ELECTRICAL CONDUCTIVITY OF GLASSES IN THE SYSTEM $CuCl\text{-}Cu_2O\text{-}(P_2O_5+MoO_3)$

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This work deals with glasses of composition 18.0 CuCl – 36.5 Cu_2O – 45.5 ($P_2O_5+MoO_3$) in which the $MoO_3/(P_2O_5+MoO_3)$ molar ratio was varied. The glasses can be classified as glasses which contain mainly one type of cation (Cu^+) and various kinds of polymeric or discrete anions. A distinct increase in conductivity (by two orders of magnitude) was observed with an increasing $MoO_3/(P_2O_5+MoO_3)$ ratio. The maximum of conductivity is of the order of $10^{-4}\Omega^{-1}cm^{-1}$. Increase in conductivity is in agreement with rapid decrease in activation energy for conduction and increase in concentration of Cu^+ conductive ions, which is due to substantial changes in glass network with increasing content of MoO_3. Electronic conductivities of glasses under study were lower by 3 orders of magnitude than their total electrical conductivities.

INTRODUCTION

The problem of production and storage of electrical energy by use of ecologically safe devices has become very interesting in the last few years. Primary and secondary electrochemical cells based on glassy materials were used successfully for production and storage of electricity. It is well-known that solid state cells with glassy materials have some advantages such as safety, long self life, durability, ease of utilization and miniaturization. Nevertheless, their greatest interest is the potential to obtain high power and energy density for room temperature applications [1].

Glass electrolytes used in these devices should meet some criteria, but the most important is high ionic conductivity at room temperature. The highest ionic conductivities ($\sigma_{25} \sim 10^{-2}\Omega^{-1}cm^{-1}$) were attained in Ag^+ containing glasses. Because of a shortage of silver it is necessary to find new chemical composition of glasses, with conductivity comparable to the Ag^+ containing glasses. Here is a good opportunity for glasses containing Cu^+ conductive ions. The similarity of electronic configuration and smaller ionic radii of Cu^+ ion in comparison with Ag^+ ion gives, from a theoretical point of view, a good chance to achieve conductivity comparable with the best Ag^+ conductive glasses [2]. The chemical composition of these glasses can be generally expressed as the system $CuX\text{-}Cu_2O\text{-}M_mO_n$ (where X = Cl, Br, I; and M_mO_n is a "glass forming" oxide).

On the other hand, some glasses which are semiconducting and chemically intercalatable with mobile ions could have patential applications as positive electrode materials [3].

The conductivity of glasses is affected not only by the type of conductive ions, but also strongly depends on "glass forming" oxide. The glass formation of many systems containing Cu^+ conductive ions was investigated [4], but glasses were prepared only in systems containing either P_2O_5 [5–8] or MoO_3 [4, 9, 10] as a "glass forming oxide". It has been found that the mixing of two glass formers yields glasses with higher electrical conductivity. Such glasses were also prepared in systems with mixed "glass forming" oxides $P_2O_5\text{-}MoO_3$ [11–18].

In the present work glasses in the system 18.0 CuCl – 36.5 Cu_2O – 45.5 ($P_2O_5+MoO_3$) with the molar ratio $Cu_2O/(P_2O_5+MoO_3)$ = 0.8 and the $MoO_3/P_2O_5+MoO_3)$ ratio ranging from 0 to 0.9 were prepared. Their electrical properties were studied, and relationships between structure and electrical conductivity are discussed.

EXPERIMENTAL

Starting materials used for glass preparation were commercial reagents of purity A.R.: P_2O_5, MoO_3, CuCl (Lachema) and Cu_2O (Reachim). A starting mixture was melted in a silica ampoule under a dry argon atmosphere (to avoid oxidation of Cu^+ ions) at 650°C for 90 min. Glass melt was rapidly quenched by pressing between two brass plates to the final thickness of 1.5 mm. The resulting disc 20 mm in diameter was kept between the plates until its temperature decreased to the room temperature. Losses in weight during melting were $\leq$ 1%. Details of glass preparation are reported elsewhere [18]. The glasses were hygroscopic (after all the glasses with high P_2O_5 content) and their exposure to air was avoided as much as possible by storing them in a desiccator.

