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CONDUCTIVE CU^{+} GLASSES IN THE SYSTEM Cu_2I_2—Cu_2O—P_2O_5

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The conductivity was measured by the complex impedance method over the frequency range of 100 Hz to 20 kHz. Compared to Cu_2O, Cu_2I_2 *has a more distinct effect on the level of conductivity. The conductivity of the glasses incerased with increasing* Cu_2I_2 *content and the opposite relationship was observed with increasing O/P ratio. The maximum conductivity was with a glass having the lowest concentration of conductive* Cu^{+} *ions, and the glass exhibited the largest molar volume. This fact indicates that electrical conductivity of glasses is not only a function of the concentration of conductive ions, as a significant part is also played by migration of ions which is given by the molar volume of the glass.*

INTRODUCTION

Ionically conductive glasses have come to the forefront of scientific interest during the last decade. This is due to the significant technological applications found by these materials (e.g. primary and secondary sources of electric power, sensors, diaphragms in ionically selective electrodes, electrochemical pumps, electrochromic displays, capacitors, etc. [1, 2]).

The highest conductivities ($\sigma = 10^{-2}\ \Omega^{-1}cm^{-1}$ at 25 °C) were achieved in systems containing AgI in combination with other silver compounds. However, the iodide content amounts up to about 80%, and this makes the materials too expensive. The lithium conductive glasses are more acceptable with respect to price, but their maximum conductivities, attaining values of the order of $10^{-6}\ \Omega^{-1}\ cm^{-1}$, do not meet the more demanding requirements. This is why new chemical compositions of glasses are seeked with the aim of satisfying both the technical and economic aspects. Conductive Cu^{+} glasses seem to be promising in this respect. The Cu^{+} ions have an electron configuration similar to that of Ag^{+} ions, but a smaller radius (Table I). The conductivity of Cu^{+} glasses can thus be expected to be equal to, or higher than, that of Ag^{+} glasses [3, 4]. However, the subject matter of Cu^{+} glasses has been paid comparatively little attention, as indicated by the small number of publications dealing with this material [5—7].

Table I

Ionic radius and electron configuration of Ag^{+} and Cu^{+} ions [3].

Cation	Radius	Configuration
Ag^{+}	0.126 nm	[Kr] $4d^{10}$
Cu^{+}	0.096 nm	[Ar] $3d^{10}$

EXPERIMENTAL

Compounds of A. R. purity were used as initial materials for the preparation of the glasses: P_2O_5 (Lachema), Cu_2O (Lachema) and CuI (Park). The homogenized raw material mixes 5 g in weight were melted in a slilica glass ampoule at 650 °C with a dwell period of 90 minutes. Considerable problems arise with oxidation of Cu^+ ions to bivalent Cu^{2+} ones, and even disproportionation to Cu_0 and Cu^{2+} can occur. The presence of copper in several oxidation stages would bring about undesirable increases in the electron component of conductivity. In order to eliminate these undesirable effects, the melting was effected in argon atmosphere. The glass melt was quenched between two aluminium plates to a final thickness of 1.1 mm. The resulting disk 20 mm in diameter was kept between the plates until its temperature decreased to that of the environment. The specimens were red-brown in colour. The melting did not bring about losses in weight which means that the actual chemical composition corresponded to the initial one. The chemical compositions of the glasses are listed in Table 2.

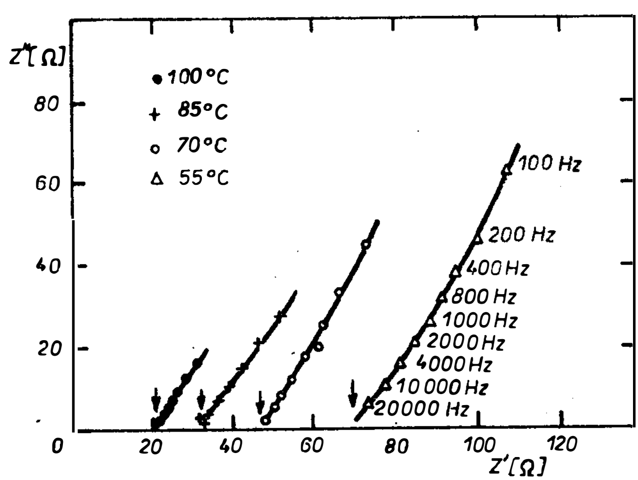

Fig. 1. A typical impedance spectrum of glasses in the system Cu_2I_2—Cu_2O—P_2O_5.

