MOLYBDENUM PHOSPHATE GLASSES MODIFIED BY Cu$_2$O

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Abstract

Glasses in the system Cu$_2$O–P$_2$O$_5$–MoO$_3$ were prepared. The transformation temperature of glasses, T_g, ranges from 122 to 436°C and depends strongly on their composition. T_g values are mainly controlled by the oxygen-packing density. The structure of glasses was studied by infrared spectroscopy. The presence of various phosphate and molybdate units, from discrete monomeric to those with three-dimensional networks, has been observed. The electrical conductivity of prepared glasses depends mainly on Cu$_2$O content and varies from $10^{-14}\Omega^{-1}$cm^{-1}, for the glass free of Cu$_2$O, to $10^{-6}\Omega^{-1}$cm^{-1}, for glasses with compositions near of the binary Cu$_2$O–MoO$_3$ composition.

Keywords: electrical conductivity, molybdenum phosphate glasses, structure, transformation temperature

Introduction

Glassy electrolytes or so-called superionic conducting glasses evoked a considerable attention because of their technological applications in batteries, electrochemical displays and sensors. These glasses are advantageous in comparison with ion-conducting crystalline materials because of isotropic properties, the absence of grain boundaries, the possibility of the formation of thin films or hollow fibres, and the possibility of continual change of their composition. Recent literature data shown that the best ionic conductors are glasses containing Ag$^+$ cations. Glasses of the general composition AgI–Ag$_x$M$_y$O$_z$ (M = P, B, S, As, Cr, Mo) have the room temperature conductivity of the order $10^{-2}\Omega^{-1}$cm^{-1}. With respect to the shortage of silver, it is interesting to replace Ag$^+$ ion by other ion with similar properties. The glasses containing Cu$^+$ cation are expected to show high conductivities, because Cu$^+$ ion has the similar electronic configuration (d^{10}) as Ag$^+$ ion and a smaller ionic radius than Ag$^+$ ion.

Transport studies shown that the ionic conductivity is strongly dependent on the structure of anionic network of glasses. A disordered network is favourable

for achieving of higher ionic conductivity. The mobility of cations also increases with polarizability of an anionic network.

The interest in molybdenum phosphate glasses is relatively high in last decade because of possibility to reach high ionic conductivity. It is known that P_2O_5 and MoO_3 form stable glasses in a wide range of compositions. The introduction of a glass-modifying oxide (usually metal oxide) offers the possibility to receive glasses with new physical properties. Recently, molybdenum phosphate glasses modified by Li_2O [1], Ag_2O [2] and K_2O [3] have been described. However, there are not available data on molybdenum phosphate glasses modified by Cu_2O.

The aim of this paper is to determine the compositional dependence of the structure, the electrical conductivity and the transformation temperature of glasses in the system $Cu_2O-P_2O_5-MoO_3$.
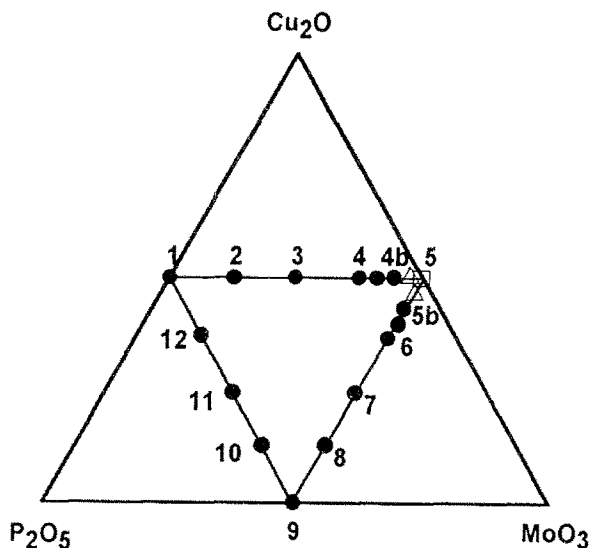

Fig. 1 Starting chemical compositions of glasses prepared in the system $Cu_2O-P_2O_5-MoO_3$ (mol%); • glass, $\triangle$ partially crystalline, $\square$ crystalline

Experimental

Glasses were prepared from commercial reagents Cu_2O, P_2O_5 and MoO_3 of purity p.a. (Lachema) by melting in a silica ampoule or a platinum crucible. In order to minimalize the influence of ambient atmosphere on melting process, the mixtures were melted under a dry argon atmosphere. Batches 15 g in weight were heated for 90 min at temperature between 750 and 1250°C, depending on the starting chemical composition. The melt was rapidly quenched between two brass plates, the disc 20 mm in diameter and ~2 mm in thickness was obtained.

