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Mechanosynthesized and ultra-fast quenched AgI–Ag_2O–B_2O_3 materials with high AgI contents

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ABSTRACT

The 78AgI, 16.5Ag_2O, and 5.5B_2O_3 mol% powder mixture, ultra-fast quenched 78AgI-16.5Ag_2O-5.5B_2O_3 glass containing α-AgI crystalline precipitates and pristine AgI were ball-milled at a high rotation speed. For all the materials, the processing did not cause formation of α-AgI phase, in contrary, it prompted α to β phase transition of the α-AgI precipitates in the glass. Nanosize scale β/γ-AgI grains were detected both in the milled powder mixture and in the glass but not in the pristine AgI powder.

The decrease of α to β phase transition temperature was observed for the milled materials during cooling from 170 °C, ca. 10 °C, 60 °C and 75 °C respectively for the AgI powder, the powder mixture and the glass. Stabilization of the α-AgI to low temperatures was related to the nanosize scale β/γ-AgI grains. The work demonstrates, that although it is not possible to stabilize α-AgI in pure silver iodide powder by ball-milling, nevertheless it is achievable for mixtures with high AgI contents.

1. Introduction

Silver ion conducting solid electrolytes has been considered as an active component of electrochemical devices [1,2]. Although, high material cost and low power density discourage to employ these materials in high power batteries but very high Ag^+ mobility and its polarizability make these superconductors attractive for application in micro-, nanobatteries or electrochemical sensors. Among many known Ag^+ conducting materials, silver iodide distinguishes oneself due to very high ion conductivity of its body-centered cubic structure phase known as α-AgI. Unfortunately under normal thermodynamic conditions this phase is stable above 147 °C, whereas below it transforms to the wurtzite type structure phase (β-AgI) or to the mixture of wurtzite and zinc blend phases (β/γ-AgI), which is a very poor ion conductor [3–5]. Therefore, there are many attempts to stabilize the α-AgI phase in low temperature and simultaneously to fabricate materials containing this phase, suitable for practical purposes. Devising of a proper route, i.e. a method and a procedure, is the key question of the problem.

In the work, we turn attention to mechanosynthesis method (MS), noticing its potential in preparation of the new materials [6,7]. Also some literature reports indicated that ball-milling could produce materials containing stable α-AgI below 147 °C [8]. A mixture of 78AgI, 16.5Ag_2O, and 5.5B_2O_3 mol% powders and pristine AgI were selected as the starting materials. As our and other earlier works shown [9–11], the α-AgI phase grains stable at room temperature, could exist embedded in the 78AgI-16.5Ag_2O-5.5B_2O_3 glass. Investigations aimed to examine, if in result of milling the alpha phase could be formed in the mixture of powders and whether the same processing applied for the pristine AgI could transform its low temperature crystal structure to body-centered cubic one. Milling was carried out applying almost the highest rotation speeds available by the used mill to provide as high as possible energy transfer from balls to the milled material.

2. Experimental

Mechanosynthesis processes were carried by means of Fritsch Pulverisette premium line planetary ball mill. Stoichiometric amount of AgI, Ag_2O and B_2O_3 reagents of 78AgI, 16.5Ag_2O, and 5.5B_2O_3 mol% overall 1.5 g mass composition was initially grounded with a mortar and a pestle. Then, the mixture was located in 20 ml WC (tungsten carbide) vials with 14 balls, 5 mm in diameter each. No control agent was added to the vials. The planetary mill operated at 1000 rpm rotation speed in a constant mode for various, fixed time — starting from 0.5 h up to 6 h. Materials obtained by ultra-fast quenching method were prepared in the following procedures: first the AgI, $AgNO_3$ and B_2O_3 substrates of 78(AgI):33(Ag_2O):5.5(B_2O_3) molar ratio were mixed with a mortar and a pestle. The mixture placed in a ceramic crucible was located in a vertical furnace. After evaporation of volatile byproducts, temperature was increased up to 800 °C and the melt was annealed for 20 min. Then, the crucible was quickly moved to the zone, which operated at about 420 °C and kept there for an additional 20 min. In the final stage, the melted material was rapidly poured out on two stainless steel rollers rotating at the speed 900 rpm. The rollers

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were additionally cooled by liquid nitrogen. Flake-like glassy samples were formed. They were carefully grounded in liquid nitrogen with a mortar and pestle when prepared for further investigations.

