

Short communication

Conductivity, thermal behavior and microstructure of new composites based on AgI–Ag₂O–B₂O₃ glasses with Al₂O₃ matrix

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Abstract

A series of Ag⁺-ion conducting composites consisting of glasses of the AgI–Ag₂O–B₂O₃ system and hard Al₂O₃ powder matrix were synthesized by a high-pressure route (pressure 7.7 GPa, temperature 100–200 °C). The composition of the glasses was described by the general formula: $x\text{AgI} \cdot (100 - x)(0.667\text{Ag}_2\text{O} \cdot 0.333\text{B}_2\text{O}_3)$, where $x = 40, 50$ and 60 . Alumina powder (2 μm average grain size) was added to the glass in 50/50 proportions (by volume).

Conductivity, thermal behavior and microstructure of these composites are reported.

Though the conductivity of the composites is lower than that of the constituent glasses, other properties like mechanical resistance to fracture are considerably improved.

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1. Introduction

Portable electronic devices, omnipresent nowadays, require small-size power sources which should be more efficient, durable, reliable and safer for the environment than those available now. To meet growing and urgent needs for such power sources it is vital to carry out the research on many prospective ideas: miniaturized fuel cells, rechargeable microbatteries, etc. One of specific tasks in this research is the development of solid electrolytes (polycrystalline, amorphous or composite) for rechargeable silver microbatteries [1,2].

Though the ionic conductivity of many silver glasses, especially those with high contents of AgI, can be suitable for battery applications at moderate temperatures, some disadvantages of those glasses such as, e.g. their brittleness or low thermal stability threshold, limit the prospects of their practical use. One of possible solutions to circumvent the drawbacks of glassy electrolytes is to produce composites based on these glasses. There have been already explored several interesting approaches to prepare composites based on AgI and other components, e.g. confining AgI particles in pores of porous alumina [3], elabo-

rating systems containing AgI and Al₂O₃ xerogels and aerogels [4] or ‘sintered’ mixtures of AgI and alumina powder [5].

A few years ago we have started studies on novel composite materials based on two components: (i) Ag⁺-ion conducting glasses of the AgI–Ag₂O–M_xO_y systems (M_xO_y = B₂O₃, V₂O₅, P₂O₅) and (ii) inert hard powders—e.g. diamond, ZrO₂, or others [6–8].

In order to produce mechanically rigid, non-porous composites we have implemented a high-pressure synthesis method, developed in the Institute of High Pressure Physics, Polish Academy of Sciences. The basic idea of this method consists in simultaneous application of high pressure and elevated temperature to a mixture and/or a sandwich system of a hard powder component (e.g. diamond, zirconia) and a soft one (e.g. ionically conducting glass, a low-melting metal, etc.). The use of both factors (i.e. high pressure and elevated temperature) at the same time causes that the softened (molten) component is forced to fill voids between the grains of the hard component. Once the applied pressure and temperature are relaxed to ambient values, the resulted sample forms a rigid composite, which is much less brittle than the constituent glass.

In this work, we report results of our current studies on conductivity, thermal behavior and microstructure of Ag⁺-ion conducting composites prepared via the high pressure method from glasses of the AgI–Ag₂O–B₂O₃ system

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and hard Al₂O₃ (corundum) powder matrix. The choice of glass compositions described by a general formula: $x\text{AgI} \cdot (100 - x)(0.667\text{Ag}_2\text{O} \cdot 0.333\text{B}_2\text{O}_3)$ for $x = 40, 50$ and 60 was justified by the fact that for these compositions the electrical conductivity reaches maximum [9]. On the other hand it is widely known that silver borate samples with high contents of AgI (exceeding ca. 55–60 mol%), prepared by a standard melt-quenching method, become partly crystalline. This was also found out by us for the compositions described by the formula: $x\text{AgI} \cdot (100 - x)(0.667\text{Ag}_2\text{O} \cdot 0.333\text{B}_2\text{O}_3)$, for $x \geq 60$ [9]. In the case of the composites, it has however been expected that due to a complicated distribution of phases in the composites and due to special conditions of their synthesis (high pressure, elevated temperature) the crystalline phases may appear at values of x lower than 60. It should be emphasized that Al₂O₃ itself does not contribute directly neither to the electrical conductivity nor to thermal events in the temperature range 20–400 °C.

