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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

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Abstract: The electrical conductivity of 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 GdCl_3 . The molar electrical 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 GdCl_3 content. The liquidus temperatures of the studied systems were determined by differential scanning calorimetry. The high-temperature Raman spectra of LiCl-GdCl_3 chloride melts were recorded. In addition, the electrical conductivity of $0.77\text{LiCl-}0.23\text{GdCl}_3$ molten system with 1 mol% of Gd_2O_3 was measured. The investigation demonstrates that the addition of gadolinium oxide results in a decrease of the electrical 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 with the optimization of the processes of electrolytic production and refining of rare earth metals, utilization and regeneration of spent nuclear fuel (SNF).¹ For example,

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pyrochemical methods of SNF reprocessing are considered as promising options in the innovative nuclear fuel cycle.^{2,3} 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.⁴

The electrical conductivity of only certain mixtures of RE chlorides with lithium chloride has been experimentally studied: LiCl–LaCl₃,⁵ LiCl–PrCl₃,⁶ LiCl–NdCl₃⁶ and LiCl–SmCl₃.⁶ In^{7,8} the electrical conductivity of molten mixtures of GdCl₃ with NaCl and KCl were investigated. Earlier we measured the electrical conductivity of molten 0.515GdCl₃–0.485KCl⁹ system and GdCl₃.¹⁰ There is no available data on the electrical conductivity of molten LiCl–GdCl₃ mixtures.

Wentao Zhou *et al.*¹¹ established the LiCl–GdCl₃ binary phase diagram based on the earlier results of differential thermal analysis and X-ray diffraction optimized using CALPHAD Thermo-Cal software. The authors¹¹ demonstrated that the phase diagram had a simple eutectic form. The eutectic point corresponds to temperature of 678 K and a concentration of GdCl₃ of 45.2 mol%. The presence of Li₃GdCl₆ 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 electrical conductivity of molten GdCl₃–LiCl systems containing up to 23 mol% GdCl₃. Based on experimental data, the calculation of molar electrical 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.¹² The presence of oxychlorides in molten RECl₃ in dissolved form or in the form of solid particles leads to a decrease in the electrical conductivity of the systems.^{9,10} Therefore, another aim of this work was to study the effect of oxygen impurities on the electrical conductivity of GdCl₃–LiCl melts. To do this the electrical conductivity of 0.77LiCl–0.23GdCl₃ 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 GdCl₃–LiCl chloride melts were obtained.

EXPERIMENTAL

Samples preparation

Lithium chloride (*puriss.* grade, “Vekton,” St. Petersburg, Russian Federation) 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. 1, A), and its temperature position 880 ± 1 K agrees with the available data for LiCl, $T_m = 883 \pm 2$ K.¹³ The enthalpy of melting ($\Delta H_m = 19.903$ kJ/mol) also agrees well with the available data¹³ ($\Delta H_m = 19.83 \pm 0.2$ kJ/mol).

