

Short communication

# XRD, SEM, Raman and DSC characterization of the materials of the AgI–Ag<sub>2</sub>O–V<sub>2</sub>O<sub>5</sub> system prepared by mechanosynthesis

J.L. Nowinski<sup>a,\*</sup>, P. Pineda Vadillo<sup>a</sup>, J.E. Garbarczyk<sup>a</sup>,  
M. Wasiucionek<sup>a</sup>, G. Zukowska<sup>b</sup>, S. Gierlotka<sup>c</sup>

<sup>a</sup> Faculty of Physics, Warsaw University of Technology, Koszykowa 75, 00-662 Warsaw, Poland

<sup>b</sup> Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland

<sup>c</sup> Institute of High Pressure Physics, Polish Academy of Sciences, Sokolowska 29/37, 01-142 Warsaw, Poland

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## Abstract

Ion conducting materials of the AgI–Ag<sub>2</sub>O–V<sub>2</sub>O<sub>5</sub> system were prepared at room temperature via mechanosynthesis. Their crystallographic structure, microstructure, local dynamics and thermal properties were monitored by X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman spectroscopy and differential scanning calorimetry (DSC), respectively. It was found that the prolonged ball-milling of mixtures described by formulae: (i)  $x\text{AgI} \cdot 0.25(100 - x)(3\text{Ag}_2\text{O} \cdot \text{V}_2\text{O}_5)$ , for  $40 \leq x \leq 70$ , and (ii)  $x\text{AgI} \cdot 0.2(100 - x)(3\text{Ag}_2\text{O} \cdot 2\text{V}_2\text{O}_5)$ , for  $0 \leq x \leq 60$ , led to the formation of amorphous materials. DSC scans and Raman spectra indicate that the thermal events in the mechanosynthesized materials and their main constituting units are similar to those observed for the glasses of the same compositions, prepared by a standard melt-quenching technique. © 2007 Elsevier B.V. All rights reserved.

**Keywords:** Mechanosynthesis; Ball-milling; Silver vanadate materials; XRD; Ionic conductors; SEM

## 1. Introduction

Silver batteries or microbatteries can be attractive as power sources for some classes of portable electronic devices operating near room temperature, taking into account high Ag<sup>+</sup>-ion conductivity (up to  $10^{-2} \text{ S cm}^{-1}$  at 25 °C) of a range of solids, amorphous or crystalline, which may serve as electrolytes in such batteries [1–3]. One class of solid silver electrolytes encompasses glasses of the AgI–Ag<sub>2</sub>O–M<sub>x</sub>O<sub>y</sub> systems (where M<sub>x</sub>O<sub>y</sub> = V<sub>2</sub>O<sub>5</sub>, B<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>, CrO<sub>3</sub> or MoO<sub>3</sub>). Glasses of these systems are usually prepared via a standard melt-quenching method. Accelerated cooling of the mixtures molten at 500–900 °C down to room temperature enables retaining amorphous, liquid-like, structure in the resulting materials. On the other hand in recent years there have been published a couple of papers, reporting that there is an alternative way to synthesize ionically conducting amorphous materials entirely at room temperature. This can be achieved by a prolonged

high-energy ball-milling, also called mechanosynthesis [4–6]. The essence of the method, developed and explored mainly for metallic systems [7,8], consists in high-energy collisions of the particles of the starting reagents among themselves but also with balls (e.g. silicon nitride) of the ball-milling devices as well as with the walls of the container. All these collisions lead to a better mixing of the components, to produce finer grains and also promote chemical reactions between resulting fine particles. Mechanosynthesis has been found to be an effective method to produce a range of materials, which could not have been prepared via standard solid state high-temperature procedures, due to e.g. problems of thermal decomposition of some reagents and/or unwanted side reactions at high temperatures. A relevant example of the superiority of the mechanosynthesis over the melt-quenching method is the synthesis of AgI–Ag<sub>2</sub>O–M<sub>x</sub>O<sub>y</sub> glasses using a commercial silver oxide as a starting reagent. The problem with Ag<sub>2</sub>O as a reagent in the standard melt-quenching preparation lies in its thermal decomposition at above ca 200 °C. To avoid this problem one often uses selected silver salts, such as e.g. silver nitrate, as starting reagents instead of Ag<sub>2</sub>O, in the preparation of the AgI–Ag<sub>2</sub>O–M<sub>x</sub>O<sub>y</sub> glasses. Mechanosynthesis can circumvent the problem of Ag<sub>2</sub>O thermal decomposition,

\* Corresponding author. Tel.: +48 22 2345026; fax: +48 22 6282171.  
E-mail address: [nowin@if.pw.edu.pl](mailto:nowin@if.pw.edu.pl) (J.L. Nowinski).

and enable a direct use of silver oxide as a starting reagent for the synthesis of  $\text{Ag}^+$ -ion conducting amorphous solids.

This work reports recent results of our studies on formation of amorphous ionic conductors of the  $\text{AgI}-\text{Ag}_2\text{O}-\text{V}_2\text{O}_5$  systems during the process of mechanosynthesis. The systems of the compositions studied in this work or their close analogs can readily be prepared by standard melt-quenching methods [9–12].