2. Experimental

Silver borate glasses of the compositions $x\text{AgI} \cdot (100 - x)(0.667\text{Ag}_2\text{O} \cdot 0.333\text{B}_2\text{O}_3)$ for $x = 40, 50$ and 60 were prepared by a standard melt-quenching method [10]. The composites consisting of ground glasses of the above compositions and α -alumina powder (Alcoa, 2 μm average grain size) in 50/50 proportion (by volume) were synthesized at 100, 150 or 200 °C under high pressure ($p = 7.7$ GPa). More details on the high-pressure synthesis are given in Ref. [6]. The resulting products were rigid pellets, much more resistant to fracture than the original glasses. Thermal events of the glasses and composites (glass transition, crystallization, etc.) were determined by differential scanning calorimetry (DSC). DSC scans were carried out on a Perkin-Elmer Pyris 1 equipment in air in the temperature range 20–220 °C (in several cases 20–350 °C) at a 20 K min⁻¹ scan rate. The scanning electron microscopy (SEM) observations were done on a LEO 1530 equipment. Impedance measurements were carried out using a fully automated setup based on a Solartron Impedance Analyzer 1260, in the 100 mHz–10 MHz frequency range. These measurements were done in the 20–170 °C temperature range in several heating–cooling stages for each sample. Prior to these measurements gold electrodes were sputtered onto opposite sides of the samples. The numerical fitting of the acquired impedance spectra was done using the FIRDAC software [11].

3. Results and discussion

3.1. DSC studies

DSC curves of the as-prepared glasses (upper curves in Fig. 1a–c) contain features typical for many amorphous systems. They start with a slight baseline shift (sometimes hardly visible) corresponding to the glass transition. Glass transition temperature T_g for all these compositions (for $x = 40, 50$ or 60) is close to 80 °C. A distinct exothermic peak following the glass transition is due to the crystallization phenomena. The corresponding crystallization temperature T_c decreases as x increases: from

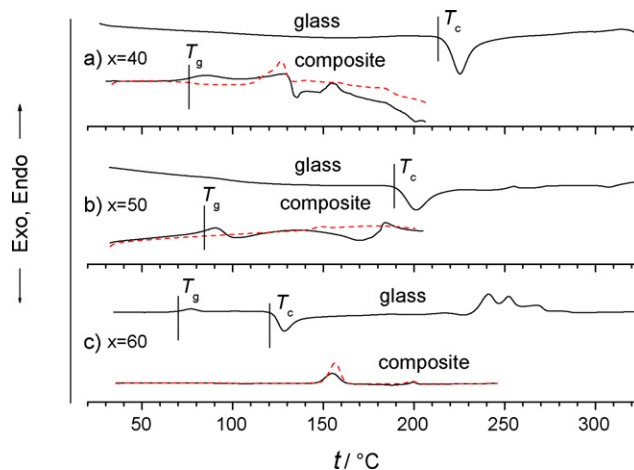


Fig. 1. DSC curves of glasses $x\text{AgI} \cdot (100 - x)(0.667\text{Ag}_2\text{O} \cdot 0.333\text{B}_2\text{O}_3)$ and corresponding composites with Al₂O₃: (a) $x = 40$, (b) $x = 50$ and (c) $x = 60$ (solid lines: first run; dashed-lines: second run).

215 °C for $x = 40$, through 190 °C for $x = 50$, to 120 °C for $x = 60$. At higher temperatures for composites based on glasses $x = 50$ or 60 one can observe an additional single endothermic peak at 250 °C ($x = 50$) or multiple peaks in the 230–270 °C range ($x = 60$) (Fig. 1b and c, respectively). These endothermic peaks may be caused by melting (single- or multi-stage) of previously crystallized grains.

