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Alpha silver iodide stabilization in mechanosynthesized AgI-Ag₂O-M_xO_y systems

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Abstract

The work presents materials formed by means of mechanosynthesis in AgI-Ag₂O-M_xO_y systems supportive to α -AgI stabilization to lower temperatures. Employed ball-milling technique allowed to easily control the synthesis process by variation of milling parameters. Stabilization of α -AgI was investigated in respect to preparation method and origin of AgI grain. As demonstrated, the stable temperature range of superionic phase depends on: silver iodide content, metal oxide chemical composition and synthesis method. We found the largest α -AgI \rightarrow β -AgI transition temperature decrease for AgI-Ag₂O-TiO₂ systems. The results demonstrate, that the temperature shift is in a correlation with Ag₂O amount; for small amounts of Ag₂O the α -AgI was stable to nearly room temperatures.

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1. Introduction

Among various silver ion conducting materials the alpha silver iodide phase (α -AgI) is one of the finest superionic conductors, and therefore has been a subject to numerous studies. At normal thermodynamic conditions the structure of the material is stable above 147 °C [1]. Therefore there were many efforts to stabilize the material to room temperatures, or to shift the phase transition temperature to lower values. In the seminal paper [2] Tatsumisago *et al.* reported formation of the α -AgI grains, stable at room temperature; the superionic phase was embedded in molybdate or borate superionic glasses prepared by means of rapid quenching. However, such obtained α -AgI grains

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are quasi-stable and after mechanical treatment (grinding, powdering or ball-milling) the phase transforms into low temperature β -AgI phase. Other attempts regarded lowering the phase transition temperature rather than stabilization of separate grains. For this purpose most works aimed forming of accurate AgI grain structures: 50 nm thick AgI nanoplates, crystallized by Guo *et al.* [3], for which α -AgI \rightarrow β -AgI/ γ -AgI phase transition temperature occurred at 95 °C; AgI nanowires grown electrochemically in a porous alumina template described Liang *et al.* with transition temperature T_{ph} about 80 °C [4]; and – the most significant decrease of T_{ph} to nearly room temperatures – size-controlled AgI grains coated with poly-N-vinyl-2-pyrrolidone (PVP) reported by Makiura *et al.* [5]. Possible evolvments routes towards stabilization of α -AgI, point to formation of material containing fine AgI grains: depending on the size of the silver iodide grain, the shift of temperature transition T_{ph} may be altered.

In this work we present materials supportive to stabilization of α -AgI formed in ternary AgI-Ag₂O-M_xO_y systems by means of ball-milling. The process is also termed as mechanosynthesis: By cause of energy transfer in high energy collisions with grinding balls, reaction of substrates chemically react and synthesize. [6, 7]. Mechanosynthesis is carried by employment of typical laboratory ball mills, thus the process may be easily controlled by varying of milling parameters [8]. The range of process variables include: milling speed, milling time, total mass of substrates (also represented as BTP ball-to-powder mass ratio [6, 8]), presence of control agent (e.g. acetone), continuity of the process, or type of employed mill. Hence, a properly adopted methodology of mechanosynthesis allows forming prototyped materials. Presented work discusses formation of heterogeneous materials containing AgI precipitates and possible stabilization range of α -AgI in regards to the preparation method and the phase composition.

2. Experimental

Mechanosynthesis of the AgI-Ag₂O-M_xO_y materials, with M_xO_y = B₂O₃, TiO₂, P₂O₅, was carried out using Fritsch Pulverisette 7 (P7) planetary ball mill. The mill operated at 600 rpm in a constant process mode. The time of milling was specified for each sample separately. The P7 mill is suitable for 45 ml Si₃N₄ vials along with 10 mm diameter grinding balls. Overall mass of synthesized substrates or ball-milled material accounted to 1.5g. The obtained products were investigated by X-ray diffraction (XRD), differential scanning calorimetry (DSC) and impedance spectroscopy (IS) methods. Phillips X'Pert Pro diffractometer with filtered Cu K α radiation set in a Bragg–Brentano configuration was used for the XRD measurements. High temperature XRD were carried out with assistance of Anton Paar 1200 X-ray oven. The DSC investigations were performed by helps of Thermal Analysis Q200 microcalorimeter. The samples were heated and cooled with the rate of 10 °C/min within 20-220 °C. Impedance spectroscopy measurements were carried out by Solartron 1260 impedance analyzer in 20-220 °C temperature range.