Further details of the sample preparation have been reported previously [4, 5]. Starting chemical compositions of glasses are shown in Fig. 1.

Non-crystallinity of prepared samples was checked by a X-ray diffraction method (Dron 2, CuK_α radiation).

The total contents of Cu, P and Mo in prepared glasses were determined by an inductivity coupled plasma emission spectroscopy (ICPES, ARL 3510-ICP).

All the samples were analyzed by DTA method in air at the scan rate of $10^\circ C$ min^{-1} (Derivatograph Q-1500 D). The transformation temperatures, T_g, were determined from the DTA curves by a shift of the base line to the endothermic direction (typical DTA curve is shown in Fig. 2). The T_g values are plotted in Fig. 3a–c.
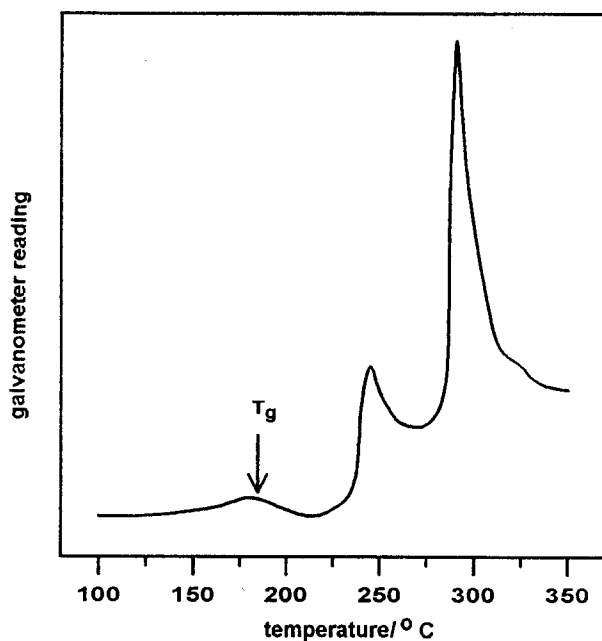

Fig. 2 Typical DTA curve of glasses in the system $Cu_2O-P_2O_5-MoO_3$ (glass 4a)

The densities of glasses were determined by a pycnometric method. Measurements were carried out at $20^\circ C$, ethanol was used as the displacement liquid.

Infrared spectra were recorded on a Perkin-Elmer 983 G double-beam dispersion spectrometer in the range $4000-180$ cm^{-1} at room temperature. The measurements were made on sample powders dispersed in CsI pellets.

