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New composite materials prepared by high-pressure infiltration of superionic glasses into diamond powder compacts

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Glassy-crystalline composites have been prepared by infiltrating highly conducting silver vanadate glasses into diamond powder compacts. The process of infiltration was carried out at a high isostatic pressure (from 1.5 to 8 GPa) and temperatures up to 800 °C. The resulting composites have conductivities comparable to those of glasses used for infiltration, but exhibit a wider range of thermal stability (up to 300 °C) than glasses. Additionally, they have much better mechanical properties, in particular, being less brittle and exhibiting higher microhardness than glasses.

Key words: *glass-crystalline composite; impedance spectroscopy; ionic conductor; silver vanadate composite; high-pressure infiltration*

1. Introduction

In recent years, the focus in the area of solid-state ionics has been shifting towards composite materials, which have become frequently used as electrodes or solid electrolytes in batteries, gas sensors, fuel cells, and electrochromic windows [1]. The advantages of composite materials over single-phase systems are well-documented, e.g. often higher conductivity, better performance in operation, improved mechanical properties without substantial loss of good electrical or electrochemical performance. The quest for novel composite materials for electrodes or electrolytes is intensive and multidirectional [2].

In this work, we present the results of studies on the electrical properties of novel composite solid ionic conductors, also characterized by X-ray diffractometry (XRD) and

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scanning electron microscopy (SEM). These materials were prepared by the infiltration of liquefied silver conducting glasses of the AgI–Ag_2O–V_2O_5 system into diamond powder compacts. The process has been carried out at high pressures (1.5–8 GPa) and elevated temperatures (200–800 °C). Such an infiltration process has been found very effective for preparing composites with metals, magnetic, and semiconducting materials introduced into diamond, SiC or other hard powder matrices.

2. Experimental

Silver-vanadate glasses were prepared by a standard melt-quenching method [3]. The process of infiltrating ion-conducting glasses into hard powder compacts matrices has been described in [4]. The composites were obtained by infiltrating $40AgI \cdot 38Ag_2O \cdot 22V_2O_5$ glass into compacts of diamond powder consisting of 0.5 or 30–40 μm grains. A pre-pressed layer of diamond powder was covered with a layer of ground glass in a graphite tube serving as a furnace. These two layers, together with ceramic boron nitride plugs, were placed in a special pressure container. The container was mounted between the anvils of a hydraulic press and heated up to 200–800 °C under high pressure (1.5–8 GPa). Under these conditions, the liquefied glass penetrated into voids between the diamond grains. The final products had the form of compact and hard cylinders, 5 mm in diameter and 2 mm thick, much more resistant to fracture than the glasses.

X-ray diffraction (XRD) analyses were carried out using a Siemens D 5000 diffractometer with a CuK_α line. The XRD patterns of the as-received glasses confirmed their amorphousness. The glass transition temperature (T_g) of the glasses used for infiltration as determined by differential scanning calorimetry (DSC) was close to 100 °C. Scanning electron microscopy (SEM) observations were carried out using LEO 1530 equipment. Impedance measurements were carried out using a computer-controlled setup based on a Solartron 1260 impedance/gain phase analyzer in the temperature range 20–300 ºC and frequency range from 10 mHz to 10 MHz. Prior to measurements, gold electrodes were sputtered onto opposite polished faces of the samples. The fitting package FIRDAC [5] was used for the numerical analysis of the impedance spectra.

3. Results

Preparation. Before obtaining composites of good quality, multiple trials had to be carried out in order to optimise the experimental conditions for infiltration. The main adjustable experimental factors were pressure and temperature. The best composites of AgI–Ag_2O–V_2O_5 glasses were obtained when infiltration was carried out at $p \approx 1.5$–3 GPa and $T \approx 200$–300 °C. Samples prepared under other conditions, in particular at higher temperatures, were of poorer quality, they contained unfilled voids and easily decomposed when subject to external forces. In these cases it was obvious that infiltration was incomplete and the distribution of the glass phase in the composite was far from homogeneous.

Microstructure and mechanical properties. SEM pictures of the composites prepared at optimum conditions (specified above) have revealed that the amorphous phase, filling the space between grains of the matrix, forms many separate small “nodules” situated at the grains of the diamond matrix. When the composite was heated up to ca. 200 ºC and then cooled down to room temperature, the “nodules” disappeared and the amorphous phase formed a continuous layer over the grain surfaces.

