

Intensification of Electrical Conductivity of Molten Electrolytes

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Abstract: *This review covers the results of the study on the behavior of molten and solid electrolytes in the external pulsed electric fields of high strength. One of the important aims was to establish the dependence of the conductivity of the molten and solid electrolytes on the electric field strength (Wien effect). These measurements were provided on the basis of the analysis of oscillograms of the microsecond pulsed electric discharges in the samples. The limiting high-voltage conductivities have been established for molten pure alkali and alkali earth halides, their binary mixtures, for the superionic conductors of the “Rubidium silver iodide family” and their melts. The limiting ionic conductivities of the molten halides obey the Nernst- Einstein and other fundamental relations.*

Another interesting result is that molten and solid electrolytes subjected to a completed electric pulse field pass into a non-equilibrium state with the significantly increased low-voltage conductivity and eliminated Raman spectra peaks. In the course of the relaxation of the non-equilibrium melts their electrical conductivities and Raman spectra tend to recovery of the values and patterns specific to equilibrium systems, in the relaxation processes during about 10 minutes. The results obtained can be considered as the direct evidence of the existence and stimulated dissociation of the complex ions in the molten salts

Keywords: *electrolytes, conductivity, spectra, high-voltage pulses, activation, prolonged relaxation.*

1. INTRODUCTION

The structures of the molten electrolytes, as well as the nature and distribution of their structural species, determine their physicochemical properties, the mechanisms and kinetic pathways that decrease energetic efficiency of metals and non-metals production technologies [1]. The concept of the formation of complex ions in molten electrolytes continues to be the subject of considerable interest and debates [2, 3]. In turn, the diversity and distribution of structural species are available for modification under the influence of external perturbing factors. For better understanding the structure of equilibrium molten electrolytes and improving electrochemical technologies, their properties should be studied in a non-equilibrium state, which can be achieved by various external influences, for example, by the action of strong electric pulses [4].

In a weak electrical field applied to the electrolytes the Ohm's law is obeyed. In a dilute electrolyte solution the equivalent conductivity of ions is

$$\lambda_i = \lambda_i^o - \Delta\lambda, \quad (1)$$

Where λ_i^o is the limiting molar conductivity of an ion at the infinite dilution of a solution, and $\Delta\lambda$ is the correction term due to the relaxation time ($\sim 0.33 \Delta\lambda$) and electrophoretic effects ($\sim 0.66 \Delta\lambda$). For the electrolytic conductors in high electric field, the deviations from Ohm's law are observed. This high field effect in the liquid electrolyte solutions was first discovered by Wien [5]. For an electrolyte solution of fixed concentration and temperature its conductivity λ is found to increase with the applied electric field strength (EFS) and tends to the limiting value λ^o . Wien effect has served as the experimental proof of the validity of the Debye- Huckel-Onsager theory of electrolyte solutions. Here, we give these well-known facts because in the literature there were no reports about the effect of Wien in molten electrolytes and their limiting conductivities to our publications [6-9]. The ionic association significantly alters the behavior of the melts. Application of this approach has been hindered by lack of the Wien effect for molten salts.

In the individual molten salts, we can not change their concentration to establish the dependence of conductivity on dilution with $c \rightarrow 0$, but we can establish the dependence of the electrical conductivity on EFS. We have constructed the high-voltage pulse setup to study this relationship and have found that electrical conductivity of molten alkaline halides and their mixtures [6-9], alkaline-earth chlorides [10-13] and their mixtures with alkaline chlorides [14, 15], solid superionic conductors [16-17] increase with increasing external EFS and strive to achieve the limiting values in the fields of the order of 1MV/m, in the same way as in the Wien effect in electrolyte solutions. The limiting high voltage conductivities of molten salts exceed their usual ones by tens of percents and obey Nernst-Einstein and Stokes-Einstein correlations. As far as we know, Wien effect in the molten salts and their limiting conductivities do not have analogues in the literature.

After the high-voltage pulsed discharges in the electrolytes having been completed, their low voltage conductivity (measured by usual ac bridge) turns out to be increased [14, 15, 18], electrode metal potentials to be changed [18, 19] and Raman spectra peaks to be disappeared [20], i.e., the “memory effect” in them is observed. The activation degree of electrical conductivity reaches up to 20 % in case of individual alkali earth metals chlorides and to 55 % in case of their mixtures with potassium chloride; it depends on the nature of the melts, temperature and parameters of activating pulses. The relaxation time of the conductance and the spectra of these melts in non-equilibrium state are anomalously prolonged and are more than ks. These observations were interpreted as a consequence of the stimulated dissociation of complex formations into simpler ions and elementary ones. These processes are followed by the recombination of complex ions during relaxation processes in the non-equilibrium melts. In this review we present some results of studying the dependence of the electrical conductivities of the molten electrolytes on EFS and the phenomenon of their activation followed by a prolonged relaxation in a non-equilibrium state.