The DSC curves of composites (lower curves in Fig. 1a–c) differ from those of the glasses (upper curves in Fig. 1a–c). For composites based on the glass with $x = 40$, there is a small shift of the baseline above 80 °C followed by exothermic peaks in the 130–200 °C range, corresponding to crystallization (Fig. 1a). On the second heating run the exothermic features disappear and a distinct endothermic peak appears with a maximum at 130 °C. For a composite based on a glass $x = 50$, the first heating run reveals a glass transition feature at $T_g = 82$ °C and an exothermic crystallization peak extending in the 140–180 °C range. On the second run the glass transition is no longer visible and a small endothermic peak appears at 145 °C. Finally for a composite based on the glass $x = 60$ in both runs one can see only an endothermic peak in the 145–165 °C range.

All these features indicate that in the as-synthesized composites based on glasses, corresponding to $x = 40$ and 50 there is still a considerable amount of the glassy phase, as indicated by the presence of glass transition in the first DSC runs (Fig. 1a and b). During heating to 200–250 °C the glassy phase undergoes crystallization, therefore in the second run one cannot see neither a glass transition nor any additional crystallization. Instead, an endothermic peak appears in the proximity of 130–150 °C (weak for the case of $x = 40$, more distinct for $x = 50$). The presence of this peak in both first and second runs of the DSC, in the case of the composite corresponding to $x = 60$ indicates that in this case the as-synthesized composite does not contain any substantial amount of the glassy phase.

The endothermic peak near 130–150 °C is characteristic for the first order phase transition of AgI crystallites from the low-temperature β -phase to the high temperature α -phase. For bulk silver iodide this transition takes place at 147 °C, however this

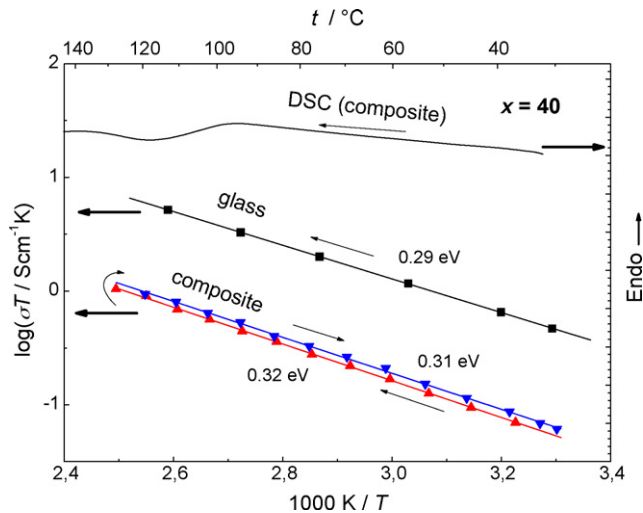


Fig. 2. Temperature dependence of the electrical conductivity of a composite $x\text{AgI}-(100-x)(0.667\text{Ag}_2\text{O}-0.333\text{B}_2\text{O}_3):\text{Al}_2\text{O}_3$ for $x=40$ during the heating (\blacktriangle) and cooling (\blacktriangledown) stages. Full squares correspond to the glass with $x=40$. A DSC trace of the composite is shown in the upper part of the figure.

temperature can depend on AgI crystallite size and/or existing mechanical stresses. In particular it can be depressed if nanosize grains of AgI are embedded in a glassy matrix [12] or confined in nanopores of porous silica [13]. Taking this size effect into account, one can interpret the substantially lower position of the peak of the phase transition for the case of $x=40$ (120–130 °C) after the first heating run, as an indication of the presence of small crystallites of AgI strongly influenced of the glassy phase surrounding these crystallites. The presence of silver iodide grains in the annealed composites was independently confirmed by our X-ray diffractometry (XRD) studies (see Section 3.4 below).