All the prepared glasses were checked by X-ray powder diffraction measurements (Dron 2) using CuK_α radiation to identify the presence of undesirable crystalline phases.

The densities of the glasses were determined by the pycnometric method using samples free of air bubbles. Measurements were carried out at 20°C, ethanol was used as the displacement liquid. The error of measurements was within 0.01 g cm^{-3}. From the densities and chemical compositions, molar volumes of glasses were calculated.

The total electrical conductivity of prepared glasses was measured by the complex impedance method over the frequency range 100 Hz - 20 kHz (Tesla BM 595 RLCG Meter) from room temperature up to ~ 100°C. Three probe technique (Au blocking electrodes prepared by cathode sputtering) was used to eliminate surface conductivity. Measurements were carried out in a dry argon atmosphere to eliminate the influence of atmospheric moisture. The complex impedance measured allowed us to obtain the bulk d.c. conductivities of glassy samples by means of the usual impedance analysis. All samples were measured twice, and obtained results were reproducible within 3%.

The contribution of electronic conductivity to the total conductivity of glasses (samples D and G) was measured by the use of an electrochemical cell

$$(-)\ \mathrm{Cu}\ /\ \mathrm{glass}\ /\ \mathrm{Au}\ (+) \tag{1}$$

by the use of the Wagner's polarisation technique [19-21]. Cu and Au are reversibile and blocking electrodes, respectively (prepared by cathode sputtering). Measurements were carried out at room temperature. The cell (1) was polarized by applying a d.c. potential below the decomposition voltage of the investigated material. At equilibrium conditions, the movement of the cuprous ions due to the electrical gradient is equal to the movemet due to the gradient of chemical potential. The total electrical current is thus carried by the electrons and/or electron holes only. According to the Wagner's analysis, the total electronic current, I, is given by the equation

$$I = I_e + I_h = \frac{\mathrm{R}TS}{L\mathrm{F}}\{\sigma_e[1-\exp(-E\mathrm{F}/\mathrm{R}T)] + \sigma_h[\exp(E\mathrm{F}/\mathrm{R}T)-1]\} \tag{2}$$

where I_e and I_h are the currents due to electrons and electron holes, respectively, R is the gas constant, T is the thermodynamic temperature, S is the area of the electrode, L is the thickness of the sample, F is the Faraday constant, E is the applied voltage, σ_e and σ_h are the conductivities due to electrons and electron holes, respectively. Dividing equation (2) by $[\exp(E\mathrm{F}/\mathrm{R}T)-1]$

$$\frac{I}{\exp(E\mathrm{F}/\mathrm{R}T)-1} = \frac{\mathrm{R}TS}{L\mathrm{F}}\left[\sigma_e\frac{1-\exp(-E\mathrm{F}/\mathrm{R}T)}{\exp(E\mathrm{F}/\mathrm{R}T)-1} + \sigma_h\right] \tag{3}$$

and when $E\mathrm{F} \gg \mathrm{R}T$

$$\frac{I}{\exp(E\mathrm{F}/\mathrm{R}T)-1} = \frac{\mathrm{R}TS}{L\mathrm{F}}[\sigma_e\exp(-E\mathrm{F}/\mathrm{R}T) + \sigma_h]\ . \tag{4}$$

A plot of $I/[\exp(E\mathrm{F}/\mathrm{R}T)-1]$ against $\exp(-E\mathrm{F}/\mathrm{R}T)$ will thus give a straight line, the slope of which gives the contribution due to electrons, while the intercept on the y axis gives the contribution due to the electron holes [21]. The reproducibility of measurements was within 5%.

