Journal of Non-Crystalline Solids 415 (2015) 51–56

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

High and low temperature syntheses of AgI–$AgPO_3$ glasses: Structural and thermal studies

P. Grabowski *, J.L. Nowinski, K. Kwatek

Faculty of Physics, Warsaw University of Technology, Koszykowa 75, 00-662 Warsaw, Poland

A R T I C L E I N F O

Article history:
Received 6 November 2014
Received in revised form 22 January 2015
Accepted 24 January 2015
Available online 2 March 2015

Keywords:
Silver phosphate;
Silver iodide;
Glass transition;
Mechanosynthesis;
MDSC

A B S T R A C T

In this work we studied the AgI–$AgPO_3$ and $AgPO_3$ glasses obtained in high and low temperature syntheses. The mechanosynthesis and melt-quenching methods were employed to prepare the amorphous materials. Samples were investigated by means of X-ray diffraction, modulated differential scanning calorimetry and Raman spectroscopy. Despite the identical overall chemical composition of the glasses, we noticed different values of glass transition, non-reversing enthalpy and unequal phase composition in elevated temperatures. The work discusses differences in the glass network and distribution of its components induced by different energy transfer mechanisms of each synthesis method.

1. Introduction

The phenomenon of superionic conductivity of glasses attracted the attention of researchers for several decades but, despite the intensive studies, still some issues require clarifications. For instance, a fundamental question whether the method of preparation affects properties of formed glass and possibly to what extent, appears in the light of the recent reports rather complex. Superionic glasses, like silver ion conducting ones, are synthesized mainly in high temperature routes (MQ), which involve melting of the constituents at high temperatures [1–4]. A different way of preparation is offered by the low temperature synthesis routes performed by the mechanosynthesis method (MS) during which the starting materials are agitated by ball-milling to react. The process is usually carried out at room temperature [5–7].

In literature, two materials of the same chemical overall composition, first prepared by the MQ and the second one by the MS method, usually are regarded as the same. Such attitude is based on experimental evidences, developed mainly by X-ray and ionic conductivity which show no significant differences between properties of these materials. For instance, in Ref. [8], the case of the glass of the overall formula $50AgI–30Ag_2O–20V_2O_5$ was studied. The material was prepared by the MS and MQ methods. In the latter one, the two different cooling rates were applied: a slow one and an ultra-fast one. The X-ray, differential scanning calorimetry (DSC), impedance spectroscopy, FTiR and Raman spectroscopy methods were used in the investigations. The study concluded that the application of substantially different preparation methods resulted in the formation of materials of very similar properties. However, on the other hand, there are reports pointing, that the method of preparation of the silver ion conducting glasses influences the properties of the final product. Mustarelli, Konidakis and Novita studied properties of the amorphous silver metaphosphate ($AgPO_3$) prepared by MQ method, using constituents of various wetness and considering other process parameters [9–11]. They observed the significant differences of a glass transition temperature T_g among the investigated materials and related those to the modifications of the glass structure by implemented water molecules; namely formation of short $(PO_4)_n$ chains and rings at the expense of the long chains. Although a direct comparison of Refs. [8] and [11] leads to ambiguous or even opposite conclusions, one should take into account the fundamental differences of the glass structure between these two materials. Whereas, in the $50AgI–30Ag_2O–20V_2O_5$ glass short $(VO_4)_n$ chains dominate, the $AgPO_3$ glass structure consists of long, almost infinite $(PO_4)_n$ chains, when the material is prepared at a very dry environment [11]. Therefore in fact, the comparison suggests that the glasses which structure is composed of long chains of $(MeO_4)_n$ tetrahedrons should be more susceptible for structural modifications than those with the short ones. Moreover, one could expect that not only the level of wetness of the starting materials is responsible for these modifications but also the way in which a final glass is formed.

