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Short communication

Ionic conductivity of all-glass composites in the $AgI–Ag_2O–P_2O_5$ system

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Abstract

All-glass composites fabricated from mixtures of the superionic $33AgI·33Ag_2O·33P_2O_5$ and $60AgI·20Ag_2O·20P_2O_5$ glasses conduct Ag^+ ions. It is demonstrated that such composites can be easily formed by high-pressure methods. Their electric properties could be modelled by an equivalent electric circuit in which the ion conductivity of the bulk of a composite is represented by a single 'effective resistance'. A related quantity—the effective ion conductivity, shows Arrhenius-like dependence. The effective activation energy and the effective preexponential factor both exhibit linear dependence on composition. The general mixing rule and the Uvarov model appeared to be unsuitable for the description of the effective conductivity of the all-glass composites as a function of composition and temperature. A new phenomenological model of effective conductivity is suggested and tested—proving its applicability.

Keywords: Superionic composites; General mixing rule; Silver phosphate glasses; Ionic conductivity

1. Introduction

Silver ion conducting glasses have been considered promising electrolytes in all-solid power sources for electronic devices operating near ambient temperature [1–5]. Their high electrical conductivity at room temperature (up to 10^{-2} S cm^{-1} at 25 °C) can be sufficient for a range of practical applications. Nevertheless, there have been undertaken several studies aimed at the additional conductivity enhancement. One of the most common approaches to reach that goal consists in preparation of composites based on the glass matrix with embedded grains of a foreign material [6]. The advances in the preparation techniques of such heterogeneous ionic conductors should be accompanied by adequate efforts in the theoretical description of these systems. The actual state of the knowledge on binary glassy-crystalline is still far from satisfactory. Even less is known about composites consisting of two different glasses. The simplest description of the averaged transport properties of ionic conducting composites is based on a concept of the "effective medium". According to it, a binary composite can be considered as a macroscopic mixture of its components. The effective electrical (ionic) conductivity is a function of individual conductivities of the components and a spatial distribution of both constituting phases [7–10]. In practice an adequate theoretical description is difficult because of complicated relations existing among effective properties composite and intrinsic properties of its constituents.

One of a number of models based on the effective medium approach [11–14] is a GMR model [2], where GMR stands for "general mixing rule". According to this model the effective conductivity σ_{eff} of a random mixture of two conducting components is given by the formula:

$$\sigma_{\text{eff}}^{\alpha} = f_1\sigma_1^{\alpha} + f_2\sigma_2^{\alpha} \quad (1)$$

where f_i and σ_i denote the volume fraction and the conductivity of the i-th phase, respectively. The parameter α in formula (1) represents the topology of the composite. According to the GMR model this parameter should fulfill the condition: $-1 < \alpha < 1$. The GMR approach was used with some success to describe the effective conductivity of a number of electron conducting composites. Unfortunately its application to composite superionic conductors has been very limited [15]. Moreover its predictions sometimes have not agreed with the experimental data. One of the best known examples, where such a disagreement was observed, is the case of $AgI:Al_2O_3$ composites (e.g. [15]). To improve the consistency between experimental data and "effective medium" model predictions, Uvarov [15] proposed

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a modification of the original GMR formula. In his version the parameter α is not a constant, but a linear function of the volume percent fractions f_i:

$$\alpha = \alpha_1 f + \alpha_2(100 - f), \quad (2)$$

where α_1 and α_2 are some phenomenological constants.

The above presented considerations have been confronted with experiments for composites consisting of crystalline phases. To the best of our knowledge there are no are literature reports related to the case of all-glass superionic composites, i.e. composites consisting of amorphous phases only.