RESULTS

Good glass forming in the system 18.0 CuCl - 36.5 Cu_2O - 45.5 (P_2O_5+MoO_3) was observed for compositions in which the $MoO_3/(P_2O_5+MoO_3)$ ratio ranged from 0 to 0.9. By X-ray diffraction, the presence of crystalline phases in the samples with a ratio higher than 0.9 was detected.

The dependence of molar volume vs. composition is presented in Fig. 1. The solid line represents the curve obtained by the least square fitting of data of molar volume. The dependence was described by equation $V_m = c_1x^2 + b_1x + a_1$, where parameters $c_1 = 7.17\pm1.70$; $b_1 = -19.66\pm1.55$; $a_1 = 40.32\pm0.23$, and $x = MoO_3/(P_2O_5+MoO_3)$. Molar volume gradually decreases by substitution of MoO_3 for P_2O_5 at a given contents of Cu_2O and CuCl. From the molar volumes and chemical compositions were calculated

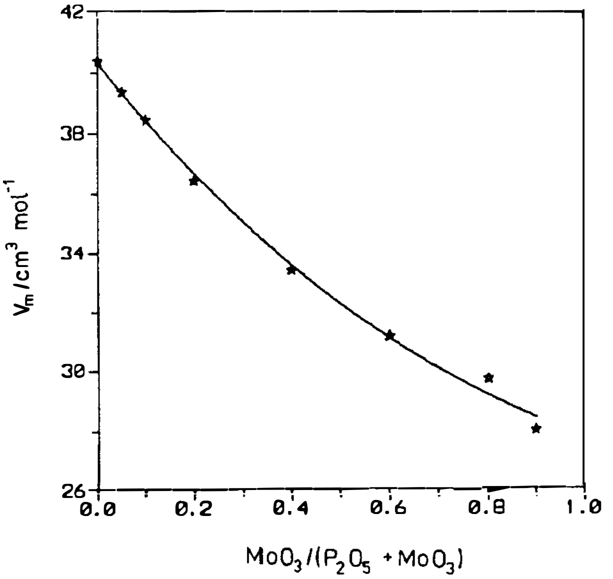

Fig. 1. The molar volume of glasses, V_m, in the system 18.0 CuCl - 36.5 Cu_2O - 45.5 (P_2O_5+MoO_3) as a function of $MoO_3/(P_2O_5+MoO_3)$ ratio.

Table I.

Compositions of glasses expressed as the molar ratio $MoO_3/(P_2O_5+MoO_3)$, total electrical conductivities, concentrations of Cu^+ ions generated from CuCl and Cu_2O, respectively, and dominant structural units

Glass	$\frac{MoO_3}{P_2O_5+MoO_3}$	σ_{25} $[\Omega^{-1}cm^{-1}]$	$[Cu^+]_{CuCl}$ $[mol\ cm^{-3}]$	$[Cu^+]_{Cu_2O}$ $[mol\ cm^{-3}]$	Dominant structural units[a]
A	0	3.03×10^{-6}	4.45×10^{-3}	1.81×10^{-2}	$(PO_3^-)_n$-chains+network
B	0.05	4.63×10^{-6}	4.57×10^{-3}	1.85×10^{-2}	$(PO_3^-)_n$-chains
C	0.1	6.59×10^{-6}	4.68×10^{-3}	1.90×10^{-2}	$(PO_3^-)_n$-chains
D	0.2	8.39×10^{-6}	4.94×10^{-3}	2.00×10^{-2}	$(PO_3^-)_n$, $P_2O_7^{4-}$
E	0.4	2.21×10^{-5}	5.38×10^{-3}	2.18×10^{-2}	$P_2O_7^{4-}$, $(PO_3^-)_n$
F	0.6	5.80×10^{-5}	5.77×10^{-3}	2.34×10^{-2}	$P_2O_7^{4-}$, PO_4^{3-}, $Mo_2O_7^{2-}$
G	0.8	1.48×10^{-4}	6.05×10^{-3}	2.45×10^{-2}	PO_4^{3-}, MoO_4^{2-}, $Mo_2O_7^{2-}$
H	0.9	3.47×10^{-4}	6.43×10^{-3}	2.61×10^{-2}	MoO_4^{2-}, PO_4^{3-}, $Mo_2O_7^{2-}$

