ELSEVIER

Journal of Alloys and Compounds 235 (1996) 143–149

Journal of
ALLOYS
AND COMPOUNDS

Electrical conductivity of molten $LnCl_3$ and M_3LnCl_6 compounds (Ln = La, Ce, Pr, Nd; M = K, Rb, Cs)

P. Gaune[a], M. Gaune-Escard[a], L. Rycerz[b], A. Bogacz[b]

[a] *IUSTI, UA 1168 CNRS, Université de Provence, Centre de St. Jérôme, Av. Escadrille Normandie Niemen, F-13397 Marseille Cedex 20, France*

[b] *Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Technical University, Wybrzeże St. Wyspiańskiego 27, 50-370 Wrocław, Poland*

Received 23 May 1995; in final form 26 September 1995

Abstract

The electrical conductivities of molten lanthanide chlorides $LnCl_3$ and definite compounds M_3LnCl_6 (where Ln = La, Ce, Pr, Nd and M = K, Rb, Cs) have been determined.

The conductivities were well represented as quadratic functions of temperature. The molar conductivities for pure lanthanide chlorides were derived and represented well by an Arrhenius-type function of temperature. Electrical conduction in investigated melts was discussed on the basis of complex formation and polymerization.

Keywords: Electrical conductivity; $LnCl_3$; Molten complex chlorides of rare earth and alkali metals

1. Introduction

Thermodynamics and electrical conductivity of $LnCl_3$ and their mixtures with alkali chlorides play an important role in the production of lanthanide metals by molten salt electrolysis.

We have initiated a general research program on the thermodynamic properties and electrical conductivity of the $LnCl_3$ and MCl–$LnCl_3$ liquid mixtures (M = Li, Na, K, Rb, Cs; Ln = lanthanide). The pure lanthanide chlorides and definite compounds M_3LnCl_6, which exist only for the heavier alkali metals (M = K, Rb, Cs), have been investigated by several experimental techniques both in the solid and liquid states. The temperatures and enthalpies of phase transitions [1,2] and heat capacities [3] of pure lanthanide chlorides ($LaCl_3$, $CeCl_3$, $PrCl_3$, $NdCl_3$, $GdCl_3$, $DyCl_3$, $ErCl_3$ and $TmCl_3$) and the M_3LnCl_6 definite compounds (Ln = La, Ce, Pr, Nd; M = K, Rb, Cs) were determined.

The enthalpies of mixing in the liquid systems $NdCl_3$–MCl (M = Li, Na, K, Rb, Cs) [4] $PrCl_3$–NaCl and $PrCl_3$–KCl [5], $NdCl_3$–$CaCl_2$ and $PrCl_3$–$CaCl_2$ [6], $DyCl_3$–NaCl, $DyCl_3$–KCl and $DyCl_3$–$PrCl_3$ [7,8] were determined for the whole range of compositions.

The present work is a part of our research program and it reports the electrical conductivities of molten $LnCl_3$ and M_3LnCl_6 compounds. The study of these conductivities is also important in understanding the structure and behaviour of ionic species in melts.

2. Experimental

2.1. Chemicals

High grade lanthanide chlorides (minimum 99.9%) were prepared from La_2O_3, CeO_2, Pr_4O_{11} produced by Hydromet Co. (Kowary, Poland) and from Nd_2O_3 produced by the Chemistry Department of the University of Lublin, Poland. The main steps of these synthesis were:

- dissolution of lanthanide oxides in hot concentrated HCl;
- crystallization of the hydrates $LnCl_3 \cdot 6H_2O$,
- partial dehydration of $LnCl_3 \cdot 6H_2O$ to obtain $LnCl_3 \cdot H_2O$;
- preparation of anhydrous $LnCl_3$;
- purification of anhydrous lanthanide chlorides by distillation under reduced pressure (about 0.1 Pa).

0925-8388/96/$15.00
SSDI 0925-8388(95)02090-X

The details of preparation procedure were described elsewhere [4].

The potassium, rubidium and caesium chlorides were Merck Suprapur reagents (minimum 99.9%). Before use they were purified and treated by progressive heating up to fusion under a gaseous HCl atmosphere. Excess HCl was removed from the melt by argon. In order to make further handling easier, both the lanthanide chlorides (very moisture sensitive) and alkali metal chlorides were ground in a glove-box and stocked in ampoules sealed under dry argon atmosphere.