The work aims to give more experimental evidences supporting that hypothesis with respect to preparation routes. It presents the case of the materials formed within the $AgI–Ag_2O–P_2O_5$, $[Ag_2O/P_2O_5] = 1$ glass system which were synthesized in various ways. Generally three groups of the materials are studied: i) prepared by high temperature method (MQ), ii) prepared by low temperature method, i.e., mechanosynthesis

---

* Corresponding author.
E-mail address: grabowski@if.pw.edu.pl (P. Grabowski).

http://dx.doi.org/10.1016/j.jnoncrysol.2015.01.018
0022-3093/

(MS) and iii) those formed first by the MQ and then ball-milled (MQ + MS). All technology operations were executed in an open air without any special precautions against moisture. Such approach was adopted to provide the same wetness conditions during preparation and to expose the role of the used methods themselves.

It is worthy to add that, according to our knowledge, the materials of the AgI–Ag_2O–P_2O_5, $[Ag_2O/P_2O_5] = 1$ system prepared by mechanosynthesis were not presented in the literature.

2. Experimental

Investigated materials were formed in high (MQ) and/or low temperature processes (MS). The high temperature synthesis was applied for preparation of both: amorphous $AgPO_3$ (material labeled as A_{MQ}) and AgI–$AgPO_3$ glasses. The former material was synthesized from $NH_4H_2PO_4$ and $AgNO_3$ substrates. The AgI–$AgPO_3$ glasses were prepared using AgI, $NH_4H_2PO_4$ and $AgNO_3$ reagents (B_{MQ} sample) or AgI and the amorphous $AgPO_3$ prepared earlier — C_{MQ} material. The next steps of the preparation procedure were the same for all MQ materials. The starting materials taken directly from the commercially packed containers, after weighting, were mixed in appropriate molar proportions and ground with a mortar and a pestle. The reagents were not pre-heated or specially dried. All operations were executed on laboratory benches in an open air without any special precautions against moisture.

The melting of the substrates was carried out in an open vertical furnace and it consisted of three stages. First, the batch was annealed from room temperature to about 300 °C and kept until the ingredients melted and volatile products of the first stage of synthesis were released to the atmosphere. Then, the temperature was raised up to about 750 °C. During this annealing some weak bubbling of the melt was still observed, indicating that the synthesis process was still in progress. After the bubbling had stopped, which marked the completion of the synthesis, the melt was additionally annealed for 15–20 min and then it was poured out between two stainless steel plates and quickly quenched. As a result 0.5–0.9 mm thick glassy plates were formed.

The low temperature syntheses were carried out by means of *Fritsch Pulverisette P7* planetary ball mill. The reagents were located in 45 ml Si_3N_4 vials. Three Si_3N_4 grinding balls were used and the total mass of the reagents in a vial was to keep the ball-to-powder mass ratio equal to 10:1. The mill operated at 600 rpm rotation speed for 6 h in a constant work mode.

Applying the procedures described above, the amorphous $AgPO_3$ and the materials of an overall formula $x \cdot AgI - (1 - x) \cdot AgPO_3$ for $x = 33, 40, 50, 55, 60, 66$ and 80 were prepared. To distinguish materials of the same overall formula but prepared by different methods, the given labels will be used. Table 1 presents the list of the materials, labels and selected preparation details.

The as-received materials were examined by means of X-ray powder diffraction (XRD) employing *Phillips X'Pert Pro* diffractometer set up in a Bragg–Brentano configuration with filtered Cu Kα radiation. High temperature X-ray measurements (HT XRD) were carried out with assistance of an *Anton Paar* oven. Thermal properties were investigated by means of modulated differential scanning calorimetry method (MDSC) using *Thermal Analysis TA Q2000* calorimeter. The device operated in a heat-flow mode within a temperature range from 0 °C to 220 °C. Modulated component of temperature oscillated with 1 °C amplitude and 3 °C period. For Raman measurements, samples were characterized by the *Renishaw InVia System*, using 633 nm circularly polarized laser: the power was adjusted to avoid heating of the samples.

The error values provided for the measured quantities were determined according to the manufacturer's guide of the *TA Q2000* and *Renishaw InVia System* including the random errors measured as the standard deviation of the average value of determined quantities relevant to the: glass transition temperature determination onset points; enthalpy integration area bounded by inflection points of heat flow signal; scattering strength ratios of Raman modes as related to the integrated area; and modes' detectability.

