Original Papers

MIXED-HALIDE PHOSPHATE GLASSES CONTAINING Cu^+ IONS

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Cuprous ion conductive glasses in the system (20-x) CuI-x CuBr-40 Cu_2O-40 P_2O_5 as well as (40-y) CuI-y CuBr-30 Cu_2O-30 P_2O_5 were prepared. The glass formation was observed in the all range of substitution of CuI by CuBr. All the prepared glasses show similar infrared spectra typical for metaphosphate glasses containing mainly chains of the (PO_3^-) anions. The conductivity of glasses at room temperature, σ_{25}, increases with an increase of total concent of cuprous halides. The significant positive deviation of the conductivity from the additivity, by substitution of Br^- for I^- anions (mixed anion effect), has not been observed in the glasses under study.

INTRODUCTION

Cuprous ion conductive materials are promising for utilization in high energy density batteries, electrochemical sensors, etc. In recent years increasing interest was devoted to the study of Cu^+ glassy solid electrolytes. Glasses have many advantages over the crystalline electrolytes because of their physical isotropy, lack of grain boundaries, possibility of continual variation in composition and good workability [1, 2].

The glass-formation of many systems containing Cu^+ conductive ions was recently investigated. Those glasses were mainly prepared in systems containing either P_2O_5 [3–6] or MoO_3 [7–9] as "glass-forming oxides". If cation-conducting glasses contain two kinds of different anions, the positive deviation of conductivity from additivity rule (mixed anion effect) in often observed. This effect was described in glasses with mixed glass-forming oxides [10, 11] as well as in glasses with mixed halides [9, 12]. Minami et al. [9] illustrate this effect in the Cu^+ conductive pseudoternary system CuI – CuBr – Cu_2MoO_4 by mixing of two kinds of anion species, I^- and Br^-. In this system the conductivity goes through maximum value near to the ratio Br/(Br+I) = 0.15.

The mixed anion effect is in striking contrast to the mixed cation effect which is characterized by negative deviation of the conductivity from additivity. Mixing of two anion species in cationic conductors could be very promising way for obtaining high conductive glassy electrolytes.

In this paper the effect of the substitution of CuBr for CuI in glasses of composition (20-x) CuI-x CuBr-40 Cu_2O-40 P_2O_5 (group A) and (40-y) CuI-y CuBr-30 Cu_2O-30 P_2O_5 (group B), has been investigated. The influence of halide substitution on the IR spectra and ion-conducting properties are mainly discussed.

EXPERIMENTAL

Glasses were prepared from commercial reagents Cu_2O and P_2O_5 (Lachema); cuprous halides CuI and CuBr were prepared according to previously described procedures [13]. A starting mixture 15 g in weight was homogenized and melted in a silica ampoule in a dry argon atmosphere to avoid the oxidation of Cu^+ ions during melting. Batches were heated for 90 min. at 700°C. Further details of the sample preparation are described elsewhere [14]. To confirm reproducibility of results, all the glasses were prepared twice. Starting compositions of glasses are given in Table I.

All samples of the prepared glasses were analyzed by X-ray powder diffraction measurements (Dron 2) using CuK_α radiation to confirm non-crystallinity. The fracture surfaces of the glasses were investigated by a scanning electron microscope (Tesla BS-300) to detect phase separation (magnification 10^4).

The densities of glasses were determined by the pycnometric method using glass fragments with a diameter of ~ 3mm. Measurements were carried out at 20°C, ethanol was used as the displacement liquid. The error of measurements was within 0.02 gcm^{-3}.

Infrared spectra were recorded on a Philips Analytical PU 9800 FTIR spectrometer in the range 4000–400 cm^{-1}. The measurements were made on glass

Table I

Starting cuprous halide contents (mol%) and the Br/(Br+I) ratios of glasses in the systems (20-x) CuI-x CuBr-40 Cu_2O-40 P_2O_5 (group A) and (40-y) CuI- yCuBr-30 Cu_2O-30 P_2O_5 (group B).

