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Crystallization processes in silver-ion conducting borate and phosphate glasses

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Crystallization processes in silver-ion conducting superionic borate and phosphate glasses_are presented. Experimental evidence indicates that these processes are determined by the dopant concentration x, glass former, molar ratio of modifier to former $\eta = [Ag_2O]/[P_2O_5]$, cooling rate of the molten glass during preparation, and by the thermal history of the glass. A crystal-free material is produced by the press-quenching method, in which the total concentration of AgI does not exceed 64–65 mol %. Rapid quenching of highly-doped borate glasses results in the formation of α-AgI crystallites in the glass. The phase deteriorates when stored for a long time or after pressure operation. Annealing prompts crystallization in solid glasses when they contain $40 < x < 65$ mol % of dopant. Only surface crystallization takes place when $0 < \eta < 1$. In the $1 < \eta < 2$ range, the surface crystallization of γ-AgI dominates, provided the annealing time is not too long. When the concentration of the modifier Ag_2O is high ($\eta > 2$), the crystalline phases precipitate in the glass bulk. Investigations point to the key role of a rigid substructure in crystallization. Some of the results indicate that primary crystallization is preceded by a pre-crystallization stage.

Key words: *crystallization; borate glass; phosphate glass; α-AgI*

1. Introduction

For a long time, crystallization effects in superionic glasses have not attracted much attention of researchers who have been mainly interested in ionic properties of this class materials. Therefore, only a limited number of papers considering the subject have been published. In consequence, details of the crystallization processes, mechanisms of crystallization, and their influence on the properties of superionic glasses are hardly known.

In one of the first papers devoted to crystallization, it has been shown that the solubility limit of silver iodide in $Ag_2O–P_2O_5$ glass matrix is about 60 mol % [1, 2].

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The excessive amount of dopant precipitated in the bulk of the glass as a mixture of β- and γ-AgI inclusions.

The properties of silver superionic glasses, prepared by rapid quenching, were reported by a group from the University of Osaka [3–14]. Their research revealed that in highly doped borate, vanadate, and germanate glasses, an α-AgI crystalline phase was formed. At normal conditions, its structure is stable above 147 °C and the compound exhibits superionic properties. Below this temperature, it transforms into a poor ion conducting β-AgI phase. The finding raised hopes for devising methods allowing the structure stabilization of compounds exhibiting superionic properties at high temperatures.

The influence of crystalline precipitates on the ion conductivity of silver iodide oxysalt glass was investigated by Adams et al. [15, 16]. An anomalous increase of conductivity was found, correlating with the interface area between the crystalline inclusion and glassy matrix. Garbarczyk et al. showed that nanocrystallization in Li_2O–V_2O_5–P_2O_5 glasses enhances the ion conductivity of the material [17].

The reported results advocate that crystalline nanoparticles embedded in a glassy matrix improve its ionic characteristics. Such glass–ceramic composites seem to be promising technologically, but their application calls for materials satisfying severe technical regimes. Therefore, the knowledge of how to design a material and control its properties is essential. To understand the nature of crystallization processes in superionic glasses is not only an academic, but also an urgent technological need.

The work aims to summarize experimental observations related to crystallization processes in silver ion conducting borate and phosphate glasses doped with silver iodide. Although the selected glasses are rather outside the interest of technology, they appear to be ideal model media, useful for fundamental investigations of ion and molecular processes in glasses.

2. Experimental

Phosphate glasses were prepared from AgI, $AgNO_3$, and $NH_4H_2PO_4$. NH_4NO_3 was added to some glasses as an additional substrate. AgI, $AgNO_3$, and H_3BO_3 were used as starting compounds in borate glass preparation. After grinding, stoichiometric amounts of the reagents were placed in a furnace. The crucible with the substrates was kept at 400 °C for about half an hour. During this stage of the reaction, the constituents melted and some ammonia and water evaporated from the melt. Next, the temperature was increased to about 650 °C, causing nitrogen oxide to be released. The melt was annealed for about 20 minutes and then, depending on the quenching method, an appropriate procedure was employed. In the case of the press-quenching method, the melt was quenched between two stainless steel plates. Disks of a cast glass, about 5 cm in diameter and 0.5 mm thick, were formed. The press-quenching method assures the cooling rate up to about 10^2 K/s. Square solid samples, with a

1 cm base, were cut out from the disks for further investigations or when necessary the glass was powdered in an agate mortar. A surface layer was removed from the sample with a very fine sand paper.