All of the glasses were analyzed by *X*-ray powder diffraction (Rigaku Denki) in order to identify any undesirable crystalline phases. The density of the glasses was determined pycnometrically.

The electrical conductivity of the glasses was measured by the complex impedance method over the frequency range of 100 Hz to 20 kHz (TESLA BM 595 RLCG Digibridge) in three-electrode configuration (vacuum deposited Pt blocking electrodes). The measuring method is described in [8]. A typical impedance spectrum is shown in Fig. 1.

EXPERIMENTAL RESULTS AND DISCUSSION

The glass-forming region of the Cu_2I_2—Cu_2O—P_2O_5 system was studied by Bartholomew et al. [9] and Liu et al. [5]; however, their results disagree considerably. Among the glasses investigated by the present authors, the best glass-forming ability was exhibited by those having the O/P ratio within the interval of 2.85 to 3.00. The Cu_2I_2 content exceeding 22 mol % caused the glasses to crystallize. The chemical compositions of the glasses investigated were in the composition range where the glass-forming abilities, specified by the two authors, overlap.

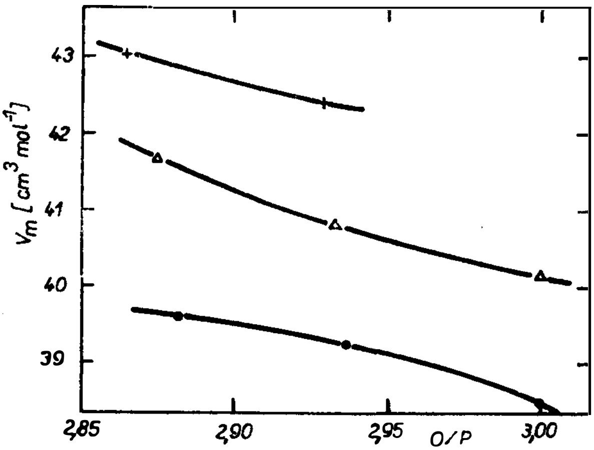

Fig. 2. Molar volume vs. chemical composition of glasses in the system Cu_2I_2—Cu_2O—P_2O_5 (● — *0.143* Cu_2I_2; △ — *0.176* Cu_2I_2; + — *0.212* Cu_2I_2).

The molar volume of the glasses was established on the basis of density determinations. Fig. 2 shows that the molar volume increases with increasing Cu_2I_2 content, while decreasing with increasing O/P ratio. The equation

$$[Cu^+] = \frac{2w_{Cu_2I_2} + 2w_{Cu_2O}}{V_m}$$

Table II

Chemical composition of the glasses prepared [mol] and some of their characteristics

Glass	Cu_2I_2	Cu_2O	P_2O_5	σ_{25} [Ω^{-1} cm^{-1}]	Cu^+ [mol cm^{-3}]
1A	0.143	0.429	0.429	1.09×10^{-4}	2.97×10^{-2}
1B	0.176	0.412	0.412	2.85×10^{-4}	2.93×10^{-2}
2A	0.143	0.400	0.457	1.01×10^{-4}	2.77×10^{-2}
2B	0.176	0.382	0.441	3.11×10^{-4}	2.73×10^{-2}
2C	0.212	0.364	0.424	5.64×10^{-4}	2.72×10^{-2}
3A	0.143	0.371	0.486	1.68×10^{-4}	2.55×10^{-2}
3B	0.176	0.353	0.470	4.48×10^{-4}	2.54×10^{-2}
3C	0.212	0.333	0.455	7.39×10^{-4}	2.53×10^{-2}

was used to determine the concentration of Cu^+ ions in the individual glasses ($w_{Cu_2I_2}$ and w_{Cu_2O} are the molar fractions of Cu_2I_2 and Cu_2O respectively, V_m is the molar volume). The concentrations of Cu^+ are listed in Table II.