3.2. Temperature dependence of conductivity

The temperature dependencies of conductivity of all the composites were studied in several cycles, each consisting of a heating and a cooling stage. These dependencies were compared with those of the constituent glasses. All of them reveal some interesting features depending on the parameter x . In the case of the samples corresponding to $x=40$ (Fig. 2), the conductivity of the composite increases on heating according to the Arrhenius formula with a single activation energy of 0.32 eV. On cooling the conductivity values at given temperatures are approximately the same as those measured on heating. The conductivity of the composite is lower than that of the glass by a factor of 7–8, but the activation energy values are in both cases similar (0.31–0.32 eV for the composite versus 0.29 eV for the glass).

The conductivity of the composites based on glasses $x=50$ exhibits somewhat different temperature dependence (Fig. 3). On the heating up to 130 °C the conductivity follows the Arrhenius formula with a single activation energy of 0.33 eV. Above 130 °C the slope of the $\log \sigma T$ versus $1000/T$ increases. After holding the sample at 150 °C the conductivity on a cooling run is systematically higher than that on the heating. Moreover the activation energy on cooling is lower than on heating (0.26 eV versus 0.33 eV). The maximum temperature of this cycle enters

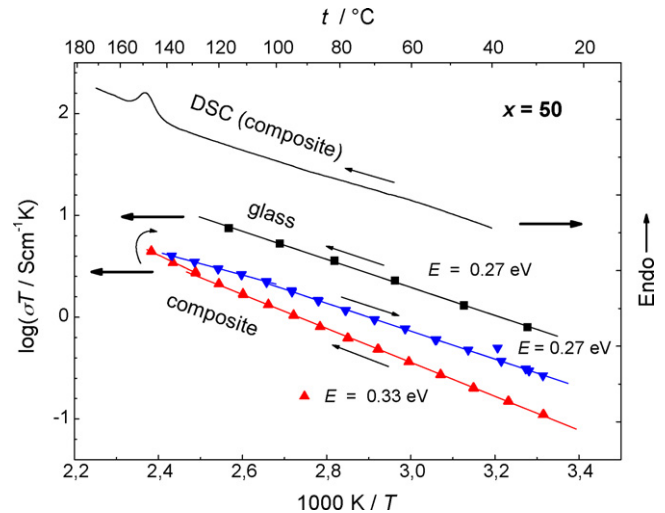


Fig. 3. Temperature dependence of the electrical conductivity of a composite $x\text{AgI}-(100-x)(0.667\text{Ag}_2\text{O}-0.333\text{B}_2\text{O}_3):\text{Al}_2\text{O}_3$ for $x=50$ during the heating (\blacktriangle) and cooling (\blacktriangledown). Full squares correspond to the glass with $x=50$. A DSC trace of the composite is shown in the upper part of the figure.

the region of the $\beta \rightarrow \alpha$ -phase transition of silver iodide crystallites formed in the composite, as can be seen on the inserted DSC trace (Fig. 3).

Finally for the composite based on the glass with the highest content of AgI ($x=60$), the temperature dependence of conductivity shows a hysteresis (Fig. 4). In the heating run up to ca. 125 °C the conductivity depends on temperature in an Arrhenius way with the activation energy of 0.31 eV. In the 125–140 °C range there is a substantial increase in conductivity. At temperatures higher than 140 °C the dependence follows the Arrhenius formula again but now with much lower activation energy of 0.16 eV. On the cooling the Arrhenius-like dependence with the same activation energy (0.16 eV) extends down to ca. 105 °C. Only below 100 °C there is a steep decrease in conductivity.