When a rapid quenching was required, the melt was heated at the temperature range 300–350 °C for about 10 minutes and then it was poured between two rollers rotating with the speed of 700–1000 rpm. Thin flakes of the material were produced. The twin-roller method allows the melt to be cooled with a rate of 10^3–10^5 K/s [4].

X-ray diffraction was carried out using a Philips X'Pert Pro diffractometer. An HTK 1200 Anton Paar X-ray diffraction camera oven, equipped with a temperature control attachment, was employed for the thermal treatment of the samples and high temperature X-ray diffraction.

Differential scanning calorimetry (DSC) measurements were performed using a Perkin-Elmer Pyris 1 instrument. A LEO 1530 field emission scanning electron microscope was used in glass microstructure investigations. Ion conductivity was measured by the impedance spectroscopy method.

3. Results and discussion

The course of the crystallization processes in phosphate and borate glasses, in general, depends on: chemical composition, i.e. dopant concentration x, the glass former, and the molar ratio of modifier to former $\eta = [Ag_2O]/[P_2O_5]$ (i), the thermal history of the glass, comprising the annealing sequences at various temperatures and of various duration(ii), the cooling rate υ of the molten glass during preparation (iii). The variety of the observed crystallization phenomena makes it difficult to specify the individual influence of each factor on the process. It is more convenient to consider separately the class of crystallization processes taking place during quenching of the glass melt and the class of crystallizations, which are initiated and proceeded by external factors (like temperature) in the glass.

3.1. Crystallization in molten glass

When the crystalline phase is formed during quenching, crystallization depends mainly on the total AgI concentration x, the chemical composition of the glass former, and on the cooling rate. Crystal-free phosphate glasses are produced when the total concentration of the dopant does not exceed about 64–65 mol % and when they are prepared by the press-quenching method [1, 2]. Increasing the cooling rate hardly affects the solubility limit of the silver iodide dopant. Also, the value of η does not influence the formation of the crystalline phase in the glass. The excess of the dopant precipitates as a mixture of β- and γ-AgI. The average size of a crystalline grain decreases with increasing cooling rate – as the broadening of the XRD lines of the rapid-quenched material suggests.