In this paper, we present experimental data on conductivity of a series of all-glass Ag^+ ion conducting composites from the AgI–Ag_2O–P_2O_5 system and their description in terms of the effective medium approach. The choice of the glasses of the silver phosphate system was natural, because: (i) the range of glass formation in this system is very wide and (ii) the electrical conductivity of the glasses with different contents of AgI could vary by several orders of magnitude. Also activation energies of ion transport depend on the glass composition. It should be noticed that the topology of the composite does not change with temperature, while the partial conductivities are temperature dependent. These features give a possibility to distinguish between the influence of intrinsic properties of the components and the effect of their spatial distribution on the effective conductivity of a composite. A series of the composites under study have been prepared from glasses of two distinctly different compositions and electrical properties: $33AgI{\cdot}33Ag_2O{\cdot}33P_2O_5$ (denoted as A) and the $60AgI{\cdot}20Ag_2O{\cdot}20P_2O_5$ (labeled B).

2. Experimental

The starting glasses of the nominal compositions $33AgI{\cdot}33Ag_2O{\cdot}33P_2O_5$ (A) and $60AgI{\cdot}20Ag_2O{\cdot}20P_2O_5$ (B) were prepared by a standard press-quenching method. Stoichiometric amounts of pre-dried reagent-grade chemicals: AgI, $AgNO_3$ and $NH_4H_2PO_4$, were ground, mixed and placed in a furnace. The crucible with the reagents was kept at 400 °C for about half an hour. During this stage the constituents melted and some ammonia and water evaporated from the melt. Next the temperature was increased to about 650 °C causing nitrogen oxides to be released. The melt was annealed for about 20 min, and then it was quenched between two stainless-steel plates. As-prepared samples were examined by X-ray diffraction for the presence of crystalline inclusions. The diffraction patterns were collected at room temperature on a Philips X'Pert Pro diffractometer set in the Bragg–Brentano geometry, using a Cu Kα line.

The preparation of a series of the all-glass composites fB + (100 − f) A, where $20 < f < 80$, started with weighing the powdered components, their mixing and uniaxially pressing in a die at 8 MPa for 5 min. For each glass composition the conductivity of the as-prepared glass and the pellet made out of the ground glass were measured as a function of temperature. It was found out that in the case of a glass A there were no detectable conductivity differences between a solid glass and a pellet. In the case of a glass B these differences were small (ca. 2–5%). Therefore, only the conductivity data for the pelletized glasses were used in further analyses.

Ionic conductivity of all investigated materials was determined by means of the impedance spectroscopy in the temperature range −60 to +50 °C and the frequency range 10 mHz to 10 MHz, using a Solartron 1260 Impedance/Gain Phase analyzer. The temperature was stabilized with precision of ±0.1 °C.

Optical observations aiming at estimating an average grain size in the powdered glasses were done using a Nikon Optic Phot microscope working in the reflectance mode.

3. Results and discussion

Optical microscope examination of the glasses ground in a mortar revealed the presence of oval grains whose linear dimensions were about 80–100 μm. Grains of the glass A were light yellow, quite distinct from the dark red colored grains of the glass B. Optical microscopy observations did not reveal pores nor cavities in the composite samples.

The impedance spectra of the component glasses (regardless whether solid or pelletized) had a very similar shape at any temperature in the studied range (−65 to +50 °C). They consisted of a slightly deformed semicircle at higher frequencies and a straight line at lower frequencies. These spectra were analyzed using a simple equivalent circuit consisting of a parallel R–CPE loop (CPE stands for a Constant Phase Element) in series with another CPE element representing a double layer capacitance.

Impedance spectra of the composites (Fig. 1) were more complicated than those of the component glasses, and their analysis was more difficult. In order to fit them adequately, a more elaborate equivalent circuit, shown in the insert in Fig. 1, had to be used. This equivalent circuit was used in the fitting procedure for all composites at all temperatures.

The conductivity values determined from the numerical analyses of the impedance spectra of the whole series of fB + (100 − f) A composites were fitted to using the equations of the GMR model (Eq. (1)) and its variant by Uvarov (Eq. (2)).