[a] Observed in IR spectra (see [18]); the presence of neutral structural units with two- or three-dimensional networks such as typical for $MoO_2(PO_3)_2$ and $(MoO_2)_2P_2O_7$ is also assumed mainly in the glasses D-G.

concentrations of Cu^+ ions generated from CuCl and Cu_2O, respectively (see Table I.)

Fig. 2. shows the temperature dependences of the total conductivity of the glasses. The conductivity data fit the Arrhenius equation

$$\sigma = \sigma_0 \exp(-E_a/RT) \qquad (5)$$

where σ_0 is the pre-exponential term, E_a is the activation energy for conduction, R is the gas constant and T is thermodynamic temperature.

Values of the conductivity at 25°C, σ_{25}, the activation energy, E_a, and the logarithm of the pre-exponential term, $\log \sigma_0$, were calculated using the least square fitting analysis of experimental conductivity data.

The plot of logarithm of conductivity at 25°C ($\log \sigma_{25}$) vs. chemical composition of glasses is shown in Fig. 3. The dependence was fitted by equation $\log \sigma_{25} = b_2 x + a_2$. Parameters $b_2 = 2.14 \pm 0.07$ and $a_2 = -5.48 \pm 0.04$ ($x = MoO_3/(P_2O_5+MoO_3)$) were obtained by using least square fitting method. It is obvious that with an increasing content of MoO_3, conductivity increases by two orders of magnitude.

The influences of chemical composition on logarithm of the pre-exponential term ($\log \sigma_0$) and activation energy for conduction (E_a) can be observed in Fig. 4. and Fig. 5., respectively. Both dependences were approximated by weighted least square fitting analysis, where the weights were defined as $1/(s_{\log \sigma_0})^2$ and $1/s_{E_a})^2$, respectively. Obtained equations can be expressed as follows: $\log \sigma_0 = d_3 x^3 + c_3 x^2 + b_3 x + a_3$, parameters $d_3 = -6.74 \pm 1.03$, $c_3 = 10.09 \pm 1.38$, $b_3 = -6.66 \pm 0.50$, $a_3 = 4.98 \pm 0.05$; $E_a = d_4 x^3 + c_4 x^2 + b_4 x + a_4$, parameters $d_4 = -50.42 \pm 10.26$, $c_4 = 71.67 \pm 13.92$, $b_4 = -53.59 \pm 5.07$, $a_4 = 59.76 \pm 0.49$, and $x = MoO_3/(P_2O_5+MoO_3)$. In

