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## Electrical conductivity of $\text{GdCl}_3\text{--LiCl}$ and $\text{GdCl}_3\text{--LiCl--Gd}_2\text{O}_3$ molten systems

ELENA V. NIKOLAEVA\*, IRINA D. ZAKIRYANOVA, ANDREY L. BOVET  
and IRAIDA V. KORZUN

*Institute of High Temperature Electrochemistry, UB RAS, 620990 Yekaterinburg, Russia*

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**Abstract:** The electrical conductivity of  $\text{LiCl--GdCl}_3$  molten systems with the gadolinium chloride additions ranging from 0 to 23 mol % was measured depending on both the temperature and concentration of  $\text{GdCl}_3$ . The molar conductivity of the molten  $\text{GdCl}_3\text{--LiCl}$  system is calculated taking into account the assumption of additivity of the molar volume of the mixture. The obtained temperature dependencies can be approximated by Arrhenius-type equation. The effective activation energy,  $E_a$ , increased with the  $\text{GdCl}_3$  content. The liquidus temperatures of the studied systems were determined by differential scanning calorimetry. The high-temperature Raman spectra of  $\text{LiCl--GdCl}_3$  chloride melts were recorded. In addition, the conductivity of  $0.77\text{LiCl--}0.23\text{GdCl}_3$  molten system with 1 mol % of  $\text{Gd}_2\text{O}_3$  was measured. The investigation demonstrates that the addition of gadolinium oxide results in a decrease of the conductivity of the chloride molten system and growth of its liquidus temperature.

**Keywords:** AC impedance; gadolinium chloride; liquidus temperature; Raman spectra.

### INTRODUCTION

Gadolinium and its compounds are widely used in many areas of science and technology, such as nuclear power engineering, electronics, medicine. The unique magnetic properties of gadolinium allow it to be used for the production of laser materials. The high capability of neutron capturing makes it possible to use gadolinium compounds for controlling the operation of nuclear reactors.

The study of the electric transfer processes of molten mixtures of rare earth metal (RE) and alkali metal (M) chlorides is of interest in connection with the development of a number of scientific and technical problems related to the optimization of the processes of electrolytic production and refining of rare earth metals, use and regeneration of spent nuclear fuel (SNF).<sup>1</sup> For example, the pyro-

\* Corresponding author. E-mail: E.Nikolaeva@ihte.uran.ru  
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chemical methods of SNF reprocessing are considered as promising options in the innovative nuclear fuel cycle.<sup>2,3</sup> The development of technologies requires knowledge of the electrochemical and thermodynamic properties of molten mixtures of rare earth and alkali metal halides. In industrial production, it is desirable to have an electrolyte with high electrical conductivity and low liquidus temperatures to reduce energy consumption. Lithium chloride has the highest electrical conductivity among alkali metal chlorides and a relatively low melting point. Thus, the main operations of the pyrochemical processing of SNF are supposed to be carried out using anhydrous technologies in molten LiCl and eutectic LiCl–KCl.<sup>4</sup>

The electrical conductivity of only certain mixtures of RE chlorides with lithium chloride has been experimentally studied: LiCl–LaCl<sub>3</sub>,<sup>5</sup> LiCl–PrCl<sub>3</sub>,<sup>6</sup> LiCl–NdCl<sub>3</sub><sup>6</sup> and LiCl–SmCl<sub>3</sub>.<sup>6</sup> The conductivity of molten mixtures of GdCl<sub>3</sub> with NaCl and KCl were investigated.<sup>7,8</sup> Earlier we measured the conductivity of molten 0.515GdCl<sub>3</sub>–0.485KCl<sup>9</sup> system and GdCl<sub>3</sub>.<sup>10</sup> There is no available data on the conductivity of molten LiCl–GdCl<sub>3</sub> mixtures.

Zhou *et al.*<sup>11</sup> established the LiCl–GdCl<sub>3</sub> binary phase diagram based on the earlier results of differential thermal analysis and X-ray diffraction optimized using CALPHAD Thermo-Cal software. The authors<sup>11</sup> demonstrated that the phase diagram had a simple eutectic form. The eutectic point corresponds to the temperature of 678 K and a concentration of GdCl<sub>3</sub> of 45.2 mol %. The presence of Li<sub>3</sub>GdCl<sub>6</sub> ternary compound with polymorphic transformation at 646 K and peritectoid decomposition at 660 K was identified in the solid phase.