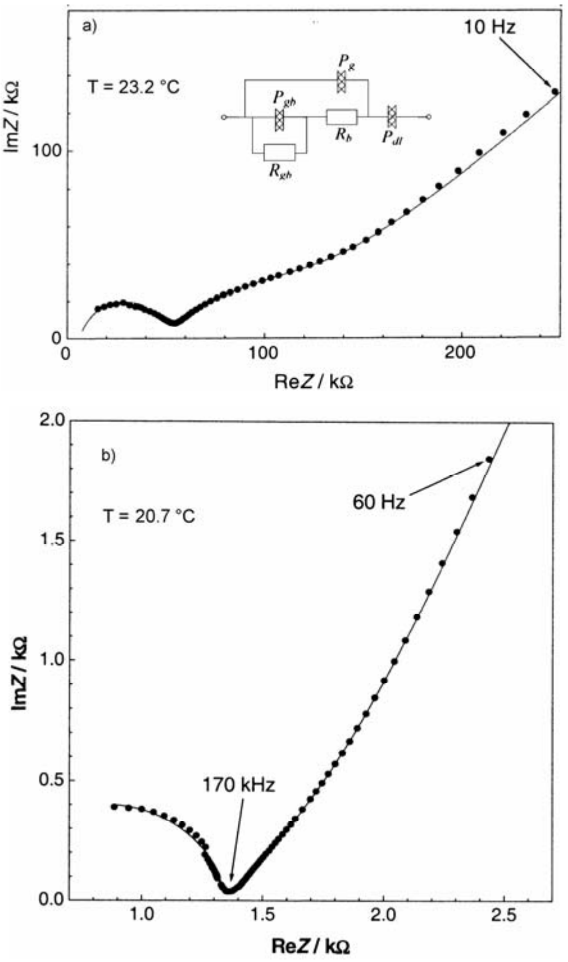

Fig. 1. Room-temperature impedance spectra of: a) composite $40AgI{\cdot}38Ag_2O{\cdot}22V_2O_5$ infiltrated in a diamond (30–40 μm) matrix, b) glass $40AgI{\cdot}38Ag_2O{\cdot}22V_2O_5$. The equivalent circuit, used for fitting the data, is shown as an inset in Fig.1a. Fits are represented by solid lines

Mechanical properties were sampled by measurements of microhardness by the Vickers method. It was found that the microhardness of the composites is more than twice higher than that of the glass (176 versus 72, respectively).

Electrical properties. Impedance spectra of the as-prepared composites were substantially different from those of the glasses used for infiltration (Fig. 1a, b, respectively). In the case of the composites, the spectra consisted of a high-frequency semicircle, followed by a suppressed arc at intermediate frequencies and a linear part inclined at about 45° to the real *Z* axis. This spectrum was fitted using the equivalent circuit shown in the inset of Figure 1a. The result of fitting (line in Fig. 1a) to the experimental spectra (points in Fig. 1a) was satisfactory. The spectra of the glasses used for infiltration (Fig. 1b) consisted of a semicircle at high frequencies and a linear spur at the low-frequency end, with a narrow intermediate region between these two main parts. Despite the differences in the shapes of the spectra of the composite and glass, the same equivalent circuit was successfully used to fit both. After a heating-cooling cycle, the impedance spectra of the composites at room temperature (Fig. 2b)

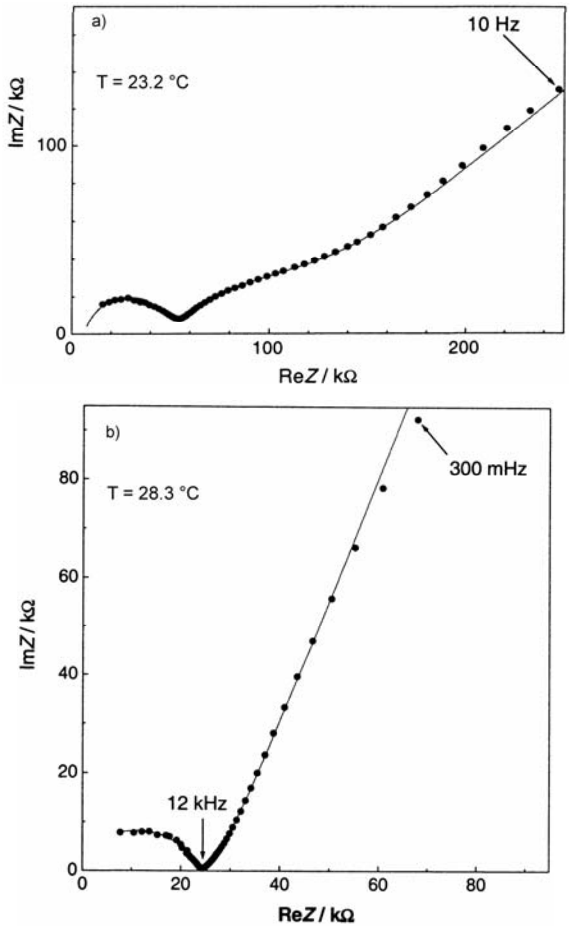

Fig. 2. Room-temperature impedance spectra of the composite $40AgI{\cdot}38Ag_2O{\cdot}22V_2O_5$ infiltrated in a diamond matrix a) before, b) after heating up to 200 °C

were different than those before the heat treatment (Fig. 2a). They were more similar to the spectra of the glasses used for infiltration (cf. Fig. 1b).