The M_3LnCl_6 compounds were prepared from the MCl and $LnCl_3$ chlorides which were weighed in the molar ratio 3:1. All the mixtures were prepared in a glove-box filled with purified and dry argon. About 20 g of each compound was synthesized in order to avoid deviation from stoichiometry. The stoichiometric mixtures of chlorides were melted in vacuum-sealed quartz ampoules in an electric furnace. The melts were homogenized by shaking and then solidified. These samples were ground in an agate mortar and placed into a cell for electrical conductivity measurements in a glove-box.

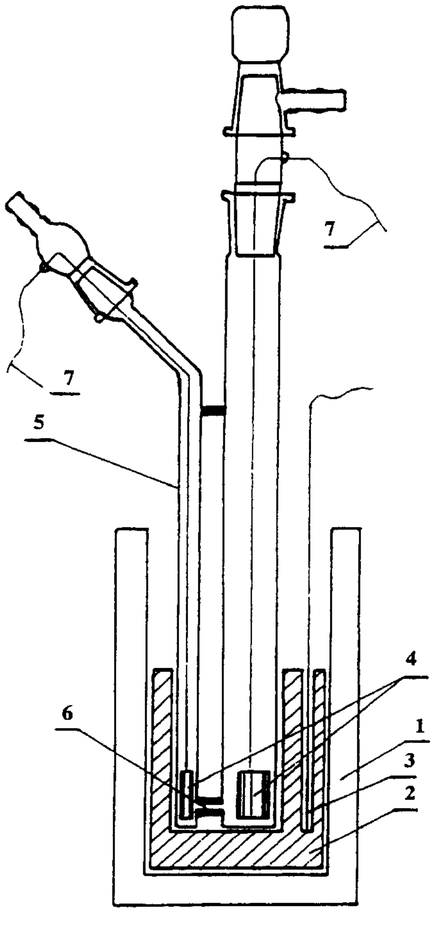

Fig. 1. Scheme of the cell for the electrical conductivity measurements: (1), electrical furnace; (2) metallic block; (3) thermocouple; (4) platinum electrodes; (5) quartz cell; (6) capillary; (7) platinum wires.

2.2. Procedure

The capillary quartz cell with platinum electrodes used in the measurements of electrical conductivity is shown in Fig. 1 [9]. The cell with compound for measurements was placed into a furnace which contained a stainless steel block in order to achieve a uniform temperature distribution. The conductivity of the compounds was measured with the conductivity meter. The conductivity of the samples was measured whilst increasing and decreasing temperature by 1 K steps. The mean value of these two measurements was used for calculations. The temperature during measurements was changed by 0.5–1 K min^{-1}. The values of temperature and conductivity were registered by a PC XT286 computer.

The accuracy of electrical conductivity measurements by the above method was estimated at ± 2%. Temperature was measured by means of Pt/Pt–Rh thermocouple with an accuracy ± 1 K. The conductivity cell was calibrated before each experimental run with NaCl pure melt [10]. Cell constants ranged from 950 to 1900 m^{-1}. All measurements were carried out under argon atmosphere.

It is well known that the variation of resistance with frequency can be expressed in the form

$$R_{meas} = R_{inf} + Cf^{-1/2} \qquad (1)$$

Where R_{meas} and R_{inf} are the measured resistance at the frequency f and the polarization-free resistance at infinite frequency respectively, and C is a constant characteristic of the studied melt. An alternative approach to R_{inf} is a least squares treatment of quadratic or linear equations in f^{-1}. The selection of the better extrapolation technique is dependent on factors such as the cell constant, concentrations, and range of frequencies [11]. In our measurement conditions, the faradaic impedance, consisting of a polarization resistance and an electrolytic capacitance, was proportional to $f^{-1/2}$. Thus Eq. (1) was used in data processing of the resistance for both pure lanthanide chlorides and M_3LnCl_6 compounds. The measurements of electrical conductivity were carried out with the frequency equal 4 kHz. To obtain the dependence of resistance on frequency, measurements with the frequency ranging from 0.5 to 16 kHz were carried out for each compound. Fig. 2 presents the resistance variation with frequency of a few of the compounds investigated.

