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Crystallization processes in superionic $AgI–Ag_2O–P_2O_5$ ($[Ag_2O]/[P_2O_5] = 3$) glasses

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Crystallization processes in superionic $AgI–Ag_2O–P_2O_5$ ($[Ag_2O]/[P_2O_5] = 3$) glasses were investigated by X-ray, DSC, SEM, and impedance spectroscopy. It was found that the crystallization process depended on the total concentration of the AgI dopant in the material and on the thermal treatment of the glass. During quenching of the glass melt, the following phases are successively formed with increasing total AgI concentration: pure glass without detectable (XRD) traces of crystalline phases, glasses containing β-AgI and some other, unidentified crystallites precipitated on the surface, and finally a composite material, namely a glass matrix in which β/γ-AgI inclusions are embedded. Glasses containing $x < 50$ mol % of AgI do not crystallize during annealing. Two bulk crystallization processes were identified in solid glasses with $50 < x < 75$ mol %. During annealing, the initial product of crystallization transforms to the final one. There is an evidence that crystallization is preceded by a pre-crystallization stage, in which the glass matrix becomes inhomogeneous, forming nano-sized volumes.

Key words: *crystallization; superionic phosphate glass*

1. Introduction

Glass-ceramic composites have been attracting attention of researchers for decades, because of their technological importance. In the case of superionic glassy composites, however, the interest has been very limited, resulting in poor knowledge of their properties and processes. Recently, some papers [1–3] reported an enhancement of ionic conductivity after introducing a crystalline phase into the superionic glass matrix. These observations highlighted the technological interest of superionic glassy composites pointing to the need for more fundamental investigations, of crystallization, in particular.

The investigated $AgI–Ag_2O–P_2O_5$ glasses are well known as useful and model materials for fundamental research of superionic processes in glasses. Due to their low

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glass transition temperatures (60–120 °C), they also appear to be convenient for the observation of crystallization phenomena. According to our knowledge, crystallization in phosphate glasses ($[Ag_2O]/[P_2O_5] = 3$) has not been reported in the literature so far.

2. Experimental

Samples of the material were prepared by the method described elsewhere [4, 5]. Crystalline phases were formed inside a glassy matrix during the quenching of the molten glass or by annealing the solid glass. Depending on the goal, thermal processing consisted of several annealing steps, at temperatures and duration times selected to achieve the required stage of crystallization. X-ray diffraction was used for material characterization, both for as-received and thermally processed samples. A Philips X'Pert Pro ($CuK_{\alpha 1}$) diffractometer, equipped with an Anton Paar high-temperature diffraction oven, was employed for room and high temperature X-ray diffractometry. Field emission scanning electron microscopy was used for microstructure investigation, using the LEO 1530 model. Ion conductivity was determined by impedance spectroscopy (Solartron 1260). Calorimetric properties were investigated and differential scanning calorimetry (DSC) was applied (Perkin-Elmer, Pyris1 model). Depending on the particular investigation, the material was powdered in a mortar and pestle, or a thin surface layer was removed by fine sand paper; in some cases as-received samples were used.

3. Results and discussion

The shapes of the X-ray diffraction patterns for the as-received samples show a correlation with the total concentration of AgI dopant. When silver iodide concentration does not exceed about 65 mol %, the diffraction patterns exhibit a 'halo' profile typical of amorphous materials (Fig. 1). For higher dopant concentrations, some diffraction lines are visible on the patterns. Powdering or removing a thin surface layer about 30–40 μm thick from the material containing $65 \leq x \leq 70$ mol % of the dopant resulted in the disappearance of these lines (Fig. 2). This observation evidently indicates that the crystalline phase is located on the surface of the glass. For materials with $x > 70$ mol %, similar mechanical processing does not change the shape of the XRD profile, suggesting bulk crystallization (Fig. 3). Concluding, there is a sequence of crystallization events with increasing total AgI concentration in the material: a glassy matrix, free from crystalline inclusions (detectable by X-ray diffraction), surface crystallization, and, finally, crystallization in the bulk. Phase analysis based on the ICDD diffraction database attributes the β/γ-AgI crystal structure to bulk precipitates and identifies a mixture of β/γ-AgI and some unknown crystalline phase on the surface of the glass.