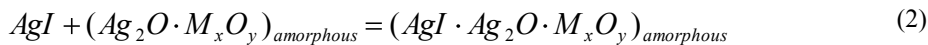
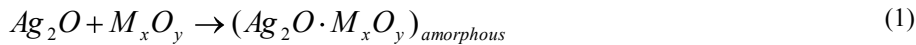
3. Results and discussion

The results section is divided in relation to the α -AgI embedding material phase. Individual route of investigation was essential for each material: parallel selection of XRD, DSC and IS methods was adopted.

3.1. Heterogeneously synthesized systems

Ball-milling of pure AgI, Ag₂O and M_xO_y reagents, (where M_xO_y = B₂O₃, WO₃, V₂O₅, P₂O₅ etc.) under certain conditions, leads to a synthesis of the substrates [9]. The occurrence of synthesis and phase composition of synthesized product depends on milling parameters and amount of substrates, forming accordingly homogeneous or heterogeneous structure.

The mechanosynthesis of reagents is modelled in two stages [10, 11]. In the first stage, a glass former and a glass modifier react together forming an interim product – usually amorphous. In the next step, silver iodide dissolves in the amorphous Ag₂O-M_xO_y matrix [12]. The occurring reaction may be described in two steps:



The uniformity of a synthesized sample depends on the molar composition of starting products: excess amounts of substrates remain unreacted during the synthesis forming crystalline products adjacent to amorphous phase. Thus, through exceeding the amount of AgI solubility defined for each system, it is possible to fabricate an amorphous structure with crystalline AgI inclusions.

Matching concept was originally adopted by Tatsumisago *et al.* for preparation of ultra-fast quenched AgI-Ag₂O-B₂O₃ materials obtained by means of steel twin rollers. The technique allowed to form a quasi-stable α -AgI crystalline originating in surplus amounts of AgI embedded in glassy matrix [2, 13, 14].

Fig. 1 shows the X-ray patterns for 78AgI-16.5Ag₂O-5.5B₂O₃ materials exposed to the process of ball-milling. The patterns given on Fig. 1 a) and Fig. 1 b) present the structure of materials obtained in mechanosynthesis of pure reagents: AgI, Ag₂O and B₂O₃ milled for 0.5 h and 6 h respectively. Patterns on Fig. 1 c) and Fig. 1 d) present the structure of a 78AgI-16.5Ag₂O-5.5B₂O₃ glasses primarily formed by means of ultra-fast quenching and subsequently exposed to ball-milling for: 0.5 h (c) and 6 h (d)). For all samples, peaks attributed to β -AgI and crystalline Ag appear. The intensity of the latter one significantly increases for the materials synthesized in prolonged processes. Taking into account, that crystalline AgI is chemically stable even against high energy milling, one must assume that Ag precipitates are products of decomposition of newly formed amorphous phase.

The transition temperatures of the embedded in the materials AgI grains were estimated by means of high temperature XRD investigations. As observed for all samples – during the heating process – the present β -AgI phase transforms into the α -AgI above ca. 140 °C. Then, after short annealing at 170 °C, the material was progressively cooled down to room temperature. On the cooling process, the α -AgI \rightarrow β -AgI phase transition occurred at various temperatures in regards to the sample preparation route (Table 1). The phase transition temperatures are higher for mechanosynthesized mixtures of starting powders (90 °C and 85 °C for 0.5h and 6h milling respectively) than for ball milled glasses (70 °C and 65 °C for 0.5h and 6h milling processes).