2. METHODOLOGY

The measurements of the EFS dependence of the electrical conductivity of any electrolyte must be carried out exclusively in the regime of short time electric pulses in order to avoid a change in the temperature of the sample and introduction of possible electrolysis products into it, which may change the electrolytic nature of the conductance, and other side phenomena. To this end, we have constructed high-voltage setup for pulsed conductometry. The descriptions of the electric circuit and the measurement cell are described in particular in the publications [13, 16]. The pulsed generator with controlled discharger yielded rectified voltage regulated up to 20 kV. The direct voltage from the transforming-rectifying system was imposed on the capacitor from which the voltage pulses with a steep front are supplied to the electrodes immersed into a sample. The setup involves the digital pulsed memory oscilloscope ASK-8 which records waveforms of attenuated current and voltage during the pulse discharge in the studied sample. The representative oscillograms (waveforms) without electric breakdown and with its presence in a molten salt are outlined in fig.1.

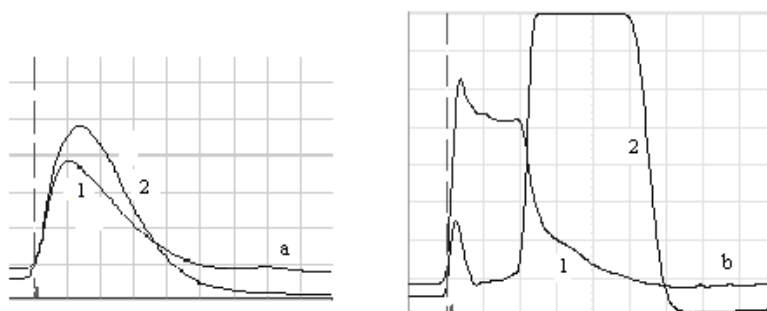


Fig1. a) Characteristic oscillograms of the voltage (curve 1) and the current (curve 2) at high-voltage discharge in molten $MgCl_2$ without the electric breakdown. The sweep rate is $0.4 \mu s/grad$. The voltage sensitivity is $340 V/grad$; the current sensitivity is $27 A/gradation$. b) The oscillograms of voltage and current at high-voltage discharge in an electrolyte at presence of electric breakdown: voltage drops to zero and current exceeds the limit of the monitor.

The waveforms show that the pulses duration is several microseconds, the current and voltage of discharge pass through maximums reached in about $1 \mu s$, and after reaching the maxima the voltage and current fall exponentially (fig.1,a); the current maximum is observed in some time after reaching the maximum of the voltage. Full pulse duration of several microseconds excludes introduction of

electrolysis products into the electrolyte and its any significant overheating. Thus, a simple pulse corresponds to a charge of about $I \cdot t = 10^{-3} \text{C}$ passing through electrolyte. At the electrochemical equivalent, for example, of magnesium $0,126 \cdot 10^{-6} \text{kg} \cdot \text{C}^{-1}$ its mass, electrochemically reduced on the cathode or in the bulk, is less than 10^{-6}g . The maximum current is not more than 1kA; the heat capacity of the electrolytes is about some kJ/kg·K. At the electrodes separated by ~1 mm the resistance of the electrolyte is less than 0, 5 Ohm, and the electrolyte mass is ~ 0,03kg; then the overheating is less than 10K, which may cause the rise in conductivity less than 1%. If we take into account that the average current is much lower than the maximum value (fig.1, a), it becomes obvious that there is no any noticeable increase in the temperature. I. Diller observed even a decrease in the temperature as result of high-pulse action on the molten aluminum electrolyte [4]. The pulsed discharges in the electrolytes under study occurred without electric breakdown (Fig.1). The above arguments confirm that the observed behavior of the molten electrolytes in used EFS takes place when the conductivity electrolytic nature is conserved.

To study the phenomenon of activation of the electrolytes we measured their conductivity by using ac bridge RLC and recorded their Raman spectra using a spectrophotometer- before the application of high-voltage pulses to the equilibrium melts and after the pulsed discharges in them having been completed. We studied Raman scattering of the molten salts excited by means of the 488nm line an argon ion (Coherent) Laser LGN-503. A laser beam passed through a Glenn-Thomson prism and then through an optical filters non transmitting radiation with $\lambda > 488\text{nm}$; then it was focused on a melt. The molten salts were contained in an optical cell, made of quartz, with two Mo-electrodes for high-voltage pulsed discharges. The relaxation dynamics of the non-equilibrium systems was defined by observing the changes in the conductivity and Raman spectra after high-voltage pulsed discharge HVPD has been completed.