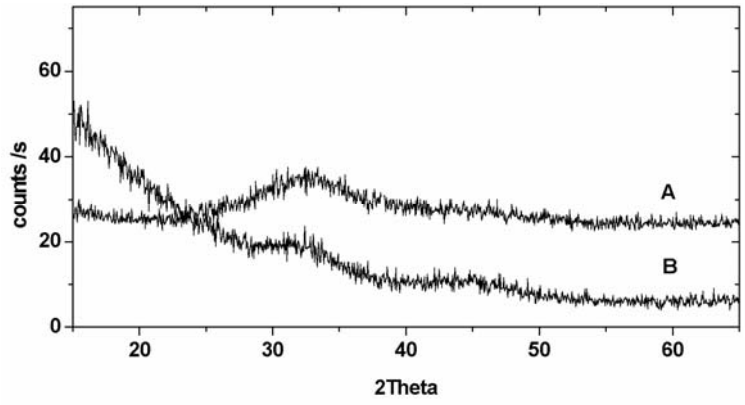

Fig. 1. X-ray diffraction patterns for the 60AgI–30Ag_2O–10P_2O_5 glass:
a) – as-received, solid sample, b) – as-received, powdered sample

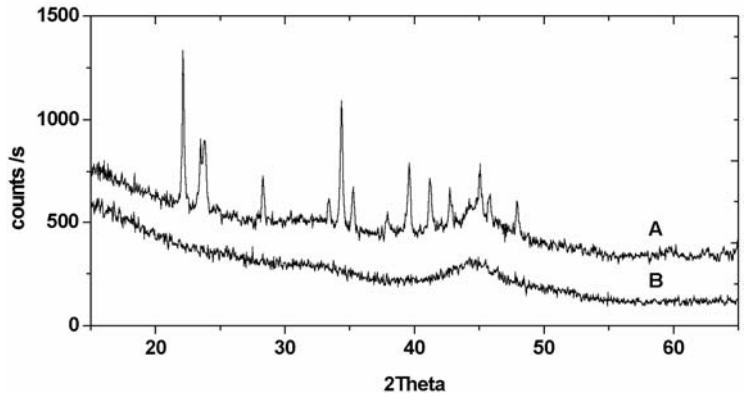

Fig. 2. X-ray diffraction patterns for the 70AgI–22.5Ag_2O–7.5P_2O_5 glass:
a) – as-received, solid sample, b) – as-received, powdered sample

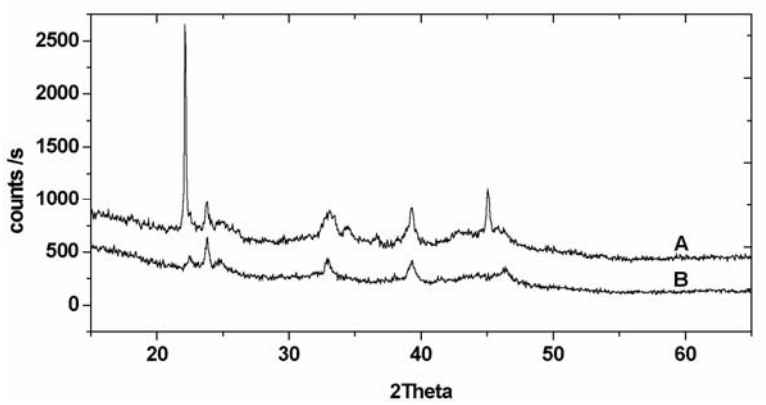

Fig. 3. X-ray diffraction pattern for the 75AgI–18.75Ag_2O–6.25P_2O_5 glass after preparation:
a) – as-received, solid sample, b) – as-received, powdered sample

It was found that crystallization in solid glasses containing more than 50 mol % of AgI could be initiated by annealing at elevated temperatures. Efforts to proceed with such crystallization for glasses with $x < 50$ mol % have not succeeded, even for long annealing (months) at various temperatures up to 160 °C. DSC investigations of glasses with $x \geq 50$ mol % revealed two crystallization processes: the first at about 62–90 °C and the second at 100–110 °C (depending on x). The glass transition temperature was found to be about 52–57 °C.