3. Results

3.1. XRD

The room temperature XRD investigations of the D_{MS} materials ($x \cdot AgI - (1 - x) \cdot AgPO_3$, $x = 33, 40, 50, 55, 60, 66, 80$) revealed, that the materials $x < 55$ were entirely amorphous, whereas for $x \geq 55$, the final products contained, apart from the amorphous phase, a crystalline one, identified as the β/γ-AgI (Fig. 1). A similar dependence between a phase composition and an overall concentration of silver iodide added to the material has been reported in the literature for the $x \cdot AgI - (1 - x) \cdot AgPO_3$ glasses obtained by the MQ method [1,2]. Therefore, results of our room temperature XRD investigations, confronted with the literature data did not indicate any substantial differences between the materials prepared by the low and high temperature methods.

For further, more detailed study, to search for the plausible differences among the materials synthesized by various routes, the glasses of the 50AgI–$25Ag_2O$–$25P_2O_5$ overall chemical composition were selected. These materials (B_{MQ}, B_{MQ+MS}, C_{MQ}, C_{MQ+MS} and D_{MS}) were prepared by low or high temperature processes and combination of the both procedures, as the labels indicate. All of them were entirely amorphous, without presence of any crystalline phases, despite, for related samples, "dissolving" high amounts of AgI in the $AgPO_3$ matrix.

The HT XRD investigations performed in a 25–200 °C temperature range for the materials from the A, B and C groups revealed no diffraction peaks on the patterns both during heating and cooling runs. A different observation was recorded for the D_{MS} material — Fig. 2 collects the relevant XRD patterns. During heating, when temperature did not exceed 80 °C, the material was amorphous, as the X-ray patterns indicated. Above, near 85 °C weak intensities attributed to the γ-AgI crystalline phase were recorded. At about 125 °C they were accompanied by the lines of the β-AgI phase. At the temperature of 140 °C, the β/γ-AgI crystalline precipitates transformed to the α-AgI phase. During cooling at 90 °C the γ-AgI lines reappeared again.

The recorded temperature of phase transition is slightly lower than the one with characteristic of pure AgI which, in normal conditions for pure AgI, occurs at 147 °C [12]. The high temperature α-AgI phase is a superionic material exhibiting high conductivity: 1.3 S/cm. This value,

Table 1

Composition, starting materials, preparation method, glass transition temperature (T_g), R_c and R_r modes and $(\Delta H)_{exo}$ and $(\Delta H)_{nr}$ enthalpies of investigated A–D materials. The N/A stands for "not applicable", MQ for "melt-quenching" and MQ + MS for "melt-quenching and mechanosynthesis".

Label	Composition	Starting materials	Preparation method	T_g/°C	R_c	R_r	$(\Delta H)_{exo}$/J/g	$(\Delta H)_{nr}$/J/g
A_{MQ}	$AgPO_3$	$NH_4H_2PO_4$, $AgNO_3$	MQ	177 (2)	1.23 (2)	N/A	0.14 (3)	0.76 (3)
A_{MQ+MS}	$AgPO_3$	$NH_4H_2PO_4$, $AgNO_3$	MQ + MS	153 (2)	1.77 (2)	6.7 (1)	0.12 (3)	0.61 (3)
B_{MQ}	50AgI–50$AgPO_3$	AgI, $AgPO_3$	MQ	88 (2)	1.75 (2)	N/A	0.55 (3)	0.33 (3)
B_{MQ+MS}	50AgI–50$AgPO_3$	AgI, $AgPO_3$	MQ + MS	85 (2)	1.83 (2)	6.3 (1)	0.41 (3)	0.13 (3)
C_{MQ}	50AgI–25Ag_2O–25P_2O_5	AgI, $NH_4H_2PO_4$, $AgNO_3$	MQ	88 (2)	1.75 (2)	N/A	0.55 (3)	0.33 (3)
C_{MQ+MS}	50AgI–25Ag_2O–25P_2O_5	AgI, $NH_4H_2PO_4$, $AgNO_3$	MQ + MS	85 (2)	1.83 (2)	6.3 (1)	0.41 (3)	0.13 (3)
D_{MS}	50AgI–50$AgPO_3$	AgI, $AgPO_3$	MS	75 (2)	1.90 (2)	1.8 (1)	0.30 (3)	0.24 (3)