3. WIEN EFFECT IN MOLTEN ALKALI HALIDES AND THEIR MIXTURES

We have established the dependence of electrical conductivity on EFS for molten alkali halides (AH) MX (M= Li, Na, K, Rb, Cs and X= F, Cl, Br, J), some of their binary mixtures at different temperatures. The conductivities of individual molten alkaline halides and their binary mixtures rise with EFS end reach the limiting values in the field of about 0, 5 MV/m. This dependence is presented in Fig.2, by way of examples, for molten pure molten LiCl and NaCl.

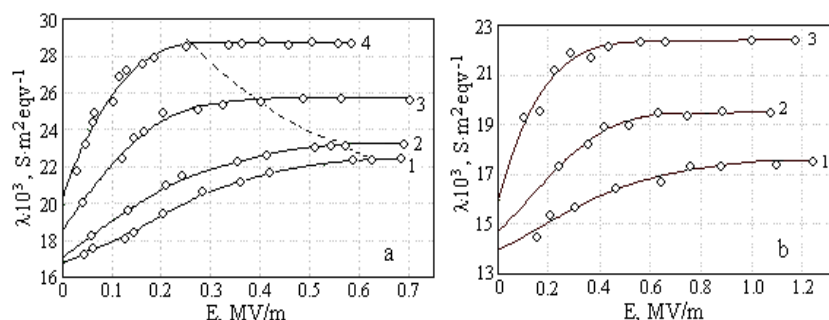


Fig2. The conductivity as function of EFS a) for the molten LiCl at 903 (1), 933(2), 1008 (3) and 1073 K (4) and b) for molten NaCl at 1103 (1), 1149 (2) u 1223 K(3)

The same dependence with of reaching of high-voltage limiting conductivities has been obtained for all alkali halides. The Table 1 presents the usual (low-voltage) equivalent conductivities $\lambda(0)$, high-voltage limiting conductivities λ^0 , high field conductance quotients $[(\lambda^0 - \lambda(0))/\lambda(0)]$, the apparent degree of dissociation- the ratio $\lambda(0)/\lambda^0$, by way of examples, for alkali chlorides and some of their binary mixture.

Table1. The low- voltage and limiting high-voltage conductivities of the pure molten alkali chlorides and some of their binary mixtures

Melt	T, K	$\lambda(0) \times 10^3$	$\lambda^0 \times 10^3$	$\Delta\lambda/\lambda(0), \%$	$\lambda(0)/\lambda^0$
		$\text{S} \cdot \text{m}^{-2} \cdot \text{mol}^{-1}$			
LiCl	903	16.80	22.40	33.3	0.75
	933	17.09	23.18	35.6	0.74
	1008	18.47	25.67	39.5	0.72
	1073	19.90	28.70	44.2	0.69
NaCl	1103	13.97	17.50	25.3	0.80
	1149	14.71	19.50	32.6	0.75
	1223	15.92	22.40	40.7	0.71

<i>RbCl</i>	1013	8.46	10.04	18.7	0.84
	1053	9.22	11.45	24.2	0.80
	1108	10.24	12.71	24.1	0.80
<i>CsCl</i>	928	7.11	7.66	7.6	0.93
	998	8.40	9.26	9.3	0.91
	1078	9.80	11.16	11.2	0.88
<i>LiCl – KCl</i>	903	9.12	13.55	48.3	0.67
	1003	9.90	15.04	51.5	0.66
	1073	10.67	16.35	53.1	0.65
<i>LiCl – RbCl</i>	1073	8.50	15.80	85.5	0.54

Table 1 shows that the high field conductance quotients decrease with the rise in cation radii and increases with the rise in temperature, at the same time the ratio $\lambda(0)/\lambda_0$ decreases with the temperature.