Glass	CuI	CuBr	Br/(Br+I)
A1	20.0	0.0	0.000
A2	17.5	2.5	0.125
A3	15.0	5.0	0.250
A4	12.5	7.5	0.375
A5	10.0	10.0	0.500
A6	7.5	12.5	0.625
A7	5.0	15.0	0.750
A8	2.5	17.5	0.875
A9	0.0	20.0	1.000
B1	40.0	0.0	0.000
B2	35.0	5.0	0.125
B3	30.0	10.0	0.250
B4	25.0	15.0	0.375
B5	20.0	20.0	0.500
B6	15.0	25.0	0.625
B7	10.0	30.0	0.750
B8	5.0	35.0	0.875
B9	0.0	40.0	1.000

powders dispersed in KBr pellets (1 wt%). All spectra were measured at room temperature with $4cm^{-1}$ resolution.

Glass discs with diameter of 20 mm and thickness of about 1.5 mm were used for electrical conductivity measurements. A guard ring electrode configuration (sputtered gold blocking electrodes) was used in order to eliminate the surface leakage and to measure the true bulk resistance of samples. The electrical conductivity measurements were carried out from room temperature up to 100°C, in a dry argon atmosphere. The signal applied across the sample was 50 mV (RLCG meter Tesla BM 595). The comlex impedance measured in the frequency range 100 Hz – 20 kHz allowed us to obtain the bulk d.c. conductivities of glassy samples by means of the usual impedance analysis [see for example 15, 16]. All samples were measured twice, and obtained results had a good reproducibility.

RESULTS AND DISCUSSION

Good glass-formation was observed in the systems (20-x) CuI-x CuBr-40 Cu_2O-40 P_2O_5 (group A) and (40-y) CuI-y CuBr-30 Cu_2O-30 P_2O_5 (group B), respectively, for the all range of substitution of CuI by CuBr. All samples were analyzed by X-ray diffraction, the presence of crystalline phases was not detected. An examination of fracture surfaces by SEM confirmed the absence of the metastable phase separation and, thus, investigated glasses were homogeneous.

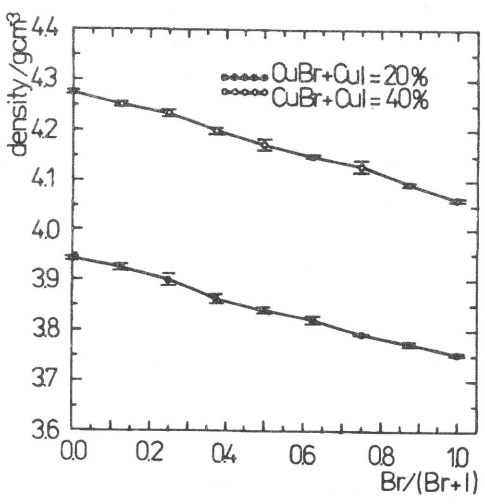

Fig. 1. Density of glasses in the system CuI – CuBr – Cu_2O – P_2O_5 as a function of the molar ratio Br/(Br+I).

In Fig. 1 is plotted density of glasses as a function of the Br/(Br+I) ratio. It is obvious that density gradually decreases by replacement of CuI by CuBr.

Densities of glasses containing 40 mol% cuprous halides are higher than those of glasses containing 20 mol% cuprous halides for each Br/(Br+I) ratio.

The dependence of the molar volume vs. the Br/(Br+I) ratio is presented in Fig. 2. The molar volume in group A decreases only slightly with increasing content of CuBr, but in group B we can observe distinct gradual decrease in the molar volume with increasing content of CuBr. This is due to higher content of cuprous halides in glasses of group B than in glasses of group A.

Structural elements of glasses were studied by IR spectroscopy. Figs. 3 and 4 show the IR spectra of some glasses (20-x) CuI-x CuBr-40 Cu_2O-40 P_2O_5 (group A) and (40-y) CuI-y CuBr-30 Cu_2O-30 P_2O_5 (group B), respectively, in the range 1500–400 cm^{-1}. In the additional range of IR measurements (4000–1500 cm^{-1}) there were no characteristic absorption bands.