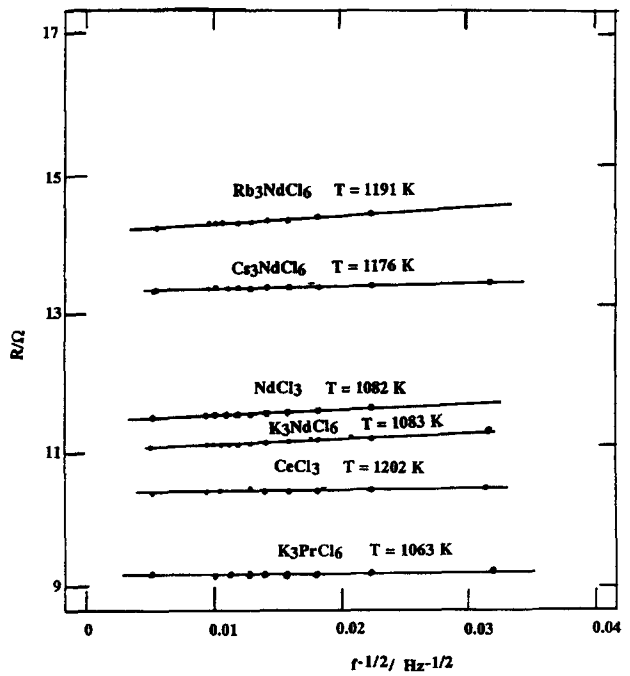

Fig. 2. Resistance variation with frequency for a few of the investigated compounds.

3. Results and discussion

3.1. Pure lanthanide chlorides

The measured electrical conductivity of the melts is well-fitted by a quadratic function of temperature

$$\kappa = a + bT + cT^2$$

The parameters a, b and c in the empirical conductivity equation of investigated chlorides are shown in Table 1. The molar conductivity of a molten salt is expressed by

$$\Lambda = \kappa V_m$$

where Λ is the molar conductivity, κ is the specific conductivity and V_m is molar volume of the salt. The V_m data were taken from the literature [12,13].

Since the lnΛ vs. $1/T$ plots for the investigated chlorides were straight lines, the molar conductivities were smoothed by Arrhenius-type equations

$$\Lambda = \Lambda_0 \exp(-E_A/RT)$$

where R is the gas constant in J mol^{-1} K^{-1}, Λ_0 is the characteristic constant of the melt, and E_A is the activation energy for electrical conduction. The values of Λ_0 and E_A are presented in Table 2.

A few investigations of the specific conductivity for molten $LaCl_3$ have been reported [14–19]. Our results are compared with literature data in Fig. 3. They are in good agreement with the results of Yaffe and van Artsdalen [15]. The maximum departure between them is no more than 0.7% in the entire investigated range. The results of Smirnov and Khokhlov [19] and Voigt and Biltz [17] are consistently smaller than our results (about 17% and 25% respectively at 1250 K).

The specific conductivity of $CeCl_3$ was measured by Bronstein et al. [20] and by Mellors and Senderoff [13]. Our results are smaller by about 7–9% than those of Mellors and Senderoff and by about 23–25% than the results of Bronstein et al. (Fig. 4). Taking account of the uncertainty of the specific conductance values of Mellors and Senderoff (estimated to be about 15% [21]) the agreement with their results is quite good.

Three investigations of the specific conductivity for molten $PrCl_3$ have been reported [17,22,23]. The results of this work are significantly smaller than those of Dworkin et al. [22] and Iwadate et al. [23] (e.g. 22% and 18% at 1090 K) but they are in good agreement with data of Voigt and Biltz [17] (Fig. 5). The maximum departure between them is no more than 2.5% in the entire temperature range investigated.

The results of measurements of specific conductivity of molten $NdCl_3$ in comparison with literature data [17,18,24] are presented in Fig. 6. The results of this

Table 2
Molar electrical conductivity (Λ/S m^2 mol^{-1}) of $LnCl_3$

Compound	Λ_0 (S m^2 mol^{-1})	E_A (kJ mol^{-1})
$LaCl_3$	1.168	29.62
$CeCl_3$	0.103	25.36
$PrCl_3$	0.143	28.32
$NdCl_3$	0.204	28.05

Table 1
Results of electrical conductivity measurements of $LnCl_3$ compounds (κ/S m^{-1})

Compound	Temperature (K)	a ($\times 10^{-2}$ S m^{-1})	b (S m^{-1} K^{-1})	c ($\times 10^{-4}$ S m^{-1} K^{-2})	SE (S m^{-1})
LaCl	1144–1234	−7.170	1.189	−3.77	0.322
$CeCl_3$	1090–1254	−3.551	0.584	−1.68	0.168
$PrCl_3$	1070–1170	−8.392	1.431	−5.38	0.113
NdCl	1017–1135	−5.191	0.869	−2.57	0.408