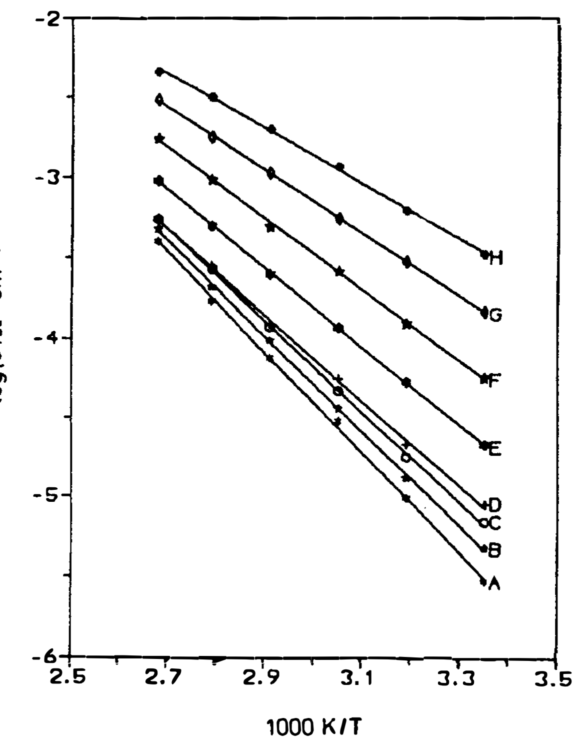

Fig. 2. The temperature dependence of logarithm of conductivity of glasses, $\log \sigma$, *in the system 18.0 CuCl - 36.5* Cu_2O *- 45.5* $(P_2O_5+MoO_3)$*.*

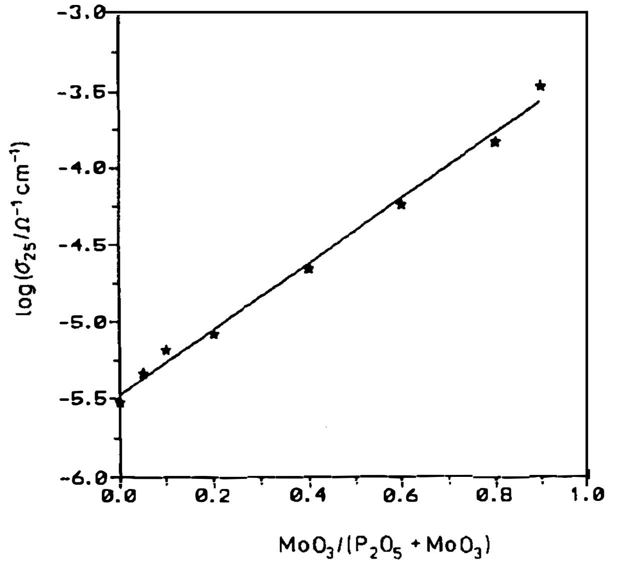

Fig. 3. The logarithm of conductivity at 25° C of glasses, $\log\sigma_{25}$, *in the system 18.0 CuCl - 36.5 Cu₂O - 45.5 (P₂O₅+MoO₃) as a function of MoO₃/(P₂O₅+MoO₃) ratio.*

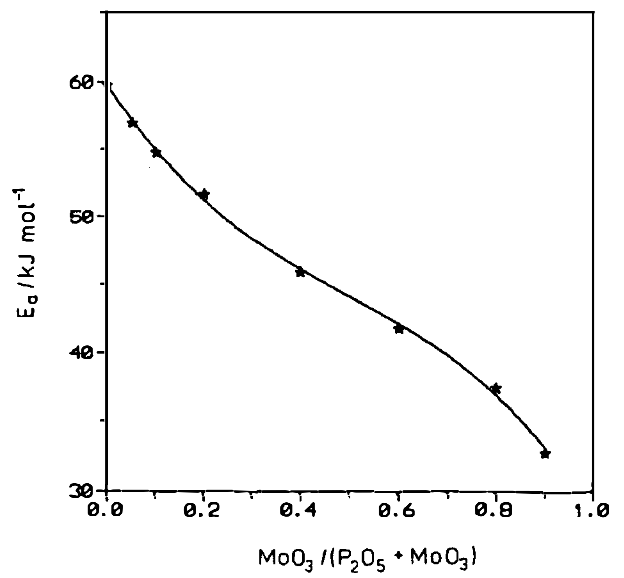

Fig. 5. The dependence of activation energy for conduction of glasses, E_a, *in the system 18.0 CuCl - 36.5 Cu₂O-45.5 (P₂O₅+MoO₃) on MoO₃/(P₂O₅+MoO₃) ratio.*

both graphs we can observe a continuous decrease in $\log\sigma_0$ and E_a, respectively, with an increasing $MoO_3/(P_2O_5+MoO_3)$ ratio.

