Short communication

XRD, SEM, Raman and DSC characterization of the materials of the AgI–Ag$_2$O–V$_2$O$_5$ system prepared by mechanosynthesis

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Abstract

Ion conducting materials of the AgI–Ag$_2$O–V$_2$O$_5$ 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) xAgI·0.25(100 − x)(3Ag$_2$O·V$_2$O$_5$), for $40 \leq x \leq 70$, and (ii) xAgI·0.2(100 − x)(3Ag$_2$O·2V$_2$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.
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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$^+$-ion conductivity (up to 10^{-2} 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$_2$O–M$_x$O$_y$ systems (where M$_x$O$_y$ = V$_2$O$_5$, B$_2$O$_3$, P$_2$O$_5$, CrO$_3$ or MoO$_3$). 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$_2$O–M$_x$O$_y$ glasses using a commercial silver oxide as a starting reagent. The problem with Ag$_2$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$_2$O, in the preparation of the AgI–Ag$_2$O–M$_x$O$_y$ glasses. Mechanosynthesis can circumvent the problem of Ag$_2$O thermal decomposition,

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

This work reports recent results of our studies on formation of amorphous ionic conductors of the AgI–Ag$_2$O–V$_2$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 AgI–Ag$_2$O–V$_2$O$_5$ system were prepared from reagent grade AgI, Ag$_2$O and V$_2$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 (Si$_3$N$_4$ from Fritsch, 20 ml volume) together with three Si$_3$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 xAgI·0.25(100 − x)(3Ag$_2$O·V$_2$O$_5$), for $0 \leq x \leq 85$. That of the second series was given by the formula xAgI·0.2(100 − x)(3Ag$_2$O·2V$_2$O$_5$), for $0 \leq x \leq 60$. The main

difference between both families is the ratio between the glass modifier (Ag$_2$O) and the network former (V$_2$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 Cu Kα 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 K min^{-1}.

Raman spectra were taken at room temperature with a Nicolet Almega 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: xAgI·0.25(100 − x)(3Ag$_2$O·V$_2$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 Ag$_2$O, whose intensity decreases with increasing x. For the materials with higher contents of 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 AgI ($x = 85$), the diffraction lines appear again in the patterns, but this time they correspond to β- and γ-phases of silver iodide.

Fig. 2 shows the micrograph of the 60AgI·30Ag$_2$O·10V$_2$O$_5$ (i.e. $x = 60$) sample observed after 210 h of milling. Within the
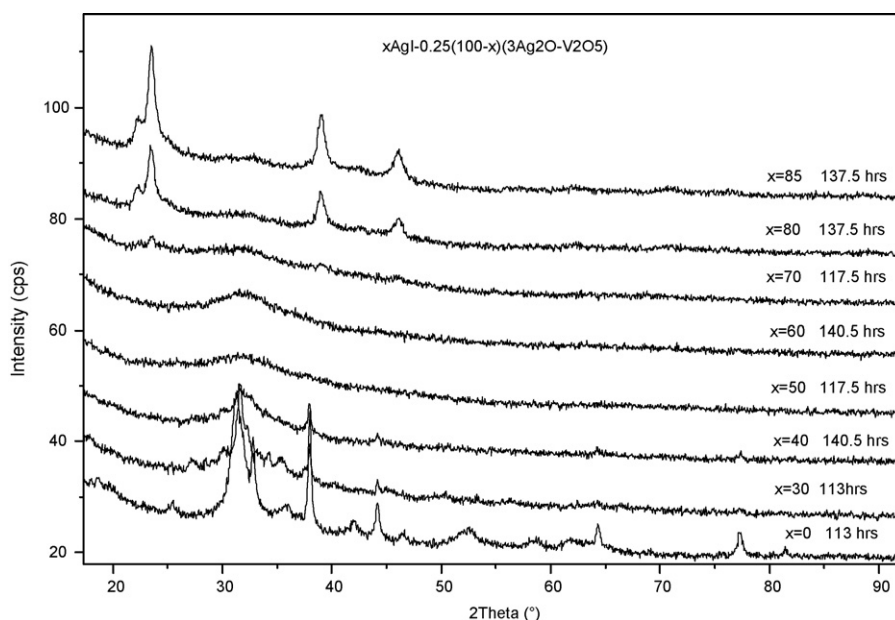
Fig. 1. XRD patterns of the xAgI·0.25(100 − x)(3Ag$_2$O·V$_2$O$_5$), for $0 \leq x \leq 85$, family, as a function of milling time at 500 rpm.
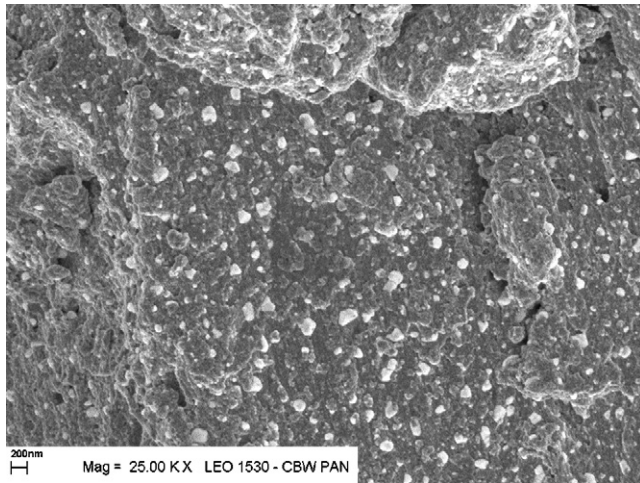
Fig. 2. SEM image of the 60AgI·30Ag₂O·10V₂O₅ ($x = 60$) material ball-milled for 210 h at 250 rpm.