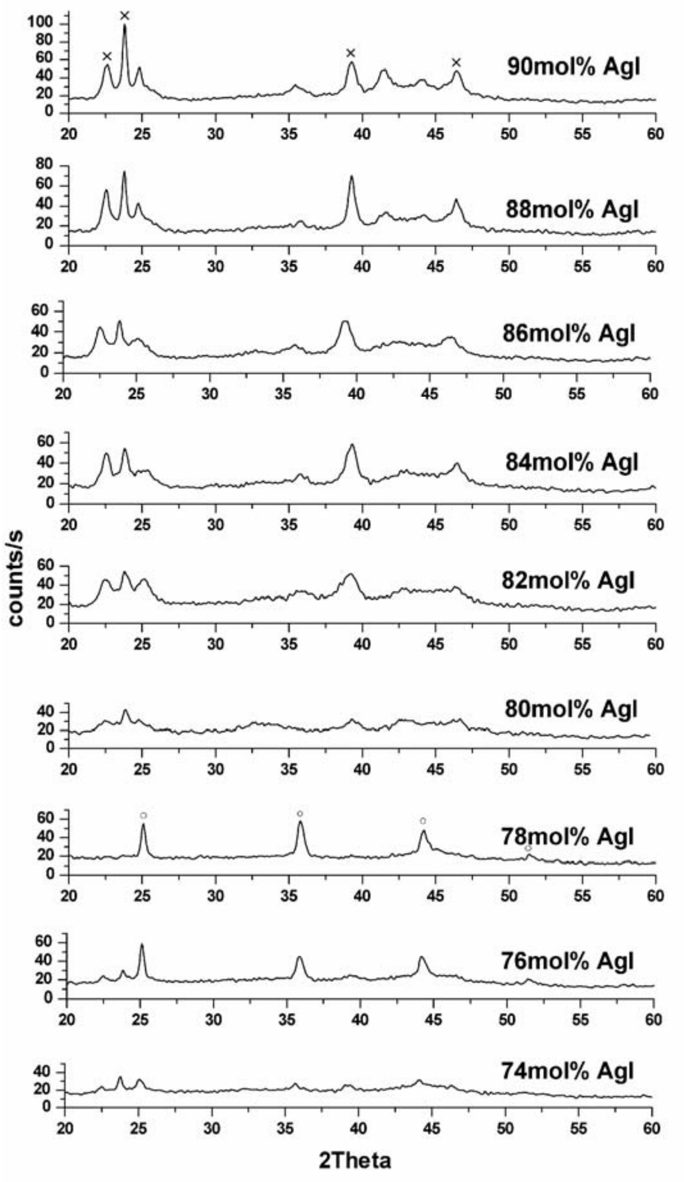

Fig. 1. X-ray patterns of xAgI–(100 – x)(0.75Ag$_2$O–0.25B$_2$O$_3$) glasses as a function of silver iodide content x; crosses denote reflections characteristic of β-AgI, open circles those characteristic of α-AgI

Crystallization in borate glasses is sensitive to the cooling rate. When the rate is relatively low, the dopant solubility limit and crystalline products are similar to those for phosphate glasses. For a high cooling rate, the crystallization route is different. Figure 1 presents the XRD patterns of borate glasses (η = 3) collected at room temperature, prepared by the twin-roller method, ordered as a function of x. The shape of the profiles and the 2θ positions of the diffraction lines suggest that the investigated materials are glass–crystalline composites comprising α-, β-, and γ-AgI. The relative contents of each crystalline phase vary with the total silver iodide concentration in the material. For $x = 78$, the diffractograms indicate that only the cubic α-AgI phase is present in the glassy matrix. There was an attempt to prepare a single α-AgI, rapidly cooling AgI melt. Also, a part of the glass melt was cooled at a lower rate. In both cases, the obtained material contained only β/γ-AgI inclusions. In another experiment, highly doped phosphate glasses were subjected to the rapid quenched procedure, resulting in the production of the glass/β/γ-AgI composite.

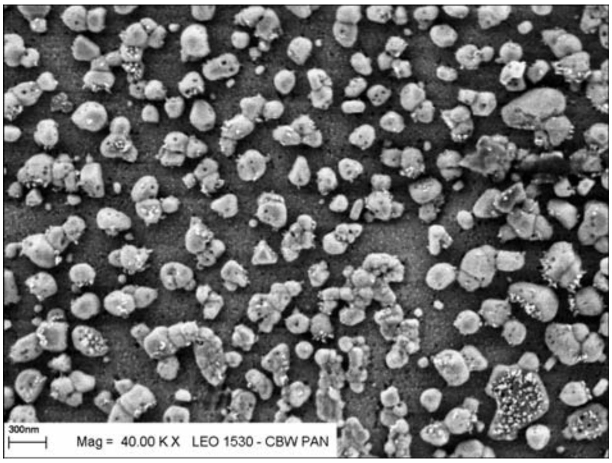

Fig. 2. SEM image of the $78AgI–16.5Ag_2O–5.5B_2O_3$ rapid quenched glass

A detailed analysis of α-AgI crystallization reveals its complex nature. Figure 2 shows a SEM photograph of the material with $x = 78$. One can see the presence of oval inclusions, about 100 nm in diameter, dispersed in the glassy matrix. The inclusions are amorphous, as indicated by XRD patterns with no diffraction lines. When the inclusions break up, forming smaller objects 20–40 nm in diameter, the diffraction lines characteristic of α-AgI appear in the XRD pattern. Tatsumisago et al. [14] found that similar oval inclusions also grow during the annealing of highly doped borate glasses following the precipitation of α-AgI nanocrystals. Our observation and reports in the literature are in agreement, that the α silver iodide phase, stable at room temperature, can be formed only if it is embedded inside a glassy matrix of a suitable chemical composition. High total dopant concentration in the glass is essential for the process. When the cooling rate is too low, thermodynamic conditions are not far from equilibrium and concentration of the AgI dissolved in the glass matrix is not high enough to prompt the formation of oval inclusions. Rapid quenching, however, at conditions far from thermodynamic equilibrium, allows a much higher concentration of silver iodide to be introduced into the glass matrix, therefore the α phase crystallizes in glasses prepared with this method.