Fig. 2 presents a set of the dependences of the parameter α versus f, at selected temperatures. These dependences are not linear as they should be, if the GMR model (Eq. (1)) is correct. In Fig. 3 there is shown the temperature dependence of a parameter α for all composites. Generally, the α values increase with the temperature. Also these dependencies are not linear.

It was found that at a given temperature and for a given composition one can find an α parameter value providing a good quality GMR fit. However these best-fit α values are strongly dependent on both temperature and composition. The temperature dependence of α (for a given composite) does not agree with the GMR principles, which assume that α reflects a topological structure of the composite and therefore should not be temperature dependent as long as the spatial distribution of both components in the composite does not change. Taking this into account one can conclude that the GMR model (represented by

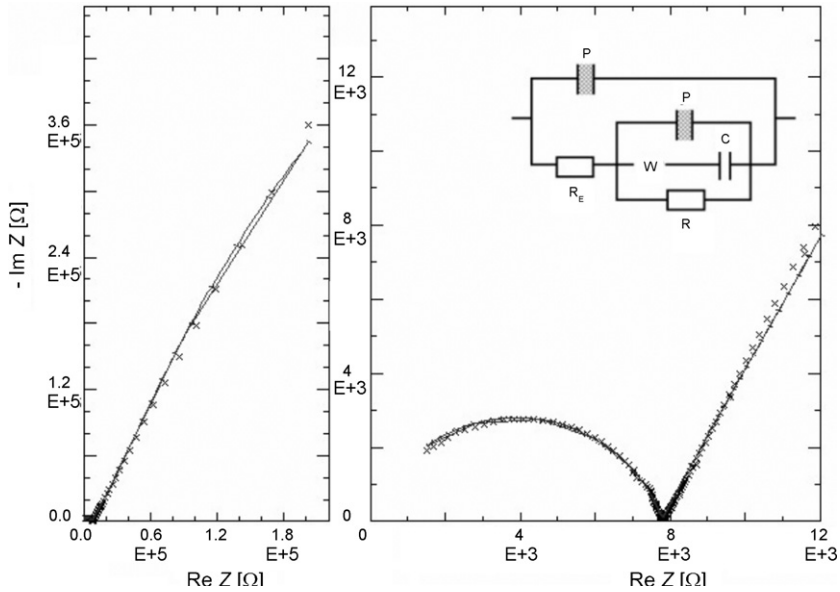

Fig. 1. The impedance spectrum of a $fB + (100 - f)$ A ($f = 40$) composite at −55 °C. Crosses represent experimental data whereas solid line correspond to numerical fits using the equivalent circuit model shown as the insert.

Eq. (1)) is not applicable to the all-glass composites studied in this work.

Also the applicability of the Uvarov model (Eq. (2)) to determine the effective conductivity of the investigated composites was tested. As it can be seen from Fig. 3 the dependence of α on f deviates from linearity at any temperature for all composites. This means that also the Uvarov's model fails to describe properly the effective conductivity of all-glass composites under study.

To improve the quality of the fit we have attempted to propose a modified model also based on effective medium approach. To do that a further analysis of the collected data was performed. Fig. 4 presents the temperature dependences of the conductivity of all investigated materials. In all cases, glasses and composites, the Arrhenius dependence is obeyed. Therefore, in the new model it was postulated that effective conductivity of a composite was the Arrhenius-like one:

$$\sigma_{\text{eff}} T = \sigma_{0\text{eff}} \exp\left(-\frac{E_{\text{eff}}}{kT}\right) \tag{3}$$

where E_{eff} and $\sigma_{0\text{eff}}$ represent effective activation energy and effective preexponential factor of the composite, respectively. Fig. 5 shows the dependence of the effective activation energy on the volume fraction f. A similar dependence for the effective preexponential factor is shown in Fig. 6. As one can notice both dependences (E_{eff} versus. f, Fig. 5 and $\sigma_{0\text{eff}}$ versus f, Fig. 6) could be represented by linear functions:

$$E_{\text{eff}} = af + b, \qquad \sigma_{0\text{eff}} = cf + d \tag{4}$$

where a, b, c and d are some phenomenological coefficients.

