. The coordination number of Cl^- ions around Er^{3+} ion was estimated at about 6 by integration of the area under the peak of $D(r)$ shown in Figs. 2 and 3. The second

Fig. 1 Correlation function $G(r)$ of Na_3ErCl_6 and K_3ErCl_6 melts.

Fig. 2 Radial distribution function $D(r)$ of Na_3ErCl_6 melt.

peak was found to be centered around 4 Å, being assignable to the $\text{Cl}^-\text{-Cl}^-$ and $\text{Er}^{3+}\text{-Er}^{3+}$ correlations. For example, the $\text{Er}^{3+}\text{-Er}^{3+}$ distance in the ErCl_3 crystal was estimated at 3.91 Å from crystallographical data.¹⁵⁾

In order to refine the short range structure of Na_3ErCl_6 and K_3ErCl_6 melts, the structural parameters for each ionic pairs are necessary to be optimized by the correlation method, using the non-linear least squares fitting of Equation (5),

$$Q \cdot i(Q) = \left[\sum_i \sum_j n_{ij} f_i(Q) f_j(Q) \exp(-b_{ij} Q^2) \sin(Q r_{ij}) / r_{ij} \right] / \left(\sum_i f_i(Q) \right)^2 \quad (5)$$

where n_{ij} , r_{ij} , and b_{ij} refer to the average coordination number, the average interatomic distance, and the temperature factor for the ionic pair i - j , respectively. Each atomic pair was presumed to be Gaussian distributed, centered at r_{ij} with a mean square displacement $2b_{ij}$. For determining the validity of model structure, the following parameter is often introduced where R is the degree of coincidence in fitting of two interference functions, observed and calculated, which is defined by Equation (6),

$$R = \frac{\sum \{ |Q \cdot i(Q)_{\text{cal}} - Q \cdot i(Q)_{\text{obs}}| \}}{\sum \{ |Q \cdot i(Q)_{\text{obs}}| \}} \quad (6)$$

As for conventional non-crystalline materials, the structural model is thought to be essentially correct in the case of $R < 0.5$.

The structural parameters obtained from $G(r)$ and $D(r)$ were used as the initial values of this process for their further refinement. Each parameter was optimized by a least squares calculation beyond $Q = 1.5 \text{ Å}^{-1}$. The parameters of the most probable model in the $Q \cdot i(Q)$ fitting are given in Table 3. The observed and calculated $Q \cdot i(Q)$'s of Na_3ErCl_6 and

Fig. 3 Radial distribution function $D(r)$ of K_3ErCl_6 melt.

K_3ErCl_6 melts are shown in Figs. 4 and 5, respectively. The R factors for the best fitted model of Na_3ErCl_6 and K_3ErCl_6 melts at intervals of $0.05 \text{ \AA}^{-1}$ in the range of $1.5 \leq Q / \text{\AA}^{-1} \leq 12.5$, converged to 0.25 and 0.42, respectively. From these results, the nearest neighbor distances were estimated at 2.61 and 2.65 $\text{\AA}$, the coordination number of Cl^- around Er^{3+} were 5.67 and 5.73, like-ion pair distances of Cl^-Cl^- were 3.90 and 3.89 $\text{\AA}$, and $Er^{3+}-Er^{3+}$ were calculated to be 5.15 and 5.17 $\text{\AA}$ for Na_3ErCl_6 and K_3ErCl_6 melts, respectively. The ratio of r_{--}/r_{+-} were 1.49 and 1.47, being close to the value for octahedral geometry 1.41.

3. 3 Medium range structure

The interionic structure, especially in the $Er^{3+}-Er^{3+}$ correlation, has been considered in terms of the molar volume and the obtained short range structural parameters. If Er^{3+} in pure $ErCl_3$ melt were distributed isotropically, the average $Er^{3+}-Er^{3+}$ pair-distance would be 5.01 $\text{\AA}$. The corresponding distance obtained from the X-ray diffraction analyses was 4.05 $\text{\AA}$. This indicates that, as to the $Er^{3+}-Er^{3+}$ pair, there is some specific configuration in the melt, which would be well interpreted by an edge-sharing

Table 3 Least squares fitted structural parameters.

a) Na_3ErCl_6 melt

ij -pair	n_{ij}	$r_{ij} / \text{\AA}$	$b_{ij} / \text{\AA}^2$	$\langle r_{ij}^2 \rangle^{1/2} / \text{\AA}$
Er-Cl	5.67	2.61	0.0367	0.271
Na-Cl	3.72	3.07	0.0457	0.302
Cl-Cl	9.49	3.90	0.1379	0.525
Er-Na	6.04	3.96	0.1438	0.536
Er-Er	4.25	5.15	0.2712	0.736

b) K_3ErCl_6 melt

ij -pair	n_{ij}	$r_{ij} / \text{\AA}$	$b_{ij} / \text{\AA}^2$	$\langle r_{ij}^2 \rangle^{1/2} / \text{\AA}$
Er-Cl	5.73	2.65	0.0459	0.303
K-Cl	3.66	3.39	0.0460	0.303
Cl-Cl	8.93	3.89	0.0989	0.445
Er-K	6.08	4.18	0.1392	0.528
Er-Er	4.10	5.17	0.1672	0.578

Fig. 4 Interference function $Q \cdot i(Q)$ of Na_3ErCl_6 melt.

Fig. 5 Interference function $Q \cdot i(Q)$ of K_3ErCl_6 melt.

model assuming flexible octahedra with variable $Er^{3+}-Cl^-$ and Cl^-Cl^- bond lengths. According to numerical calculations, another plausible possibility is a non-linear arrangement of octahedral ions on the basis of corner-sharing in which two octahedra are twisted with each other.⁷⁾ But corner-sharing is less probable than edge-sharing because of the steric hindrance between Cl^- ions, although corner-sharing has been expected from numerical calculations on Raman frequencies.⁹⁾ It is, thus, of much interest to study how the linkage of octahedra change in the melts with compositions of two intermediate compounds. As listed in Table 3, the average $Er^{3+}-Er^{3+}$ pair distances are 5.15 and 5.17 $\text{\AA}$ in Na_3ErCl_6 and K_3ErCl_6 melts, respectively. These distances are elongated extremely from the corresponding distance 4.05 $\text{\AA}$ obtained from the X-ray diffraction analysis of pure $ErCl_3$ melt. This finding is due to that the edge-sharing and / or corner-sharing octahedra of the type $Er_2Cl_{10}^{4-}$, $Er_2Cl_{11}^{5-}$, and so on are decomposed into the discrete octahedra of the type $ErCl_6^{3-}$ and the alkali cations tend to be located among the discrete octahedral complex ions.

4 Conclusions

According to X-ray diffraction, the existence of octahedral complex ions, $ErCl_6^{3-}$, in Na_3ErCl_6 and K_3ErCl_6 melts as well as in pure $ErCl_3$ melt is confirmed. Also found is the decomposition of the clustered octahedra into the discrete octahedra by addition of alkali chlorides.

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