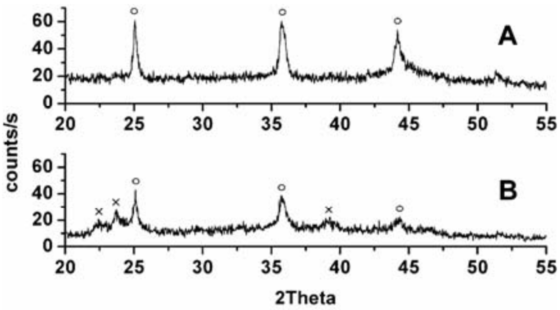

Fig. 3. X-ray patterns for the $78AgI–16.5Ag_2O–5.5B_2O_3$ glass:
a) just after rapid quenching, b) after storing at RT for 3 months; crosses denote reflections characteristic of β-AgI, open circles those characteristic of α-AgI

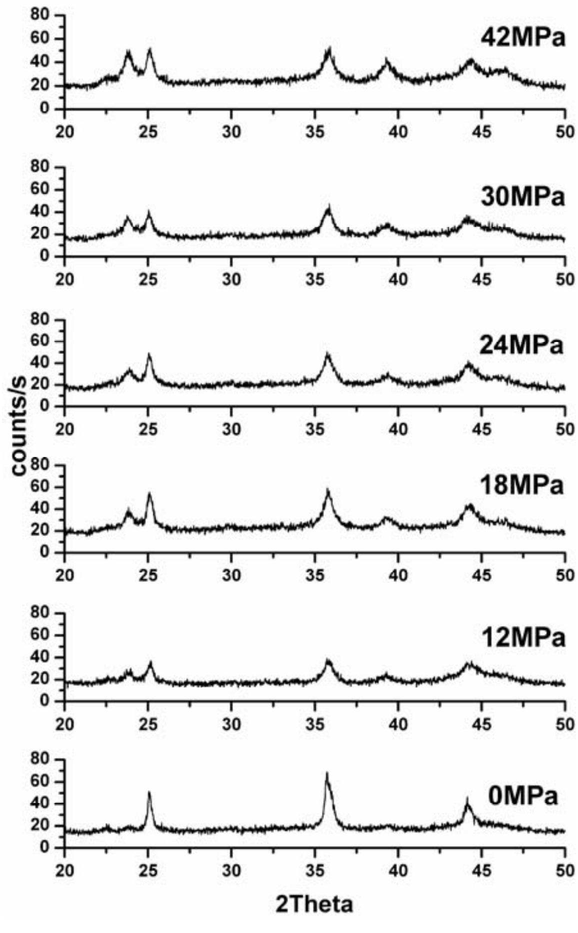

Fig. 4. X-ray patterns for the $78AgI–16.5Ag_2O–5.5B_2O_3$ glass after pressure application: a) as quenched, b) after storage at RT for 3 months; crosses denote reflections characteristic of β-AgI, open circles those characteristic of α-AgI

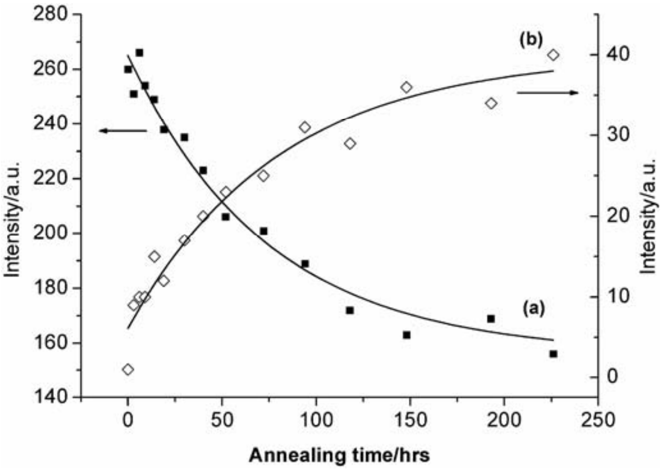

Fig. 5. The XDR intensity of the peak $2\theta = 35.8°$, characteristic of α-AgI (a), and the diffraction line $2\theta = 22.4°$ attributed to β-AgI (b) as a function of the annealing time at 60 °C for the $78AgI–16.5Ag_2O–5.5B_2O_3$ glass