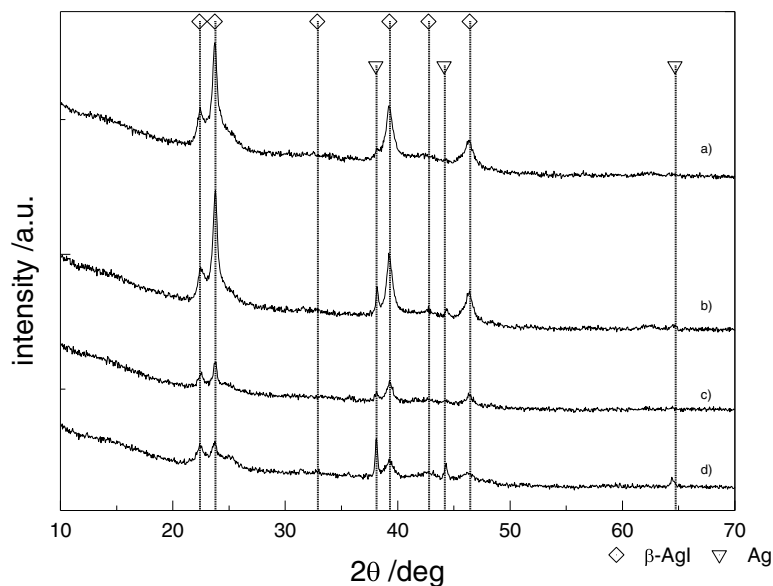


Fig. 1 XRD patterns AgI-Ag₂O-B₂O₃ system prepared by means of: mechanosynthesis (milling time a) 0.5h b) 6h) and ultra-fast quenching and subsequent mechanosynthesis (milling time c) 0.5h d) 6h)).

3.2. AgI glass crystallization

The second section concerns materials containing α -AgI inclusions formed as a result of crystallization occurring in a heated glass. The properties of 50AgI-25Ag₂O-25P₂O₅ system will be discussed. The values of substrates molar proportions situate the selected composition within a glass forming region for silver phosphate system [15]. Preparation procedure consisted of two steps: at first the host AgPO₃ glass was obtained by standard melt-quenching procedure, subsequently a synthesis of appropriate amount of AgI was performed by means of ball-milling. Such consecutive synthesis in literature is described as mechanoinsertion – the succeeding synthesis performed in room temperatures aims to interpose a crystalline substance into a host glass and to preserve the amorphous structure [16]. Resulting product of both syntheses was identified to be amorphous.

This methodology approach – unlike a standard melt quenching technique – allows to obtain a phosphate glasses characterized by low crystallization temperature; the crystallization of AgI in 50AgI-25Ag₂O-25P₂O₅ glass prepared in presented route occurs at 75 °C. The silver iodide crystallizes in low-temperature β -AgI phase, which is expected to transform, in elevated temperatures above 147 °C, to highly conducting α -AgI. Fig. 2. presents results of high temperature X-ray investigations of 50AgI-25Ag₂O-25P₂O₅ material collected during heating and cooling within a 20 - 240 °C temperature range. As presented, above 145 °C peaks ascribed to β -AgI phase decrease to the noise level, while the ones related to α -AgI appear simultaneously. Remarkably, while heating up to 160 °C the material becomes amorphous again; the α -AgI dissolves in the heated glass. The amorphous phase is present again on cooling process – a first peaks related to crystalline phases, namely β -AgI, appear at 110 °C. Closer inquiry on the α -AgI phase requires conductivity investigations of the material during both: heating and cooling processes.

Fig. 3 presents the ionic conductivity dependency. Below the 120 °C the activation energy of the 50AgI-25Ag₂O-25P₂O₅ material is equal $E_a = 0.33$ eV. In elevated temperatures the value of E_a decreases down to 0.16 eV. Despite the dissolvent of the crystalline phase, the conductivity value is constantly elevated in both states: crystalline and amorphous. As the temperature ranges, both the phase composition and activation energy level are uniform. Even on cooling process the value of activation en energy is constant. At 120 °C, when the β -AgI peaks appear, the E_a raises up to 0.38 eV. The correlation of impedance spectroscopy results with high temperature XRD analysis shows, that the stabilization of highly conducting AgI phase, in case of 50AgI-25Ag₂O-25P₂O₅ material may be sustained down to 120 °C.

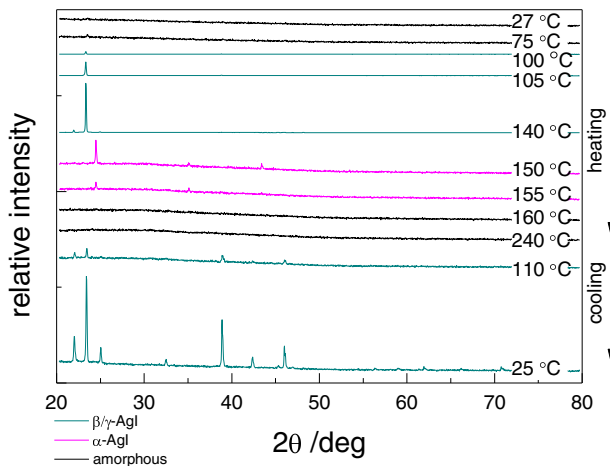


Fig. 2 XRD patterns of 50AgI-25Ag₂O-25P₂O₅ prepared by means of mechanoinsertion exposed to heating and cooling processes.