The purpose of this work was to determine the specific conductivity of molten GdCl<sub>3</sub>–LiCl systems containing up to 23 mol % GdCl<sub>3</sub>. Based on the experimental data, the calculation of molar conductivity was carried out.

Lanthanide chlorides are known to be extremely hygroscopic. When the temperature rises, they react with their own crystallization water to form very stable oxychlorides, which can dissolve in RE chlorides when the latter are melted.<sup>12</sup> The presence of oxychlorides in molten RECl<sub>3</sub> in dissolved form or in the form of solid particles leads to a decrease in the electrical conductivity of the systems.<sup>9,10</sup> Therefore, another aim of this work was to study the effect of oxygen impurities on the electrical conductivity of GdCl<sub>3</sub>–LiCl melts. To do this, the conductivity of 0.77LiCl–0.23GdCl<sub>3</sub> system containing 1 mol % of gadolinium oxide was investigated.

The liquidus temperatures were determined for all investigated chloride and oxide-chloride systems. In order to analyze the structural changes occurring in the chloride melt, the Raman spectra of homogeneous GdCl<sub>3</sub>–LiCl chloride melts were obtained.

## EXPERIMENTAL

*Samples preparation*

Lithium chloride (*puriss* grade, “Vekton,” St. Petersburg, Russia) was heated in vacuum with a gradual increase in temperature to 673 K and melted in an argon atmosphere. The resulting melt was additionally purified by directional crystallization (zone melting). According to the DSC curve (thermal analyzer STA 449C Jupiter (NETZSCH)) of the purified LiCl, a single peak is observed, which corresponds to the salt melting (Fig. 1A), and its temperature position  $880\pm 1$  K agrees with the available data for LiCl,  $T_m = 883\pm 2$  K.<sup>13</sup> The enthalpy change of melting ( $\Delta H_m = 19.903$  kJ/mol) also agrees well with the available data<sup>13</sup> ( $\Delta H_m = 19.83\pm 0.2$  kJ/mol).

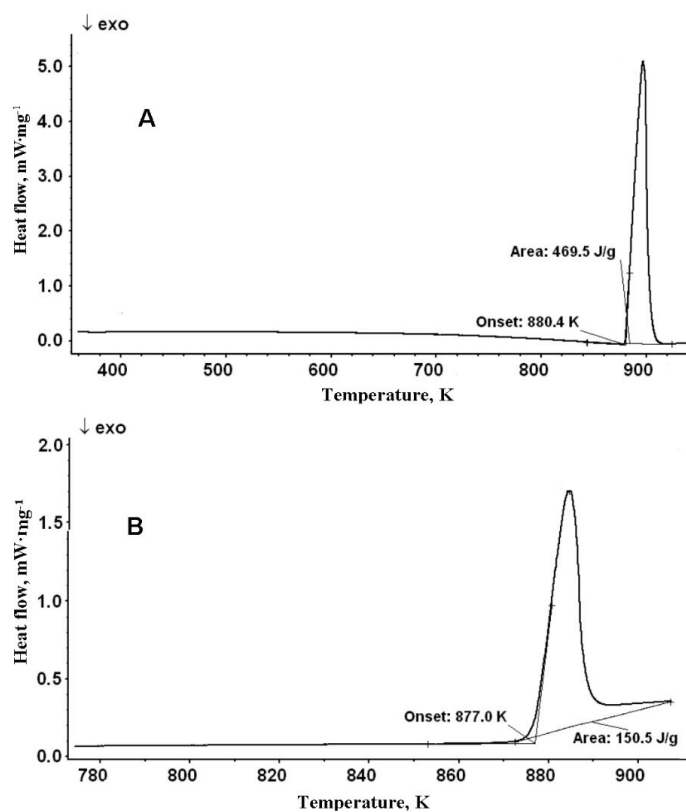


Fig 1. DSC curves for LiCl (A) and GdCl<sub>3</sub> (B).