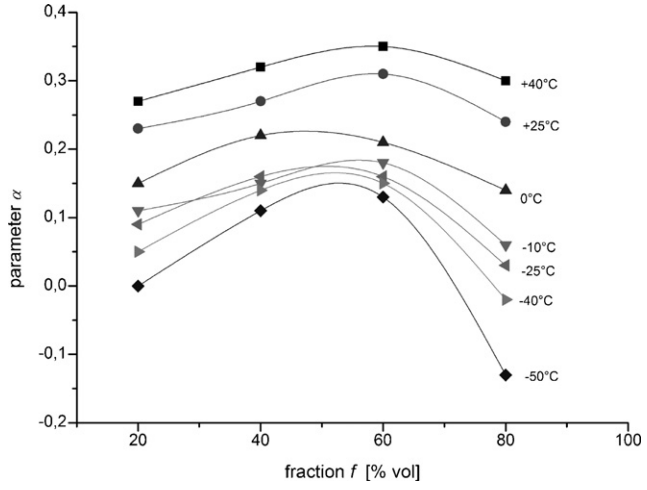

Fig. 2. The dependence of the parameter α vs. composition at selected temperatures. The lines are the guide to the eye.

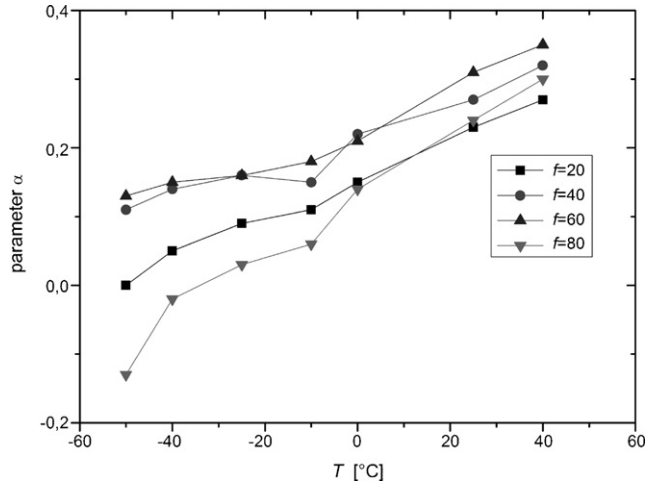

Fig. 3. The α parameter as a function of temperature for selected compositions. The lines are the guide to the eye.

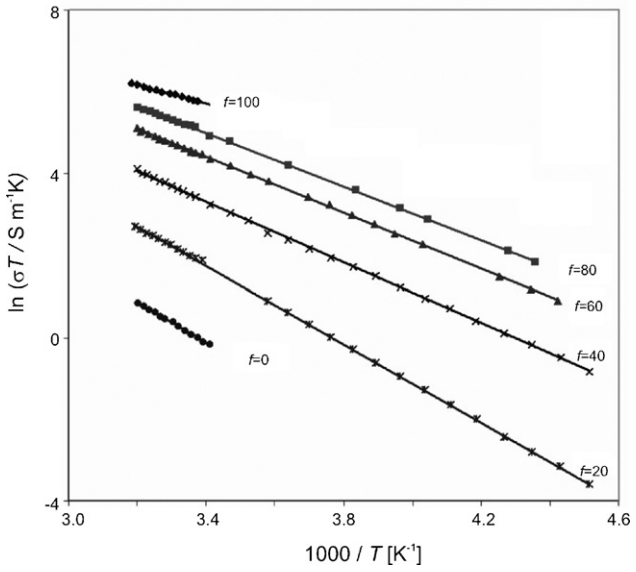

Fig. 4. The temperature dependences of conductivity of the all-glass composites.