## 2. Experimental

The materials of the  $\text{AgI}-\text{Ag}_2\text{O}-\text{V}_2\text{O}_5$  system were prepared from reagent grade  $\text{AgI}$ ,  $\text{Ag}_2\text{O}$  and  $\text{V}_2\text{O}_5$ . For a given synthesis, the appropriate amounts of the starting chemicals were ground and preliminarily mixed in a mortar. Then a 3 g premixed batch was placed in a grinding bowl ( $\text{Si}_3\text{N}_4$  from Fritsch, 20 ml volume) together with three  $\text{Si}_3\text{N}_4$  balls of the 12 mm diameter, and 10 ml of acetone. Acetone served as a process control agent inhibiting the agglomeration of substrate particles. Two milling devices were used for preparation of the materials. The first one, a Fritsch Planetary Micro Mill Pulverisette 7, worked at the rotation speed of ca. 500 rpm. The second mill, home-made, enabled planetary motion at the rotation speed of 250 rpm. Two milling schemes were applied: (i) the prolonged continuous milling, for times over 100 h with the aim to produce an amorphous material, and (ii) the intermittent mode which was employed for monitoring the changes occurring in the processed batch. In the latter case (ii), during each pause, a small amount of the processed material was taken for inspection, dried, measured and then placed back to the bowl to continue the milling process.

The former scheme (i.e. long continuous milling) was applied in the preparation of two families of the vanadate-based materials. The nominal composition of the first one was  $x\text{AgI}\cdot 0.25(100-x)(3\text{Ag}_2\text{O}\cdot\text{V}_2\text{O}_5)$ , for  $0 \leq x \leq 85$ . That of the second series was given by the formula  $x\text{AgI}\cdot 0.2(100-x)(3\text{Ag}_2\text{O}\cdot 2\text{V}_2\text{O}_5)$ , for  $0 \leq x \leq 60$ . The main

difference between both families is the ratio between the glass modifier ( $\text{Ag}_2\text{O}$ ) and the network former ( $\text{V}_2\text{O}_5$ ). In the case of the former family it is equal 3 while in the latter it is 1.5. This ratio affects the state of the disruption of the glass network by the modifier.

X-ray diffraction (XRD) patterns were collected at room temperature using  $\text{Cu K}\alpha$  radiation on a Philips X'Pert Pro diffractometer set in the Bragg–Brentano geometry. Identification of the crystalline phases was carried out using Philips X'Pert High Score, Philips X'Pert Plus and PCPDFWIN software (PDF-2 version of the ICDD database).

A LEO 1530 Field Emission Scanning Electron Microscope (FE-SEM) was used in microstructure investigations.

Thermal properties were studied by means of differential scanning calorimetry (DSC) method (Perkin-Elmer DSC Pyris 1). The heating rate was set to  $20 \text{ K min}^{-1}$ .

Raman spectra were taken at room temperature with a Nicolet Omega spectrometer. A 532 nm line was used for excitation.

## 3. Results and discussion

Fig. 1 presents the XRD patterns collected for the vanadate materials of the composition given by the formula:  $x\text{AgI}\cdot 0.25(100-x)(3\text{Ag}_2\text{O}\cdot\text{V}_2\text{O}_5)$ ,  $0 \leq x \leq 85$ . The investigated materials were milled in the Fritsch mill continuously for over 100 h. The patterns of the resulting materials corresponding to  $0 \leq x \leq 40$  contain X-ray lines of  $\text{Ag}_2\text{O}$ , whose intensity decreases with increasing  $x$ . For the materials with higher contents of  $\text{AgI}$  ( $40 \leq x \leq 70$ ), the XRD patterns contain only a wide halo, typical for amorphous systems, with no diffraction peaks. However for the highest contents of  $\text{AgI}$  ( $x = 85$ ), the diffraction lines appear again in the patterns, but this time they correspond to  $\beta$ - and  $\gamma$ -phases of silver iodide.

Fig. 2 shows the micrograph of the  $60\text{AgI}\cdot 30\text{Ag}_2\text{O}\cdot 10\text{V}_2\text{O}_5$  (i.e.  $x = 60$ ) sample observed after 210 h of milling. Within the

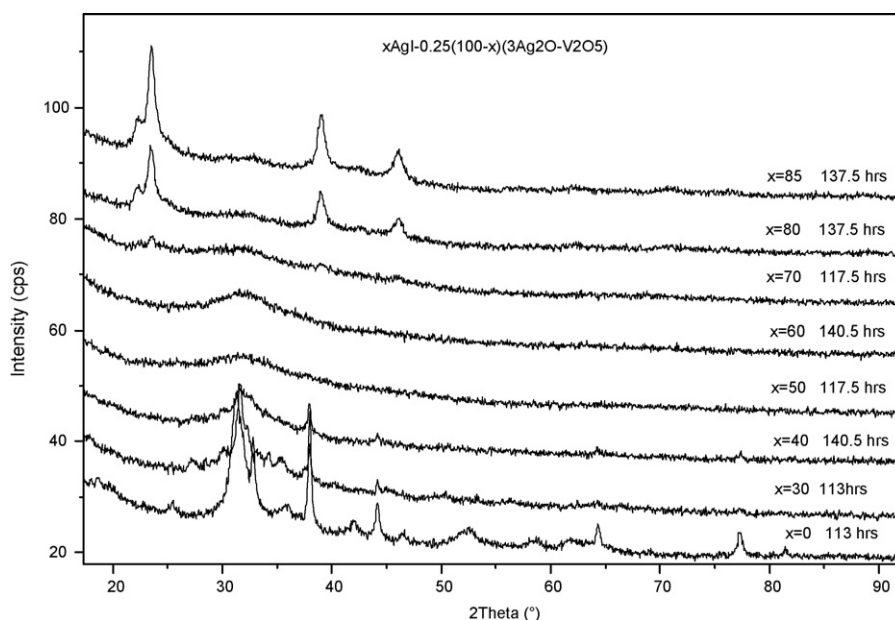


Fig. 1. XRD patterns of the  $x\text{AgI}\cdot 0.25(100-x)(3\text{Ag}_2\text{O}\cdot\text{V}_2\text{O}_5)$ , for  $0 \leq x \leq 85$ , family, as a function of milling time at 500 rpm.

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