Gadolinium chloride was prepared from gadolinium oxide (*puriss* grade, “Vekton,” St. Petersburg, Russia) according to the well-known technique, a detailed description of which was given in literature.<sup>10</sup>

The quality of anhydrous GdCl<sub>3</sub> was investigated by a well-proven visual method for determining the transparency of a salt solution in distilled water. On the DSC curve (Fig. 1B) of synthesized GdCl<sub>3</sub> one peak corresponding to the melting of the salt is observed, and its temperature position  $877\pm 1$  K is consistent with the available data for GdCl<sub>3</sub>.<sup>14-17</sup>

The Gd<sub>2</sub>O<sub>3</sub> powder was dried at 973 K for 4 h. X-ray diffraction and Raman spectroscopy confirmed the monophasic nature of the obtained product.<sup>10</sup>

All the operations with the prepared reagents were carried out in a glove box in a dry nitrogen atmosphere.

#### *Electrical conductivity measuring technique*

The experiments to determine the electrical conductivity of the GdCl<sub>3</sub>–LiCl melt were carried out in a cell with parallel platinum electrodes. The electrical conductivity was measured using a Z-1500J impedance meter, which allows the measurements to be carried out in the frequency range of alternating current from 1 to 1.5 MHz. The scheme of the experimental cell and the method of conducting the experiment are described in detail in the literature.<sup>18</sup>

The measuring set was calibrated in molten LiCl for which the explicit data on the conductivity within 917–1056 K are known.<sup>5</sup> The electrical conductivity measurements were performed at the temperatures above the liquidus temperature of each electrolyte composition. There were at least three consequential measurements in a series of experiments.

GdCl<sub>3</sub> was gradually added to molten LiCl in small portions without disturbing the gaseous atmosphere of the cell. After each addition, the system was kept at a certain temperature until the values of electrical resistance became stable. Only after this, the measurements of the temperature dependence of the electrical conductivity started. The concentration of GdCl<sub>3</sub> was determined after the experiment in a frozen float by the emission spectral analysis with inductively coupled plasma (Optima 4300 DV, "Perkin Elmer" USA).

#### *Determination of liquidus temperature using differential scanning calorimetry*

Liquidus temperatures were obtained by differential scanning calorimetry (DSC) using an STA 449C Jupiter® NETZSCH thermal analyser (Germany). The studies were carried out with a heating rate of 10 K/min in a high purity argon atmosphere in Pt–Rh crucibles. The uncertainty of the liquidus temperature values was less than 1 K. The liquidus temperature of each sample was determined during heating for the second measurement.<sup>19</sup>

#### *High-temperature Raman spectra technique*

Raman spectra of solid samples and melts were recorded using the Ava-Raman fiber-optic spectrometric complex (Avantes, the Netherlands), which includes a 50 mW laser source of monochromatic radiation with a wavelength of  $\lambda = 532$  nm. When registering the spectra, an 180° optical scattering scheme was used. The device of a high-temperature optical prefix was described earlier.<sup>19</sup> Platinum crucible was used as a container; the experiment was carried out in an argon atmosphere.

## RESULTS AND DISCUSSION

### *Liquidus temperature of LiCl–GdCl<sub>3</sub> system*

DSC curves were obtained for LiCl–GdCl<sub>3</sub> systems containing up to 23 mol % of GdCl<sub>3</sub>. As an example, Fig. 2 demonstrates the DSC and TG curves obtained for the 0.85LiCl–0.15GdCl<sub>3</sub> system. According to Zhou *et al.*<sup>11</sup> the temperatures of 647.7 and 664.3 K correspond to the temperatures of phase transitions in solid state. The solidus temperature is 680 K. The liquidus temperature for this composition is 819.3 K.

Liquidus temperatures for all the studied systems are given in Table I. Our data are in good agreement with the literature.<sup>11</sup>

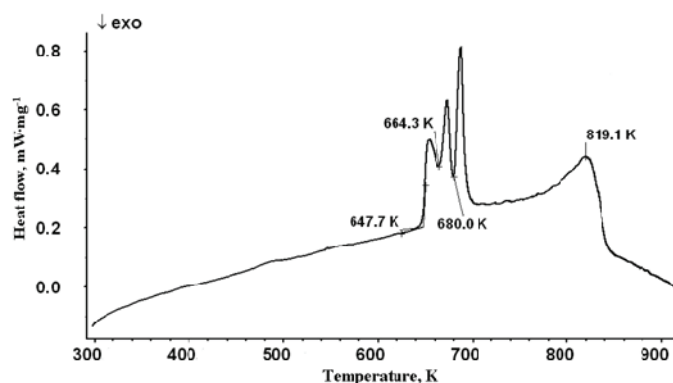


Fig. 2. DSC curve for the system 0.84LiCl–0.16GdCl<sub>3</sub>.