Fig. 4. The glass forming regions in the AgI–Ag₂O–V₂O₅ system after Taka-hashi et al. [9] (fast quenching, grey region) and Kaushik and Hariharan [12] and Minami [13] (melt-quenching, hatched region). The straight lines correspond to the materials of the compositions with [Ag₂O]/[V₂O₅] ratios equal to 3:1 and 3:2, synthesized and investigated in this work.

continuous matrix some small, oval inclusions, about 100 nm diameter each, are visible, indicating the presence of at least two phases in the mechanosynthesized material. The concentration of the inclusions seems to be sufficiently high to be detectable by XRD, if the inclusions are crystalline. However the diffraction patterns (Fig. 1) show no presence of crystalline phases. It is therefore likely that the inclusions observed in the SEM micrograph (Fig. 2) are amorphous.

Analogous investigations were carried out for the other vanadate family: xAgI·0.2(100 − x)(3Ag₂O·2V₂O₅), for $0 \leq x \leq 60$, prepared in the same way. X-ray diffractograms for the compositions corresponding to $x > 20$ contain solely a wide halo—an indicative of absence of crystalline phases (Fig. 3). For materials with lower AgI contents ($0 \leq x \leq 20$) one can see a small peak near 37.5°, whose position matches with the [2 0 0] diffraction line of Ag₂O.
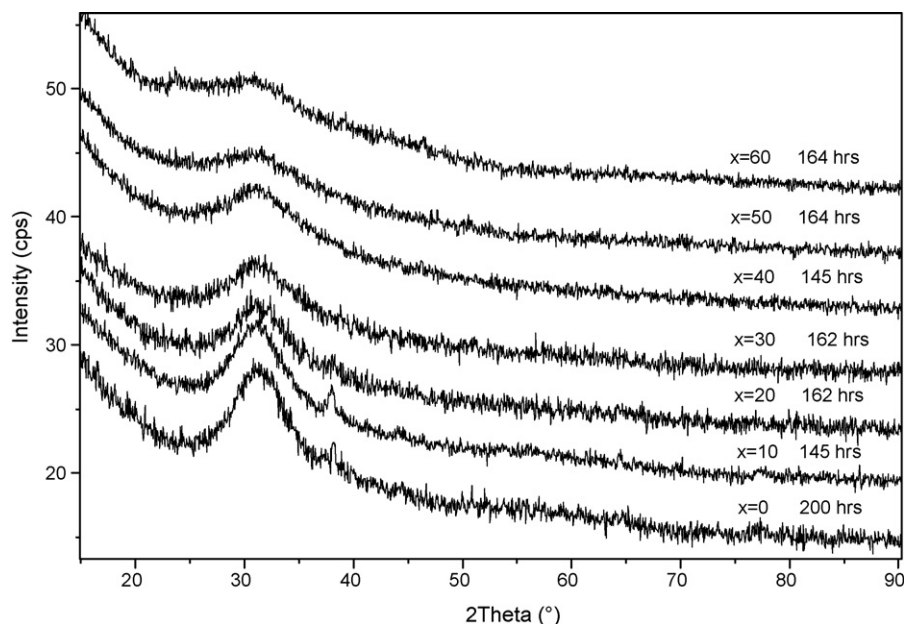
These results can be compared with the data published earlier for materials of the same composition but prepared by the melt-quenching technique (Minami [13] and Kaushik and Hariharan [12]). Both those works showed a relatively small glass-forming island (a hatched region in Fig. 4). Takahashi et al. [9] who also studied glass formation in this system, but employing a rapid quenching technique, found out somewhat extended glass forming area (grey region in Fig. 4). The straight lines marked in these diagrams correspond to the compositions in which the [Ag₂O]/[V₂O₅] ratio is constant, equal either 3:1 or 3:2, i.e. that of both xAgI·0.25(100 − x)(3Ag₂O·V₂O₅) and xAgI·0.2(100 − x)(3Ag₂O·2V₂O₅) families investigated in this work. The ball-milled amorphous materials of the