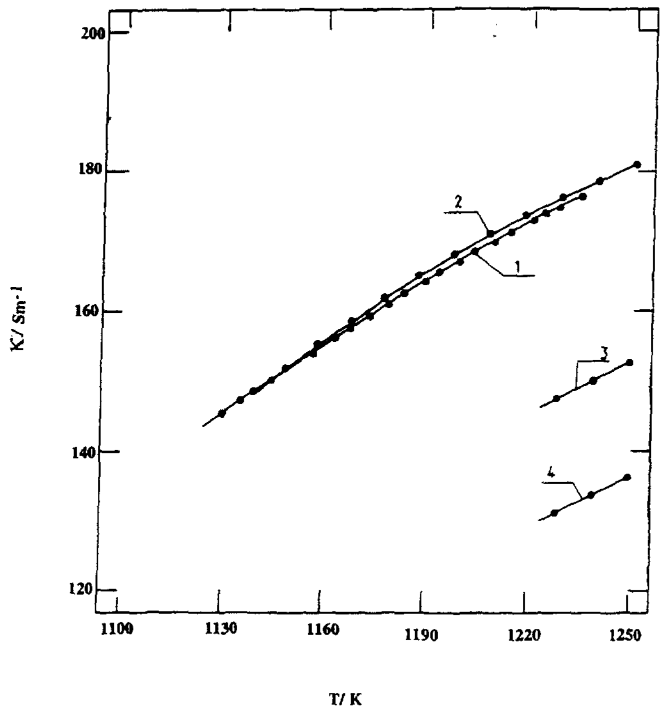

Fig. 3. Dependence of specific conductivity of $LaCl_3$ on temperature: (1), this work; (2), Yaffe and van Artsdalen [15]; (3), Smirnov and Khokhlov [19]; (4), Voigt and Biltz [17].

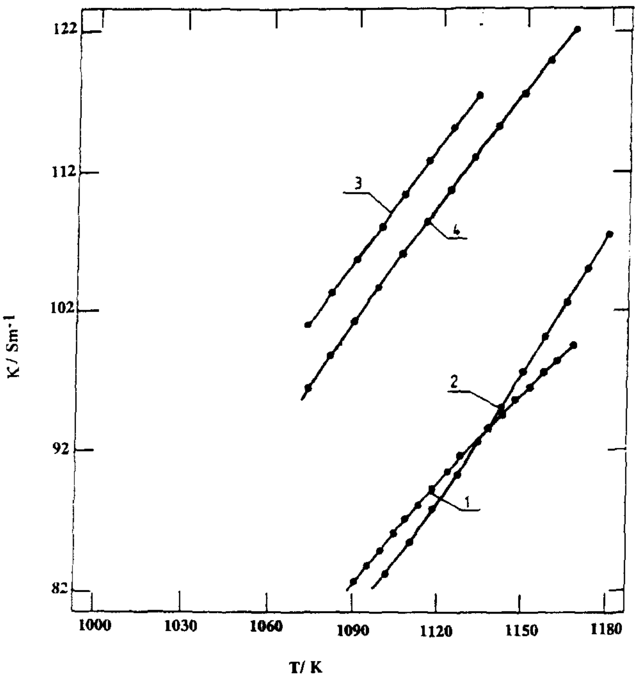

Fig. 5. Dependence of the specific conductivity of $PrCl_3$ on temperature: (1), this work; (2), Voigt and Biltz [17]; (3), Dworkin et al. [22]; (4), Iwadate et al. [23].

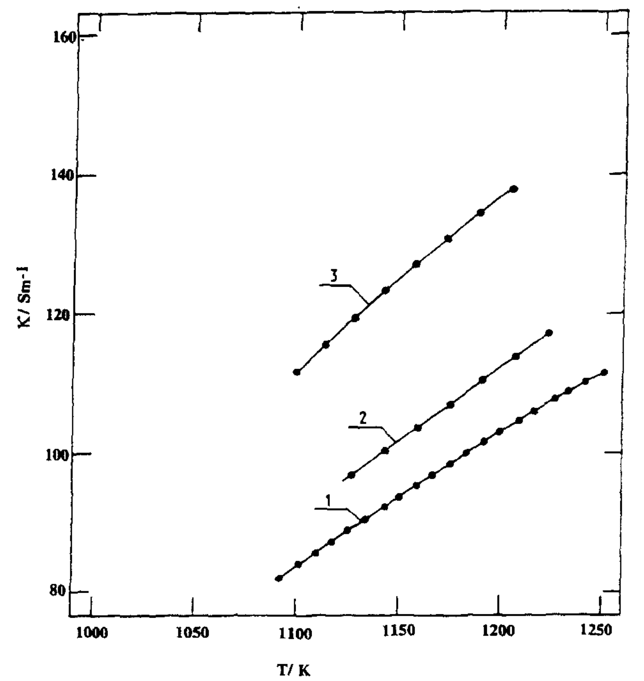

Fig. 4. Dependence of the specific conductivity of $CeCl_3$ on temperature: (1), this work; (2), Mellors and Senderoff [13]; (3), Bronstein et al. [20].

