

Structure Modification and Electrochemical Properties Intensification of Molten Chloride Electrolytes by Stimulated Dissociation of Complex Structural Units

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Abstract: In the molten chloride electrolytes the Wien effect and the related phenomenon the dissociation field effect are observed. The conductivity of molten magnesium and rare earth metals chlorides and their mixtures with the alkali metals chlorides rise with increasing electrical field intensity and strive to achieve the limiting values in the fields of the order of 1 MV/m. The field conductance quotient achieves up to the hundreds of percent. Under influence of completed microsecond strong electrical pulses the melts manifest the transition into a non-equilibrium state with modification of the structure and intensification of the electrochemical properties. As a result of prolonged structural relaxation in non-equilibrium melts, their electrochemical parameters and structure tend to restore their equilibrium values and singularities.

Keywords: molten electrolytes, Wien effect, activation, non-equilibrium state, structural relaxation

INTRODUCTION

The molten electrolytes (ME) are widely used for the production of most metals of the periodic table by electrochemical and pyrometallurgical methods, sometimes they are irreplaceable. Magnesium and aluminum are among the metals most used in modern industries, the rare earth metals (REM) are finding increasing use in the modern technologies. These ME are strongly structured; their structure, the nature and distribution of structural species in them determine their physicochemical properties, the mechanisms and kinetic pathways that decrease energetic efficiency of the metals production technologies [1]. The high ionic conductivities and diffusivities with low viscosities of molten alkali and alkaline earth metal salts and their mixtures are desirable features both from the point of view of power. The most commonly used salts are chlorides, fluorides, and chloride-fluoride mixtures. Chlorides offer the advantages of a lower operating temperature and of a greater choice of electrode and container materials [2].

Structural features of molten chloride electrolytes have been studied by modern spectroscopy and diffraction methods on a high level. On the pair radial distribution functions (PDF) $g_{+-}(r)$, $g_{++}(r)$ and $g_{--}(r)$ in molten $MgCl_2$ are observed high first peak and second peak, they show structural features not readily explained in purely ionic framework [3, 4]. Moreover, measurement of the partial structure factors of molten $MgCl_2$ by N-diffraction method [5, 6] has shown the presence of "pre-peak" in the structural factor $S_{++}(k)$ which is believed to long-range polymeric ordering of basic $MgCl_4^{2-}$ -structural species and to the presence of intermediate-range order in ionic framework. Investigation of the Raman spectra of the molten mixtures $MgCl_2$ -KCl indicates that the melts involve equilibrium between structural units $MgCl_4^{2-}$ and $Mg_2Cl_7^{3-}$ [7], the melts are among those, in which accordingly Raman spectra the intermediate order in the formation of the ion network is presented, as it was shown by the diffraction data; in these mixtures the complex ions content increases and they become more stable compared with the individual molten $MgCl_2$ [8].

The Raman spectroscopic and neutron diffraction studies for the simple molten REM chlorides $LnCl_3$ and their mixtures $LnCl_3$ -MCl (M=Li, Na, K) have shown that the predominant species in these melts are isolated species-

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octahedral complex LnCl_6^{3-} -ions forming polynuclear structures, i.e., these melts consist of distorted LnCl_6^{3-} -octahedral sharing chlorides and forming a loose “network” structure [9-12].

These particular liquids indeed are strongly organized at unusually long distances arising at the nanometer length scale interactions [6]. Energy efficiency of electrochemical technologies depends on the Faraday efficiency (equilibrium decomposition potential of MX_n with considering the overpotentials at the electrodes) and ohmic overpotential (or IR drop). These main two factors are dependent on the structure of ME, the nature and distribution their structural units. Although the structural and electrochemical properties of ME are investigated in an equilibrium or weakly perturbed state, relatively little is known about these systems in a non-equilibrium state. Meanwhile, these parameters can change, and sometimes considerably, in a favorable direction, if the systems are transformed into a non-equilibrium state under the influence of external influences at a given composition and temperature. One way to achieve this is to impact on the molten systems by short electrical pulses of high energy causing the modification or simplifying their structure. The stimulated dissociation of complex ions can be manifested in the change in the spectra of the melts, in the increase of their electrical conductivity, the electrolysis current density, and in the decrease in the decomposition potential of the salts. These changes could provide the insight into the equilibrium electrolytes structure and reducing the energy intensity of electrochemical technologies.