Fig. 3. XRD patterns of the xAgI·0.2(100 − x)(3Ag₂O·2V₂O₅), $0 \leq x \leq 60$, family as a function of milling time at 500 rpm.
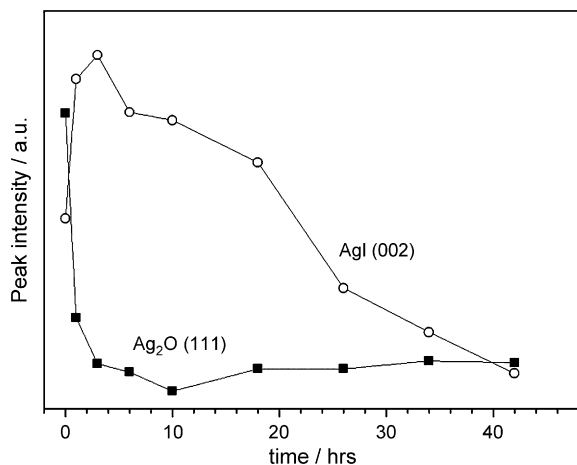
Fig. 5. The relative intensity of the (0 0 2) γ-AgI and the (1 1 1) Ag_2O peaks in the diffraction patterns of the material of the $60AgI \cdot 30Ag_2O \cdot 10V_2O_5$ nominal composition as functions of the milling time at the speed of 250 rpm.

Fig. 6. DSC trace for the $60AgI \cdot 30Ag_2O \cdot 10V_2O_5$ material formed after 140.5 h of milling at 500 rpm. The heating rate was set to 20 K min^{-1}.

series $xAgI \cdot 0.25(100 - x)(3Ag_2O \cdot V_2O_5)$, where $50 \le x \le 70$, are located outside the glass forming island determined by Takahashi, whereas those described by the formulae: $xAgI \cdot 0.2(100 - x)(3Ag_2O \cdot 2V_2O_5)$, $0 \le x \le 40$ and the $xAgI \cdot 0.25(100 - x)(3Ag_2O \cdot V_2O_5)$, $50 \le x \le 70$, are placed outside glassy islands determined by Minami [13] and Kaushik and Hariharan [12] (Fig. 4). This means that mechanosynthesis may be an effective and convenient method of preparation superionic, amorphous materials of compositions inaccessible by melt-quenching techniques, either standard or rapid ones.

Furthermore, temporal changes of the XRD patterns collected at the early stages of the milling reveal other interesting features. When the normalized intensities of the diffraction lines (here lines [0 0 2]) of γ-AgI and [1 1 1] Ag_2O are plotted versus the milling time, one can see that the intensity of lines of Ag_2O decreases faster than that of AgI (Fig. 5). The observed unequal rates of reactions consuming starting Ag_2O and AgI reagents were accompanied by broadening of their corresponding XRD lines. The latter observation reflects a decrease in the average size of crystallites of the corresponding compounds (i.e. Ag_2O or AgI). All these facts indicate that the reaction of incorporation of Ag_2O into the amorphous structure of the ternary system AgI–Ag_2O–V_2O_5 proceeds at higher rate than the 'dissolution' of AgI in the amorphous matrix, progressively formed during the ball-milling process. During those reactions the crystalline grains of the AgI and Ag_2O get smaller at a discernible rate before they finally are consumed by chemical reactions during mechanosynthesis. It should be noted however, that the mechanosynthesis not always leads to a complete amorphousness or to a full transformation of the starting reagents in the materials containing AgI, Ag_2O and V_2O_5.