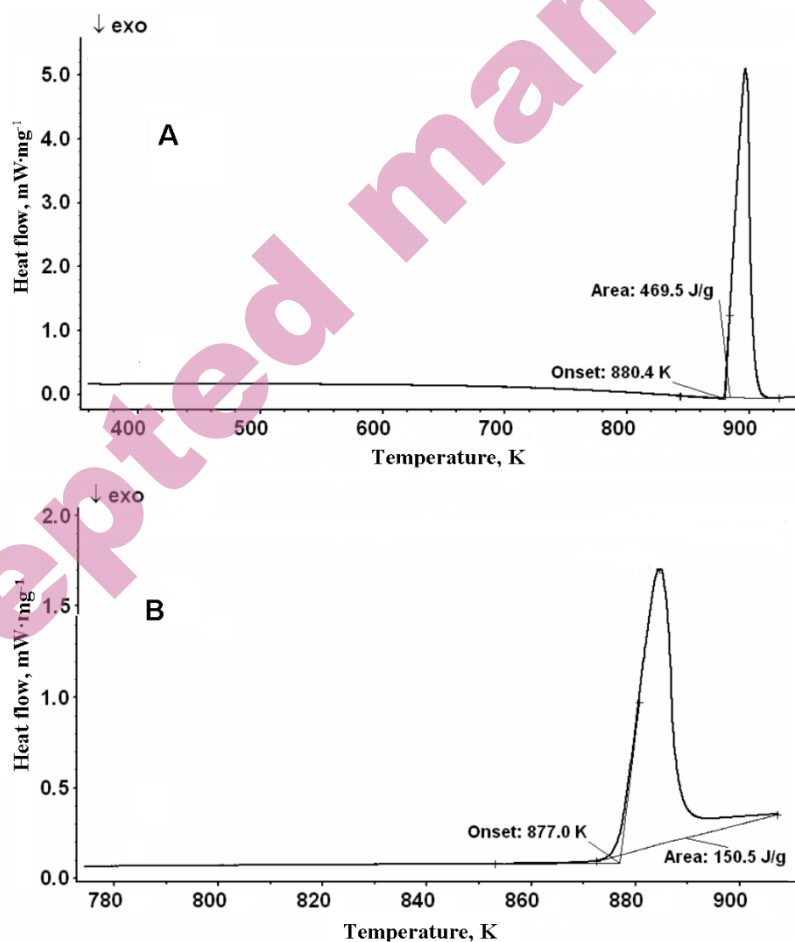


Fig 1. DSC curves for LiCl (A) and GdCl₃ (B).

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

The quality of anhydrous GdCl₃ was investigated by a well-proven visual method for determining the transparency of a salt solution in distilled water. On the DSC curve (Fig. 1, B) of synthesized GdCl₃ one peak corresponding to the melting of the salt is observed, and its temperature position 877 ± 1 K is consistent with the available data for GdCl₃.¹⁴⁻¹⁷

The Gd₂O₃ powder was dried at 973 K for 4 h. X-ray diffraction and Raman spectroscopy confirmed the monophasic nature of the obtained product.¹⁰

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

Electrical conductivity measuring technique

Experiments to determine the electrical conductivity of the GdCl₃–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 measurements to be carried out in the frequency range of alternating current from 1 MHz to 1.5 MHz. The scheme of the experimental cell and the method of conducting the experiment are described in detail in.¹⁸

The measuring set was calibrated in molten LiCl for which the explicit data on the electrical conductivity over 917-1056 K are known.⁵ 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.

GdCl₃ 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, measurements of the temperature dependence of the electrical conductivity started. The concentration of GdCl₃ was determined after the experiment in a frozen float by 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.¹⁹

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.¹⁹ Platinum crucible was used as a container; the experiment was carried out in an argon atmosphere.

RESULTS AND DISCUSSION

Liquidus temperature of LiCl–GdCl₃ system

DSC curves were obtained for LiCl–GdCl₃ systems containing up to 23 mol% of GdCl₃. As an example, Fig. 2 demonstrates the DSC and TG curves obtained

for the 0.85LiCl–0.15GdCl₃ system. According to Wentao Zhou et al.¹¹ 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.

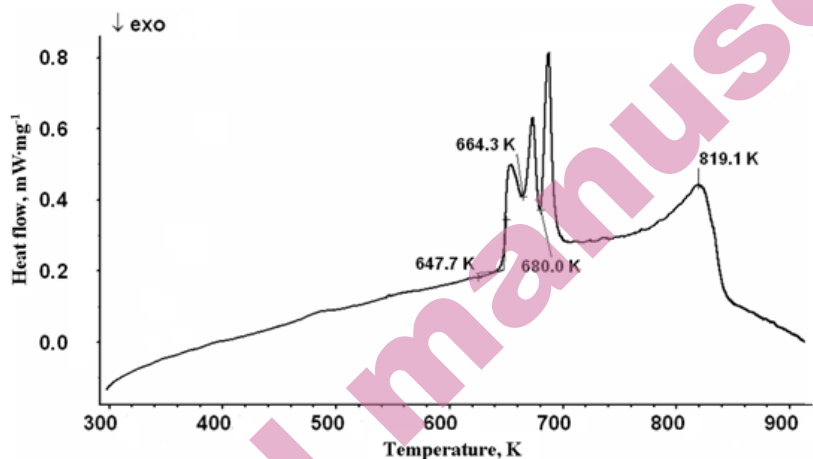


Fig 2. DSC curve for the system 0.84LiCl–0.16GdCl₃.