Evaluation of the impedance spectra yielded the values of specific electrical conductivity [Ω^{-1} cm^{-1}] for the individual temperatures. These were plotted as log σ vs. $1/T$ (Fig. 3). All of the relationships conform to Rasch-Hinrichsen's equation expressing the electrical conductivity of glasses ($\log \sigma = A - B/T$). The linear course of the relationship over the temperature interval studied indicates that there is no change from the ionic conductivity to the electronic one or vice versa,

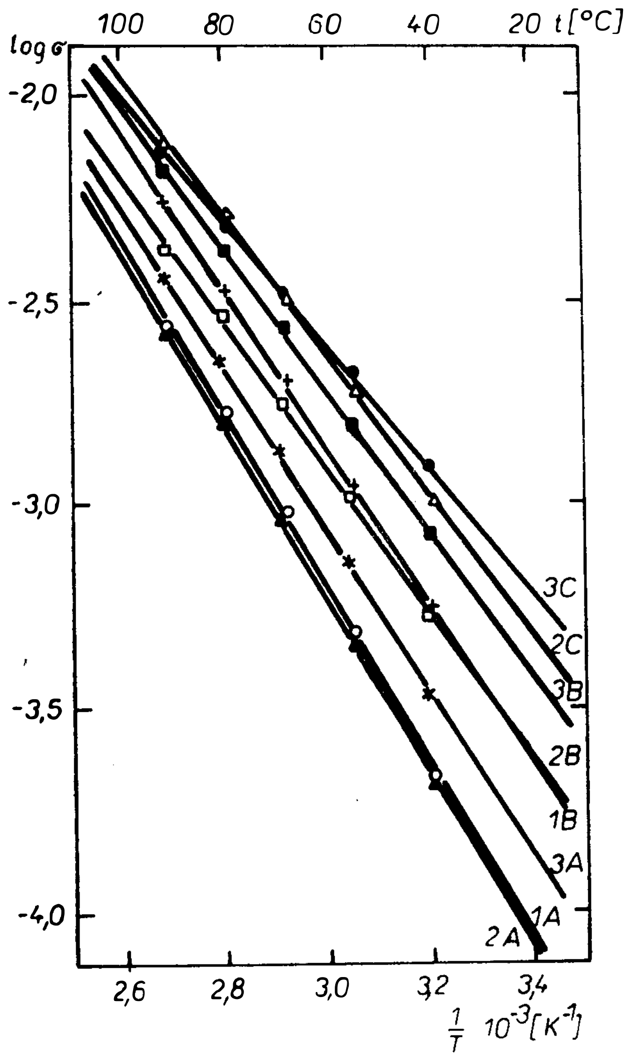

Fig. 3. Temperature dependence of the electrical conductivity of glasses in the system Cu_2I_2—Cu_2O—P_2O_5.

as this would be revealed by an inflection on the temperature dependence [10]. The relationship between log σ_{25} and the chemical composition of the glasses is plotted in Fig. 4. There is a distinct effect of Cu_2I_2 on electrical conductivity, the latter increasing with increasing iodide content. The changes in conductivity due to changes in Cu_2O content are not so significant as in the case of Cu_2I_2. The conductivity of the glasses decreases with increasing *O/P* ratio. The maximum electrical conductivity was achieved with the glass having the lowest concentration of conductive Cu^+ ions (cf. Table 2). This remarkable finding can be explained so that glasses with a high iodide content and a low oxide content have the highest molar volume which affects favourably the migration of Cu^+ ions. From this fact

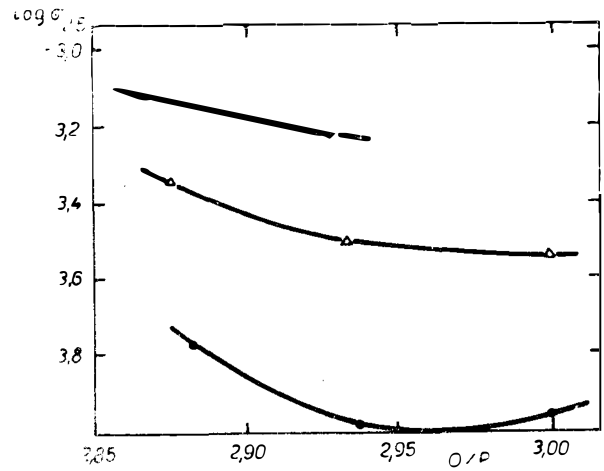

Fig. 4. Log σ_{25} *vs. the chemical composition of glasses in the system* Cu_2I_2—Cu_2O—P_2O_5 (● — *0.143* Cu_2I_2; △ — *0.176* Cu_2I_2; + — *0.212* Cu_2I_2).