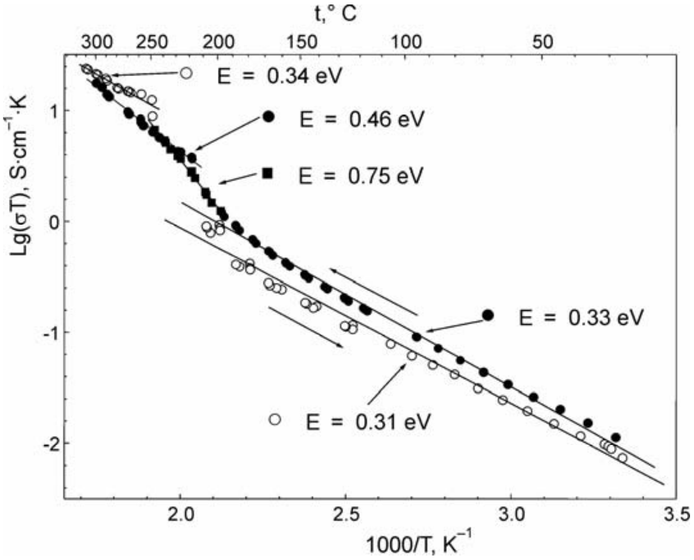

Fig. 3. Temperature dependences of the total ionic conductivity of the composite ($40AgI{\cdot}38Ag_2O{\cdot}22V_2O_5$ +diamond 30–40 μm) during heating (○) and cooling (•)

The temperature dependence of the total conductivity of the composites based on $40AgI{\cdot}38Ag_2O{\cdot}22V_2O_5$ glass in a diamond matrix with a grain size of 30–40μm (Fig.3) follows the Arrhenius formula from room temperature up to ca. 170ºC. On heating the activation energy in this range is equal to 0.31 eV, while on cooling it is slightly higher, 0.33 eV. In the range 180–250 ºC, the slope of the conductivity dependence visibly increases. The corresponding activation energy during cooling is 0.75 eV, and on heating it is even higher. Above 250 ºC, the activation energy decreases to 0.34 eV on heating, and to 0.46 eV on cooling. There is additionally some hysteresis between absolute conductivity values measured during heating and cooling.

4. Discussion

The differences in the shapes of impedance spectra observed for glasses and composites based on these glasses can be justified by the differences between the microstructures of the systems. The presence of a well-visible middle arc in the impedance spectra of composites (Fig. 1a) and its absence for bulk glasses (Fig. 1b) is related to a specific distribution of a glassy phase in the composites. As can be seen on the SEM micrographs of composites obtained by infiltration, glass forms a number of small round “nodules” in the space between grains of the ceramic matrix (in this case diamond). It was found that after heating the composites to above 200 ºC, these “nodules” disappear and the glassy phase forms a continuous layer covering the grains of the matrix. This change in glass distribution following heating is accompanied by a modification of the impedance spectra (Fig. 2b), which are similar to those of bulk glasses (Fig. 1b). The reason for this similarity lies in a continuous distribution of the conducting phase in glasses and annealed composites. In the case of freshly prepared composites, the conducting phase contains many boundaries, mainly between glassy nodules, which can discernibly impede, or, more generally, modify ion transport conditions in the system. The presence of these boundaries may cause the appearance of an additional arc in the impedance spectrum like that in Fig.1a.

A linear temperature dependence of the conductivity in the (log σT vs. $1/T$) coordinates) observed at temperatures up to ca. 170 ºC means that the activation energy is constant in this range. Its value, close to 0.3 eV, is typical of bulk glasses containing considerable amounts of AgI. The increase in activation energy in the 180–250 ºC range and its decrease at higher temperatures point to the presence of some amount of crystalline AgI in the composites. Bulk crystals of AgI undergo a phase transition from a low conducting β to highly conducting α phase at 147 ºC [2]. The fact that for the composites under study the change in conductivity is observed at higher temperatures (ca. 170 C, Fig. 3) than for bulk AgI (147 ºC) should be ascribed to the dispersion of AgI in the composite and to its strong interactions with the glassy phase as well as diamond particles.

5. Conclusions

It has been demonstrated that it is possible to prepare attractive composites based on $AgI–Ag_2O–V_2O_5$ glasses infiltrated into diamond powder. Such composites exhibit improved thermal stability and better mechanical characteristics as compared to those of as-received glasses. The conductivities of these materials are comparable to that of the infiltrated glasses, in spite of a lower share of conductive phase in these composites compared to bulk glasses.

Acknowledgements

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