Liquidus temperatures for all the studied systems are given in Table 1. Our data are in good agreement with.¹¹

TABLE I. Liquids temperatures and coefficients in eq. (1) for LiCl–GdCl₃ and LiCl–GdCl₃–Gd₂O₃ systems

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

Electrical conductivity of GdCl₃–LiCl molten systems

The temperature dependences of the specific electrical conductivity of the GdCl₃–LiCl molten systems containing up to 23 mol% of GdCl₃ were investigated in the range from the temperature above the liquidus temperature of each mixture up to 1073 K (for composition 0.23GdCl₃–0.77LiCl up to 1153 K). The obtained experimental data are shown in Fig.3 together with the available data for LiCl.⁵ It can be seen that the addition of GdCl₃ reduces the electrical conductivity of the systems. The temperature dependences of the specific electrical conductivity of LiCl–GdCl₃ melts were approximated by linear equation:

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

here κ is specific electrical conductivity, T – temperature (K), a and b are constants. The coefficients of eq. (1) are given in Table I.

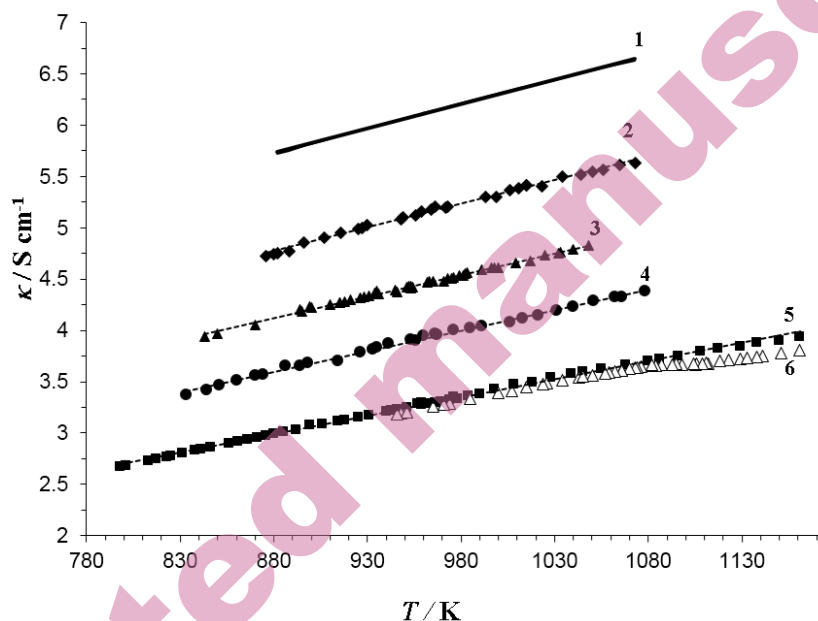


Fig 3. Temperature dependence of the specific electrical conductivity of molten LiCl^5 (1); molten LiCl , containing GdCl_3 (mol %): 6 (2); 11 (3); 16 (4); 23 (5); $0.77\text{LiCl}-0.23\text{GdCl}_3$ containing 1 mol% Gd_2O_3 (6).

Figure 4 shows the isotherms of the normalized conductivity of the $\text{LiCl} - \text{GdCl}_3$ system containing from 0 to 23 mol% GdCl_3 . It can be seen that the specific electrical 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_3 reduces the specific electrical conductivity of the system by almost 40%. The largest changes in the electrical conductivity of the system occur at low temperatures.