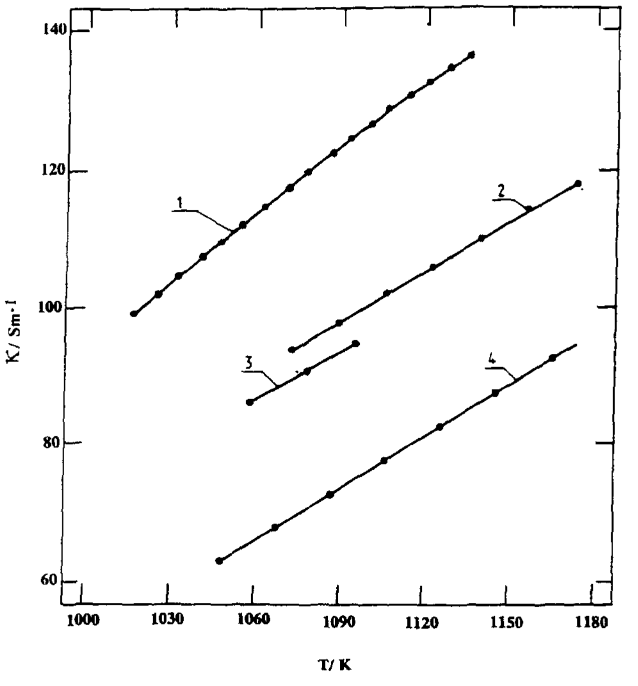

Fig. 6. Dependence of the specific conductivity of $NdCl_3$ on temperature: (1), this work; (2), Förthmann et al. [18]; (3), Mochinaga and Iwadate [24]; (4), Voigt and Biltz [17].

work are significantly higher than literature data (e.g. the departure between them and the Förthmann et al. results [18] is about 25%).

The lanthanide chlorides used for electrical conductivity measurements in this work were previously used in calorimetric investigations [1]. The values of enthalpy of fusion obtained for them are in excellent agreement with literature data. The $\Delta_{fus}H_m$ and T_{fus} values are as follows: $LaCl_3$, 55.7 kJ mol^{-1} and 1127

K; $CeCl_3$, 55.5 kJ mol^{-1} and 1086 K; $PrCl_3$, 52.1 kJ mol^{-1} and 1061 K; $NdCl_3$, 48.1 kJ mol^{-1} and 1032 K. This respectively compares with literature data of: 54.3 kJ mol^{-1} and 1128 K [25], 53.5 kJ mol^{-1} and 1090 K [26]; 50.6 kJ mol^{-1} and 1059 K [27]; 50.2 kJ mol^{-1} and 1032 K [27]. This agreement of temperatures and enthalpies of fusion confirms the purity of compounds used in investigations.

From the results of X-ray diffraction analysis [28] and Raman spectroscopy, the existence of octahedral complex anions of $NdCl_6^{3-}$ has been inferred in the $NdCl_3$ melt [24]. A similar situation was suggested for the $PrCl_3$ melt [23]. The dimer species $Pr_2Cl_{11}^{5-}$ and $Nd_2Cl_{11}^{5-}$ were also estimated to exist in the melt [28]. The dimers can be formed from monomers according to the reactions

$$2NdCl_6^{3-} \rightarrow Nd_2Cl_{11}^{5-} + Cl^-$$

$$2PrCl_6^{3-} \rightarrow Pr_2Cl_{11}^{5-} + Cl^-$$

The Cl^- ions with higher ionic mobility are formed in these reactions. The quantity of Cl^- ions depends on the degree of polymerization. It is known from the measurements of enthalpy of mixing in the systems $PrCl_3$–$CaCl_2$ and $NdCl_3$–$CaCl_2$ [6] that the degree of polymerization is higher for $NdCl_3$. Thus the quantity of Cl^- ions is higher in the $NdCl_3$ melt and explains the higher conductivity of molten $NdCl_3$ compared with the $PrCl_3$ melt.

According to Savin [29], the formation of 'chain structure' takes place during the melting of $LaCl_3$. Probably, the degree of polymerization for $LaCl_3$ is higher and the quantity of Cl^- ions with higher ionic mobility is also higher. This results in the higher electrical conductivity of molten $LaCl_3$. Unfortunately, there is no information about the structure of molten $CeCl_3$.