#### Electrical conductivity of GdCl<sub>3</sub>–LiCl molten systems

The temperature dependences of the specific electrical conductivity of the GdCl<sub>3</sub>–LiCl molten systems containing up to 23 mol % of GdCl<sub>3</sub> were investigated in the range from the temperature above the liquidus temperature of each mixture up to 1073 K (for composition 0.23GdCl<sub>3</sub>–0.77LiCl up to 1153 K). The obtained experimental data are shown in Fig. 3 together with the available data for LiCl.<sup>5</sup> It can be seen that the addition of GdCl<sub>3</sub> reduces the conductivity of the systems. The temperature dependences of the specific conductivity of LiCl–GdCl<sub>3</sub> melts were approximated by the linear equation:

$$\kappa = a + Bt \quad (1)$$

here  $\kappa$  is the specific conductivity,  $T$  – the temperature (K),  $a$  and  $b$  are constants. The coefficients of Eq. (1) are given in Table I.

TABLE I. Liquidus temperatures and coefficients in Eq. (1) for LiCl–GdCl<sub>3</sub> and LiCl–GdCl<sub>3</sub>–Gd<sub>2</sub>O<sub>3</sub> systems

System	$T_{\text{liq}}$ K	$A$ S cm <sup>-1</sup>	$B$ S cm <sup>-1</sup> K <sup>-1</sup>	$\kappa$ / S cm <sup>-1</sup>		
				923 K	1023 K	1103 K
0.94LiCl–0.06GdCl <sub>3</sub>	873	0.7125	0.00461	5.07	5.54	–
0.89LiCl–0.11GdCl <sub>3</sub>	843	0.4292	0.00419	4.43	4.86	–
0.84LiCl–0.16GdCl <sub>3</sub>	819	0.0691	0.00401	3.87	4.28	–
0.77LiCl–0.23GdCl <sub>3</sub>	752	–0.1441	0.00356	3.16	3.51	3.79
[0.77LiCl–0.23GdCl <sub>3</sub> ]–Gd <sub>2</sub> O <sub>3</sub> (1 mol %)	1090	0.9872	0.00243	–	–	3.67

Fig. 4 shows the isotherms of the normalized conductivity of the LiCl–GdCl<sub>3</sub> system containing from 0 to 23 mol % GdCl<sub>3</sub>. It can be seen that the specific conductivity gradually decreases with an increase in the concentration of gadolinium chloride, deviating from additive magnitudes towards smaller values. Thus, at 1023 K, the addition of 20 mol % GdCl<sub>3</sub> reduces the specific conduct-

ivity of the system by almost 40 %. The largest changes in the conductivity of the system occur at low temperatures.

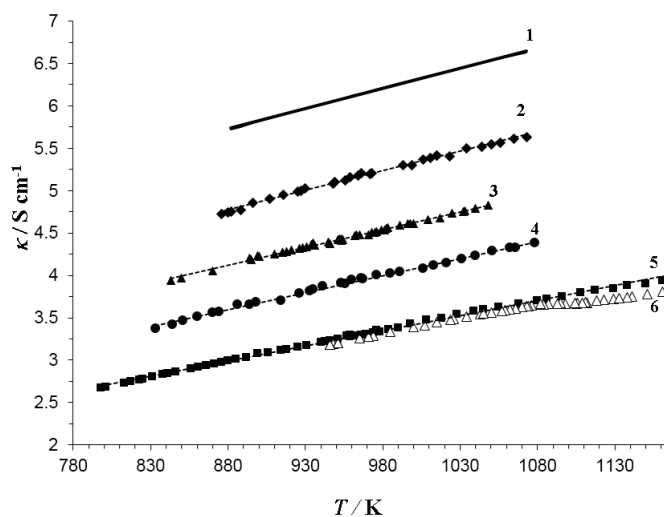


Fig. 3. Temperature dependence of the specific electrical conductivity of molten LiCl (1);<sup>5</sup> molten LiCl, containing GdCl<sub>3</sub> (mol %): 6 (2); 11 (3); 16 (4); 23 (5); 0.77LiCl–0.23GdCl<sub>3</sub> containing 1 mol % Gd<sub>2</sub>O<sub>3</sub> (6).