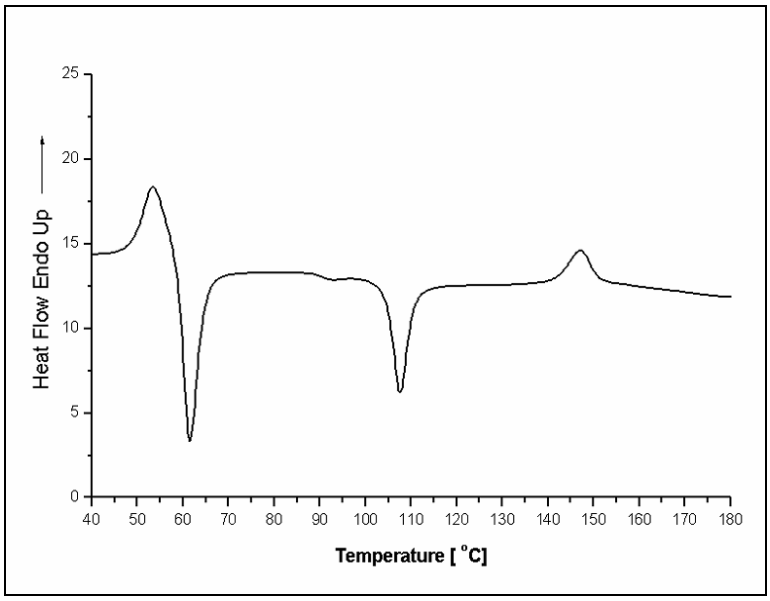

Fig. 4. DSC trace for the 75AgI–18.75Ag_2O–6.25P_2O_5 as-received glass

Figure 4 presents, as an example, the DSC curve for the glass 75AgI–18.75Ag_2O –6.25P_2O_5. XRD investigations also confirmed the existence of these two crystallizations. Figure 5 shows diffraction patterns for 60AgI–30Ag_2O-10P_2O_5, recorded after various thermal treatments. Profile (d), obtained after annealing at 64 °C for 145 min, differs from profile (e), observed after annealing at 64 °C for 145 min and additionally at 66 °C for 418 min. None of the lines visible in profile (d) are repeated in pattern (e). Similarly, two characteristic shapes of the X-ray patterns exhibited other, thermally treated glasses, containing ca. 60–75 mol % of the dopant (Fig. 6). According to the ICDD database, the lines observed in both patterns represent unknown crystalline phases. Some of the weak reflections in Fig. 5e can be attributed to γ-AgI. Since during annealing the diffraction lines assigned to the first crystallization continuously decreased, whereas those ascribed to the second crystallization increased, it was concluded that the final product of crystallization was formed at the expense of the initial crystalline phase.