4. CORRELATIONS OF TRANSPORT PROPERTIES IN THE MOLTEN ALKALI HALIDES

In the extremely diluted electrolyte solutions the ions are moving independently and Kohlrausch law is obeyed. In the individual molten salts the ions cannot have the limit mobilities constant, independent of the nature of the salt, and dependent only on the temperature; as a consequence the Kohlrausch law is not obeyed. If we check the product of the limiting conductance and the viscosity of the melt $\lambda_0 \cdot \eta$ at different temperatures, we can see that within the limits $T_m + 100$ K these products $\lambda_i^0 \cdot \eta$ for the ions, hence and the products $\lambda^0 \cdot \eta$ for the salts, will vary little, remaining constant within the measurement errors for conductivity λ_0 and viscosity η :

$$\lambda^0 \cdot \eta = (\lambda_+^0 + \lambda_-^0) \cdot \eta = const \quad (2)$$

The limiting molar conductivities of ions "corrected" on the viscosity of the salts exhibit quite satisfactory constancy not only for the salt when the temperature varies, but also in passing from the one salt to another salt. If we average the productions $\lambda_i^0 \cdot \eta$ for the given salt, and then $\lambda_+^0 \cdot \eta$ for each cation in its halides and $\lambda_-^0 \cdot \eta$ for the anion in the corresponding halides of alkali metals, we obtain their characteristic values $\lambda_i^0 \cdot \eta$ suitable for the set of molten alkali halides. It is easy to calculate the absolute "corrected" ion nobilities $u_i^0 \cdot \eta = \lambda_i^0 \cdot \eta / F$ of them which are constant and independent of the temperature and nature of the salt to which they belong. The "corrected" limiting conductivities of molten salts are constant at least within the limits of 100 K above their melting temperatures T_m . They are shown in the Table 2.

Table2. 'Normalized' absolute ion mobilities in molten alkali halides

	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺	Cl ⁻	Br ⁻	I ⁻
$\lambda_i^0 \cdot \eta, \frac{10^{-5} N \cdot s}{Ohm \cdot mole}$	1.66	1.13	0.83	0.73	0.65	0.60	0.56	0.51
$u_i^0 \cdot \eta, 10^{-10} N/V$	1.72	1.17	0.86	0.76	0.67	0,62	0.58	0.53
$\lambda_i^0 \cdot \eta \cdot r_i, \frac{10^{-15} N \cdot m \cdot s}{Ohm \cdot mol}$	1.13	1.11	1.10	1.09	1.07	1.09	1.11	1.12

The Stocks law

$$\lambda_i^0 = \frac{|z_i| e^2 N_A}{6\pi\eta r_i} = \frac{|z_i| F^2}{6\pi N_A \eta r_i} \quad (3)$$

is not obeyed for the conductivity of electrolyte solution at infinite dilution and for low-voltage electrical conductivity of the molten salts. Expressing λ^0 in S·m²·mol and η in Pa·s, one can to present the equation (3) in the form

$$\lambda_i^0 \cdot \eta = |z_i| 0,82 \cdot 10^{-15} / r_i \quad (4)$$

And for 1:1 electrolyte

$$\lambda^0 \eta = (\lambda_+^0 + \lambda_-^0) \eta = 0,82 \cdot 10^{-15} (1/r_+ + 1/r_-) \tag{5}$$

From the above data (Table 2) it follows that the limiting molar conductivity of molten alkali metal halides obeys Stokes law. This dependence is a straight line passing through the origin with the slope that exceeds $1.1 / 0.82 = 1.34$ times the slope that follows from the equation 5. In other words, the product $\lambda_i^0 \cdot \eta \cdot r_i$ is constant (Table 2).

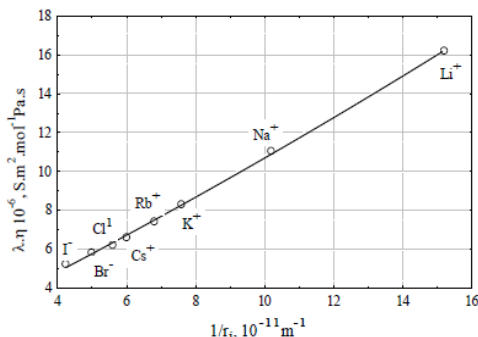


Fig3. Variation of the product $\lambda_i^0 \cdot \eta$ as function of inverse ion radii of alkali halides

The average value of the product $\lambda_i^0 \cdot \eta \cdot r_i = 1,1 \cdot 10^{-15} N \cdot S \cdot m \cdot s \cdot mol^{-1}$ with maximum deviation $\pm 2, 17\%$, it is constant for all ions in molten alkali metal halides. They satisfy the Stokes' law in the form

$$\lambda_i^0 = 1,1 \cdot 10^{-5} / \eta \cdot r_i = F^2 / 4,48\pi \cdot N_A \eta \cdot r_i, \tag{6}$$

Instead of the Eq. 4.