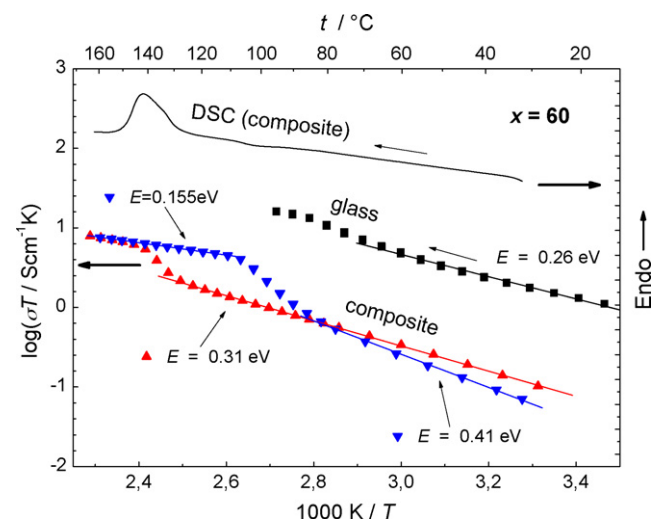


Fig. 4. Temperature dependence of the electrical conductivity of a composite $x\text{AgI}-(100-x)(0.667\text{Ag}_2\text{O}-0.333\text{B}_2\text{O}_3):\text{Al}_2\text{O}_3$ for $x=60$ during the heating (\blacktriangle) and cooling (\blacktriangledown) stages in the third thermal cycle (reaching 170 °C). Full squares correspond to the glass with $x=60$. A DSC trace of the composite is shown in the upper part of the figure.

Below 80 °C the dependence is characterized by the activation energy of 0.41 eV, somewhat higher than that observed in the heating run (0.31 eV). The corresponding DSC trace shows that the endothermic peak of the $\beta \rightarrow \alpha$ transition of AgI overlaps with the hysteresis region (Fig. 4). The hysteresis in the conductivity of the AgI based composites (usually consisting of AgI crystallites thoroughly mixed with a second powdered phase) has been reported a number of times. Very recently however a study was published devoted entirely to that problem [14]. It has been clearly shown by DSC experiments carried out at very low heating/cooling rates that the hysteresis is larger for smaller grains [14].

The fact that the conductivity of any of the composites is lower than that of the corresponding component glass (Figs. 2–4) should be ascribed mainly to the percolation effects. The composite, on a submicron scale, is a mixture of the conducting phase (partly crystallized Ag^+ -conducting glass) and a non-conducting one (Al_2O_3 grains), each occupying 50% of the volume. The high share of the insulating phase (50% vol.) leads to the overall decrease in the conductivity. This effect differs from that observed in AgI: Al_2O_3 composites [5], for which one observes an increase in the low-temperature conductivity, compared to the parent β -AgI phase, at contents of Al_2O_3 even as high as 60 vol.%. The major difference between the case described here and that studied in Ref. [5] is that in the latter case, β -AgI is a poorly conducting phase (conductivity is a few orders of magnitude lower than that of α -AgI), while glasses or partly crystallized glasses studied here are highly conducting materials also at low temperatures. Therefore it is relatively easy to enhance the overall conductivity of the AgI: Al_2O_3 composites due to formation of defective well-conducting regions at the interfaces between grains of β -AgI and Al_2O_3 . Formation of such interfacial regions in the case of composites of highly conducting glasses with Al_2O_3 matrix and its effect on overall conductivity can be of secondary importance.

3.3. Microstructure

SEM studies confirm that the composites consist of uniformly distributed components: a glassy phase and alumina powder. In the SEM micrograph (Fig. 5) (acquired in a phase-view mode) of the as-synthesized composite ($x = 50$), one can clearly distinguish between alumina (darker grains) and glassy phase (lighter regions). The fraction of pores is negligible. The SEM picture confirms that the important part of the volume of the composite sample (i.e. grains of Al_2O_3) is excluded from the ionic conduction. Apart from these two major constituents one can see smaller “droplets” of dimensions ca. 50 nm covering surfaces of the glass and of the alumina grains. The nature of these droplets is not known yet, however they can be either residuals of the glassy phase or precursors of AgI nanocrystallites.

