Journal of Non-Crystalline Solids 408 (2015) 66–70

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

Extension of α-AgI stabilization range in AgI–Ag_2O–M_xO_y systems by mechanosynthesis processing

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ARTICLE INFO

Article history:
Received 18 August 2014
Received in revised form 13 October 2014
Accepted 19 October 2014
Available online xxxx

Keywords:
α-AgI;
Stabilization range;
Mechanosynthesis;
Glasses;
Grain size

ABSTRACT

The ultra-fast quenching method and mechanosynthesis processing were employed to prepare the AgI–Ag_2O–M_xO_y glasses (where M_xO_y = B_2O_3, WO_3, MoO_3, V_2O_5) containing AgI crystalline inclusions. After heating in elevated temperatures the α-AgI superionic phase was formed: regarding the composition and preparation method its stabilization to lower temperatures was investigated. X-ray diffraction, differential scanning calorimetry and scanning electron microscope methods were used. The study showed that employment of both methods outrivals the solely applied ultra-fast quenching or mechanosynthesis methods, giving the final product with a wider α-AgI stability range.

1. Introduction

The alpha silver iodide phase is one of the best superionic conductors, therefore it has been a subject to various studies. Unfortunately the structure of the material is stable above 147 °C at normal thermodynamic conditions [1,2]. There were many attempts to stabilize the phase to lower temperatures. Tatsumisago et al. in the seminal paper [3–7] reported the formation of the α-AgI grains to be stable at room temperature, embedded in rapidly quenched superionic glasses. Guo et al. crystallized 50 nm thick AgI nanoplates, for which α-AgI to β/γ-AgI phase transition temperature T_{ph} occurred at 95 °C [8]. The work of Liang et al. describes AgI nanowires grown electrochemically in a porous alumina template: recorded T_{ph} for such prepared materials occurred at 80 °C [9]. However, the most significant decrease of T_{ph} down to nearly room temperatures was reported by Makiura et al. for size-controlled AgI grains coated with *poly-N-vinyl-2-pyrrolidone* (PVP) [10].

In our previous paper [11] we showed, that there was a possibility to stabilize to lower temperatures the α-AgI phase by means of mechanosynthesis method (MS). Milling a mixture of AgI, Ag_2O and B_2O_3 powders resulted in the formation of a material in which the α-AgI phase was stable at some temperature T_{ph} lower than 147 °C. The temperature difference $\Delta T = 147\ ^\circ C - T_{ph}$ was directly related to the milling parameters. Investigations indicated that ΔT was, in fact, a function of a size of AgI grains constituting the material, following the general relation: the smaller the grain the lower the temperature of the α-AgI → β-AgI phase transition. The lowest recorded temperature, 87 °C, was achieved for high energy milling at a rotation speed of 1000 rpm, the maximal available for *Fritsch Pulverisette Premium Line* mill. Thus, in our efforts to decrease transition temperature in the way of milling we found a technical obstacle.

To overcome the problem, we introduced an idea to assist the milling with another process in order to enhance the effectiveness of granulation of the AgI grains. The attention was turned to the ultra-fast quenching method (UFQ) [3,4,12]. We were aware that this process itself, when applied to the glasses with a high silver iodide contents, might lead to the formation of the α-AgI phase stable even at room temperature. But the essence of our goal was to demonstrate that such assisted milling is possible and workable. Then combination of UFQ and subsequent MS methods (UFQ + MS) was applied to the mixture of AgI, Ag_2O and B_2O_3 compounds. High temperature X-ray based investigation revealed that the AgI phase present in a final material exhibits T_{ph} at about 70 °C. In this paper we study in detail, the impact of the UFQ + MS method on T_{ph} of AgI–Ag_2O–M_xO_y (where M_xO_y is a glass former oxide) including additional MoO_3, WO_3 and V_2O_5 glass forming oxides. Differential scanning calorimetry (DSC) method supported by scanning electron microscopy (SEM) analysis was principally used.