3.2. M_3LnCl_6 compounds

The specific electrical conductivity of M_3LnCl_6 compounds in the liquid state is also well-fitted by a quadratic function of temperature. The parameters *a*, *b* and *c* in the empirical conductivity equation of investigated compounds are presented in Table 3.

Owing to the lack of molar volume data for the investigated compounds, the calculation of the activation energy for electrical conduction used the equation

$$\kappa = \kappa_0 \exp(-E_A/RT) \qquad (2)$$

where κ_0 is a characteristic constant of the melt. Eq. (2) can be recalculated as follows:

$$\ln k = a + b/T$$

where $a = \ln\kappa_0$ and $b = -E_A/R$

The values *a*, *b* and E_A are presented in Table 4. In the literature there is limited data on the electrical conductivity of M_3LnCl_6 compounds. There are data for K_3NdCl_6 compound [18,24], K_3PrCl_6 compound [18,23] and values for Rb_3LaCl_6 and Cs_3LaCl_6 compounds only at 1195 K [18]. The electrical conductivity of the compounds M_3CeCl_6, Rb_3PrCl_6, Cs_3PrCl_6, Rb_3NdCl_6 and Cs_3NdCl_6 was measured for the first time in this work.

The comparison of results of this work with literature data for K_3PrCl_6 and K_3NdCl_6 is shown in Figs. 7 and 8. The results of this work are about 20% lower compared with the results of Iwadate et al. [23] for K_3PrCl_6 and about 35% higher compared with the results of Mochinaga and Iwadate [24] for K_3NdCl_6.

Table 4
Specific electrical conductance of molten M_3LnCl_6 compounds

Compound	*a* (S m^{-1})	*b* (K^{-1})	E_A (kJ mol^{-1})
Rb_3LaCl_6	6.153 ± 0.006	−1951.4 ± 6.7	16.22 ± 0.06
Cs_3LaCl_6	5.954 ± 0.015	−1956.8 ± 17.1	1627 ± 0.14
K_3CeCl_6	6.493 ± 0.053	−2062.7 ± 56.9	17.15 ± 0.47
Rb_3CeCl_6	6.167 ± 0.016	−2046.8 ± 17.9	17.02 ± 0.15
Cs_3CeCl_6	5.933 ± 0.011	−1949.4 ± 12.5	16.21 ± 0.10
K_3PrCl_6	6.428 ± 0.002	−1918.8 ± 2.4	15.95 ± 0.02
Rb_3PrCl_6	6.086 ± 0.003	−1936.8 ± 3.6	16.10 ± 0.03
Cs_3PrCl_6	5.899 ± 0.004	−1908.8 ± 5.5	15.87 ± 0.05
K_3NdCl_6	6.907 ± 0.008	−1891.9 ± 8.5	15.73 ± 0.07
Rb_3NdCl_6	6.759 ± 0.013	−2189.7 ± 14.2	18.21 ± 0.12
Cs_3NdCl_6	6.059 ± 0.008	−2040.1 ± 9.7	16.96 ± 0.08

Table 3
Results of electrical conductivity measurements of M_3LnCl_6 compounds (κ/S m^{-1})

Compound	Temperature (K)	*a* ($\times 10^{-2}$ S m^{-1})	*b* (S m^{-1} K^{-1})	*c* ($\times 10^4$ S m^{-1} K^{-2})	SE (S m^{-1})
Rb_3LaCl_6	1000–1146	−1.820	0.353	−1.05	0.305
Cs_3LaCl_6	1040–1215	−0.344	0.077	+0.12	0.769
K_3CeCl_6	1090–1132	−3.825	0.723	−2.58	2.608
Rb_3CeCl_6	1010–1142	−1.556	0.296	−0.79	0.557
Cs_3CeCl_6	1070–1220	−2.025	0.372	−1.18	0.370
K_3PrCl_6	939–1060	−1.832	0.374	−1.00	0.060
Rb_3PrCl_6	1030–1180	−1.546	0.297	−0.80	0.113
Cs_3PrCl_6	1085–1253	−1.667	0.307	−0.88	0.215
K_3NdCl_6	968–1096	−2.857	0.580	−1.44	0.924
Rb_3NdCl_6	1050–1191	−1.484	0.270	−0.25	1.011
Cs_3NdCl_6	1105–1249	−2.241	0.399	−1.22	0.296