It is known that the Wien effect has served as the experimental proof of the validity of the Debye-Huckel-Onsager theory of electrolyte solutions and is used as a method of physico-chemical research. Prior to our publications, for example [13-15], in the literature have not been articles on the Wien effect in molten salts. We established the regularities of this effect in molten alkali halides and their binary mixtures [16], in molten alkaline earth chlorides and their mixtures with potassium chloride [17-20], in aluminum chloride electrolyte [21, 22], and also in some molten rare-earth chlorides and in their mixtures with potassium chloride [23, 24]. The obtained high-voltage limiting conductivities of individual molten salts obey the Nernst-Einstein ratio [16-20]. These regularities have been established by analyzing the waveforms of high-voltage pulsed (HVP) discharges in them. After exposure to the molten salts of microsecond pulses, the low-voltage conductivity and the current density of electrolysis are significantly increased [21-29], i.e. the phenomenon of activation with their transition into a non-equilibrium state is observed. The activated state exhibits a significantly prolonged relaxation. The activation phenomenon was not observed in the case of simple and unstructured melts- the molten alkali halides. In this brief review, we present some results on the Wien effect and a related the dissociation field effect obtained for chloride melts of polyvalent metals; they have no analogues in the literature.

EXPERIMENTAL

The measurements of dependence of the electrical conductivity of any electrolyte on electric field strength (EFS) must be carried out exclusively in the regime of the short time electric pulses in order to avoid a change in the temperature of a sample and introduction of possible electrolysis products into it. To this end in view, we have constructed HVP- setup for the pulsed conductometry method. The descriptions of the electric circuit and the measurement cell are presented, in particular, in the publications [18, 26]. The pulse generator provides rectified voltage regulated up to 15 kV. The direct voltage from the increase - rectification of voltage system was imposed on the capacitor from which the voltage pulses with a steep front supplied through an attenuator to the electrodes immersed into a melt. The setup involves the digital pulsed memory oscilloscope ASK-8 which records oscillograms (waveforms) of attenuated current and voltage during the pulse discharge in the sample under study. The representative waveforms without the electric breakdown in a molten salt are outlined in Fig. 1.

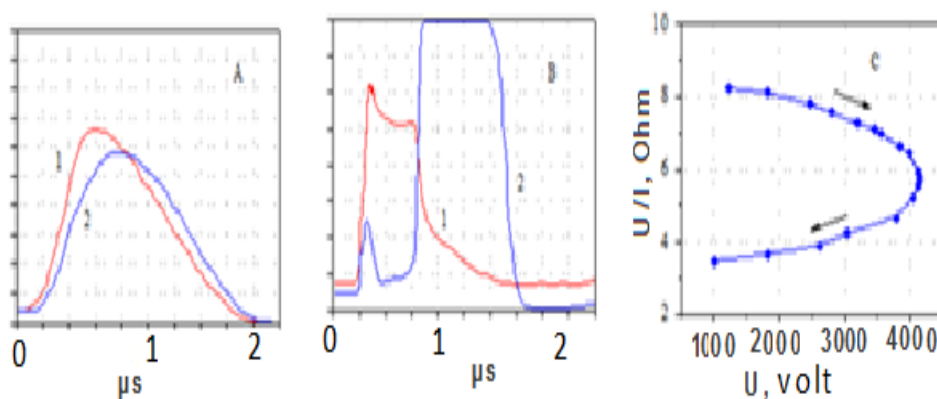


Fig1. a) The characteristic waveforms of voltage (curve 1) and current (curve 2) of HVP discharge in molten $MgCl_2$ without the breakdown. The sweep rate is $0.2 \mu s/div$ (axe x). The voltage sensitivity (axe y) is 680 volt/div , the current sensitivity is 150 A/div (axe y); **b)** The waveforms of voltage and current of the discharge in an electrolyte at the electric breakdown presence. Voltage drops to zero, and current exceeds the limit of the monitor; **c)** Dependence of U/I as function of U before (curve \rightarrow) and after (curve \leftarrow) reaching the current maximum.

The waveforms show that the HVP duration is several microseconds, the current and voltage of discharge pass through the maximums reached in about $1 \mu s$; after reaching the maximum they fall exponentially (fig. 1a). The pulse full duration excludes introduction of electrolysis products into the electrolyte and it's any significant overheating. This analysis and electroluminescence spectra of molten salts [16, 19] confirm that regularities observed in behavior of the electrolytes in strong fields (that we used) at breakdown absence take place with maintaining the electrolytic nature of the conductance. The high-voltage resistance of the electrolytes was determined as U/J at instant of the current maximum, when the quasistationary condition $dI/dt = 0$ and Ohm's law are satisfied. As can be seen from fig. 1c, at high voltages the Ohm's law is not fulfilled, that is shown from different values of $R=U/J$ for a given voltages before and after reaching the current maximum; the initial R value (curve \rightarrow) is not equal to U/J at $U \rightarrow 0$ (curve \leftarrow). These values become equal in the vicinity of the voltage when the current reaches maximum.