X-ray powder diffraction (XRD) patterns for all components and obtained materials were collected using a Phillips X'Pert Pro diffractometer with filtered Cu Kα radiation set in a Bragg–Brentano configuration. High temperature X-ray investigations were carried out with assistance of Anton Paar X-ray oven.

3. Results and discussion

Fig. 1 presents the X-ray patterns collected for the 78AgI, 16.5Ag_2O, and 5.5B_2O_3 mol% mixture after application of the MS method for various milling time. On the X-ray patterns for the unprocessed mixture, the β-AgI and traces of γ-AgI peaks accompanied by the line characteristic for Ag_2O (111) and (200), and also B_2O_3 (310) are visible (Fig. 1a). After 0.5 h of milling, the Ag_2O and B_2O_3 lines disappear, whereas those attributed to beta silver iodide structure transform to reflections assigned to γ-AgI phase. Only a weak 22.36° (100) β-AgI peak one can observe (Fig. 1b). The extension of the milling time to 6 h resulted in decreasing intensity of (100) β-AgI and (111), (220), (311) lines related to γ-AgI. Simultaneously the new line appears, which is attributed to silver metal (Fig. 1c and 2). Rough estimation of a grain size in these materials, based on Scherrer formula [12], gives values 25–35 nm.

Analysis of the XRD patterns for the as-received 78AgI-16.5Ag_2O-5.5B_2O_3 glassy material reveals, apart from a glass phase, the presence of the lines assigned to α-AgI and β/γ-AgI phases (Fig. 1d). The shape of a pattern changes after milling. Even short processing (0.5 h) caused disappearance of the alpha-phase lines indicating its destruction. Simultaneously, the increase of intensity of the X-ray peaks related to the β-AgI structure is observed. Some weak peaks attributed to WC compound and also to metallic silver are detected for the product after 6 h of milling. Estimated average AgI grain size is about 20–25 nm.

The XRD investigations show, that milling of the AgI component alone, i.e. a pristine AgI powder, prompts transformations of a crystal structure of this compound, depending on the process duration. The AgI powder used in the investigation is a mixture of β/γ phases. After 0.5 h of milling, the strong lines assigned to the γ-AgI phase and very weak (100) reflection of β-AgI are observed (Fig. 3a), similarly like for the milled 78AgI, 16.5Ag_2O, and 5.5B_2O_3 mol% mixture. Longer, 6 h milling, produces the material which X-ray diffraction profile is almost identical with the profile of an unprocessed AgI

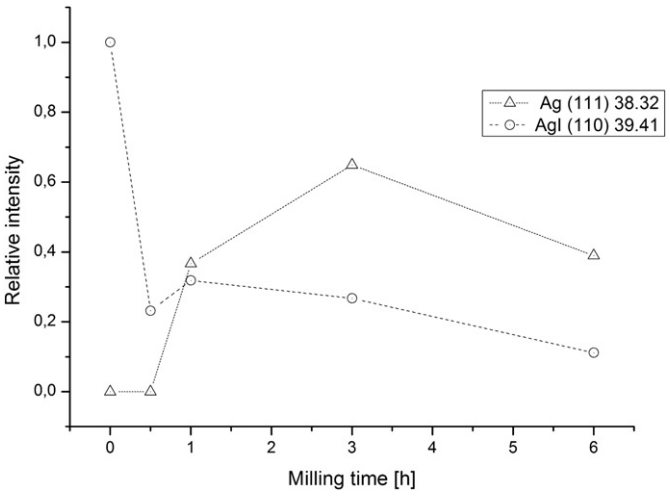

Fig. 2. The relative intensity of X-ray reflection at 2θ 39.41 ° ((110) β-AgI) (○) and 38.32 ° ((111) Ag) vs. milling time (Δ).

powder (Fig. 3b). Inspection of the XRD patterns shows no lines attributed to elemental Ag. Some low intensity reflections related to WC, the compound of which milling vials are made off, are visible. Also no significant broadening of the line width is detected.