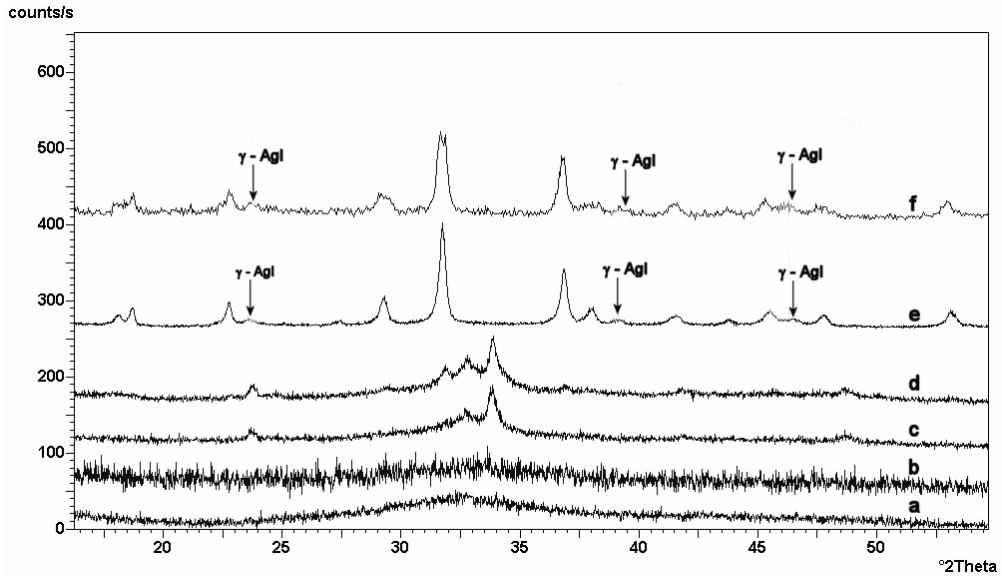

Fig. 5. X-ray diffraction patterns for the 60AgI–30Ag_2O–10P_2O_5 glass: as-received material (a) and after annealing at 60 °C for 12 min (b), at 60 °C for 12 min and additionally at 64 °C for 74 min (c), at 60 °C for 12 min and at 64 °C for 145 min (d), at 60 °C for 12 min, at 64 °C for 145 min, and at 66 °C for 418 min (e), at 60 °C for 12 min, at 64 °C for 145 min, at 120 °C for 12 min (f); the reflections attributed to γ-AgI are marked

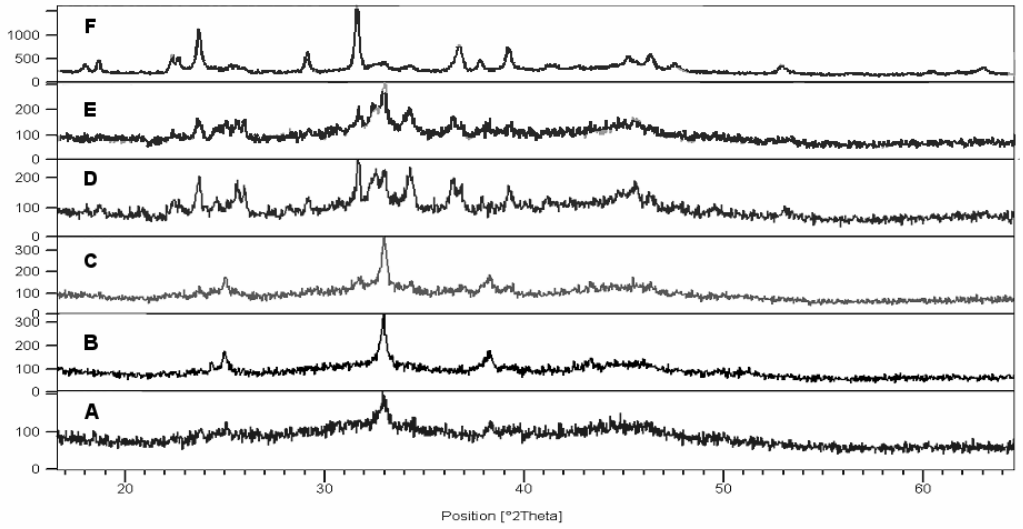

Fig. 6. X-ray diffraction patterns for the 70AgI–22.5Ag_2O–7.5P_2O_5 glass: as-received material (a); after annealing for 10 minutes at: 60 °C (b), 80 °C (c), 100 °C (d), 110 °C (e), and 120 °C (f)

Correlated XRD, SEM, and impedance spectroscopy revealed some interesting features of crystallization process in the glass. It was observed that ion conductivity in

$60AgI–30Ag_2O\text{-}10P_2O_5$ after annealing at 60 °C for 12 min increased about twice compared to that of the as-received glass. Further annealing at 64 °C resulted in an abrupt decrease of conductivity. The relevant diffraction patterns showed no lines after annealing at 60 °C, and no reflections characteristic of the first crystallization after annealing at 64 °C.