To study the phenomenon of the electrolytes activation, their conductivity was measured by using AC Bridge RLC, and the Raman spectra were recorded using a spectrophotometer - both before exposure of HVP on the equilibrium melts and after the pulsed discharges in them were completed. We studied Raman scattering of some molten salts excited by means of the 488 nm line an argon ion (Coherent) Laser LGN-503. The relaxation dynamics of the non-equilibrium systems was defined by observing the changes in the conductivity and Raman spectra after pulsed discharges having been completed.

EXPERIMENTAL RESULTS

Dependence of the conductivity of molten chlorides on the electric field strength

We have established regularities in the dependence of the electrical conductivity of the molten simple salts $MgCl_2$, $CaCl_2$, $CeCl_3$, $NdCl_3$ and their binary mixtures with potassium chloride on the electric field strength (EFS); they are illustrated in figures 2-6.

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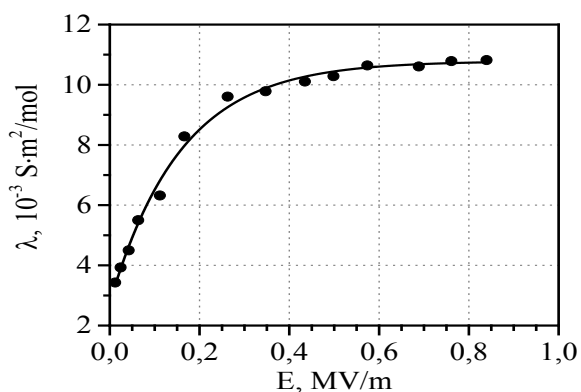


Fig2. The dependence of equivalent conductivity of molten MgCl_2 on applied electric field strength at 1000 K

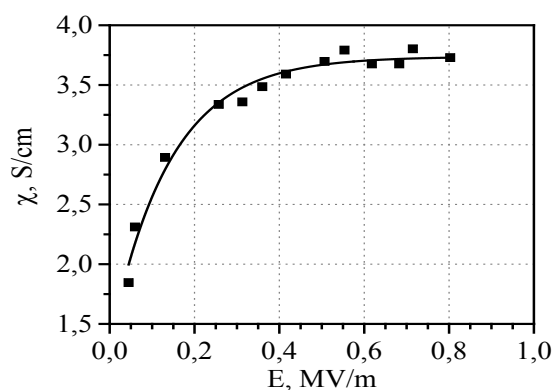


Fig3. The dependence of specific conductivity of molten $\text{MgCl}_2(0.2)\text{-KCl}$ on applied electric field strength at 1000 K

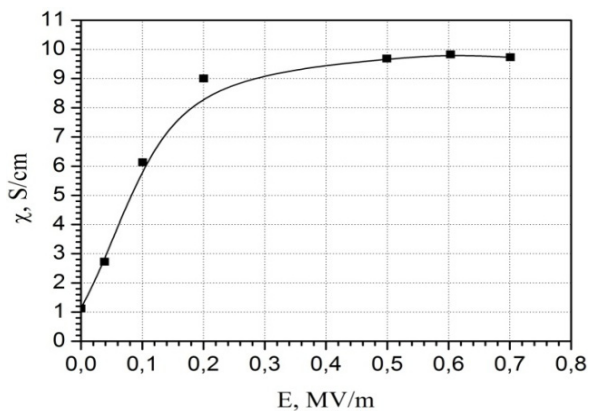


Fig4. The dependence of specific conductivity of molten CeCl_3 on applied electric field strength at 1100 K

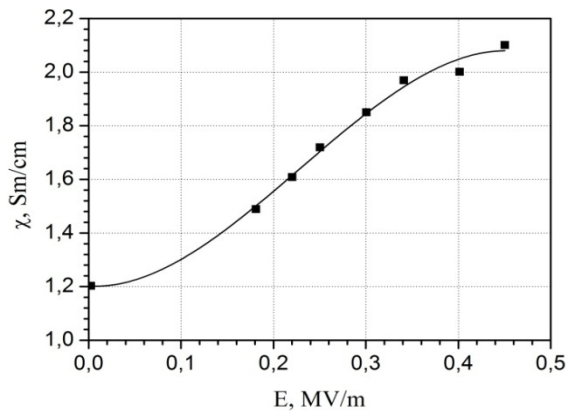


Fig5. The dependence of specific conductivity of molten $0.2\text{CeCl}_3\text{-KCl}$ on applied electric field strength at 1110 K