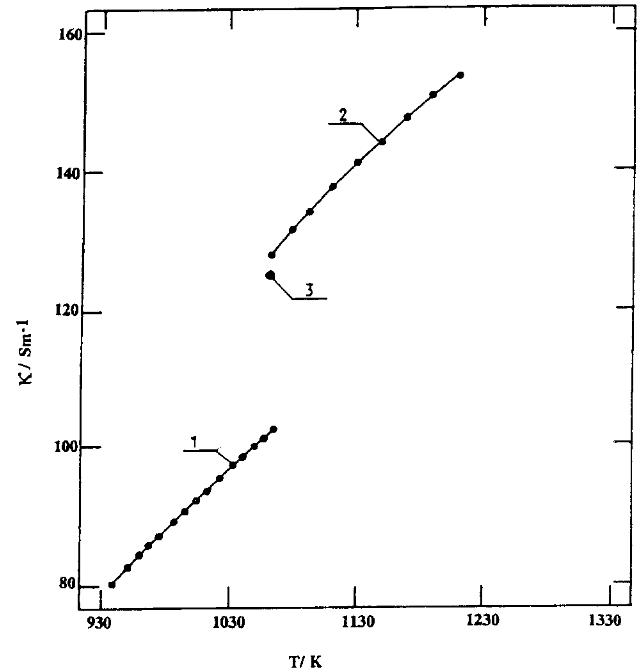

Fig. 7. Dependence of the specific conductivity of K_3PrCl_6 on temperature: (1), this work; (2), Iwadate et al. [23]; (3), Förthmann et al. [18].

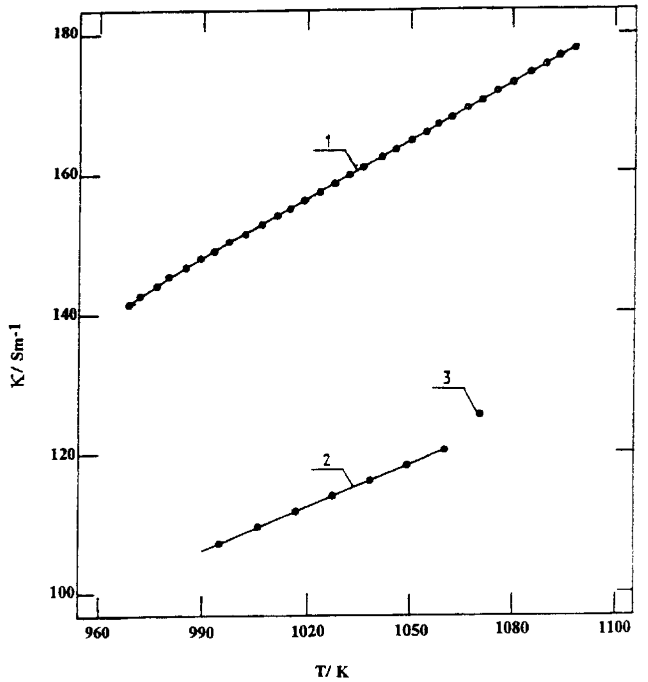

Fig. 8. Dependence of the specific conductivity of K_3NdCl_6 on temperature: (1), this work; (2), Mochinaga and Iwadate [24]; (3), Förthmann et al. [18].

Our results for Rb_3LaCl_6 and Cs_3LaCl_6 at 1195 K are 90.1 S m^{-1} and 75.0 S m^{-1}, compared with 130.7 S m^{-1} and 101.19 S m^{-1} respectively obtained by Förthmann et al. [18].

It can be seen from the data given in Table 4 that the activation energy of electrical conductivity does not depend significantly on alkali metal cation. The electrical conductivity of the investigated compounds decreases with increasing ionic radius of the alkali metal cation. It also depends on the lanthanide complex anion formed in the melt.

In the case of K_3LnCl_6 compounds, electrical conductivity of K_3NdCl_6 compound is significantly higher than for K_3PrCl_6 and K_3CeCl_6 compounds. This can be explained by polymer formation.

It was shown that in the melt KCl–$LnCl_3$ complexes, $LnCl_6^{3-}$ are formed [23,24]. The formation of dimers $Ln_2Cl_{11}^{5-}$ also takes place [24]. As a product of dimerization, free Cl^- ions with higher ionic mobility are produced. The possibility of dimerization or polymerization is higher for compound K_3NdCl_6, and the electrical conductivity of this compound is higher than the others.

For the Rb_3LnCl_6 compounds, electrical conductivity for Rb_3NdCl_6 is also significantly higher than for Rb_3LaCl_6, Rb_3PrCl_6 and Rb_3CeCl_6 compounds. Probably the dimerization can also take place but the degree of dimerization is lower than for K_3NdCl_6 compound.