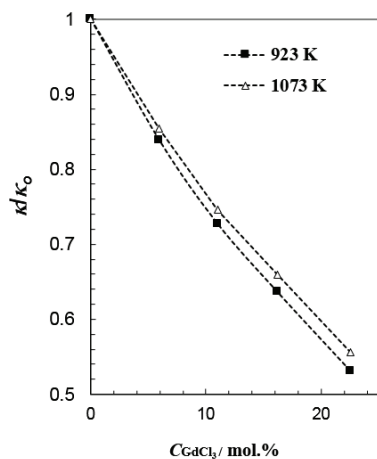


Fig. 4. Isotherms of normalized electrical conductivity of LiCl–GdCl<sub>3</sub> molten system at different temperatures ( $\kappa_0$  – specific conductivity of LiCl).

#### *Molar conductivity of molten GdCl<sub>3</sub>–LiCl mixtures*

The specific conductivity is the conductivity of a single volume of liquid. It is the value directly measured in the experiment. For the purposes of further analysis, it has the disadvantage that a single volume of different liquids (melts) contains a different number of molecules of the studied substances and, thus, a direct comparison of specific conductivity does not quite correctly reflect the properties

of the compared melts. It is more correct to compare the molar conductivity, that is, the conductivity of one mol of each melt.

The molar conductivity ( $A$ ) of LiCl-GdCl<sub>3</sub> melt can be calculated according to the equation:

$$A = \kappa V_m \quad (2)$$

where  $V_m$  is the molar volume.

Most mixtures of alkali and RE halides are formed with an increase in volume compared to its additive value.<sup>20</sup> Common to all systems is the effect of increasing deviations of the molar volume from the additive values as the size of the alkali metal cation increases.

Thus, according to the literature<sup>5,20,21</sup> for binary mixtures of RE chlorides with LiCl maximum the relative deviations of the additivity of the molar volume are less than 1 %. While when RE chlorides are mixed with cesium chlorides, this value can reach 4–5 %.

Therefore, the molar volume of the melt  $x\text{LiCl}-y\text{GdCl}_3$  can be represented by the following expression:

$$V_m = x(M_1/d_1) + y(M_2/d_2) \quad (3)$$

where  $M_1$  and  $d_1$  are the molecular weight and density of the melt LiCl;  $M_2$  and  $d_2$  are the molecular weight and density of the melt GdCl<sub>3</sub> (extrapolated to the studied temperature range),  $x$  and  $y$  are the molar fractions of the corresponding melt components.

The values of molar electrical conductivity of LiCl-GdCl<sub>3</sub> melts calculated in this way are shown in Fig. 5 (curves 2–5) in coordinates  $\ln A+1/T$ . In these coordinates, the values of molar conductivity can be approximated by the linear equation:

$$\ln A = A - E_a/(RT) \quad (4)$$

where  $A$  – constant;  $T$  is the absolute temperature (K);  $R$  – universal gas constant ( $\text{J K}^{-1} \text{mol}^{-1}$ );  $E_a$  is the activation energy of conductivity.

Fig. 5 also shows the molar conductivity values for LiCl (curve 1) and GdCl<sub>3</sub> (curve 6) melts calculated on the basis of the available data on specific conductivity<sup>5,10</sup> and density.<sup>5,21</sup> The values of the molar conductivity at 923 and 1023 K are given in Table II. The molar conductivity of LiCl is several times higher than of GdCl<sub>3</sub> whereas the activation energy of the GdCl<sub>3</sub> conductivity is 3 times higher than of LiCl. The addition of gadolinium chloride to molten LiCl reduces electrical conductivity of the systems. A slight increase in the activation energy can be noted with an increase in the concentration of GdCl<sub>3</sub> up to 23 mol %.