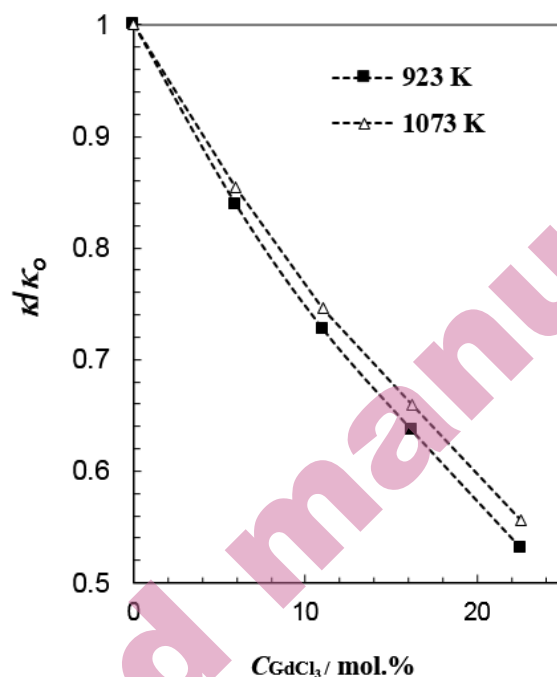


Fig 4. Isotherms of normalized electrical conductivity of LiCl–GdCl₃ molten system at different temperatures (κ_0 - specific electrical conductivity of LiCl).

Molar electrical conductivity of molten GdCl₃–LiCl mixtures

Specific electrical conductivity is the electrical 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 electrical conductivity does not quite correctly reflect the properties of the compared melts. It is more correct to compare the molar electrical conductivity, that is, the electrical conductivity, of one mole of each melt.

Molar electrical conductivity (Λ) of LiCl–GdCl₃ melt can be calculated according to the equation:

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

where κ is the specific electrical conductivity, V_m is the molar volume.

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

Thus, according to^{5,20,21} for binary mixtures of rare earth metal 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_3 (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_3 melts calculated in this way are shown in Figure 5 (curves 2-5) in coordinates $\ln(\Lambda) - 1/T$. In these coordinates, the values of molar electrical conductivity can be approximated by the linear equation

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

where Λ is the molar electrical conductivity ($\text{S cm}^2 \text{ mol}^{-1}$); 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 electrical conductivity.

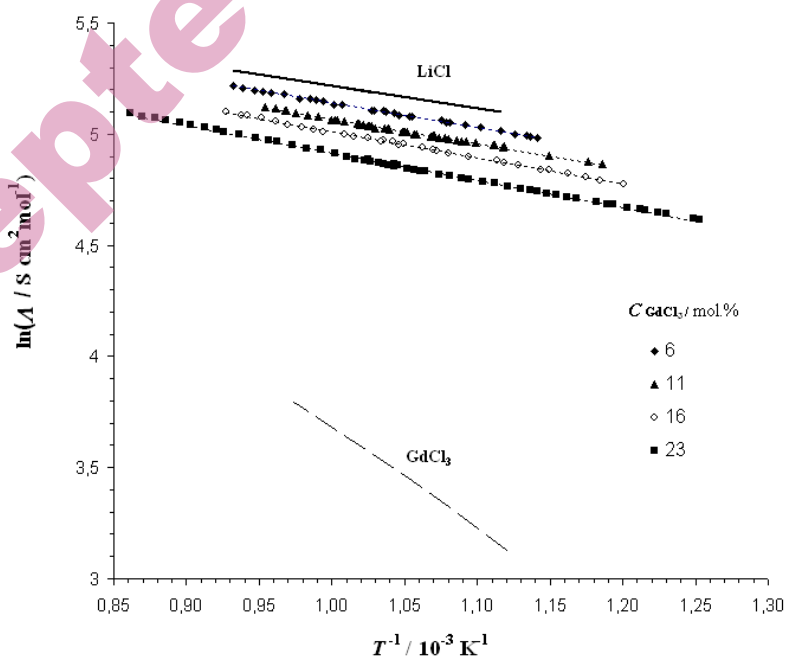


Fig 5. Temperature dependence of the molar conductivity of molten LiCl;⁵ GdCl_3 ;^{10,21} LiCl containing 6; 11; 16 and 23 mol% of GdCl_3 .

Figure 5 also shows the molar electrical conductivity values for LiCl (curve 1) and GdCl₃ (curve 6) melts calculated on the basis of the available data on specific electrical conductivity^{5,10} and density.^{5,21} The values of the molar electrical conductivity at 923 K and 1023 K are given in Table 2. The molar electrical conductivity of LiCl is several times higher than of GdCl₃ whereas the activation energy of the GdCl₃ electrical 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 GdCl₃ up to 23 mol%.