All the prepared glasses show quite similar spectra. Five major absorption bands (with maxima at about 1270, 1090, 890, 760 and 520 cm^{-1}) were observed in each glassy sample an they are marked out in Figs. 3 and 4. The assignment of each significant absorption band in the IR spectra was made by using reference data for phosphate glasses [17–22]. The bands at about 1270, 1090 and 520 cm^{-1} are assigned to the ν_{as} (PO_2), ν_s(PO_2) and δ(PO_2) modes, respectively, of $(PO_3^-)_n$ chain groups. The broad bands with maxima near 890 nad 760 cm^{-1} consist of bands belonging to ν_{as} (POP) and ν_s (POP) modes, respectively, of $(PO_3^-)_n$ chain groups and, in part, by corner-shared chains of $(PO_3^-)_n$ in two- or three-dimensional network. Other bands or shoulders with lower intensities near 1020 and 1170 cm^{-1} can be assigned to the

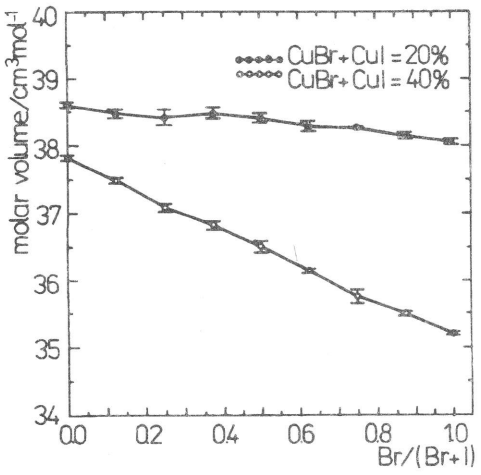

Fig. 2. Molar volume of glasses in the system CuI – CuBr – Cu_2O – P_2O_5 as a function of the molar ratio Br/(Br+I).

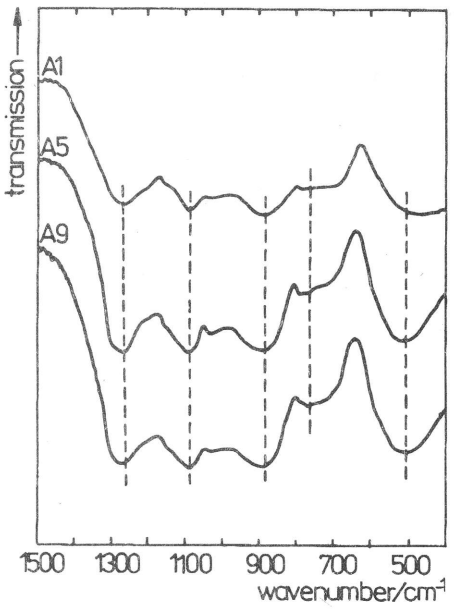

Fig. 3. Infrared spectra in KBr pellets of glasses in the system (20-x)CuI – xCuBr – 40Cu_2O – 40P_2O_5.

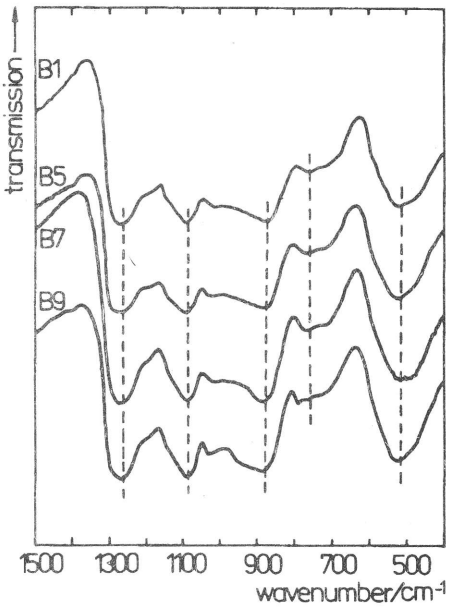

Fig. 4. Infrared spectra in KBr pellets of glasses in the system (40-y)CuI – yCuBr – 30Cu_2O – 30P_2O_5.