It is known that the equivalent conductivities λ_D of molten salts largely exceed the ordinary (low-voltage) conductivities $\lambda(0)$ when they (λ_D) are calculated using the experimental ion self-diffusion coefficients according to the Nernst - Einstein (NE)

$$\lambda_D = \frac{F^2}{RT} \sum_i z_i D_i, \tag{7}$$

This indicates to the existence in the molten salts of a discrete structural species that make non-equivalent contributions to the kinetic coefficients of the mass and charge transfer. The limiting high-voltage conductivities λ^0 correlate with λ_D calculated according NE equation; in the state of complete dissociation of molten salts, the elementary ions make the equivalent contributions to the kinetic coefficients of the mass and charge transfer. This, in turn, enables to evaluate the ion self-diffusion coefficients using the ion limiting conductivities by the equation

$$D_i = t_i RT \lambda^0 / F^2 \tag{8}$$

Where t_i is the transport number of ion. These results are presented in the Table 3 by way of example for the molten alkali chlorides.

Table3. The feasibility of Nernst-Einstein relation for molten alkali chlorides

Melt	T, K	λ_D	λ^0	$D_+ \cdot 10^8, M^2/s$		$D_- \cdot 10^8, M^2/s$	
		$10^{-3} S \cdot m^2 \cdot mol^{-1}$		exper	Equ.10	exper	Eq.10
LiCl	1100	27.20	29.30	1.73	2.09	0.95	0.79
NaCl	1103	16.78	17.50	0.92	1.12	0.69	0.60
KCl	1073	13.98	12.50	0.71	0.69	0.63	0.51
	1100	14.86	13.36	0.77	0.76	0.69	0.56
RbCl	1108	12.90	2.71	0.68	0.67	0.59	0.58
CsCl	1100	13.3	11.71	0.61	0.60	0.69	0.55

As seen from the Tables 1 and 3, the mass and charge transfer coefficients correlate accordingly to NE equation when one uses the limiting high-voltage conductivity of the molten salt.

5. WIEN EFFECT IN MOLTEN ALKALINE EARTH CHLORIDES AND THEIR MIXTURES WITH KCL

Since the individual molten alkaline earth (AEM) chlorides and their binary mixtures with potassium chloride are more structured than molten AH and their mixtures, it was possible to expect the higher field effects in the AEM. Their conductivities also rise with rising EFS and reach the limiting values in the field of about 0, 7 MV/m. This dependence is presented in Fig.4, by way of examples, for the molten pure MgCl₂ and binary mixtures MgCl₂-KCl.

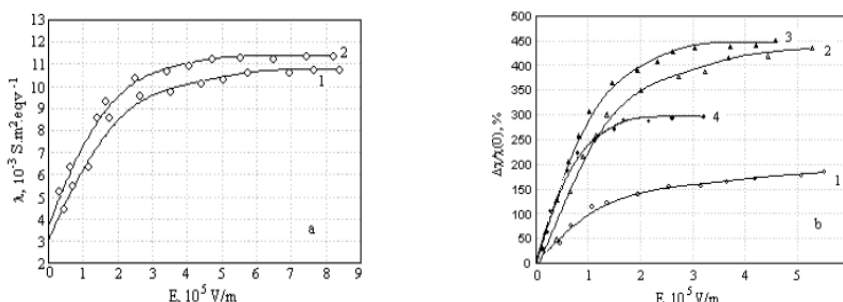


Fig4. a) The equivalent conductivity of molten MgCl₂ as function of EFS at 1000K (1) and 1040 K (2); b) Dependence of high field specific conductivity quotient on the EFS for mixtures MgCl₂-KCl with content of MgCl₂ 0, 2 mol% (curve 1), 0, 4 (2), 0,6 (3) and 0,8 (4); T=T_{liquidus}+90K.

The high field conductance quotients for the mixtures exceed considerably the corresponding values for the pure MCl₂ (M=Mg, Ca, Sr, Ba) and KCl. Extrapolation of the $\Delta\lambda / \lambda(0), r^{-2}$ - dependence to $r^{-2} \rightarrow 0$ for AE chlorides yields its value about 20 %. This means that up to 20 % of the observed value of Wien effect corresponds to elimination of the relaxation inhibition, while key contribution to the observed effect in the salt melts is made by their stimulated dissociation, as in the second Wien effect and as it was predicted by Faraday. The limiting high-voltage conductivities of molten AE chlorides correlate with the NE equation (7). They are presented in the Table 4 together with experimental self-diffusion coefficients of the ions [21].