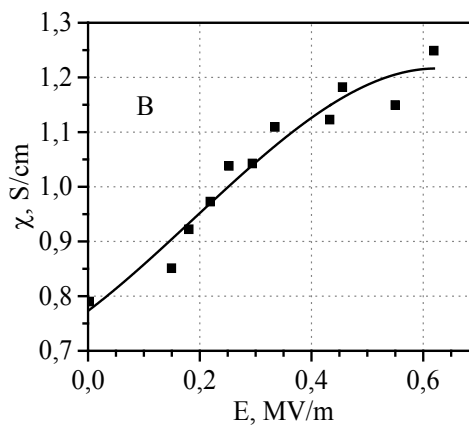
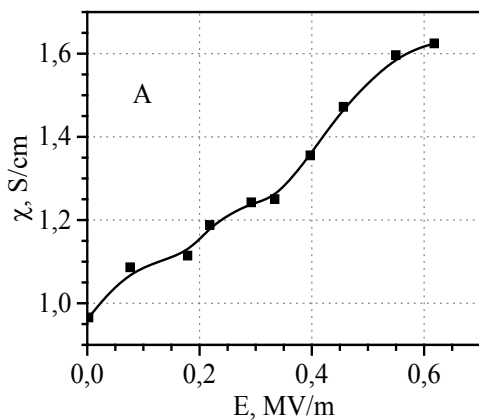


Fig6. The dependence of specific conductivity of molten NdCl_3 (a) and the mixture $0.8\text{NdCl}_3 - 0.2\text{KCl}$ (b) on applied electric field strength at 1000 K.

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Analogy dependence has been obtained for the different compositions and temperatures of these melts. We found that the conductivity of individual molten salts and their mixtures increases with increasing EFS and tend, in the fields of about 1 MV/m, to the limiting high-voltage values depending on the melt nature, composition, and temperature. The limiting high-voltage conductivity of molten MgCl_2 , CaCl_2 , CeCl_3 , and NdCl_3 surpasses their usual (low-voltage) values $\chi(0)$ by 265%, 38%, 782 % and 79%, respectively; the high field conductance quotient $\frac{\Delta\chi}{\chi(0)} = \frac{\chi^0 - \chi(0)}{\chi(0)}$ characterizes the melt degree of its structuredness; χ^0 - specific conductivity. The $\frac{\lambda(0)}{\lambda^0}$ value, which is considered as a dissociation degree, is equal to 0.3-0.6;

λ is molar conductivity. These parameters will be presented below in the summarizing table 1.

Electrochemical potentials of the metals in activated molten chlorides

To determine the values of electrochemical potentials of metals in non-equilibrium melts we measured EMF of electrochemical chains of the type $\text{Ag}_n\text{M} / \text{MCl}_n - \text{NaCl} - \text{KCl} - \text{NaCl} - \text{KCl} - \text{AgCl} / \text{Ag}$ with 10 mol % of AgCl and MCl_n ($\text{M} = \text{Ag}, \text{Mg}, \text{Al}, \text{Zn}$). EMF of the cells were measured initially under equilibrium conditions, and then - after the electrolyte in one of the half-cell being subjected to the HVP action. The observed change in the EMF of the cell is obviously equal to the change in the potential of the metal in the electrolyte, which was transferred to non-equilibrium state. In our experiments, the equilibrium EMF of silver-magnesium cell at 1086 K was 1932 mV. After activation of the magnesium electrolyte MgCl_2 - NaCl - KCl by series of pulses with the amplitude of voltage of 8 kV, the EMF of the cell became equal to 1630 mV. Consequently, the potential of the magnesium electrode in its activated chloride electrolyte became more positive by 15.6%. Similar results were obtained for other metals. These results allow expecting that the decomposition potentials of metal chlorides in non-equilibrium state would be less than in "equilibrium" state. To obtain such experimental data, the study was performed employing linear sweep voltammetry of the magnesium, aluminum and cerium chloride electrolytes.