All isotherms of molar conductivity, both obtained by us for the GdCl<sub>3</sub>-LiCl system and the available data for the LaCl<sub>3</sub>-LiCl,<sup>5</sup> PrCl<sub>3</sub>-LiCl,<sup>6</sup> NdCl<sub>3</sub>-LiCl<sup>6</sup> and SmCl<sub>3</sub>-LiCl<sup>6</sup> systems, have a similar layout. As the RECl<sub>3</sub> concentration increases, the molar conductivity of the LiCl-RECl<sub>3</sub> mixtures gradually dec-

reases, deviating from additivity towards lower values. The maximum deviations from additivity are achieved when the  $\text{RECl}_3$  content in the melt is about 25 mol % and does not exceed 10–12 %. In this work, for the  $\text{GdCl}_3$ – $\text{LiCl}$  system containing 23 mol % gadolinium chloride, the deviation of the molar conductivity from the additive values is 10 %.

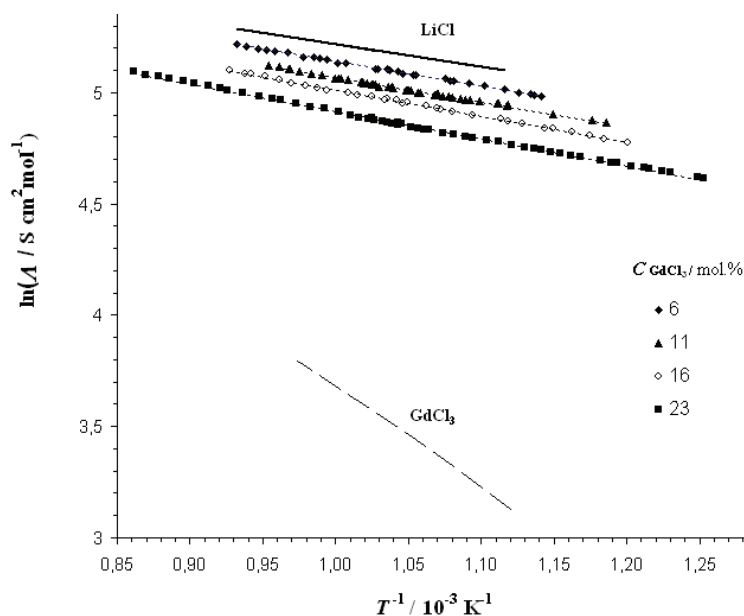


Fig. 5. Temperature dependence of the molar conductivity of molten  $\text{LiCl}$ ;<sup>5</sup>  $\text{GdCl}_3$ ;<sup>10,21</sup>  $\text{LiCl}$  containing 6, 11, 16 and 23 mol % of  $\text{GdCl}_3$ .

TABLE II. Coefficients of Eq. (3) for  $\text{LiCl}$ – $\text{GdCl}_3$  molten system

$c_{\text{GdCl}_3} / \text{mol } \%$	Temperature range, K	$A$	$E_a / \text{kJ mol}^{-1}$	$A / \text{S cm}^2 \text{mol}^{-1}$	
				923 K	1023 K
0 <sup>5</sup>	917–1056	6.2367	8.48	169.33	188.64
6	873–1070	6.2395	9.14	155.82	175.06
11	840–1045	6.1921	9.36	144.32	162.61
16	830–1063	6.1777	9.71	135.99	153.89
23	795–1158	6.1437	10.20	123.25	140.36
100 <sup>10,21</sup>	893–1028	8.1969	37.55	27.35	43.62

In the  $\text{GdCl}_3$ – $\text{NaCl}$  and  $\text{GdCl}_3$ – $\text{KCl}$  systems, the molar conductivity isotherms show deeper minima. At  $\text{GdCl}_3$  concentrations of 30–40 mol %, the deviation of molar conductivity from additive values reaches 30–50 %.<sup>7</sup>

The ionic potential of alkali metal cations is substantially lower than that of  $\text{RE}^{3+}$ . Therefore,  $\text{RE}^{3+}$  act as complexing agents, coordinating chlorine anions around themselves and displacing alkali metal cations into the second coordin-



ation sphere. When a small amount (on the order of magnitude of a few mol %) of RECl<sub>3</sub> is added to the MCl melt, strong 6-coordinate GdCl<sub>6</sub><sup>3-</sup> complexes are formed in the second coordination sphere of which there are alkali metal cations. This fact has been proven by many independent research methods.<sup>22-25</sup>

With an increase in the RECl<sub>3</sub> concentration, an increasing number of Cl<sup>-</sup> are required for the formation of six-coordinated complexes. The theoretical limit is 25 mol % RECl<sub>3</sub> when all anions are coordinated around RE<sup>3+</sup>. At higher RECl<sub>3</sub> concentrations, the melt structure becomes more complicated due to the inclusion of RECl<sub>6</sub><sup>3-</sup> octahedra in more complex ionic groups.