Table4. The low-voltage and high-voltage limiting conductivities of molten MCl₂ and feasibility of the Nernst-Einstein relation

Melt	T, K	D ₊	D ₋	λ(0)	λ ⁰	λ _D	Δλ/λ(0),%
		10 ⁻⁹ m ² /s		10 ⁻³ S·equ ⁻¹			
MgCl ₂	1000	6.00	0.40	2.95	10.78	13.90	265.0
	1040			3.20	11.3		253.0
CaCl ₂	1073	2.14	2.98	5.70	7.80	7.69	38.0
	1138	2.52	3.77	6.52	9.10	8.66	39.6
SrCl ₂	1168	2.06	3.96	6.06	7.76	7.74	28.0
	1200	2.20	4.30	6.46	8.43	8.12	30.5
BaCl ₂	1250	1.74	4.40	6.89	8.41	7.06	22.1
	1280	1.89	4.81	7.27	8,91	7.51	22.6

The proximity of the values of λ_D and λ⁰ means that the structure of molten salts exposed to strong electrical impulses is simplified and ion displacement contributes equivalently to the mass and charge transfer. In the Table 5 the low-voltage specific conductivity χ(0) and high-voltage limiting conductivities χ⁰ of binary melts MgCl₂-KCl are compared.

Table5. Usual low-voltage and high-voltage limiting specific conductivities of the melts in the system MgCl₂-KCl

Melt	T,K	χ(0)	χ ⁰	Δχ / χ(0) ,%
		10 ² S·m ⁻¹		
KCl	1073	2.24	2.54	13
	1113	2.33	2.69	15
0.8KCl-0.2 MgCl ₂	976	1.32	3.7	185
	1033	1.43	3.7	160
0.6KCl-0.4MgCl ₂	843	0.90	5.1	465
	909	1.05	5.6	433
0.4KCl-0.6MgCl ₂	870	0.97	5.32	550
0.2KCl-0.8MgCl ₂	1005	1.18	4.69	297
	MgCl ₂	1000	1.05	3.48
	1040	1.12	3.96	253

6. ACTIVATION OF THE MOLTEN AND SOLID ELECTROLYTES

The above results were obtained when analyzing the waveforms of the discharges in molten and solid electrolytes. After the discharges have been completed, the low-voltage conductivity of the electrolytes measured by an ac bridge turns out increased significantly (“memory effect”). Fig.5 presents some curves as a samples of quotient $[\chi(t)-\chi(0)]/\chi(0)=\Delta\chi/\chi(0)$, vs the time after discharges for the melt $MgCl_2$ -KCl, where $\chi(0)$ is the low-voltage conductivity before the discharge and $\chi(t)$ is it after the discharge. The value $\chi(t)$ at $t=0$ can be accepted as the activation degree of the electrolyte.

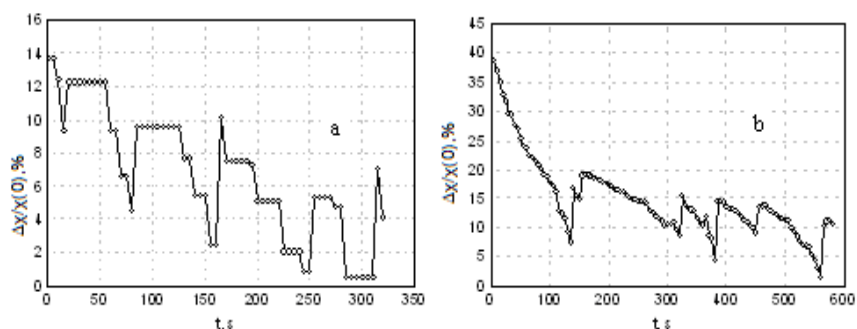


Fig5. Change of the relative values $\Delta\chi/\chi(0)$,% in the time in the molten mixture $MgCl_2(0,2)$ -KCl activated by one pulse of voltage amplitude: a) 2,2kV, and b) activated by 3 pulses of the amplitude 10kV.

The graphs of Fig.5 show that the value of the activation degree increases with increasing voltage amplitude of single activating pulse from 14% at $U=2, 2$ kV (curve a) to 36% at $U=10$ kV (curve b). It is obtained that the activation degree increases with increasing number of activating pulses from 14% for one pulse of 10kV to 38% for three pulses of the same voltage amplitude. For the electrolytes studied, the activation degree tends toward the saturation with increasing voltage amplitude for a given number of the pulses and with increasing amounts of activating pulses in the series of given voltage amplitude.

Superconducting α -phase of the solid conductors also exhibit the “memory effect”. Fig. 6 shows the conductivity relaxation dynamics for activated α -AgJ and α -KAg₄I₅.