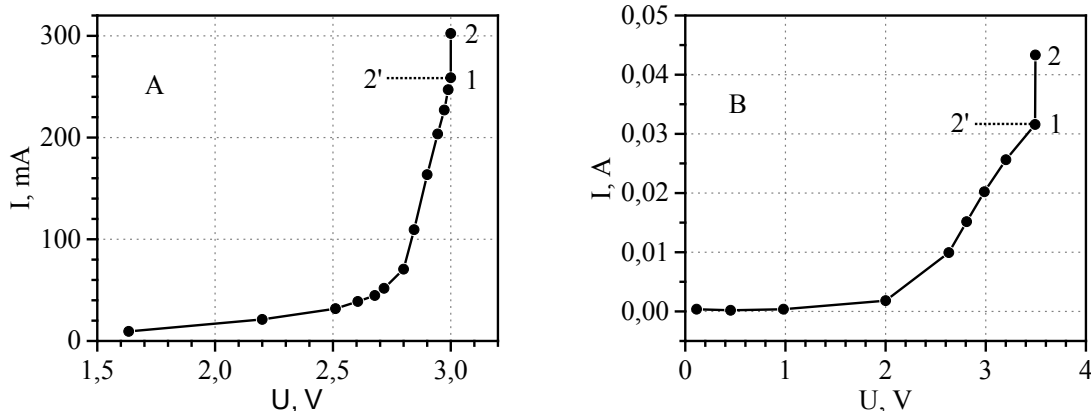


Fig7. Linear sweep voltammograms in molten MgCl_2 - NaCl - KCl (a) and NaCl - KCl - CeCl_3 (b).

Derived from this dependence the values of the decomposition potentials of MgCl_2 and CeCl_3 in non-perturbed melts were found equal to 2.73 V and 2.1 V, respectively, in good agreement with the literature. After exposure to the molten electrolytes of 10 pulses with the voltage amplitude of 6 kV, electrolyze current is increased by more than 20%, while the electrolysis voltage was maintained equal to the initial value (points 1-2). In its turn, while maintaining the same initial value of the electrolysis current, the voltage on the cell is correspondingly reduced (1'-2'). This means that the decomposition potentials of the MCl_n salts decrease upon activation of their electrolytes. A similar analysis was performed and similar results have been found for the electrolysis of aluminum and neodymium chloride electrolytes. The degree of electrolyze intensification rises with increasing number of activating pulses and their voltage amplitude, tending to the saturation.

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Intensification of conductivity of molten metal chloride electrolytes

An analysis of the waveforms in Figure 1,c shows that U/I for full discharge sweep at $U \rightarrow 0$ in the lower curve (after reaching the maximum current) is lower than the initial value (at $\tau \rightarrow 0, U \rightarrow 0$) determined from the upper curve. In our experiments on Wien effect, every next voltage pulse was applied to an electrolyte only after the initial low-voltage conductivity was restored. This indicates that the electrical conductivity of a sample measured by a conventional AC Bridge increases as a result on subjecting it to a large electric pulse electric field; that is, the «memory effect” is observed. The activation degree is expressed as $\Delta\chi / \chi(0) = [\chi(\tau) - \chi(0)] / \chi(0)$, where $\chi(0)$ is the initial (low-voltage) conductivity and $\chi(\tau)$ is the low-voltage conductivity at the time $\tau=0$ after the end of a high-voltage pulse. The conductivity activation degree also rises with increasing number of pulses and their voltage amplitude, and tends to the saturation. In Figure 8, as examples, these dependences are presented for a magnesium electrolyte

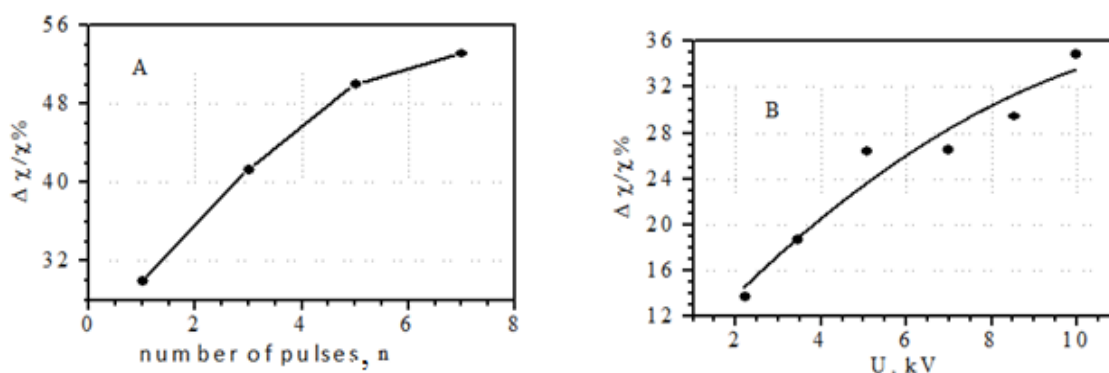


Fig8. Dependence $\Delta\chi / \chi(0)$ of the molten mixture 0,2MgCl₂ - 0,8KCl on the number n of activating pulses in series with the voltage amplitude of 8,5 kV (a) and this dependence on the voltage amplitude of single pulses (b) at 983K.