With the results of the X-ray investigations one could explain that during ball-milling some specific processes take place in the milled materials: some chemical reactions in both the 78AgI, 16.5Ag_2O, and 5.5B_2O_3 mol% powder mixture and the 78AgI-16.5Ag_2O-5.5B_2O_3 glass, whereas phase transitions take place in the AgI powder. Disappearing of Ag_2O and B_2O_3 lines with simultaneous decrease of the peak intensity for AgI reflections, observed during initial stages of milling of the powder mixture, suggests consumption of the components. Because, for this stage, there is no experimental evidence indicating chemical decomposition, then, we adopted that the substrates should participate in some synthesis which fabricated some new amorphous phase or phases. So, consequently after the first stage, the processed material consists of the amorphous phase and unreacted silver iodide. Precipitation of metallic silver occurring during longer milling suggests subsequent reaction-decomposition. As our investigation shows, AgI is chemically stable against even high energy milling. Therefore one can assume, that crystalline AgI present in the powder mixture is also stable and in

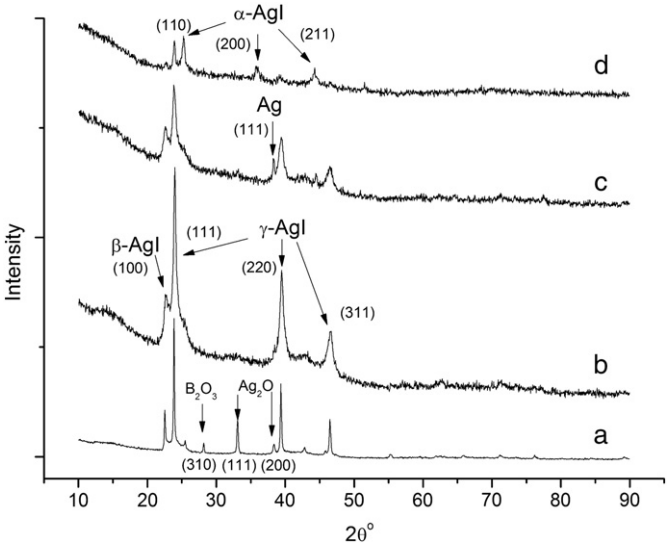

Fig. 1. X-ray powder patterns of the 78AgI–16.5Ag_2O–5.5B_2O_3 mol% mixture: a) as-mixed; b) after ball-milling, applying 1000 rpm rotation speed for 0.5 h and c) after 6 h of milling; d) after ultra-fast quenching.

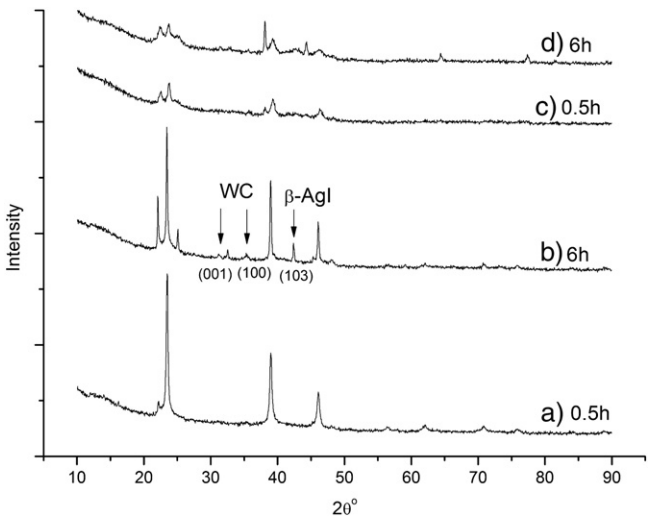

Fig. 3. XRD patterns of the materials milled at 1000 rpm rotation speed for: a) pristine AgI after 0.5 h, b) pristine AgI after 6 h, c) 78AgI–16.5Ag_2O–5.5B_2O_3 glass after 0.5 h, and d) 78AgI–16.5Ag_2O–5.5B_2O_3 glass after 6 h.