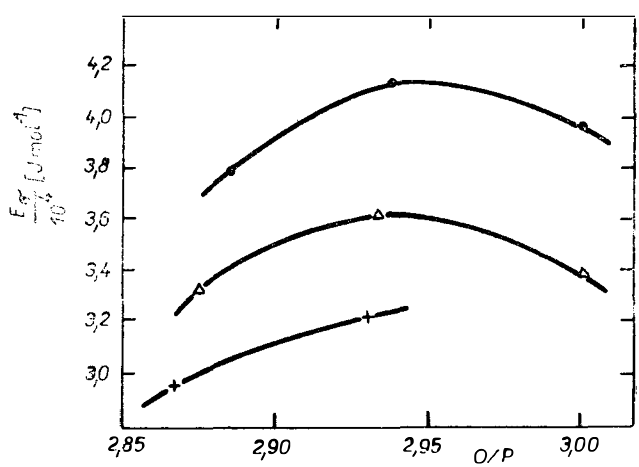

Fig. 5. Activation energy E_σ *vs. the chemical composition of glasses in the system* Cu_2I_2—Cu_2O—P_2O_5 (● — *0.143* Cu_2I_2; △ — *0.176* Cu_2I_2; + — *0.212* Cu_2I_2).

it follows that the conductivity is not merely a simple function of concentration of conductive ions in the system.

Using the Arrhenius relation $\sigma = \sigma_0 \exp(-E/RT)$, the activation energies of the conductivity process E were calculated (Fig. 5), together with the values of the pre-exponential factor σ_0 (in Fig. 6, the σ_0 values are presented as $A = \log \sigma_0$). At a constant $OP/$ ratio, an increasing Cu_2I_2 content reduces the activation energy E_σ of the conductivity process, as well as decreasing the value of the pre-exponential factor σ_0. With the glasses being investigated, one can observe opposite effects of E_σ and σ_0 on the resulting conductivity while changing the Cu_2I_2 content. However, a dominant part is played by a decrease of activation energy, as on the whole, the conductivity increases with increasing Cu_2I_2 content. The behaviour of the system due to a change in the O/P ratio is similar, showing a distinct maximum at $O/P = 2.94$. The peak values of E_σ and σ_0 are probably associated with the structural aspects of the glasses; however, no detailed explanation of phenomenon has yet been suggested.

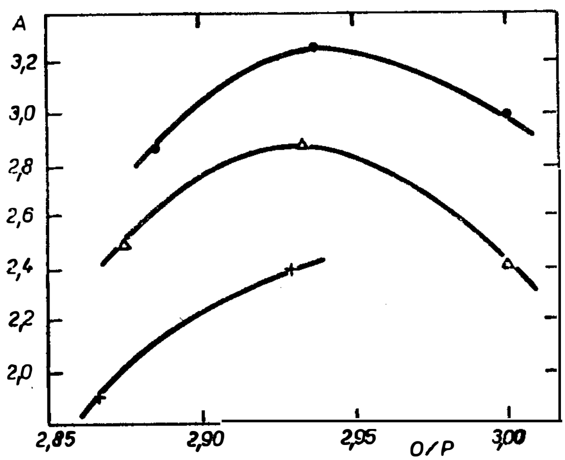

Fig. 6. A ($A = \log \sigma_0$) vs. the chemical composition of glasses in the system Cu_2I_2—Cu_2O—P_2O_5 (● — *0.143* Cu_2I_2; △ — *0.176* Cu_2I_2; + — *0.212* Cu_2I_2).

CONCLUSION

The conductivity of the best glass prepared within the framework of the system Cu_2I_2—Cu_2O—P_2O_5 amounted to $7 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$, which is a value lower by one and a half order of magnitude than that of the best conductive Ag^+ glasses. In principle, the conductivity could be further increased by raising the Cu_2I_2 content or by optimizing the Cu_2I_2/Cu_2O ratio. However, owing to their crystallization ability, preparation of these highly conductive glasses requires application of more efficient cooling techniques. The results obtained indicate that conductive Cu^+ glasses fully deserve the attention they have been paid recently.