The α-AgI crystalline precipitates deteriorate when the material is stored for several months at RT or subject to high pressure (Figs. 3 and 4). Annealing at elevated temperatures also causes the disappearance of the precipitates. It was observed that decreasing α-AgI content correlates with increasing γ-AgI content in the glass (Fig. 5), suggesting that this phase is formed due to the consumption of the former one.

3.2. Crystallization in solid glasses

Crystallization processes are relatively better recognized in phosphate glasses. For this reason, the discussion will be mainly focused on that group of crystallizations. Among various external and internal factors affecting the composite microstructure of the material, the most significant are: dopant concentration x, the parameter η, and thermal history. The influence of these factors on crystallization can be represented in the two-dimensional phase space of x and η (Fig. 6).

The most interesting phase volume for crystallization covers the $40 < x < 65$ mol % range. Below and above this range, the process is difficult to initiate by annealing. Generally, for this phase crystallization volume, experimental evidence indicates that the more AgI is dissolved in the glass, and the higher temperature and longer annealing time, the easier crystallization proceeds. The type of the crystallization, namely bulk (homogeneous) or surface (heterogeneous), is strongly governed by the parameter η. Employing the phase space approach, one can indicate the area of the most probable occurrence of the crystallization type (Fig. 6). Only surface crystallization takes place when $0 < \eta < 1$. For the $1 < \eta < 2$ range, the surface crystallization of γ-AgI dominates, provided the annealing time is not too long. When thermal treatment lasts several days and the applied temperature does not exceed 20–50 °C above the glass transition temperature, the γ-AgI phase disappears and the bulk crystallization of $Ag_{16}I_{14}P_2O_7$ proceeds. [18]. Crystallization for glasses with $1 < \eta < 2$ can change if an additional NH_4NO_3 substrate is added during preparation. Usually, ammonia nitrate is used to prevent the decomposition of silver compounds. During annealing the molten substrate, NH_4NO_3 decomposes, producing gaseous ammonia and nitrogen oxides. The ionic properties of the glasses prepared with and without ammonia nitrate are identical, but their crystallization properties are different. While in the former precipitates crystallize on the surface, in the latter they locate inside the glassy matrix.

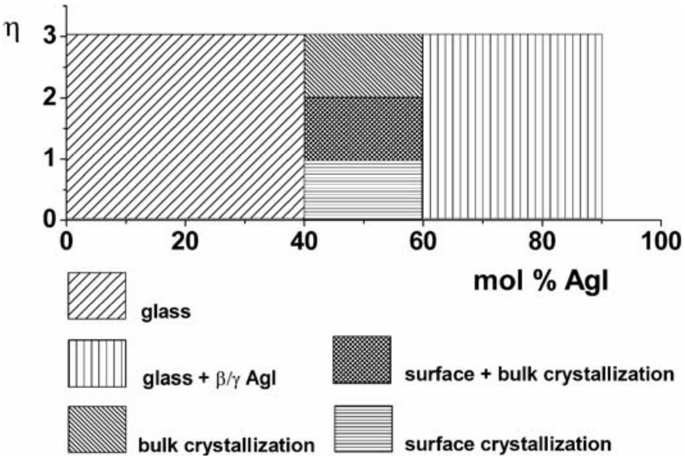

Fig. 6. Phase diagram of the crystallization process in the AgI–Ag_2O–P_2O_5 glasses; $\eta = [Ag_2O]/[P_2O_5]$

When the concentration of the modifier Ag_2O is high ($\eta > 2$), the crystalline phase precipitates in the glass bulk. The process exhibits a characteristic two-stage course. In the beginning, a transitional phase first precipitates, then during annealing it gradually disappears and a second crystalline phase is formed at the expense of the first one. Both phases have unknown structures, as the analysis of XRD patterns reveals [19].