As our other investigations of the binary mixtures of Ag_2O and V_2O_5 (or CrO_3) have shown, even the long lasting, high speed ball-milling had not produced fully amorphous materials. In those cases the diffraction lines of starting oxides were always present. The only effect of ball-milling visible in the XRD patterns was the broadening of these lines, pointing out to a progressively decreasing grain size.
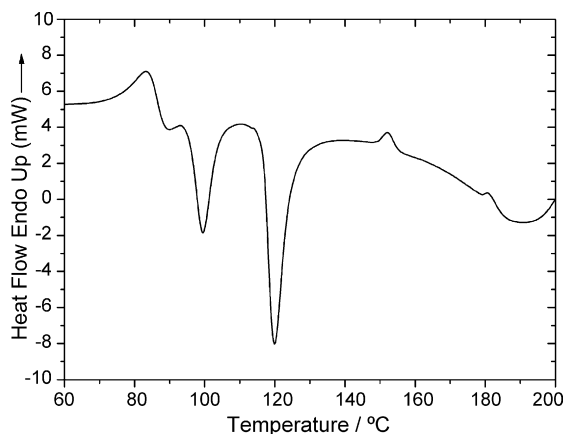
Dalvi and Shahi [14] studied and discussed the mechanism of formation of amorphous phases in AgI–Ag_2O–M_xO_y ($M_xO_y = CrO_3$, V_2O_5 and MoO_3) systems prepared by ball-milling [15]. They noticed, that the annealing of the fully amorphous material at sufficiently high temperature, led to precipitation of the crystalline grains of Ag_2CrO_4, Ag_3VO_4, $Ag_4V_2O_7$, $Ag_8I_4V_2O_7$ or Ag_2MoO_4, respectively, embedded in the amorphous matrix. They concluded, that during mechanical processing of the mixture of the starting reagents (AgI, Ag_2O and M_xO_y), firstly some crystalline binary phases of the Ag_2O–M_xO_y system were formed. Only afterwards the diffusion of the Ag^+ and I^- ions from AgI into these crystallites led to the destruction of their crystalline structure and formation of the amorphous medium. Our experimental observations indicate that the transient phases, if they appear, are amorphous.

The DSC scan of the material $60AgI \cdot 30Ag_2O \cdot 10V_2O_5$ formed after 140.5 h of milling is shown in Fig. 6. It starts from an endothermic feature at around $74\,^{\circ}C$, attributed to the glass transition. Its presence confirms the conclusion from the XRD patterns, that the materials formed after prolonged milling are amorphous. It is known for a number of ternary AgI–Ag_2O–M_xO_y glasses that at high contents of AgI (e.g. 60 mol%) their glass transition temperature is close to ca $80\,^{\circ}C$. The exothermic peaks at around 90, 99 and $120\,^{\circ}C$ may indicate multistage crystallization processes. Similar, though less pronounced and less numerous, exothermic events on DTA scans of the ball-milled samples of the AgI–Ag_2O–V_2O_5 system were reported by Dalvi and Shahi [14]. The main of these crystallization events occurred at $90\,^{\circ}C$ [14].