The electronic conductivity was determied on the glass C (with a high content of P_2O_5) and G (with a high content of MoO_3) with values: for glass C: $\sigma_{25el} = 4.2 \times 10^{-9}\ \Omega^{-1}cm^{-1}$; and for glass G: $\sigma_{25el} = 3.8 \times 10^{-7}\ \Omega^{-1}cm^{-1}$).

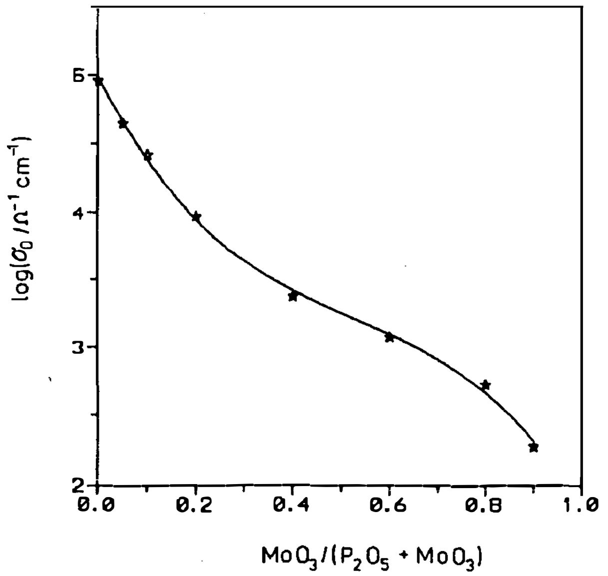

Fig. 4. The dependence of logarithm of pre-exponential term of glasses, $\log\sigma_0$, *in the system 18.0 CuCl - 36.5 Cu₂O - 45.5 (P₂O₅+MoO₃) on MoO₃/(P₂O₅+MoO₃) ratio.*

DISCUSSION

The structure of glasses in the system 18.0 CuCl - 36.5 Cu_2O - 45.5 $(P_2O_5+MoO_3)$ was studied by IR spectroscopy and, in part, by Raman spectroscopy [18]. Structure of glasses changes significantly with varied molar ratio $MoO_3/(P_2O_5+MoO_3)$ (see Table I.). The glasses can be classified as glasses which contain one type of cation and various kinds of polymeric or discrete anions. The presence, in small concentrations, of structural units with networks such as typical for $MoO_2(PO_3)_2$ and $(MoO_2)_2P_2O_7$, is also assumed. A phosphate glass without MoO_3 (A), is assumed to be made up of chains of $(PO_3^-)_n$ and by corner shared chains of $(PO_3^-)_n$ in a two- or three-dimensional network. In glasses in which the ratio of $MoO_3/(P_2O_5+MoO_3)$ increases, a gradual degradation of the network structural units and $(PO_3^-)_n$ chains and increasing content of a variety of low-condensed or monomeric phosphate and molybdate anions was observed. For example glasses B, C and D contain mainly $(PO_3^-)_n$ chains and some lower-condensed phosphate ions in small amounts ($P_3O_{10}^{5-}$, $P_2O_7^{4-}$). On the other hand, glasses G and H with the highest content of MoO_3 are composed mainly of discrete anions, such as MoO_4^{2-} and PO_4^{3-}, and partly of condensed molybdate anions of the "$Mo_2O_7^{2-}$" type. These changes in the structure of glasses affect strongly interactions of Cu^+ ions with negatively charged non-bridging oxygens belonging to phosphate and molybdate sructural units.

The temperature dependences of logarithm of conductivity (Fig. 2) of glasses in the system 18.0 CuCl - 36.5 Cu_2O - 45.5 (P_2O_5+MoO_3) are linear in the examined temperature interval. That means, mechanism of charge transport in glasses does not change from ionic to electronic or vice versa, which would be indicated by the non-linearity of plots.