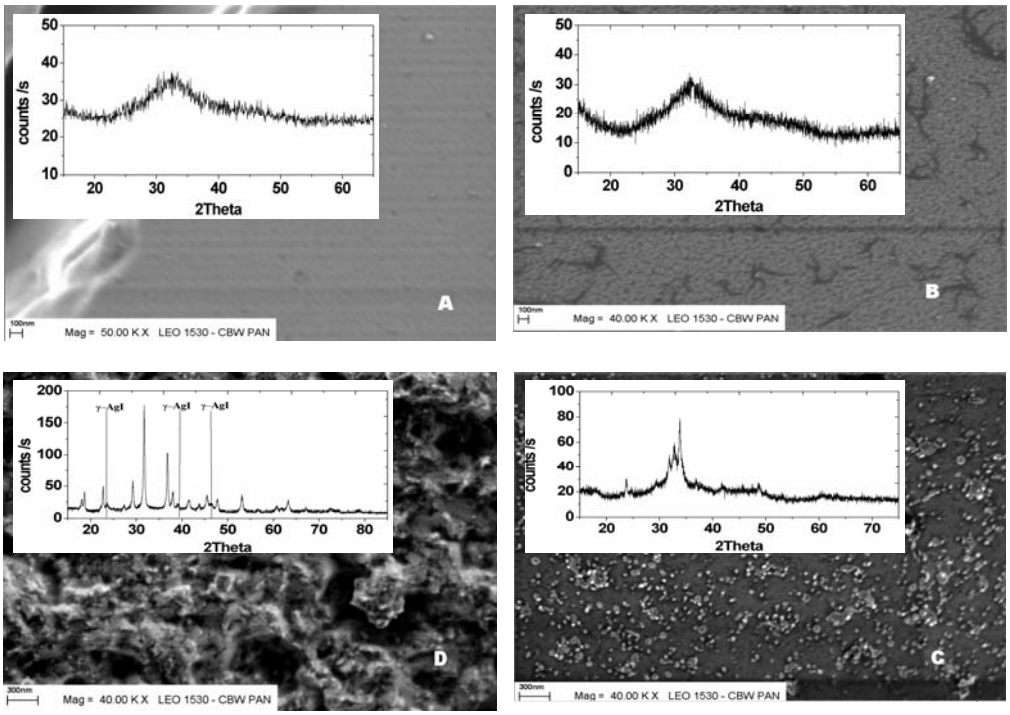

Fig. 7. SEM images of the $60AgI–30Ag_2O–10P_2O_5$ glass: a) as-received; after annealing at 60 °C for 12 min (b), at 60 °C for 12 min and at 64 °C for 145 min (c), at 60 °C for 12 min, at 64 °C for 145 min, and at 66 °C for 418 min (d)

The SEM image of the as-received glass bulk showed a uniform structure, in which few small inclusions are embedded (Fig. 7a). On the contrary, SEM images of the glass after annealing at 60 °C manifested a complex microstructure, whose shape suggests rather inhomogeneities of the glass phase (nano-sized) than the precipitation of some foreign inclusions (Fig. 7b). The presence of such inclusions was exhibited only by SEM images recorded for the glass annealed at 64 °C (Fig. 7c). It seems that annealing at 60 °C results in a phase separation in the glass and that such material appears to be a better ion conductor than the untreated one. These results suggest that mainstream crystallization is preceded by a pre-crystallization stage. It is very likely that during this stage elements of the glass structure, previously uniformly distributed, begin to regroup and form volumes or domains, enabling the further growth of crystallization seeds.

4. Conclusions

Crystallization processes in superionic AgI–Ag_2O–P_2O_5 ($[Ag_2O]/[P_2O_5]$ = 3) glasses are determined by the total concentration of AgI dopant in the material and by thermal treatment of the glass. In as-received (thermally untreated) glasses, the following phases are successively formed with increasing total AgI concentration: pure glass without detectable (XRD) traces of crystalline phases, glasses containing β-AgI and some other, unidentified crystallites precipitated on the surface, and, finally, a composite material being a glass matrix with embedded β/γ-AgI. Two bulk crystallization processes were identified in solid glasses with $50 < x < 75$. During annealing, the initial product of crystallization transforms into the final one. There is an evidence that crystallization is preceded with a pre-crystallization stage, in which the glass matrix becomes inhomogeneous, forming some nano-size volumes.

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