Similar results were obtained for other compositions of molten mixtures [19, 27-29]. The results obtained in Sections 3.1 and 3.3 are collected in the summarizing Table 1

Table1. Wien effect and activation degree of some molten chloride electrolytes

Melt	T, K	$\chi(0)$, S/m	χ^0 , S/m	$\frac{\lambda(0)}{\lambda^0}$	$\frac{\Delta\chi}{\chi(0)}$, % (Wien effect)	$\frac{\Delta\chi}{\chi(0)}$, % (Activation)
MgCl ₂	1000	105	378	0.30	265	14
0.8KCl-MgCl ₂	980	140	372	0.38	166	35
CaCl ₂	1073	212	292	0.72	38	12
0.8KCl ₂ -CaCl ₂	1073	168	258	0.65	54	20
CeCl ₃	1110	110	970	0.12	782	17
0.8KCl-CeCl ₃	1110	120	212	0.57	77	32
NdCl ₃	1082	95	165	0.58	79	15
0.8NdCl ₃ -KCl	1082	79	125	0.63	58	18

Relaxation in activated molten chloride electrolytes

The above values relate to the degree of activation at the time $t = 0$ after the completion of the pulses. In this section, the regularities of the change in the degree of activation $\Delta\chi / \chi(0) = [\chi(t) - \chi(0)] / \chi(0)$ in time are described; here $\chi(t)$ is the low-voltage conductivity of the melts at time t after the pulse action completion. The activated molten electrolytes are in the non-equilibrium state with the increased conductivity. These systems tend to the equilibrium state with the restoration of the equilibrium values of the electrical conductivity at unchanged temperature; in these systems the relaxation processes take place. The figures below show some examples of the relaxation curves in some non-equilibrium molten electrolytes.

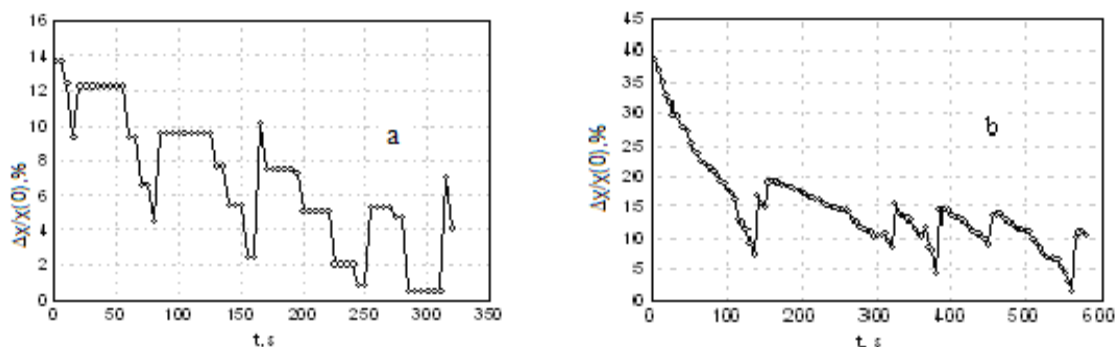


Fig9. Change of the relative values $\Delta\chi/\chi(0),\%$ in time in the molten mixture $MgCl_2(0,2)-KCl$ **A)** activated by one pulse of voltage amplitude 2,2 kV, and **B)** activated by 3 pulses of the amplitude 10 kV. $T=983 K$