Under the above assumptions (Eq. (4)) the effective conductivity of the all-glass binary composite can be written in an approximate form:

$$\sigma_{\text{eff}}(T, f) = \frac{cf + d}{T} \exp\left(-\frac{af + b}{kT}\right) \quad (5)$$

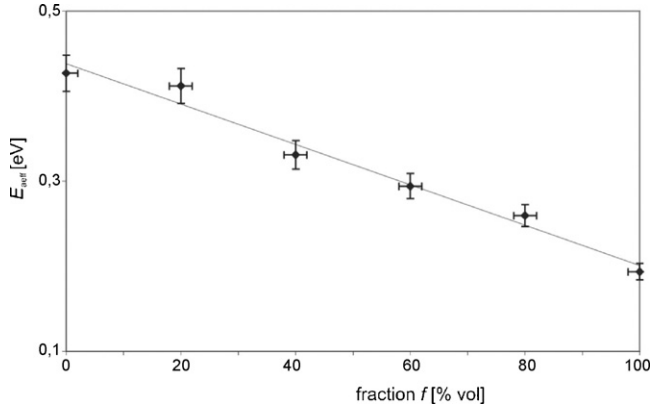

Fig. 5. The dependence of the effective activation energy on the volume fraction f of the component B.

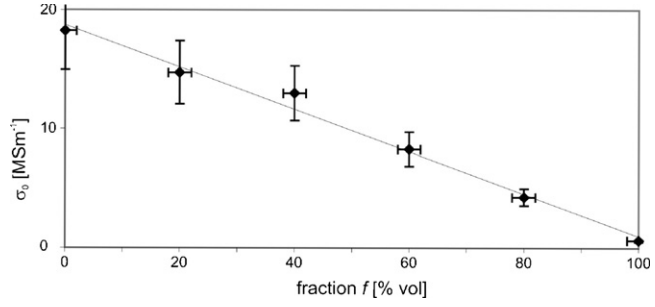

Fig. 6. The dependence of the effective pre-exponential factor on the volume fraction f of the component B.

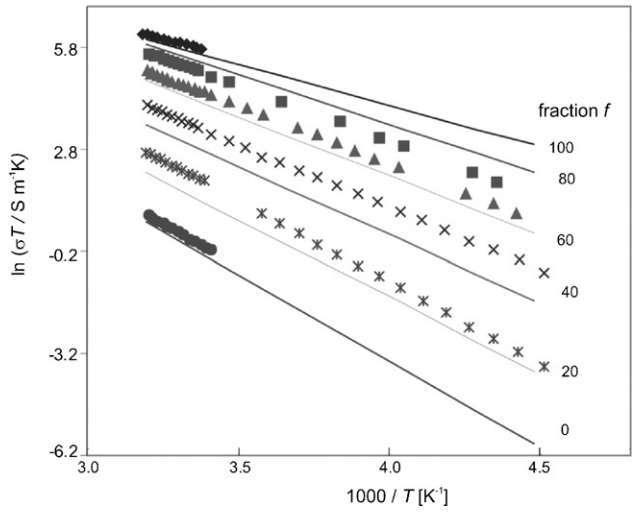

Fig. 7. The temperature dependences of conductivity of the all-glass composites: measured (symbols) and calculated using the Eq. (5) (lines).

Fig. 7 shows temperature dependences of the conductivity: experimental and calculated using the Eq. (5). Both dependences are similar in terms of the activation energy but somehow systematically shifted one versus another. These departures are most pronounced in the case of the composite corresponding to $f = 80$, but even then is does not exceed 4%. The actual small divergences between the experimental absolute values of the conductivity and calculations based on the proposed Eq. (5) should be minimized in the near future.

4. Conclusions

Electrical conductivity of a series of all-glass composites based on Ag^+-ion conducting glasses of the $AgI–Ag_2O–P_2O_5$ system, measured in a wide temperature cannot be properly described using neither the general mixing rule nor the Uvarov model. A new phenomenological model based on the effective medium approach was proposed. The tests of this model showed its applicability to describe temperature dependence of conductivity of the composites.

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