2. Experimental

The AgI, $AgNO_3$ and M_xO_y (where M_xO_y = B_2O_3, WO_3, MoO_3, V_2O_5) compounds of 7 g total mass were taken with appropriate molar proportion: 78AgI–22($Ag_2O \cdot M_xO_y$). The ratio of the glass matrix regarded the glass former and was fixed at 3:1, 2:1 and 1:1 for B_2O_3, MoO_3 and

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http://dx.doi.org/10.1016/j.jnoncrysol.2014.10.017
0022-3093/

WO_3 or V_2O_5 respectively [3,13,14]. Grounded mixtures were loaded into a crucible and then located in a vertical furnace at 350 °C. The reagents melted releasing some vapor byproducts. Thereafter, when the process of decomposition had ended, the temperature was raised up to 800 °C and the melt was annealed for 20 min. Then, the melt was rapidly quenched between stainless steel twin-rollers rotating at the speed of 900 rpm. The flake-like samples were formed.

Mechanosynthesis process was performed employing *Fritsch Pulverisette Premium Line* planetary ball mill. The obtained flakes, 0.75 g mass for each material, were located inside tungsten carbide vials filled with tungsten carbide balls, 1 mm in diameter each. Ball-to-powder ratio of 15:1 was kept fixed for all MS processes. The mill operated at a constant 1000 rpm rotation speed for 0.5 h or 1 h. After processing a powder product was formed.

The obtained materials were investigated by X-ray diffraction (XRD), DSC and SEM methods. *Phillips X'Pert Pro* diffractometer with filtered Cu Kα radiation set in a Bragg–Brentano configuration was used for the XRD measurements. High temperature XRD was carried out with the assistance of *Anton Paar 1200* X-ray oven. The average size of silver iodide grains was estimated by Scherrer method [15]. The DSC investigations were performed with the help of a *TA Instruments Q200* microcalorimeter. The samples were heated and cooled at a rate of 10 °C/min within 20–170 °C. SEM images were recorded by *Nova NanoSEM D9983* scanning electron microscope. The standard deviation value was used as a measurement of uncertainty in the grain size estimations.

3. Results

3.1. XRD

The XRD investigations revealed, for the B_2O_3 and MoO_3 based materials obtained by the UFQ method, diffraction peaks characteristic for β/γ- and α-AgI phases. In the case of the WO_3 and V_2O_5 based materials, only the lines ascribed to β/γ-AgI were detected. For all the materials prepared by UFQ + MS method the X-ray patterns show only lines attributed to the β/γ-AgI phase: there were no lines characteristic for the α-AgI even for the B_2O_3 and MoO_3 materials, which had exhibited these peaks previously, i.e. after the UFQ processing. Fig. 1 shows the exemplary X-ray patterns of the UFQ B_2O_3 and WO_3 materials — before and after MS processing.

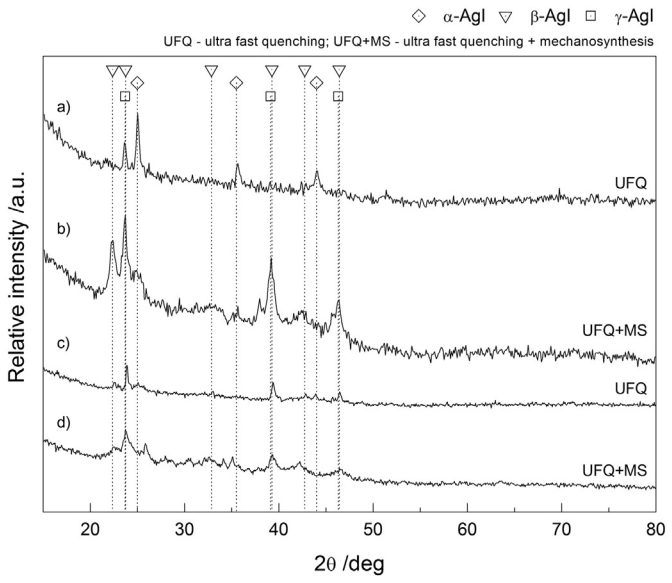

Fig. 1. X-ray powder patterns of the B_2O_3 based material prepared by a) UFQ; b) UFQ + MS; WO_3 based material prepared by c) UFQ and d) UFQ + MS.