The electrical conductivity of prepared glasses was measured by a complex impedance method in the frequency range 100 Hz–20 kHz. Measurements were carried out in the temperature interval from room temperature up to $30^\circ C$ below T_g of glass (Tesla BM 595). Conductivities of glasses at various temperatures
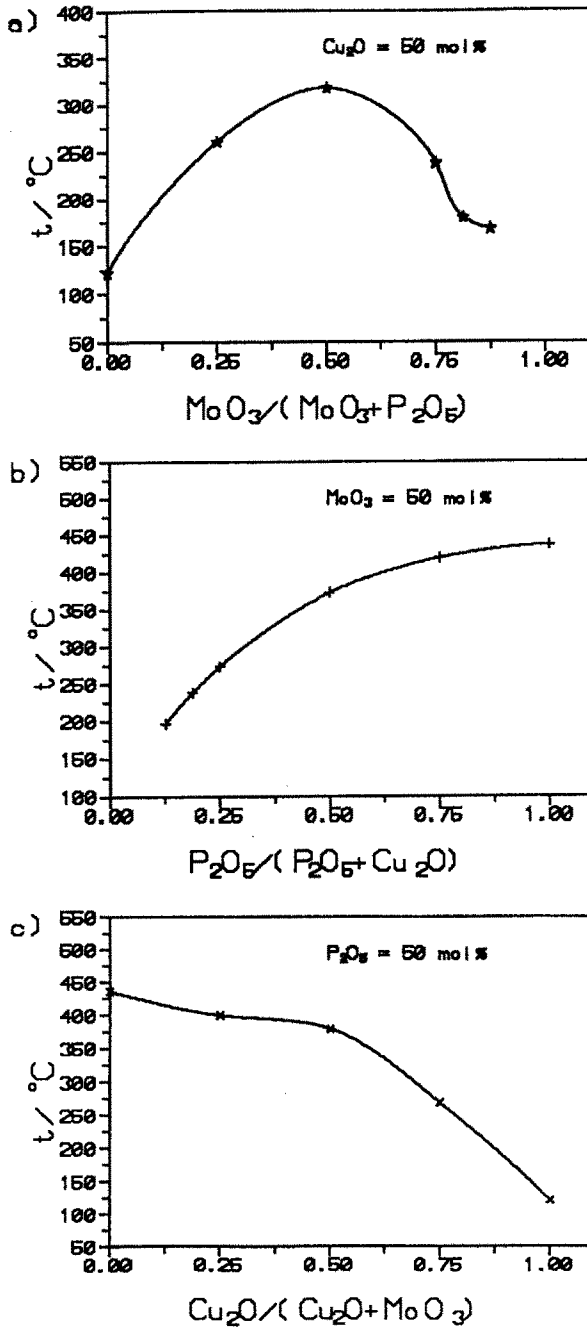
Fig. 3 Transformation temperatures, T_g, of glasses in the system $Cu_2O–P_2O_5–MoO_3$; a) subsystem $50Cu_2O–(50–x)P_2O_5–xMoO_3$; b) subsystem $(50–y)Cu_2O–yP_2O_5–50MoO_3$; c) subsystem $zCu_2O–50P_2O_5–(50–z)MoO_3$

were obtained by means of usual impedance analysis (typical impedance spectra are plotted in Fig. 4).
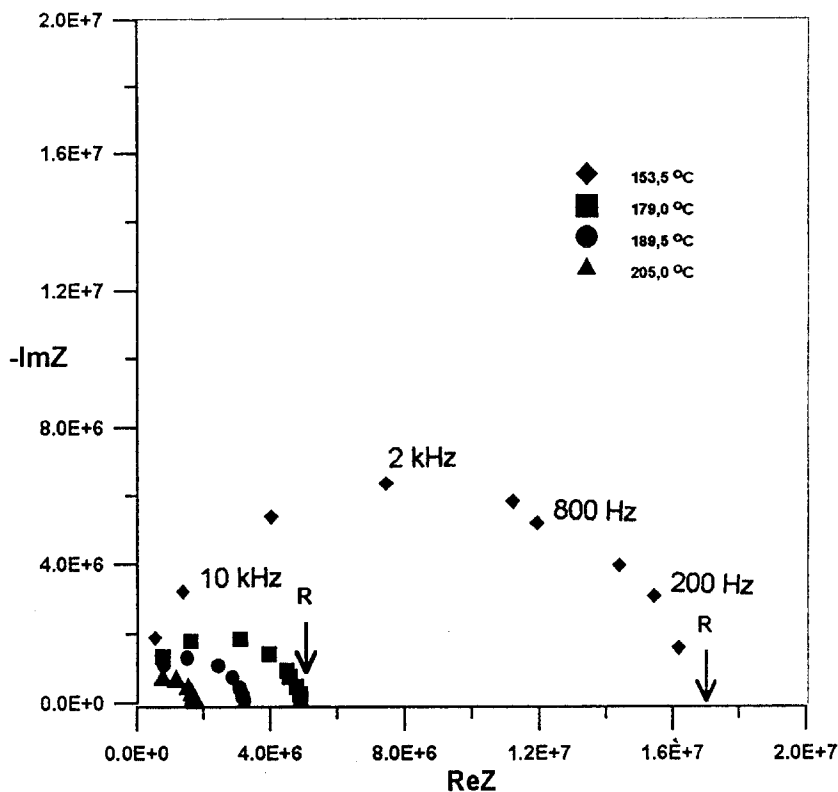

Fig. 4 Impedance spectra of glass 11 at various temperatures (measured in frequency range 100 Hz–20 kHz)

Results and discussion

Glasses in the system $Cu_2O–P_2O_5–MoO_3$ were obtained in a wide range of compositions. Very good glass-formation was observed for glasses with low content of Cu_2O. The presence of crystalline phases of composition Cu_2MoO_4 and $Cu_2Mo_2O_7$ was identified for low-phosphate samples with the molar ratio Cu_2O/MoO_3 (samples 4c, 5 and 5a).