ν_s(PO_3) and ν_{as}(PO_3) modes, respectively, of PO_3 "end groups" of various condensed phosphates [17]. It seems that there are no other significant absorption bands in any glasses and there are no changes in the band structures of these IR spectra with a substitution as well as with total content of halide anions. These results suggest that all the prepared glasses

consist mainly of cuprous ions Cu^+, halide anions X^- (X=I, Br) and condensed phosphate macroanions, as expected from their chemical composition [17, 22], and they do not contain monomeric PO_4^{3-} anions.

The relationships log σ vs. $1/T$ were obtained by evaluation of the impedance spectra recorded at various temperatures. Values of the total conductivity at 25°C, σ_{25}, the activation energy, E_a, and the logarithm of the pre-exponential term, log σ_0, for each glass, were calculated using the least square fitting analysis of relationships log σ vs. $1/T$. The data fit well the Arrhenius equation,

$$\sigma = \sigma_0 \exp(-E_a/RT) \,. \qquad (1)$$

where σ_0 and E_a are defined in previous text, R is the gas constant and T is the temperature.

The compositional dependence of σ_{25} of the glasses in the system CuI-CuBr-Cu_2O-P_2O_5 for group A and B, respectively, is plotted in Fig. 5. It can be seen that the total conductivity of glasses containing 40 mol% cuprous halides is always higher in comparison with the conductivity of glasses containing 20 mol% cuprous halides. So we can conclude that the conductivity of glasses substantially incerases with increasing total content of cuprous halides for each Br/(Br+I) ratio.

From Fig. 5. is obvious that changes in conductivity due to changes in Br/(Br+I) ratio are negligible in comparison with those due to changes in total content of cuprous halides in glasses. Conductivities of "end glasses" in group A (A1, A9) and B (B1, B9), respectively, are almost the same. Moreover there are no observable systematic trends of increase in conductivity due to mixing of two anion species, I^- and Br^-. The moderate increase of conductivity we can observe only for the Br/(Br+I) ratio = 0.750 (group B).

The activation energy, E_a, of glasses containing 20 mol% cuprous halides is practically independent on the Br/(Br+I) ratio (Fig. 6). For glasses of group B we can similarly observe that the activation energy of "end glasses" (B1 and B9) is almost the same, but the others have lower activation energy. A significant decrease in the activation energy is observed for glasses with the Br/(Br+I) ratio 0.625 and 0.750, respectively.

The dependence of the log σ_0 vs. the Br/(Br+I) ratio (Fig. 7) is generally very similar to that of the

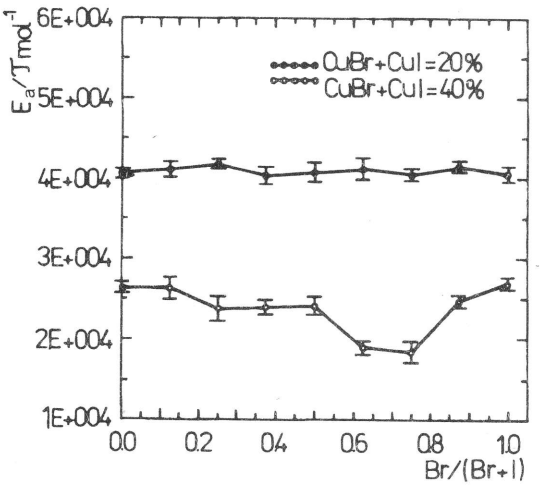

Fig. 6. Activation energy, E_a, of glasses in the system CuI - CuBr - Cu_2O - P_2O_5 as a function of the molar ratio Br/(Br+I).