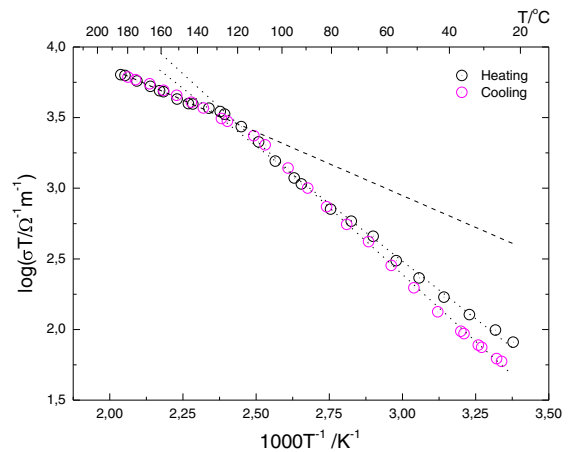


Fig. 3 Ionic conductivity of 50AgI-25Ag₂O-25P₂O₅ sample prepared by means of mechanoinsertion.

3.3. Composite AgI systems

Despite many composite AgI based systems were investigated to successfully decrease the α -AgI phase transition temperature [17 - 19], according to author's knowledge, there were no attempts to involve ternary AgI-Ag₂O-M_xO_y systems, typically used to form amorphous structures. Unlike discussed heterogeneous samples enclosing amorphous and crystalline phases, the composite structure must be formed with oxide that does not form a glass matrix within AgI-Ag₂O-M_xO_y system. The aim of approach for composite materials is to form a structure comprising small AgI grains modeled within the crystalline grains of metal oxide. Hence, the AgI-Ag₂O-TiO₂ system was selected for closer investigations. Preparation of the materials was performed by means of mechano-synthesis: pure reagents of AgI, Ag₂O and TiO₂ were ball-milled using 600 rpm rotation speed proceeded for 6 h.

Fig. 4 collects the patterns of 50AgI-(50-x)Ag₂O-xTiO₂ system for x=0; 5; 15; 25; 35; and 45 mol%. Resulting composite products were identified to be crystalline; lines of all starting substrates are present on recorded X-ray patterns. However, the intensity of X-ray peaks strongly correlates to the molar composition of the system, predominantly to the amount of Ag₂O network modifier. Noticeably, the composition with the lowest amount of silver oxide is characterized by the lowest peak intensity.

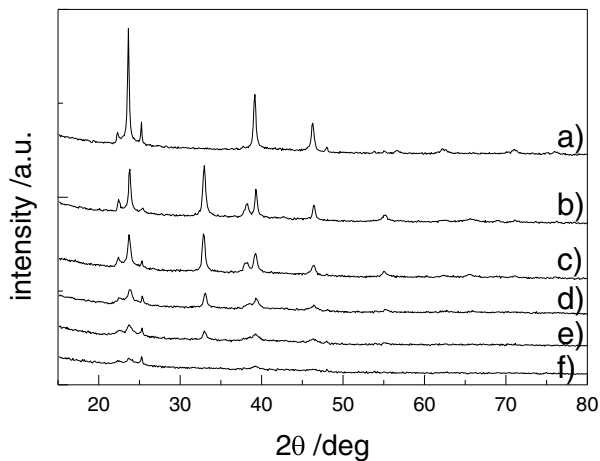


Fig. 4 XRD patterns of 50AgI-xAg₂O-(50-x)TiO₂ system where x = a) 0; b) 45; c) 35; d) 25; e) 15; f) 5.

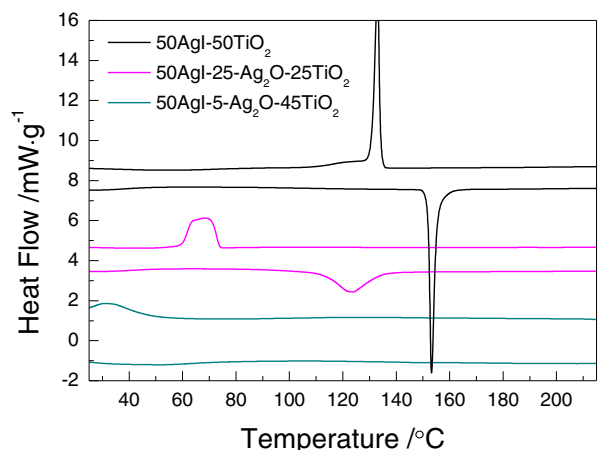


Fig. 5 DSC signals of selected materials formed in AgI-Ag₂O-TiO₂ system.