TABLE II. Coefficients of (3) for LiCl–GdCl₃ molten system

$c_{\text{GdCl}_3} / \text{mol}\%$	Temperature range, K	A	$E_A / \text{kJ mol}^{-1}$	$A / \text{S cm}^2 \text{mol}^{-1}$	
				923K	1023K
0 ⁵	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 ^{10,21}	893–1028	8.1969	37.55	27.35	43.62

All isotherms of molar electrical conductivity, both obtained by us for the GdCl₃–LiCl system, and available data for the LaCl₃–LiCl,⁵ PrCl₃–LiCl,⁶ NdCl₃–LiCl,⁶ SmCl₃–LiCl⁶ systems look in the similar way. As the RECl₃ concentration increases, the molar electrical conductivity of the LiCl–RECl₃ mixtures gradually decreases, deviating from additivity towards lower values. The maximum deviations from additivity are achieved when the RECl₃ content in the melt is about 25 mol% and does not exceed 10–12%. In this work, for the GdCl₃–LiCl system containing 23 mol% gadolinium chloride, the deviation of the molar electrical conductivity from the additive values is 10%.

In the GdCl₃–NaCl and GdCl₃–KCl systems, the molar electrical conductivity isotherms show deeper minima. At GdCl₃ concentrations of 30–40 mol%, the deviation of molar electrical conductivity from additive values reaches 30–50%.⁷

The ionic potential of alkali metal cations is substantially lower than that RE³⁺ cation. Therefore, RE³⁺ ions act as complexing agents, coordinating chlorine anions around themselves and displacing alkali metal cations into the second coordination sphere. When a small amount (on the order of a few mole percent) of RECl₃ is added to the MCl melt, strong 6-coordinate GdCl₆³⁻ 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.²²⁻²⁵

With an increase in the RECl₃ concentration, an increasing number of Cl⁻ anions are required for the formation of six-coordinated complexes. The theoretical limit is 25 mol. % RECl₃ when all anions are coordinated around RE³⁺ cations. At

higher RECl₃ concentrations, the melt structure becomes more complicated due to the inclusion of RECl₆³⁻ octahedra in more complex ionic groups.

Analysis of the available data⁵⁻¹⁰ shows that the electrical conductivity of molten salt mixtures gradually decreases with the addition of RE chloride to alkali metal chloride, while the transfer numbers of chlorine anions decrease, since a large number of Cl⁻ ions bind to complexes and do not participate in the transfer of electricity.

Alkali metal cations are displaced into the second coordination sphere, the mobility of Na⁺ and K⁺ cations decreases slightly with increasing RECl₃ concentration²⁶ whereas in LiCl–RECl₃ mixtures, in the concentration range from 0 to 80 mol % RECl₃, the mobility of Li⁺ cations decreases by half.²⁷ The ionic potential of Gd³⁺ is only 2.4 times greater than the ionic potential of Li⁺,²⁸ so the counter-polarizing effect of three Li⁺ ions can lead to strong distortions and dissociation of GdCl₆³⁻ complexes. This can explain the fact that the deviations of molar electrical conductivity of molten LiCl–RECl₃ mixtures from additive values are small.

Raman spectra of LiCl–GdCl₃ 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. Figure 6 shows the Raman spectra of LiCl–GdCl₃ melts containing 0; 15; 25 mol. % GdCl₃. 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 stable complex structural groupings in it.^{29,30} A band at 252 cm⁻¹ was recorded in gadolinium-containing melts, which is attributed to the valence symmetric oscillation of the complex grouping GdCl₆³⁻. An increase in the normalized intensity of this vibrational band was noted with an increase in the content of gadolinium chloride in the melt (Fig. 6), which is associated with an increase in the concentration of such groupings.