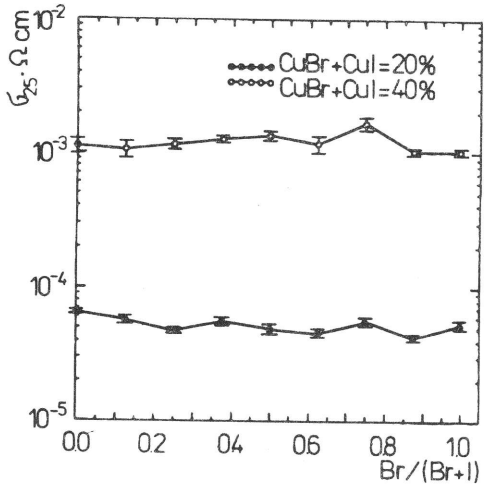

Fig. 5. Total room temperature conductivity, σ_{25}, of glasses in the system CuI - CuBr - Cu_2O - P_2O_5 as a function of the molar ratio Br/(Br+I).

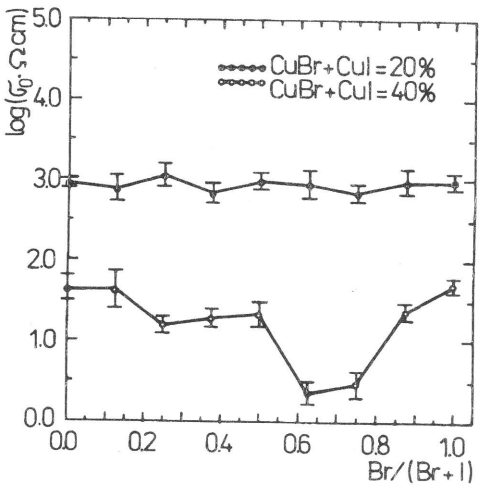

Fig. 7. Logarithm of pre-exponential term, log σ_0, of glasses in the system CuI - CuBr - Cu_2O - P_2O_5 as a function of the molar ratio Br/(Br+I).

activation energy. The log σ_0 does not change significantly with the change in the Br/(Br+I) ratio for glasses of group A. On the other hand, for glasses of group B, we can observe the singificant minimum in the dependence of the log σ_0 for the Br/(Br+I) ratios 0.625 and 0.750, which corresponds with minimum observed in the dependence of the activation energy (Fig. 6). However, the main structural elements of the glasses B6 and B7 are, probably, consistent with those supposed in the other glasses of group B (see Fig. 4). According to the equation (1), the activation energy, E_a, and the pre-exponential term, σ_0, have a controversial influence on conductivity. From Fig. 5 is obvious, however, that the total conductivity changes with the Br/(Br+I) ratio only slightly, so we can conclude that neither the activation energy nor the pre-exponential term has an outweighing effect on conductivity. The decrease in the activation energy is compensated by the decrease in the pre-exponential term, which results only in slight changes in the conductivity at 25°C.

CONCLUSIONS

a) Good glass-formation of investigated samples is observed. Substitution of CuBr for CuI does not influence the glass-forming ability in the system (20-x) CuI-x CuBr-40 Cu_2O-40 P_2O_5 (group A) and (40-y) CuI-y CuBr-30 Cu_2O-30 P_2O_5 (group B), respectively.

b) The network of all prepared glasses in the system CuI-CuBr-Cu_2O-P_2O_5 consists mainly of condensed phosphate macroanions, such as chains of $(PO_3^-)_n$ and, in part, corner-shared chains of $(PO_3^-)_n$ in two- or three-dimensional network. IR spectra indicate that cuprous halides are not incorporated into the glass network and do not affect the phosphate structural units.

c) The total conductivity of glasses in the system CuI-CuBr-Cu_2O-P_2O_5 is strongly dependent on total content of cuprous halides. The room temperature conductivity of glasses containing 40 mol% cuprous halides is higher nearly by 2 orders of magnitude than the total conductivity of glasses containing 20 mol% cuprous halides. The dependence of the room temperature conductivity on the Br/(Br+I) ratio indicates that no pronounced positive deviation of the conductivity from additivity rule was observed. It seems that the mixing of two halide anion species in the system CuI-CuBr-Cu_2O-P_2O_5 is not an effective way for enhancement of the electrical conductivity.