Due to low intensity of the peaks for samples with low amount of Ag₂O, for the verification of α -AgI phase existence and its transition temperatures both methods were employed: HTXRD and DSC. Correlation of HTXRD results with observed on DSC curves thermal events indicate, that the endothermic processes occurring on heating runs of DSC scans correspond to β -AgI \rightarrow α -AgI transition whereas the exothermic reactions present on cooling runs match the α -AgI \rightarrow β -AgI transition. Fig. 5 presents the DSC traces for selected samples with x = 0; 5 and 25 mol% of Ag₂O. The position of the exothermic peak on cooling runs varies as the amount of Ag₂O decreases. The transition temperature was hence estimated at the signal maximum temperature: detailed values of the phase transition temperatures are collected in Table 1 One can notice following dependence: the lower amount of Ag₂O is used in the system, the lower value of α -AgI \rightarrow β -AgI transition temperature was recorded. However, the absence of Ag₂O results in a shifting of the T_{ph} to 133 °C – slightly below the value for pure AgI.

Table 1. Detailed values of $\alpha \rightarrow \beta$ AgI phase transition temperatures of prepared materials.

No.	Formula	Preparation methodology (MS – mechanosynthesis)	$\alpha \rightarrow \beta$ AgI phase transition temperature (°C)
1.	78AgI-15.5Ag ₂ O-5.5B ₂ O ₃	MS 0.5 h	90
2.	78AgI-15.5Ag ₂ O-5.5B ₂ O ₃	MS 6 h	85
3.	78AgI-15.5Ag ₂ O-5.5B ₂ O ₃	Ultra-fast quenching + MS 0.5 h	70
4.	78AgI-15.5Ag ₂ O-5.5B ₂ O ₃	Ultra-fast quenching + MS 6 h	65
5.	50AgI-25Ag ₂ O-25P ₂ O ₅	Mechanoinsertion (6 h)	120
6.	50AgI-45Ag ₂ O-5TiO ₂	MS 6 h	97
7.	50AgI-35Ag ₂ O-15TiO ₂	MS 6 h	93
8.	50AgI-25Ag ₂ O-25TiO ₂	MS 6 h	61
9.	50AgI-15Ag ₂ O-35TiO ₂	MS 6 h	44
10.	50AgI-5Ag ₂ O-45TiO ₂	MS 6 h	30
11.	50AgI-50TiO ₂	MS 6 h	133

Presented methodologies of mechanosynthesized AgI-Ag₂O-M_xO_y systems lead to formation of materials composed of “embedding” phase (amorphous or crystalline) and separate AgI grains. The silver iodide grains originated from: exceeding amount of AgI above the solubility level in mechanosynthesized products; thermal crystallization of a glass; AgI-Ag₂O mixture coating TiO₂ crystals. As observed for all samples, after heating above 147 °C and subsequent cooling, the α -AgI crystallines were stable below the usual transition temperature.

4. Conclusions

We presented results of effective stabilization of α -AgI to lower temperatures for various AgI-Ag₂O-M_xO_y systems – differing in structure and composition. For all materials, and also in systems discussed in other literature reports, the stabilization of α -AgI originates as the AgI particles are present: nanoscale of AgI grains is necessary for stabilization of the alpha silver iodide to lower temperatures. One may conclude, that lowering of the T_{ph} is possible only in a range limited by accessible decrease of a grain size. However, as demonstrated, a companion of other foreign phases – whether amorphous or crystalline – also plays significantly supportive role for the stabilization range.

We demonstrated, that α -AgI stabilization to lower temperatures occurs in materials comprising AgI particles fabricated by means of ball-milling of AgI with a mixture of Ag₂O and M_xO_y powders. The α -AgI stabilization temperature range in AgI-Ag₂O-M_xO_y systems depends on silver iodide content, selected metal oxide and synthesis method. All fabrication routes adopted following methodology: formation of facilitating matrix – amorphous, heterogeneous or composite – enclosing AgI grains. We detected the largest transition temperature decrease for AgI-Ag₂O-TiO₂ systems with low Ag₂O amounts. Moreover, presented temperatures shifts are a consequence of an effective approach, pointing towards further stabilization possibilities within related composite materials.

Acknowledgements

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