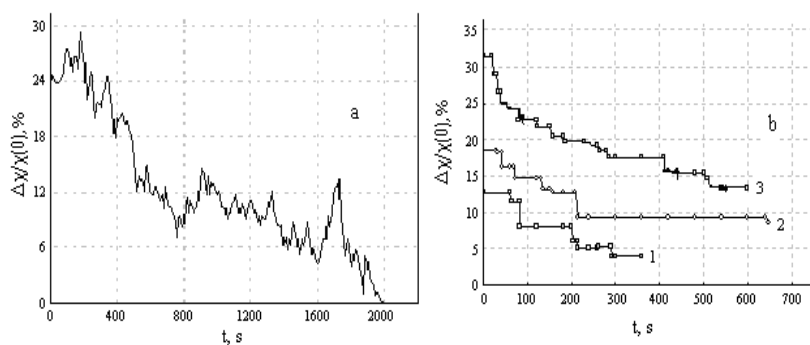


Fig6. Conductivity relaxation curve for a) α -AgJ activated by a single high-voltage pulse with the amplitude of 3 kV; 636 K. b) α -KAg₄I₅ activated by the pulse with the voltage amplitude of 4.4 (curve 1), 5.1 (2), and 6.1 kV (3) at 100 °C.

The increased electrical conductivity of activated molten and solid electrolytes decreases with the time and tends to the initial (equilibrium) values, the relaxation of conductivity occurs in multi-step and oscillatory regime.

The above results can be regarded as the experimental manifestation and evidence of the existence of (auto) complexes in the equilibrium molten salts as well as of dissociation of these complexes due to the high-voltage treatment. But in the literature there are no direct evidences of stimulated dissociation of the complexes and their prolonged structural relaxation in the ionic halide molten electrolytes. The dissociation of complex formations can be displayed by comparison of the Raman spectra of the molten salts in equilibrium and in non-equilibrium states at given temperature and composition. We have carried out such experiments with the highly structured molten salts. The spectra for the molten $MgCl_2$ and $ZnCl_2$, normalized using the total polarized scattered intensity, are shown in

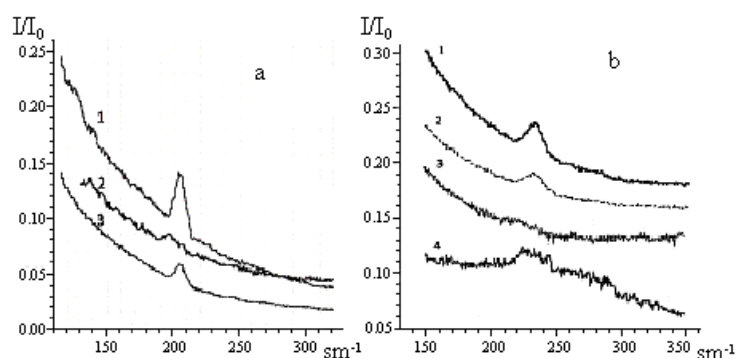


Fig7. Raman spectra of the equilibrium salts and of these salts subjected to activating high-voltage pulses. a) Raman spectra of equilibrium molten $MgCl_2$ (curve 1) and spectra of its melt subjected to 3 electric pulses of voltage amplitude 8kV (curve 2). The curve 3 represents the Raman spectra of the non-equilibrium melt in the relaxation processes 10 minutes after activation; $T= 973 K$

b) Raman spectra of solid $ZnCl_2$ (curve 1), of its equilibrium melt at 624 K (curve 2); the spectrum of the melt subjected to 5 electric pulses of voltage amplitude 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.

As a result of previous high-voltage pulses influence, the spectral peaks disappear almost completely due to the melts transition to a nonequilibrium state with dissociated complexes. In continuation of the relaxation processes in non-equilibrium melts, their Raman spectra restore and strive to initial peaks typical for equilibrium systems.

7. DISCUSSION

The structure and electrochemical properties of molten and solid electrolytes are studied mainly in their equilibrium or slightly non-equilibrium states; they are determined by the nature and distribution of structural species in them. For the molten alkali halides [22] and alkali earth halides [23] the structural auto complex model has been a priori assumed according to which molten salts may be considered as mixture of MX_4^{n-4} anions and M^{n+} cations as structural elements. Later, as a result of the development of spectroscopic methods, it was proved that auto complexes in individual molten halides of alkali and alkaline earth metals are not a priori abstraction but can quite reliably be fixed in Raman spectra [24, 25]. From the low-frequency Raman spectra a conclusion is drawn that in molten alkali halides and their mixtures the configurations of MX_4^{-n+1} exist in during the time intervals (0.5ps) sufficient to a collision complex to execute several vibrations.