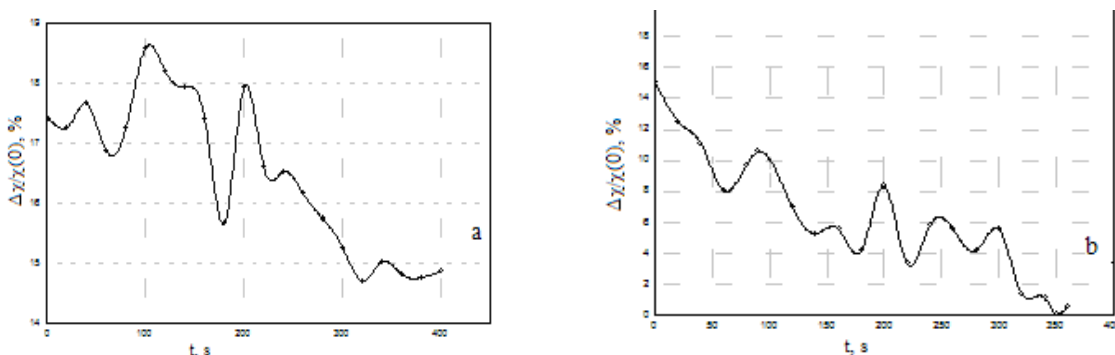


Fig10. Change of the relative values $\Delta\chi/\chi(0),\%$ in time in molten mixtures $LaCl_3 - 0,6KCl$ **(a)** and $NdCl_3 - 0,8KCl$ **(b)** activated by single pulses of the voltage amplitude 6 kV at 1082 K

It is seen from Figs. 9-10 that the degree of electrical conductivity activation $\Delta\chi/\chi(0)$ reaches 45%, the increased electrical conductivity of the electrolytes in the non-equilibrium state decreases in time and tends to the initial (equilibrium) values in 5-10 min. Relaxation in non-equilibrium electrolytes occurs in a step-oscillatory regime (Fig.9,A), or in a purely oscillatory regime (Fig.9,B and Fig.10).

Changes in Raman spectra of molten $MgCl_2$ and $ZnCl_2$ upon the transition to a non-equilibrium state

The results presented above indicate a modification or simplification of the structure of the molten electrolytes due to stimulated dissociation of complex ions under the action of HVP. Stimulated dissociation of long-lived complex structural units was confirmed by Raman spectra of structured melts $MgCl_2$ and $ZnCl_2$ in the equilibrium and non-equilibrium states. Initially, we have reproduced known literary equilibrium characteristics of Raman spectra of $MgCl_2$ [1] and $ZnCl_2$ [30]. Then we recorded their spectra after being subjected to high

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voltage microsecond pulses. The spectra for the molten $MgCl_2$ and $ZnCl_2$, normalized using the total polarized scattered intensity, are shown in fig.11. The Raleigh background signals were removed from all spectra via standard baseline subtraction and all spectra are normalized into a unit area. The obtained spectra of individual equilibrium molten salts are in good agreement with literature data.

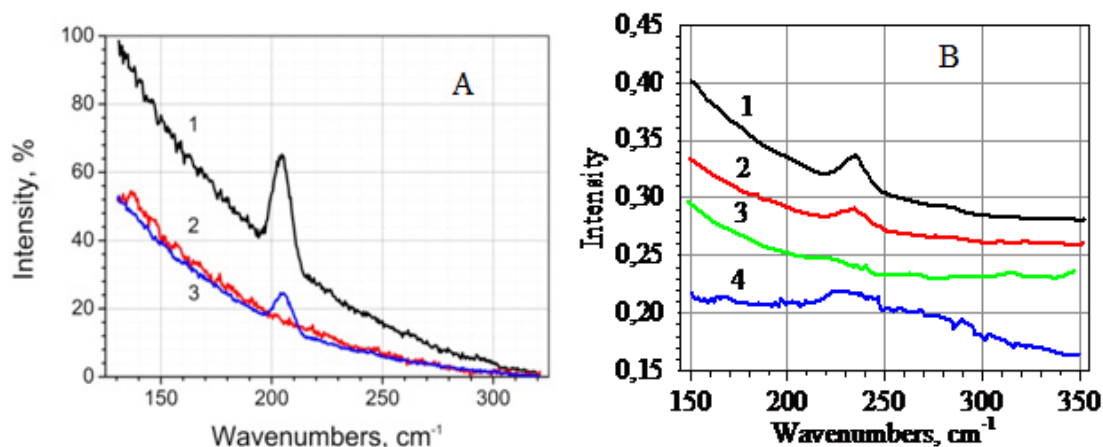


Fig11. A) Raman spectra of equilibrium molten $MgCl_2$ (curve 1) and of its melt subjected to 3 electric pulses of voltage amplitude of 8kV (curve 2) at 973 K. The curve 3 is Raman spectrum of the non equilibrium melt 10 minutes after activation; **B)** Raman spectra of solid $ZnCl_2$ (curve 1), of its equilibrium melt at 624 K (curve 2) and of the melt subjected to 5 electric pulses of voltage amplitude of 8kV (curve 3) at 624 K. The curve 4 represents the Raman spectrum of the non-equilibrium melt in the relaxation processes 10 minutes after activation.