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Cu^+ FOSFOREČNÉ SKLÁ OBSAHUJÚCE ZMIEŠANÉ HALOGENIDY

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V oblasti výskumu sklených elektrolytov dominuje snaha o prípravu vysokovodivých skiel vhodných pre použitie v batériách a iných elektrochemických zariadeniach. V literatúre je popísané [9–12], že miešaním dvoch aniónov

v katiónovo vodivom skle možno dosiahnuť zvýšenie vodivosti skiel (tzv. jav zmiešaných aniónov).

Cu^+ iónovo vodivé sklá boli pripavené v systéme CuI-CuBr-Cu_2O-P_2O_5. Skúmal sa vplyv zámeny halogenidov medi v sklách zloženia (20-x) CuI – x CuBr – 40 Cu_2O – 40 P_2O_5 (skupina A) a (40-y) CuI – y CuBr – 30 Cu_2O – 30 P_2O_5 (skupina B) na štruktúru a elektickú vodivosť (zloženie skiel je uvedené v Tab. I).

Sklá vykazovali dobrú sklotvornosť v celom rozsahu náhrady CuBr za CuI. Z infračervených spektier sa zistilo, že základný skelet skiel je tvorený z rovnakých štruktúrnych jednotiek s dominantným obsahom reťazcov metafosforečnanových aniónov $(PO_3^-)_n$. Halogenidy medi nie sú súčasťou základného skeletu a neovplyvňujú fosforečnanové štruktúrne jednotky. Vodivosť skiel sa určila metódou merania komplexnej impedancie. Vyhodnotením teplotných závislostí vodivostí sa určili hodnoty celkovej špecifickej vodivosti pri laboratórnej teplote, σ_{25}, aktivačnej energie, E_a, a predexponenciálneho faktora, σ_0. Z Obr. 5 je zrejmé, že vodivosť skiel s celkovým obsahom halogenidov medi 40 mol% je takmer o 2 poriadky vyššia ako u skiel s obsahom halogenidov 20 mol%, pre všetky pomery Br/(Br+I). To znamená, že celkový obsah halogenidov v sklách má významný vplyv na ich vodivosť. Naproti tomu sa nepozorovali podstatné zmeny vodivosti pri zmene pomeru Br/(Br+I), tak v skupine skiel A ako i B. Na základe uvedených skutočností možno konštatovať, že miešanie dvoch halogenidov sa nejaví ako efektívny spôsob zvýšenia vodivosti skiel v študovanom systéme.

Obr. 1. Hustota skiel v systéme CuI-CuBr-Cu_2O-P_2O_5 ako funkcia mólového pomeru Br/(Br+I).

Obr. 2. Mólový objem skiel v systéme CuI-CuBr-Cu_2O-P_2O_5 ako funkcia mólového pomeru Br/(Br+I).

Obr. 3. Infračervené spektrá skiel v systéme (20-x)CuI-xCuBr-40Cu_2O-40P_2O_5 (merané metódou KBr tabliet).

Obr. 4. Infračervené spektrá skiel v systéme (40-y)CuI-yCuBr-30Cu_2O-30P_2O_5 (merané metódou KBr tabliet).

Obr. 5. Celková špecifická vodivosť pri laboratórnej teplote, σ_{25}, skiel v systéme CuI-CuBr-Cu_2O-P_2O_5 ako funkcia mólového pomeru Br/(Br+I).

Obr. 6. Aktivačná energia, E_a, skiel v systéme CuI-CuBr-Cu_2O-P_2O_5 ako funkcia mólového pomeru Br/(Br+I).

Obr. 7. Logaritmus predexponenciálneho faktora, log σ_0, skiel v systéme CuI-CuBr-Cu_2O-P_2O_5 ako funkcia mólového pomeru Br/(Br+I).