Raman spectrum of the binary material of composition $60Ag_2O \cdot 40V_2O_5$ formed after 200 h of ball-milling of the mixture of V_2O_5 and Ag_2O and spectra of those two starting oxides are shown in Fig. 7. The spectrum of the synthesized material is completely different from the spectra of the starting components. This means that due to the ball-milling the starting mixture underwent a chemical reaction and formed a new material. Fig. 8 presents a series of Raman spectra of the $xAgI \cdot 0.25(100 - x)(3Ag_2O \cdot V_2O_5)$, $30 \le x \le 70$, materials ball-milled for long time. The corresponding XRD patterns are shown in Fig. 1. All spectra of the materials containing from
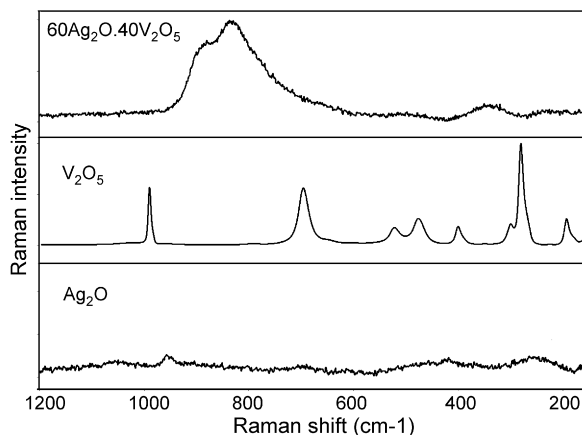
Fig. 7. Raman spectra of starting reagents: Ag_2O and V_2O_5 used for the synthesis of the $60Ag_2O\cdot40V_2O_5$ binary material, and the spectrum of that material formed after 200 h of ball-milling at 500 rpm.
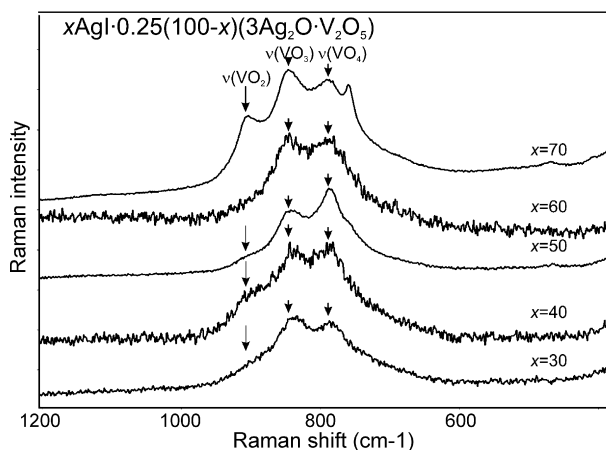

Fig. 8. Raman spectra for the $xAgI\cdot0.25(100-x)(3Ag_2O\cdot V_2O_5)$, $30 \leq x \leq 70$, materials formed by prolonged ball-milling at 500 rpm. The corresponding X-ray diffraction patterns are shown in Fig. 1.

30 to 60 mol% of AgI are alike. They contain two bands at $787\,cm^{-1}$ and $847\,cm^{-1}$. For the material, corresponding to $x = 70$, two distinct additional bands at 780 and $900\,cm^{-1}$ are visible. The Raman spectra for the second vanadate family $xAgI\cdot0.2(100-x)(3Ag_2O\cdot2V_2O_5)$ are similar to those presented in Fig. 8. They also contain two bands at $840\,cm^{-1}$ and $890\,cm^{-1}$, but the band at ca. $790\,cm^{-1}$ is absent.

Raman spectra acquired in this study were compared to those of the glasses of the $AgI–Ag_2O–V_2O_5$ system, prepared by the melt-quenching technique [9,16]. The band centred near $842\,cm^{-1}$ in the spectra of the mechanosynthesized materials of the family with $xAgI\cdot0.2(100-x)(3Ag_2O\cdot V_2O_5)$ (Fig. 8) was also present, at slightly shifted position (ca. $850\,cm^{-1}$),

in the spectra of glasses prepared by melt quenching [16]. This band is attributed to vibrations of pyrovanadate units [16]. The other band (at ca. $890\,cm^{-1}$) correlates well with that of the anti-symmetric mode of the VO_2 group in metavanadates [16].

It should be noted that the Raman spectroscopy studies indicate that the AgI content has little effect on the Raman spectra. Similar negligible effect of AgI content on Raman spectra was observed for $AgI–Ag_2O–V_2O_5$ glasses [16].

From XRD, Raman, SEM and DSC investigations presented in this work it can be concluded that the local structure of the silver vanadate materials under study prepared by ball-milling is similar to the structure of the glasses prepared by melt quenching.

4. Conclusions

The prolonged ball-milling of the mixture of appropriate quantities of AgI, Ag_2O and V_2O_5 leads to chemical reactions between these compounds and to the amorphization of the final material. Local structure of the materials prepared by mechanosynthesis contains of units similar to those present in the structure of the melt-quenched glasses of the same chemical composition.

It has been shown, that mechanosynthesis is an alternative method of preparation of the amorphous silver ion conducting materials, including those which cannot be prepared by other techniques.

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