The ICPES measurements confirmed good correspondence between starting total contents of Cu, P and Mo and those in prepared glasses.

Transformation temperature T_g, of oxide glasses is increased with the cross-link density of the network, with increasing strength of the chemical bonds and with the "closeness-of-packing" of the oxide network [6]. The measure of the "closeness-of-packing" is the oxygen density – the molar content of oxygen per

unit volume (Table 1). The maximum T_g was observed for glass 9, which is free of Cu_2O. The absence of a glass-modifying oxide results in high cross-link densities as well as in close packing, which is characterized by the maximum of the oxygen density. Generally, the introduction of a glass modifier into the glass is accompanied by significant changes in the glass structure. In the system $Cu_2O-P_2O_5-MoO_3$, the strong covalent P–O and Mo–O bonds in the glass network are replaced by substantially weaker ionic bonds of the Cu^+-O^- - type. It is obvious that T_g decreases gradually with an increase in the Cu_2O content. This decrease in T_g correlates with reduction of the cross-link density and weakening of mean bond strength. This latter observation is consistent with the decrease in the oxygen density. The dependence of T_g of glasses containing 50 mol% of Cu_2O (glasses 1–4b) is also in good agreement with the trends in the oxygen-packing density. It is obvious a well defined maximum for glass 3 with the molar ratio $P_2O_5/MoO_3 = 1$, which is in correspondence with maximum in T_g. Based on presented results we suggest that the oxygen-packing density is the dominant factor affecting T_g values of glasses in the system $Cu_2O-P_2O_5-MoO_3$.

Main structural units of glasses were determined on the basis of IR spectra in the region $1500–200$ cm^{-1}. The structure of glasses strongly depends on their chemical composition. Glasses studied we can classify as glasses containing

Table 1 Main structural units and some physical characteristics of glasses in the system $Cu_2O-P_2O_5-MoO_3$

Glass	Oxygen-packing density / $mol \cdot cm^{-3} \times 10^{-2}$	Room temperature conductivity, σ_{25} / $\Omega^{-1}cm^{-1}$	Main structural units
1	7.94	$1.6 \cdot 10^{-8}$	$(PO_3^-)_n$
2	7.96	$1.7 \cdot 10^{-8}$	$(PO_3^-)_n$, $P_2O_7^{4-}$, $Mo_2O_7^{2-}$
3	8.13	$4.9 \cdot 10^{-7}$	PO_4^{3-}, $Mo_2O_7^{2-}$, $P_2O_7^{4-}$
4	7.98	$2.7 \cdot 10^{-6}$	PO_4^{3-}, $Mo_2O_7^{2-}$, $P_2O_7^{4-}$
4a	7.92	$4.1 \cdot 10^{-6}$	MoO_4^{2-}, PO_4^{3-}
4b	7.77	$7.2 \cdot 10^{-6}$	MoO_4^{2-}, PO_4^{3-}
5b	8.08	$7.5 \cdot 10^{-6}$	MoO_4^{2-}, PO_4^{3-}
5c	8.40	$4.4 \cdot 10^{-6}$	MoO_4^{2-}, PO_4^{3-}, $Mo_2O_7^{2-}$
6	8.58	$1.4 \cdot 10^{-6}$	$Mo_2O_7^{2-}$, PO_4^{3-}, $(MoO_2)_2P_2O_7$
7	8.62	$2.6 \cdot 10^{-7}$	$(MoO_2)_2P_2O_7$, $Mo_2O_7^{2-}$, PO_4^{3-}
8	8.73	$1.4 \cdot 10^{-10}$	$MoO_2(PO_3)_2$, $(PO^{3-})_n$
9	9.26	$4.8 \cdot 10^{-14}$	$MoO_2(PO_3)_2$
10	9.06	$4.8 \cdot 10^{-12}$	$MoO_2(PO_3)_2$, $(PO_3^-)_n$
11	8.83	$1.1 \cdot 10^{-11}$	$(PO_3^-)_n$, $MoO_2(PO_3)_2$
12	8.39	$5.7 \cdot 10^{-11}$	$(PO_3^-)_n$, $MoO_2(PO_3)_2$