The compositional dependence of $\log\sigma_{25}$ is plotted in Fig. 3. The conductivity gradually increases with increasing MoO_3 content in glasses. This trend is in good agreement with increase in concentration of mobile Cu^+ ions in prepared glasses (Table I). Electronic conductivities of glasses in this system were lower by 3 orders of magnitude in comparison with conductivities determined by the complex impedance analysis. Hence, the transport number of Cu^+ ions in these glasses in only slightly lower than unity.

It is evident from the equation (5) that conductivity is an increasing function of the pre-exponential term (σ_0) and decreasing function of the activation energy (E_a).

The activation energy for conduction of the glasses is plotted in Fig. 5 as a function of the $MoO_3/(P_2O_5+MoO_3)$ ratio. Anderson and Stuart [22] suggest that the total activation energy is the sum of two parts - electrostatic binding energy (E_b) which is determined by the electrostatic interactions acting on mobile ions, and elastic strain energy (E_s) which is associated with the expansion of the local structure to allow the ion to move between sites. After several approximations they propose that for an ion of valency z

$$E_a = E_b + E_s = \frac{\beta z z_0 e^2}{\gamma(r + r_0)} + \quad (6)$$
$$+ 4\pi G r_D (r - r_D)^2$$

where z_0 and r_0 are the valency and radius of the non-bridging oxygen, respectively, β is the lattice parameter depending on the distance between neighbouring sites, r is the cation radius, r_D is the radius of the normal (unexpanded) doorways in the glass, G is the elastic modulus and γ is the "covalency parameter". Ingram [23] concluded that a fall in activation energy could be associated with an increase in concentration of mobile ions either because of (a) decrease in the lattice parameter, β, consequent upon the cation sites being moved closer together, (b) an increase in the "covalency parameter", γ, consequent upon the rise in the polarizability of the oxide atoms or (c) decreases in G and r_D, consequent upon a disruption of the network and an increase in the number of non-bridging oxygens.

In the system 18.0 CuCl - 36.5 Cu_2O - 45.5 (P_2O_5+MoO_3) activation energy gradually decreases with increasing the $MoO_3/(P_2O_5+MoO_3)$ ratio. This decrease is explicable in terms of increase of concentration of Cu^+ ions in glasses (Table I) in the sequence A - G. Lattice parameter, β, decreases that means decrease jump distances for movement of Cu^+ ions. For movement of Cu^+ ions in glass structure also the nature of anion distribution in the network is important. Structure of glasses changes significantly with increasing $MoO_3/(P_2O_5+MoO_3)$ ratio [18]. With increasing content of MoO_3 in glasses increases the number of non-bridging oxygens which is associated with increase in polarizability of oxygen atoms. This results in decrease of activation energy with increasing content of MoO_3 in glasses under study.

From plot in Fig. 4 we can observe gradual degradation of $\log\sigma_0$ as a function of the $MoO_3/(P_2O_5+MoO_3)$ ratio. It is obvious (equation 5) that increase in conductivity should be associated with increase in pre-exponential term. But in Fig. 3 and Fig. 4 we can observe contradictory trends in $\log\sigma_{25}$ and $\log\sigma_0$. So, we can conclude that in these glasses variation in activation energy E_a has an outweighing effect on conductivity as compared with variation in pre-exponential term.

CONCLUSIONS

(i) The conductivity of glasses in the system 18.0 CuCl - 36.5 Cu_2O - 45.5 (P_2O_5+MoO_3) increases with increasing $MoO_3/P_2O_5+MoO_3)$ ratio and reaches the maximum of the order of 10^{-4} $\Omega^{-1}cm^{-1}$.

(ii) The increase of the conductivity with increasing ratio $MoO_3/(P_2O_5+MoO_3)$ is essentially due to the changes in activation energy, but not in pre-exponential term. The activation energy decreases as a result of decreasing jump distances of Cu^+ ions, increasing number of non-bridging oxygens and increasing polarizability of oxygen atoms.