Analysis of the available data<sup>5-10</sup> shows that the conductivity of molten salt mixtures gradually decreases with the addition of RE chlorine anions to an alkali metal chloride, while the transfer numbers of chlorides decrease, since a lot of Cl<sup>-</sup> bind to complexes and do not participate in the transfer of electricity.

The alkali metal cations are displaced into the second coordination sphere, the mobility of Na<sup>+</sup> and K<sup>+</sup> decreases slightly with increasing RECl<sub>3</sub> concentration<sup>26</sup> whereas in LiCl-RECl<sub>3</sub> mixtures, in the concentration range from 0 to 80 mol % RECl<sub>3</sub>, the mobility of Li<sup>+</sup> decreases by half.<sup>27</sup> The ionic potential of Gd<sup>3+</sup> is only 2.4 times greater than the ionic potential of Li<sup>+</sup>,<sup>28</sup> so the counter-polarizing effect of three Li<sup>+</sup> can lead to strong distortions and dissociation of GdCl<sub>6</sub><sup>3-</sup> complexes. This can explain the fact that the deviations of molar conductivity of molten LiCl-RECl<sub>3</sub> mixtures from additive values are small.

#### *Raman spectra of LiCl-GdCl<sub>3</sub> melts*

*In situ* Raman spectroscopy has been used to obtain information about the structural features and characteristic vibrational frequencies of complex groupings in chloride melts containing lithium and gadolinium ions. Fig. 6 shows the Raman spectra of LiCl-GdCl<sub>3</sub> melts containing 0; 15; 25 mol. % GdCl<sub>3</sub>. No vibrational bands are recorded in the LiCl melt (Fig. 6). This fact directly indicates the predominantly Coulomb type of interparticle interaction in this system and the absence of a stable complex structural groupings in it.<sup>29,30</sup> A band at 252 cm<sup>-1</sup> was recorded in gadolinium-containing melts, which is attributed to the valence symmetric vibration of the complex grouping GdCl<sub>6</sub><sup>3-</sup>. The increase in the normalized intensity of this vibrational band was noted with the growing content of gadolinium chloride in the melt (Fig. 6), which is associated with an increase in the concentration of such groupings.

The obtained results made it possible to explain the results of the study of the conductivity of these systems. Indeed, when gadolinium ions are introduced into the melt, part of the chlorides binds to the GdCl<sub>6</sub><sup>3-</sup> grouping, which leads to a decrease in their mobility, and, as a consequence, to a difficulty in electrical transfer and to an increase in the activation energy of this process.

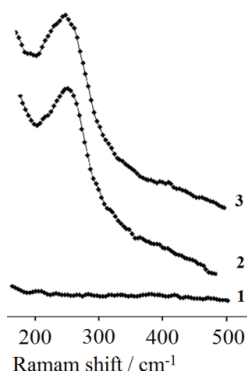


Fig 6. The Raman spectrum of the molten LiCl (1) and of the molten LiCl after the addition of GdCl<sub>3</sub> (mol %): 15 (2); 25 (3) at 898 K.

#### *Conductivity and liquidus temperature of the GdCl<sub>3</sub>–LiCl–Gd<sub>2</sub>O<sub>3</sub> molten mixture*

The temperature dependence of the electrical conductivity when introducing 1 mol % gadolinium oxide into the 0.23GdCl<sub>3</sub>–0.77LiCl system is shown in Fig. 3. Two sections with different slopes can be distinguished on the curve. The temperature at which the slope changes corresponds to the liquidus temperature of the system. Thus, the introduction of 1 mol % of gadolinium oxide leads to a significant increase in the liquidus temperature from 751 to 1090 K, which is obviously due to the low solubility of gadolinium oxide in the melt under study.