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Cu^+ VODIVÉ SKLÁ V SÚSTAVE $Cu_2I_2—Cu_2O—P_2O_5$

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V práci sa skúmala závislosť elektrickej vodivosti skiel v sústave $Cu_2I_2—Cu_2O—P_2O_5$ od ich chemického zloženia. Vodivost sa merala komplexnou impedančnou metódou vo frekvenčnom rozsahu 100 Hz—20 kHz. Cu_2I_2 má v porovnaní s Cu_2O výraznější vplyv na úroveň vodivosti. Pri stúpajúcom obsahu Cu_2I_2 sa vodivosť skiel zvyšovala, pri stúpajúcom pomere *O/P* sa pozorovala opačná závislosť. Maximum vodivosti sa dosiahlo u skla s najnižšou koncentráciou Cu^+ vodivých iónov, pričom mólový objem skla bol najvyšší. Táto skutočnost nasvedčuje tomu, že vodivosť skiel nie je len funkciou koncentrácie vodivých iónov, ale že významnou mierou sa uplatňuje i možnosť migrácie iónov daná veľkosťou molárného objemu skiel.

Obr. 1. Typické impedančné spektrum skiel v sústave $Cu_2I_2—Cu_2O—P_2O_5$.

Obr. 2. Závislosť mólového objemu do chemického zloženia skiel v sústave $Cu_2I_2—Cu_2O—P_2O_5$ (● — *0.143* Cu_2I_2; △ — *0.176* Cu_2I_2; + — *0.212* Cu_2I_2).

Obr. 3. Teplotná závislosť elektrickej vodivosti skiel v sústave $Cu_2I_2—Cu_2O—P_2O_5$.

Obr. 4. Závislosť log σ_{25} *od chemického zloženia skiel v sústave* $Cu_2I_2—Cu_2O—P_2O_5$ (● — *0.143* Cu_2I_2; △ — *0.176* Cu_2I_2; + — *0.212* Cu_2I_2).

Obr. 5. Závislosť aktivačnej energie E_σ *od chemického zloženia skiel v sústave* $Cu_2I_2—Cu_2O—P_2O_5$ (● — *0.143* Cu_2I_2; △ — *0.176* Cu_2I_2; + — *0.121* Cu_2I_2).

Obr. 6. Závislosť A (A = log σ_0) *od chemického zloženia skiel v sústave* $Cu_2I_2—Cu_2O—P_2O_5$ (● — *0.143* Cu_2I_2; △ *0.176* Cu_2I_2; + — *0.212* Cu_2I_2).

Cu ПРОВОДЯЩИЕ СТЕКЛА В СИСТЕМЕ Cu_2I_2—Cu_2O—P_2O_5

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В предлагаемой работе исследуется зависимость электропроводности стекол в системе Cu_2I_2—Cu_2O—P_2O_5 от их химического состава. Проводимость измеряли с помощью комплексного метода импеданса в пределах частотности 100 Гц—20 кГц. Cu_2I_2 в сопоставлении с Cu_2O оказывает более резкое влияние на уровень проводимости. При растущем содержании Cu_2I_2 проводимость стекол повышается, при растущем отношении O/P наблюдали обратную зависимость. Максимум проводимости получается у стекла с наиболее низкой концентрацией Cu^+ проводящих ионов, причем мольное содержание больше. Данный факт является свидетельством того, что проводимость стекол не является только функцией концентрации проводящих ионов, но что и в значительной степени действует даже возможность миграции ионов, данная величиной мольного объема стекол.

Рис. 1. Типичный спектр импеданса стекол в системе Cu_2I_2—Cu_2O—P_2O_5.

Рис. 2. Зависимость мольного объема от химического состава стекол в системе Cu_2I_2—Cu_2O—P_2O_5 (● — 0,143 Cu_2I_2; △ — 0,176 Cu_2I_2; + — 0,212 Cu_2I_2).

Рис. 3. Температурная зависимость электропроводности стекол в системе Cu_2I_2—Cu_2O—P_2O_5.

Рис. 4. Зависимость $\log \sigma_{25}$ *от химического состава стекол в системе* Cu_2I_2—Cu_2O—P_2O_5 (● — 0,143 Cu_2I_2; △ — 0,176 Cu_2I_2; + — 0,212 Cu_2I_2).

Рис. 5. Зависимость энергии активации E_σ *от химического состава* (● — 0,143 Cu_2I_2|; △ — 0,176 Cu_2I_2; + — 0,212,Cu_2I_2).

Рис. 6. Зависимость A ($A = \log \sigma_0$) *от химического состава стекол в системе* Cu_2I_2—Cu_2O—P_2O_5 (● — 0,143 Cu_2I_2; △ — 0,176 Cu_2I_2; + — 0,212 Cu_2I_2).