The beginning of crystallization in this glass exhibits unusual features. Complementary XRD, SEM, and impedance spectroscopy investigations revealed that primary crystallization is preceded by a pre-crystallization stage, in which a uniform glass matrix transforms and produces a domain-like area, in which crystallization probably initiates; the details are presented in [19].

3.3. Mechanism of crystallization

Trying to understand the experimental evidence discussed earlier, it is necessary to consider the susceptibility of the glass structure to change under certain thermodynamics conditions. The rigid part of the glass structure comprises chains of PO_4 tetrahedra sharing corners. The length of a chain depends on the value of η. Very long chains are formed if $\eta \approx 1$. In the case of $\eta = 2$, short chains consisting of two tetrahedra are present, while for $\eta = 3$ only single PO_4 tetrahedra exist. Among these crystal units, Ag^+ and I^- ions locate in a disordered manner, constituting a so-called ionic substructure. During crystallization, the structure units exhibit a long-range order. One can assume that ordering proceeds only within one of the substructures or within the whole structure. According to the classical theory of crystallization [20], a foreign phase can grow only if crystallization seeds of suitable size are present in the material. In the case of the discussed glasses, in the molten state, local fluctuations could form some volumes occupied by silver and iodine ions only. For low and intermediate doping, the volumes are too small to reach a critical size. In contrary, in highly doped glasses, fluctuations can produce the appropriate volumes required for crystallization. Therefore, the ions order during quenching, forming AgI. Since the critical size of the crystallization seed is determined by the chemical composition of the volume, one could conclude that the critical size should be the same or similar in all silver oxysalt superionic glasses. That would explain why the solubility limit of AgI is practically the same in all these glasses [21–23].

In solid glasses at normal conditions, elements of the rigid substructure are immobile, inhibiting any crystallization. At elevated temperatures, they are more movable, depending on the lengths of polyhedron chains. Due to fluctuations in the local density of the chains, volumes containing silver and iodine ions, free of chains, can be formed in some places. Inside them, critical size seeds can be formed. The probability of forming such a seed increases with the total concentration of the dopant, with temperature, and with the annealing time. On the other hand, longer polyhedron chains are less mobile. Therefore, in agreement with our observations, it is difficult, if at all possible, to proceed with bulk crystallization for glasses with $\eta \approx 1$ and relatively easy for those with $x > 60$ mol % ($\eta \approx 3$). When chains are short enough and the dopant concentration is about 40–60 mol %, the chance to form a critical seed of AgI is rather low. The involvement of entire units of the structure is more favourable, first in the formation of volumes with an appropriate chemical composition, and next in their ordering. Such a mechanism would explain the presence of the pre-crystallization microstructure observed in glasses with $\eta = 3$ and the formation of some crystalline phases with unidentified structures. Also, crystallization in glasses with $\eta = 2$, where silver iodine phosphate was identified, firmly supports the suggested mechanism. $Ag_{16}I_{12}P_2O_7$ can be formed from $(P_2O_7)Ag_4$ chains, Ag^+ and I^- ions.

The nature of the process leading to the formation of α-AgI in borate glasses seems to be an intriguing and challenging problem. Evidence advocates the phase separation of glass. The nanometer size of the α silver iodide precipitate indicates an important role of the surface energy in stabilization. On the other hand, ordinary, nanocrystalline AgI exists only as a β structure [24]. Therefore, the glass matrix stabilizes the α structure also. Why, then, does the borate matrix stabilize and the phosphate one does not? What property of the matrix decides about stabilization? Pressure investigations expose the role of internal friction as a stabilization factor. Unfortunately, the state of present knowledge does not give a satisfactory answer for these questions.

4. Conclusions

It was shown that crystallization processes in silver-ion conducting borate and phosphate glasses are governed by the chemical composition of the glass and its thermal history, including the quenching of the melt. It is difficult to suggest one universal crystallization scheme common for all glasses, because of the variety of crystallization routes and complex ordering mechanisms. An analysis of the experimental evidence points to the key role of the mobility of the rigid substructure during crystallization. Some of the results indicate that primary crystallization is preceded by a pre-crystallization stage.

α-AgI crystallization is interesting and technologically promising. Investigations revealed that under specific conditions, such as high pressure or long-lasting storage at room temperature, the phase deteriorated. The mechanism of this crystallization needs further investigations.

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