The section of the temperature dependence of the conductivity above the liquidus temperature was approximated by a linear equation of the form  $\kappa = A + BT$ , the coefficients of which are given in Table I. The decrease in the specific conductivity of the system 0.77GdCl<sub>3</sub>–0.23LiCl after the addition of 1 mol % Gd<sub>2</sub>O<sub>3</sub> in the range of 1093–1143 K is 3–4 %.

Gadolinium oxide is known<sup>10</sup> to react with gadolinium chloride, according to the reaction:



The observed patterns of changes in the specific electrical conductivity of the GdCl<sub>3</sub>–LiCl melt, when gadolinium oxide is added, can be explained by the formation of complex oxychloride groups when gadolinium oxychloride is dissolved in the liquid phase.

According to the results of studies of the local structure and ion dynamics in molten systems 0.5LiCl–0.5GdCl<sub>3</sub>, with a Gd<sub>2</sub>O<sub>3</sub> concentration up to 2 mol % obtained by *ab initio* molecular dynamics and *in situ* Raman spectroscopy,<sup>31</sup> gadolinium oxide in the chloride melt dissociated to form [Gd<sub>2</sub>OLi] groups, which were incorporated into the network-like structure of the original chloride melt.

#### CONCLUSIONS

The specific conductivity of the molten GdCl<sub>3</sub>–LiCl system was investigated depending on the temperature and concentration of GdCl<sub>3</sub> up to 23 mol %.

A significant decrease of conductivity with the concentration of gadolinium chloride was shown. So at 923 K, the additive of 20 mol % GdCl<sub>3</sub> reduces the conductivity of the system by 40 %. An increase in the system temperature slightly slows down the decrease in the conductivity of the system with an increase in the concentration of GdCl<sub>3</sub>.

The molar conductivity of the molten GdCl<sub>3</sub>–LiCl system is calculated taking into account the assumption of additivity of the molar volume of the mixture. The temperature dependences of the molar conductivity were approximated by Arrhenius type equation. A slight increase in the activation energy of molar conductivity can be noted with an increase in the concentration of GdCl<sub>3</sub>.

The spectral studies have shown that when gadolinium ions are introduced into the LiCl melt, part of the chlorine anions binds to the GdCl<sub>6</sub><sup>3-</sup> grouping. This leads to a decrease in their mobility, and, as a consequence, the difficulty of electrical transfer and an increase in the activation energy of this process.

The introduction of 1 mol % of gadolinium oxide to GdCl<sub>3</sub>–LiCl melt leads to a significant increase in the liquidus temperature of the system and a decrease in conductivity. This can be explained by the formation of complex oxychloride groups during the dissolution of gadolinium oxide in the liquid phase.

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## ИЗВОД

ПРОВОДЉИВОСТ РАСТОПА GdCl<sub>3</sub>–LiCl И GdCl<sub>3</sub>–LiCl–Gd<sub>2</sub>O<sub>3</sub>

ELENA V. NIKOLAEVA, IRINA D. ZAKIRYANOVA, ANDREY L. BOVET и IRAIDA V. KORZUN

*Institute of High Temperature Electrochemistry, UB RAS, 620990 Yekaterinburg, Russia*

Мерена је проводљивост растопа LiCl–GdCl<sub>3</sub> са додатком гадолинијум-хлорида у распону од 0 до 23 mol % при различитим температурама и концентрацијама GdCl<sub>3</sub>. Моларна проводљивост растопа GdCl<sub>3</sub>–LiCl је рачуната уз претпоставку адитивности моларне запремине смеше. Добијене температурне зависности се могу апроксимирати Аренијусовским типом једначине. Ефективна енергија активације,  $E_a$ , је расла са повећањем садржаја GdCl<sub>3</sub>. Температуре ликвидуса испитиваних растопа су одређиване методом диференцијалне скенирајуће калориметрије. Снимљени су високо-температурни Раманови спектри растопа LiCl–GdCl<sub>3</sub>. Поред тога, измерена је проводљивост растопа 0,77LiCl–0,23GdCl<sub>3</sub> са 1 mol % Gd<sub>2</sub>O<sub>3</sub>. Испитивања су показала да додатак гадолинијум-оксида смањује електричну проводљивост хлоридних растопа и повећава њихову температуру ликвидуса.

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