(iii) Electronic conductivities of glasses in this system are lower by 3 orders of magnitude in comparison with total conductivities; the transport number of Cu^+ ions in these glasses is only slightly lower than unity.

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ELEKTRICKÁ VODIVOSŤ SKIEL V SYSTÉME $CuCl-Cu_2O-(P_2O_5+MoO_3)$

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V práci sa skúmali elektrické vlastnosti skiel v sústave 18.0 CuCl – 36.5 Cu_2O – 45.5 $(P_2O_5+MoO_3)$ v závislosti od zmeny chemického zloženia, ktoré je vyjadrené pomerom $MoO_3/(P_2O_5+MoO_3)$.

Skúmané sklá možno klasifikovať ako sklá obsahujúce jeden typ katiónu (Cu^+) a viacero typov polymérnych a diskrétnych fosforečnanových a molybdénanových aniónov. Predpokladá sa aj prítomnosť neutrálnych štruktúrnych celkov typu $MoO_2(PO_3)_2$ a $(MoO_2)_2P_2O_7$ [18]. Pre pohyb iónov Cu^+ je rozhodujúca distribúcia aniónov v skelete skiel.

Celková elektrická vodivosť sa určila metódou merania komplexnej impedancie, elektrónová vodivosť sa určila Wagnerovou polarizačnou metódou. Celková vodivosť pripravených skiel sa zvyšuje so vzrastajúcim pomerom $MoO_3/(P_2O_5+MoO_3)$ a dosahuje maximálnu hodnotu poriadku 10^{-4} $\Omega^{-1}cm^{-1}$. Toto zvýšenie je v súlade s poklesom aktivačnej energie vodivostného procesu (E_a). Pokles (E_a) je spôsobený zväčšením koncentrácie Cu^+ iónov v systéme ako dôsledok zmeny štruktúry základného skeletu skiel. Zväčšenie koncentrácie Cu^+ iónov má za následok zmenšenie vzdialeností pre ich preskok do priľahlej polohy. So zväčšujúcim sa obsahom MoO_3 v sklách sa zväčšuje počet nemostíkových kyslíkov a zvyšuje sa polarizovateľnosť kyslíkových aniónov, z čoho rezultuje výrazné zmenšenie aktivačnej energie. Elektrónové vodivosti skiel boli menšie v porovnaní s celkovými vodivosťami o 3 poriadky, z čoho vyplýva, že prevodové čísla iónov Cu^+ sú blízke 1.

Obr. 1. Mólový objem skiel, V_m, v systéme 18.0 CuCl – 36.5 Cu_2O – 45.5 $(P_2O_5+MoO_3)$ ako funkcia pomeru $MoO_3/(P_2O_5+MoO_3)$.

Obr. 2. Teplotná závislosť logaritmu vodivosti skiel, $\log\sigma$, v systéme 18.0 CuCl – 36.5 Cu_2O – 45.5 $(P_2O_5+MoO_3)$.

Obr. 3. Logaritmus vodivosti skiel pri 25° C, $\log\sigma_{25}$, v systéme 18.0 CuCl – 36.5 Cu_2O – 45.5 $(P_2O_5+MoO_3)$ ako funkcia pomeru $MoO_3/(P_2O_5+MoO_3)$.

Obr. 4. Závislosť logaritmu predexponenciálneho faktora skiel, $\log\sigma_0$, v systéme 18.0 CuCl – 36.5 Cu_2O – 45.5 $(P_2O_5+MoO_3)$ od pomeru $MoO_3/(P_2O_5+MoO_3)$.

Obr. 5. Závislosť aktivačnej energie skiel, E_a, v systéme 18.0 CuCl – 36.5 Cu_2O – 45.5 $(P_2O_5+MoO_3)$ od pomeru $MoO_3/(P_2O_5+MoO_3)$.