The Raman peaks at 205 cm^{-1} in unperturbed molten $MgCl_2$ and 230 cm^{-1} in liquid $ZnCl_2$ are in accordance with the literature data. As a result of previous pulses influence, the spectral peaks disappear almost completely due to dissociation of complex ions and the melts transition to a non-equilibrium state. As a result of relaxation processes in non-equilibrium melts, the Raman spectra of the equilibrium melts are restored within 10 minutes [29, 31].

DISCUSSION

For the molten halides of alkali [32] and alkaline earth metals [33], an autocomplex model was proposed a priori, according to which the molten salts can be considered as a mixture of anions MX_4^{Z-4} and cations M^{Z+} as structural units. Later, as a result of the development of spectroscopic methods, it was proved that the structural units- autocomplexes in these halides are not a priori abstraction but can quite reliably be fixed in Raman spectra [34]. Raman spectra indicate presence in the molten equilibrium electrolytes of diversity of structural units of different symmetry and lifetimes. The observed behavior of the molten electrolytes in the Wien effect, in the dissociation field effect (the second Wien effect), and in the activation phenomenon can be understood on the basis of stimulated dissociation of the complex ions under action of strong electric pulses.

It is seen from Figs. 9 that the degree of electrical conductivity activation $\Delta\chi/\chi(0)$ reaches 45%, the increased electrical conductivity of the electrolytes in the non-equilibrium state decreases in the time and tends to the initial (equilibrium) values in 5-10 min. The non-equilibrium molten electrolytes tend to the equilibrium state, to reestablish the equilibrium electrochemical parameters, characteristic structural species diversity and their distribution. The drop and jumps in electrical conductivity in Fig. 9 can be associated with successive recombination of complex ions and their dissociation with the release of simple ions. Relaxation of conductivity occurs in the oscillatory regime, which is clearly expressed. Performing a Fourier analysis of the time series

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for the relaxation in non-equilibrium molten $MgCl_2 - KCl$ leads to the conclusion about realization of a quasi-periodic regime of oscillation and about deterministic chaos; the dimensionality of a phase space corresponds to five [29, 35]. This phase space corresponds to the five structural spaces in this system above; from the fig.9 it is shown that the number of drops of the conductivity from the steps and the number of jumps are also equal to five. The observed structural relaxation in non-equilibrium systems exhibit all the signs of the self-organization and it is obvious that entropy is decreased in the recombination reactions of the structural units - complex ions of different symmetry.

The idea of the activation of molten electrolyte by HVP ("blue dream") and its experimental realization was first published by Diller in the case of cryolite-alumina melt electrolysis [36, 37]. The authors [39] repeated the Diller experiments, but they did not find a significant influence of the HVPs on the electrochemical properties of this molten electrolyte. Our reports of significant activation of molten chloride electrolytes and their prolonged relaxation in the activated state also raised the questions and doubts at various conferences on physical chemistry and electrochemistry of molten and solid electrolytes. On the instructions of the Academy of Sciences of the USSR, the expert commission repeated the experiments on the activation of molten chloride magnesium electrolyte in our laboratory. They confirmed qualitatively the phenomenon of activation of electrical conductivity and prolonged relaxation of the molten chloride electrolyte in a non-equilibrium state. Cryolite-alumina electrolytes differ from the chloride electrolytes in that in the first the covalent stable complexes $AlOF_2^{2-}$ and $Al_2OF_{2x}^{4-2x}$ are formed [38], in the second one – the long-lived or short-lived ionic complexes $MgCl_n^{2-n}$, $Mg_2Cl_6^{2-}$ complexes [7], and $LnCl_6^{3-}$ - octahedral sharing chlorides forming a loose "network" structure [10]. The substructure of the melt $ZnCl_2$ is formed by mixing a variety of tetrahedra participating in "open," "cluster," and "chain" networks which are bound to each other by bridged halides [30]. Strong impulses at a given temperature destroy the substructure to smaller fragments, the dissociation of complex structural units, as well as a rise in temperature.

CONCLUSIONS

The molten chloride electrolytes of polyvalent metals subjected to the high voltage microsecond pulses exhibit the phenomenon of activation and the transition to a non-equilibrium state with increased electrical conductivity, disappeared characteristic Raman peaks and prolonged structural relaxation. The results obtained provide new insight in the physical chemistry of molten electrolytes and can serve as a scientific basis for the intensification of electrochemical technologies. The presented results have no analogues in the literature.

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