The observed behavior of the melts can be understood on the basis of their equilibrium structure and its changes under the influence of external perturbation action. The local structure of molten metal halides has been quite extensively studied in using neutron and X-ray scattering techniques. In summary, they lead to conclusion that alkali halides have a simple local structure. The maximum of the first peak is related to the association between the cations and the anions. The mixtures of alkali halides are more structured, in the mixtures with the lithium salts a relatively long-live configuration appears, even a pre-peak was observed [26].

The structure of the molten alkali earth metal chlorides is determined in terms of the RDF $g_{\alpha\beta}(r)$ [26]. On the RDF $g_{\alpha\beta}(r)$ for the molten $MgCl_2$ and $ZnCl_2$ are observed the high first peaks that not readily explained in purely ionic framework. Moreover, measurement of their partial structure factors shown the presence of the “pre -peak” in the structural factor $S^{++}(k)$ which is believed to long-range polymeric ordering of basic structural species indicating the presence of intermediate-range order (IRO) in ionic framework. The RDF of molten $SrCl_2$ and $BaCl_2$ can be reproduced by purely ionic potentials [26]. Raman spectra of the molten $MgCl_2$ [54] indicate the presence of a discrete tetrahedral $MgCl_4^{2-}$ species in equilibrium with complex $Mg_2Cl_7^{3-}$ ions, they confirm the presence of variety of structural species and IRO in ionic framework of molten $MgCl_2$. According to the authors [28], the content of the species $MgCl_4^{2-}$ and $Mg_2Cl_7^{3-}$ in the pure melt is about 30%. The addition of

the KCl to alkali earth chlorides MCl_2 causes more stabilization of complex ions than in the pure molten MCl_2 . The molten mixtures become more structured, the content of the complex ions in the mixtures KCl - $MgCl_2$ rises up to 85% [28].

These extremely important and interesting experimental data do not cause any doubt, they explain the observed behavior of the equilibrium real melts. It is also clear that if we could change the structural characteristics of the molten electrolytes, it is possible to observe significant changes in their properties. Our results on the dependence of the electrical conductivity of the individual molten chlorides of s^2 -metals (Table 4) and their mixtures with KCl (Table 5) on the EFS agree fully with the expected changes in the melts structure and their conductivity. The limiting high-voltage conductivity surpasses the usual values up to 265% in the pure molten $MgCl_2$ and up to 550% in the molten mixtures $MgCl_2+KCl$ that is a testament to the equilibrium melts being strongly associated and to the complete dissociation of ionic complexes in high fields.

After the high-voltage pulsed discharges in the molten and solid salts are completed, their low voltage conductivity turns out increased. As a consequence of the transition of the melt to a non-equilibrium state with dissociation of the complex ions on the elementary or simpler ions; its conductivity is significantly increased. The system tends to the equilibrium state, to reestablish its equilibrium characteristic structural species diversity and their distribution. As can be seen from Fig. 6 and Fig. 7, the relaxation has the anomalous duration reaching up to ten minutes. The conductivity failures from the steps can be attributed to a recombination of complex ions. The relaxation of conductivity occurs in multi-step and oscillatory regime obviously expressed, with the increase of the amplitude and the amount of activating pulses stepwise-oscillating nature of the relaxation curve is reduced, and it becomes just an oscillatory one. The activation degree and the duration of the activated state rise with raising voltage amplitude and number of activating pulses.

The Raman spectra of individual equilibrium molten salts obtained agree well with literature data 205 cm^{-1} for the $MgCl_2$ [29] and $230\text{-}235\text{ cm}^{-1}$ for $ZnCl_2$ [30]. As a consequence of the transition of the melts to a non-equilibrium state, the typical for the melts spectral peaks disappear almost completely. During the structural relaxation processes in non-equilibrium melts their Raman spectra and the conductivities are restored to the values and patterns characteristic for equilibrium molten salts.

8. CONCLUSION

In the molten electrolytes the Wien effect is observed with reaching the limiting high-voltage conductivity. The ionic limiting conductivities in the molten salts obey the fundamental Stokes, Stokes-Einstein and Nernst-Einstein relations. The molten electrolytes subjected to a microsecond pulses of high intensity exhibit the phenomenon of activation with their transition to a nonequilibrium state with increased conductivity and the disappearance of the peaks of the Raman spectra characteristic of the equilibrium molten salts. During the structural relaxation processes in non-equilibrium melts their conductivities and Raman spectra are restored to the values and patterns characteristic for equilibrium systems. Anomalous prolonged relaxation of the non-equilibrium electrolytes occurs in stepwise - oscillatory regime. The high-field effects in the conductivity and in Raman spectra of molten salts are interpreted as the direct display and evidence of the existence and stimulated dissociation of the complex ions in them.

The results presented in the article have no analogues in the literature. The authors have no conflicts of interests.

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