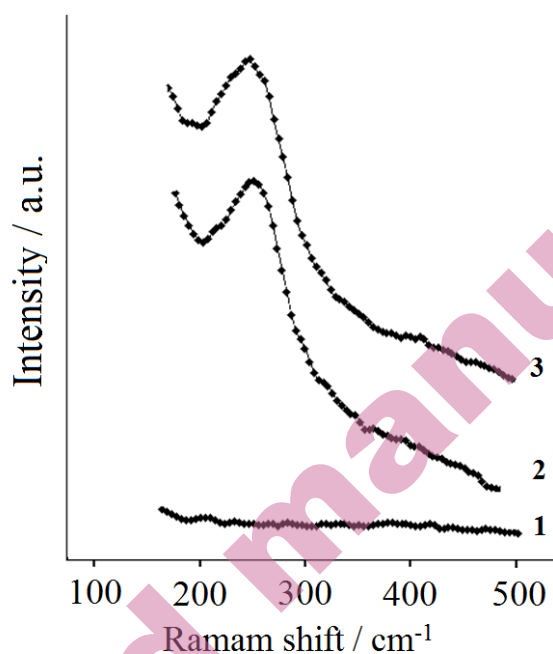


Fig 6. The Raman spectrum of the molten LiCl (1) and of the molten LiCl after the addition of GdCl₃ (mol%): 15 (2); 25 (3) at 898 K.

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 chlorine anions binds to the GdCl₆³⁻ grouping, which leads to a decrease in their mobility, and, as a consequence, difficulty in electrical transfer and an increase in the activation energy of this process.

Electrical conductivity and liquidus temperature of the GdCl₃-LiCl-Gd₂O₃ molten mixture

The temperature dependence of the electrical conductivity when introducing 1 mol. % gadolinium oxide into the 0.23GdCl₃-0.77LiCl 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 751K to 1090K, which is obviously due to the low solubility of gadolinium oxide in the melt under study.

The section of the temperature dependence of the electrical 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 1. The decrease in the specific electrical conductivity of the system 0.77GdCl₃-0.23LiCl after the addition of 1 mol% Gd₂O₃ in the range of 1093–1143 K is 3–4 %.

Gadolinium oxide is known¹⁰ to react with gadolinium chloride, according to the reaction:



The observed patterns of changes in the specific electrical conductivity of the GdCl_3 – 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_3 with a Gd_2O_3 concentration up to 2 mol% obtained by *ab initio* molecular dynamics and *in situ* Raman spectroscopy³¹ gadolinium oxide in the chloride melt dissociated to form $[\text{Gd}_2\text{OLi}]$ groups, which were incorporated into the network-like structure of the original chloride melt.

CONCLUSIONS

The specific electrical conductivity of the molten GdCl_3 – LiCl system was investigated depending on the temperature and concentration of GdCl_3 up to 23 mol%.

A significant decrease of electrical conductivity with the concentration of gadolinium chloride was shown. So at 923 K, the additive of 20 mol% GdCl_3 reduces the electrical conductivity of the system by 40%. An increase in the system temperature slightly slows down the decrease in the electrical conductivity of the system with an increase in the concentration of GdCl_3 .

The molar electrical conductivity of the molten GdCl_3 – LiCl system is calculated taking into account the assumption of additivity of the molar volume of the mixture. The temperature dependences of the molar electrical conductivity were approximated by Arrhenius type equations. A slight increase in the activation energy of molar electrical conductivity can be noted with an increase in the concentration of GdCl_3 .

Spectral studies have shown that when gadolinium ions are introduced into the LiCl melt, part of the chlorine anions binds to the GdCl_6^{3-} 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.

Introduction of 1 mol% of gadolinium oxide to GdCl_3 – LiCl melt leads to a significant increase in the liquidus temperature of the system and a decrease in electrical 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

ЕЛЕКТРИЧНА ПРОВОДЉИВОСТ РАСТОПА $\text{GDCL}_3\text{-LiCl}$ И $\text{GDCL}_3\text{-LiCl-GD}_2\text{O}_3$

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Мерена је електрична проводљивост растопа LiCl-GdCl_3 са додатком гадолинијум-хлорида у распону од 0 до 23 mol% при различитим температурама и концентрацијама GdCl_3 . Моларна електрична проводљивост растопа $\text{GdCl}_3\text{-LiCl}$ 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_3 . Температуре ликвидуса испитиваних растопа су одређиване методом диференцијалне скенирајуће калориметрије. Снимљени су високо-температурни Раманови спектри растопа LiCl-GdCl_3 . Поред тога, измерена је електрична проводљивост растопа $0,77\text{LiCl-0,23GdCl}_3$ са 1 mol% Gd_2O_3 . Испитивања су показала да додаток гадолинијум-оксида смањује електричну проводљивост хлоридних растопа и повећава њихову температуру ликвидуса.

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