The results of the high temperature XRD investigations are visualized in Fig. 2, where the example of the B_2O_3 material is shown. Starting from the bottom of Fig. 2, the recorded X-ray patterns are ordered with increasing temperature up to 180 °C and then with decreasing temperature down to 40 °C. The positions of the strongest β/γ-AgI lines are marked by the full circles, whereas the full triangles point the diffraction lines ascribed to α-AgI. One can notice, that during heating, in the 85–120 °C range, some β/γ-AgI peaks become stronger. Above 130 °C, the peaks characteristic for the α-AgI phase are visible on the pattern. They disappear below 65 °C.

3.2. DSC

Thermal properties of the studied materials were determined by DSC method. Results of the investigations were divided into two subgroups in respect to α-AgI occurrence in UFQ materials: a) B_2O_3, MoO_3 based materials containing α-AgI and b) materials formed with WO_3, V_2O_5 comprising only low temperature phases — β/γ-AgI. The results of DSC investigations for selected materials from each group are presented in Fig. 4.

3.2.1. B_2O_3 and MoO_3

On a DSC trace recorded for the heating run for the as-prepared UFQ B_2O_3 or MoO_3 based materials (solid lines in Fig. 4a) and b)), the following processes are visible: a weak endothermic process in 50–70 °C range, a broad, weak exothermic reaction occurring in the range 70–120 °C and a strong endothermic one peaking around 150 °C. During cooling, for the MoO_3 material only a single exothermic peak at 129 °C was detected; for the B_2O_3 material the exothermic events were split

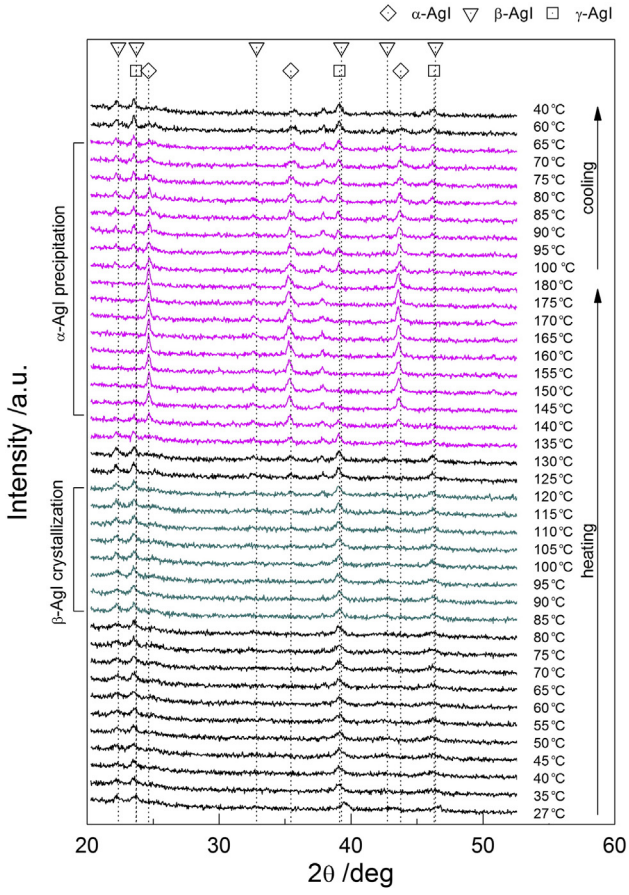

Fig. 2. High temperature X-ray powder patterns of the B_2O_3 based material formed by means of UFQ + MS method.