Cu^+ cations and, in part, Cu^{2+} cations (as a result of oxidation-reduction processes, which can occur during melting), various types phosphate and molybdate anions (monomeric, low-condensed and polymeric chains) and also structural units with a two- or three-dimensional network. Glasses with the molar ratio $Cu_2O/(P_2O_5 + MoO_3)\sim 1$ are built up mainly by discrete and low-condensed phosphate and molybdate anions such as MoO_4^{2-}, PO_4^{3-}, $P_2O_7^{4-}$ and $Mo_2O_7^{2-}$ or by chains of metaphosphate anions $(PO_3^-)_n$ (Table 1). The structure of most of glasses with the molar ratio $Cu_2O/(P_2O_5 + MoO_3) < 1$ is mainly three-dimensional, built up by neutral phosphate-molybdate structural units with networks typical of glasses of compositions $MoO_2(PO_3)_2$ and $(MoO_2)_2P_2O_7$ [7]. There is no observable evidence in the IR spectra of prepared glasses for the reduction of Mo^{6+} ions to Mo^{5+} ions; the presence of Mo^{5+} does not affect the intensity and positions of IR absorption maxima.

The values of the electrical conductivity, σ, obtained by evaluation of the impedance spectra were plotted as log σ vs. $1/T$. All the dependencies fit the Arrhenius equation (1)

$$\sigma = \sigma_o \cdot \exp\left(-\frac{E_a}{RT}\right) \qquad (1)$$

where σ_o is the pre-exponential term, E_a is the activation energy, R is the gas constant and T is the thermodynamic temperature. The room temperature electrical conductivities, σ_{25}, were calculated by least squares fitting analysis of experimental data.

The electrical conductivity of glasses in the system Cu_2O–P_2O_5–MoO_3 varies from $10^{-14}\Omega^{-1}cm^{-1}$, for glass free of Cu_2O, to $10^{-6}\Omega^{-1}cm^{-1}$, for glasses with compositions near of the binary Cu_2O–MoO_3 composition. The electrical conductivity increases with increasing content of the glass modifying oxide, Cu_2O. At a given content of Cu_2O the conductivity increases by substitution of MoO_3 for P_2O_5. The electrical conductivity of molybdenum phosphate glasses without Cu_2O is due to the hopping mechanism in which the electrical charge transfers from Mo^{5+} to Mo^{6+} sites by hopping of electrons [8]. With respect to the presence of Cu^+, Cu^{2+}, Mo^{6+} and Mo^{5+} in glasses studied, we can conclude that the total electrical conductivity is due mainly to movement of Cu^+ ions and partly to the hopping of electrons between atoms of copper and molybdenum in various valency states as well as to the hopping of electrons between the same atoms in different valency states.

Generally, the use of glasses as solid electrolytes is limited by their low electronic conductivity. For glasses in the system under study it means to minimalize the presence of Cu^{2+} and Mo^{5+} ions. Preliminary ESR measurements (Bruker SRC-200 D) shown that the lowest contents of these paramagnetic ions are in glasses near of binary Cu_2O–MoO_3 composition.

Conclusions

The measurements confirmed strong dependence of the structure of glasses on their chemical composition. The direct reflection of structural changes are also values of the transformation temperature and the electrical conductivity. The best thermal stability was observed for glasses with compositions near binary system $P_2O_5-MoO_3$, however, the electrical conductivity is very low. The highest conductivity in the system $Cu_2O-P_2O_5-MoO_3$ reach glasses with compositions near of binary system Cu_2O-MoO_3, which also have relatively good thermal stability. Introduction of cuprous halides (CuI, CuBr or CuCl) into the glasses enhances additionally the electrical conductivity. Enhancement by 2 orders of magnitude (up to $10^{-4}\Omega^{-1}cm^{-1}$) was observed for glasses of similar composition with CuCl content of 40 mol% [9]. These values of the electrical conductivities are comparable to those of corresponding Ag^+ conducting glasses.

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