3.4. Identification of crystalline phases by XRD

The XRD patterns of the composites indicate that the originally amorphous ion-conducting component had become partly crystalline during the synthesis of the composite. Fig. 6 shows a

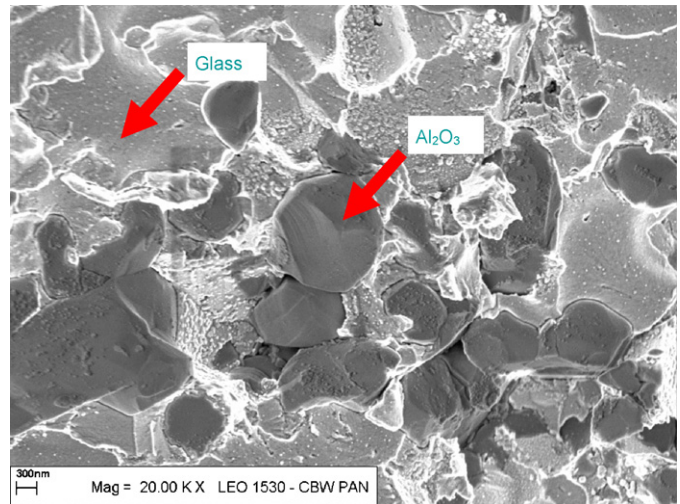


Fig. 5. SEM micrograph of a composite based on a glass $x = 50$ (a phase view).

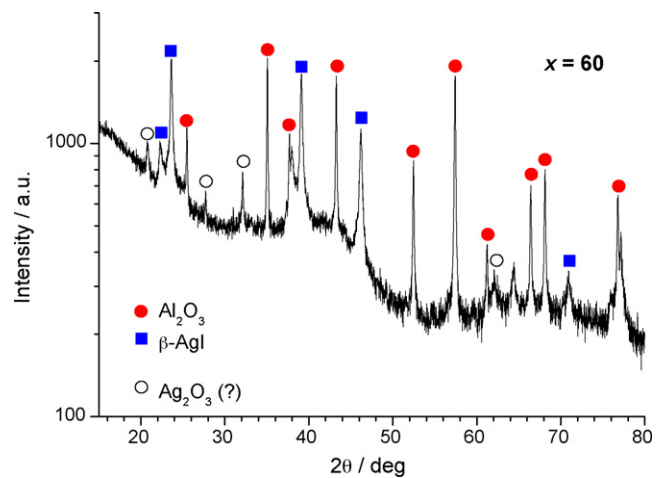


Fig. 6. XRD pattern of a composite based on the glass $x = 60$. Lines of Al_2O_3 marked by (●), lines of β -AgI (■) and other crystalline phase— Ag_2O_3 (?) (○).

XRD pattern of the composite based on a glass with $x = 60$. The pattern contains, as expected, lines corresponding to Al_2O_3 (its α -phase or corundum) and to β -phase of silver iodide. There are also additional lines, which match those of Ag_2O_3 from JPDS databases. However, it can also be that these lines originate from some residuals of a high-pressure AgI-III phase of the rocksalt structure [15], which remained after the high-pressure synthesis of the composite.

4. Conclusions

Ionically conducting composites based on AgI-rich glasses of the AgI– Ag_2O – B_2O_3 system and α - Al_2O_3 were synthesized by a high-pressure route. Their high ionic conductivity is slightly lower than that of the constituent glasses. This deficiency is partly compensated by their non-brittleness, which makes the polishing, cutting and handling of the samples much easier, than in the case of the glasses. It was shown that due to the synthesis procedure some fraction of the original glassy phase undergoes crystallization. The conductivity of the composites

can be increased by thermal treatment at appropriate temperatures. For composites based on glasses with the highest AgI content ($x = 60$) there is a distinct hysteresis of the temperature dependence of the conductivity. The hysteresis was ascribed to the effect of presence of small grains of AgI strongly strained by their environment.

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