In the case of Cs_3LnCl_6 compounds, the dimerization is not possible and the values of electrical conductivity of all compounds are very close to each other because of the similarity of the lanthanide cations.

References

[1] M. Gaune-Escard, L. Rycerz, W. Szczepaniak and A. Bogacz, *J. Alloys Comp.*, *204* (1994) 193.
[2] M. Gaune-Escard, L. Rycerz, A. Bogacz and W. Szczepaniak, *J. Alloys Comp.*, *204* (1994) 189.
[3] M. Gaune-Escard, L. Rycerz, A. Bogacz and W. Szczepaniak, in preparation.
[4] M. Gaune-Escard, A. Bogacz, L. Rycerz and W. Szczepaniak, *Thermochim. Acta*, *236* (1994) 67.
[5] M. Gaune-Escard, L. Rycerz, W. Szczepaniak and A. Bogacz, *Thermochim. Acta*, *236* (1994) 59.
[6] M. Gaune-Escard, L. Rycerz, W. Szczepaniak and A. Bogacz, *Thermochim. Acta*, *236* (1994) 51.
[7] R. Takagi, L. Rycerz and M. Gaune-Escard, *Denki Kagaku*, *62* (3) (1994) 240.
[8] M. Gaune-Escard, L. Rycerz and A. Bogacz, *J. Alloys Comp.*, *204* (1994) 185.
[9] W. Szczepaniak, Hexabromo- and hexaiodouranates (IV) of alkali metals as solid electrolytes, *Scientific Papers of the Institute of Inorganic Chemistry and Metallurgy of Rare Elements of the Technical University of Wrocław no. 62*, Monographs 30, Wrocław, 1990.
[10] G.I. Janz, *Mater. Sci. Forum*, *73–75* (1991) 707.
[11] R.P.T. Tomkins, G.I. Janz and E. Andalaft, *J. Electrochem. Soc. Electrochem. Sci. Technol.*, *117* (1970) 906.
[12] K. Igarashi and J. Mochinaga, *Z. Naturforsch.*, *42a* (1987) 777.
[13] G.W. Mellors and S. Senderoff, *J. Phys. Chem.*, *64* (1960) 294.
[14] W. Biltz and W. Klemm, *Z. Anorg. Chem.*, *152* (1926) 225, 267.
[15] J.S. Jaffe and E.R. van Artsdalen, Chemistry Division *Semian-*

nual Progress Rèp. ORNL-2159, Oak Ridge National Laboratory, 1956, p. 77.

[16] A.S. Dworkin, H.R. Bronstein and M.A. Bredig, *Discuss. Faraday Soc., 32* (1961) 188.

[17] A. Voigt and W. Biltz, *Z. Anorg. Chem., 133* (1924) 277.

[18] R. Förthmann, G. Vogel and A. Schneider, *Z. Anorg. Allg. Chem., 367* (1969) 19.

[19] M.W. Smirnov and V.A. Khokhlov, *Zh. Prikl. Khim., 2* (1970) 302.

[20] H.R. Bronstein, A.S. Dworkin and M.A. Bredig, *J. Phys. Chem., 66* (1962) 44.

[21] G.I. Janz, F.W. Dampier, G.R. Lakshminarayanan, P.K. Lorenz and R.P.T. Tomkins, *Molten Salts: Vol. 1, Electrical Conductance, Density and Viscosity Data, NSRDS-NBS 15*, 1968, p. 8.

[22] A.S. Dworkin, H.R. Bronstein and M.A. Bredig, *J. Phys. Chem., 66* (1962) 1201.

[23] Y. Iwadate, K. Igarashi and J. Mochinaga, *J. Electrochem. Soc. Electrochem. Sci. Technol., 133* (6) (1986) 1162.

[24] J. Mochinaga and Y. Iwadate, *J. Electrochem. Soc., 138* (12) (1991) 3588.

[25] R. Thoma, The rare eath halides, in L. Eyring (ed.), *Progress in the Science and Technology of the Rare Earths*, Pergamon, 1960.

[26] A.S. Dworkin and M.A. Bredig, *High Temp. Sci., 3* (1971) 81.

[27] A.S. Dworkin and M.A. Bredig, *J. Phys. Chem., 67* (1963) 697.

[28] M. Ikeda, Y. Miyagi, K. Igarashi, J. Mochinaga and H. Ohno, *The 20th Symp. on Molten Salt Chemistry, C303, Yokohama, Japan, November 10, 1988.*

[29] W.D. Savin, *Zh. Fiz. Khim., 60* (3) (1986) 554.