

MECHANOCHEMICAL SYNTHESIS OF SILVER VANADATE AND SILVER CHROMATE AMORPHOUS SUPERIONIC CONDUCTORS

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Abstract. The work presents the results of investigation of materials obtained in the AgI-Ag₂O-M_xO_y (M_xO_y = V₂O₅, CrO₃) systems by means of mechanosynthesis. The X-ray diffraction and field emission scanning electron microscopy methods were employed in the investigations. The milling speed, apart from the milling time, appeared to be a key factor for the effectiveness of the formation of the amorphous chromate and vanadate materials.

The model of the synthesis process is discussed and suggested. During initially stages of milling Ag₂O and chromium or vanadium oxides react together forming some new phases. Then this intermediate products act as a solid solvent dissolving in itself silver iodide component of the mixture forming finally an amorphous phase.

1. INTRODUCTION

An electrolyte is a vital and operational part of each electrochemical device such as a battery or a sensor. The demand for miniaturization and easy assembly of the component parts in these devices favours solid materials over the liquid ones. Solid electrolytes satisfy such requirements [1-4]. A potentially important class of solid electrolytes are superionic glasses. In particular, those of the AgI-based, exhibit especially high conductivity at room temperature due to high mobility of silver ions in the glass matrix [5].

In standard glass preparation route starting materials are melted at high temperature. This step may lead to some undesired side effects. In consequence, for some chemical compositions glasses are not formed. In recent years there were

successful attempts employing low temperature methods, such as ball milling [6,7], for preparation of amorphous, superionic materials [8] and for intercalation of lithium into graphite [9]. Dalvi et al. in series of papers [10-14] investigated ionic conductivity and kinetics of crystallization of materials formed by ball-milling in the AgI-Ag₂O-M_xO_y (M_xO_y = B₂O₃, MoO₃, V₂O₅, and CrO₃) systems. Hayashi et al. described preparation and investigated ionic conductivity of Li₂S-P₂S₅ [15,16] and Li₂S-SiS₅ [17] glass electrolytes prepared by ball-milling. Despite of these reports the literature devoted to ball milling in superionic glass is very poor, in comparison to the numerous works concerning metallic glasses. In consequence the state of knowledge, understanding of the nature of the processes taking place during milling are unsatisfactory.

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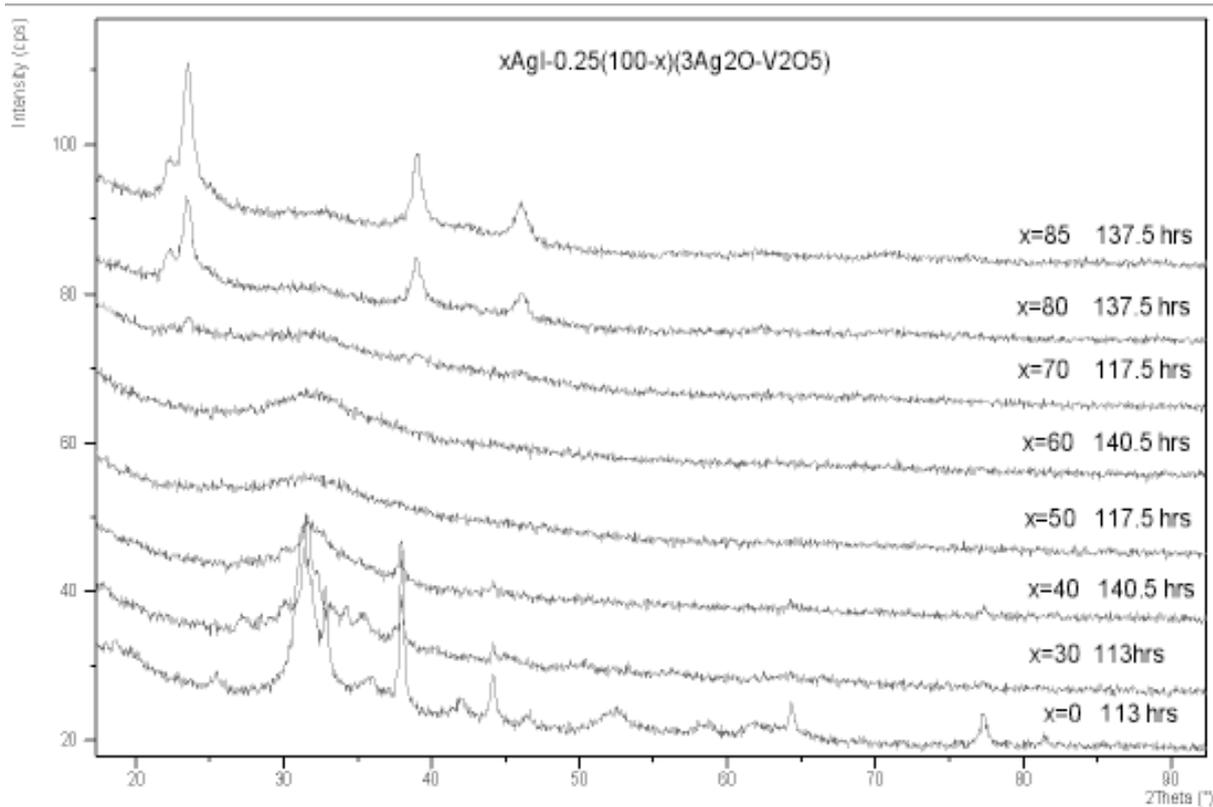


Fig. 1. The diffraction patterns of the $x\text{AgI}-0.25(100-x)(3\text{Ag}_2\text{O}-\text{V}_2\text{O}_5)$, $x \in (0,85)$ family as a function of milling time. Fritsch Planetary Micro Mill Pulverisette 7 was used in preparation.

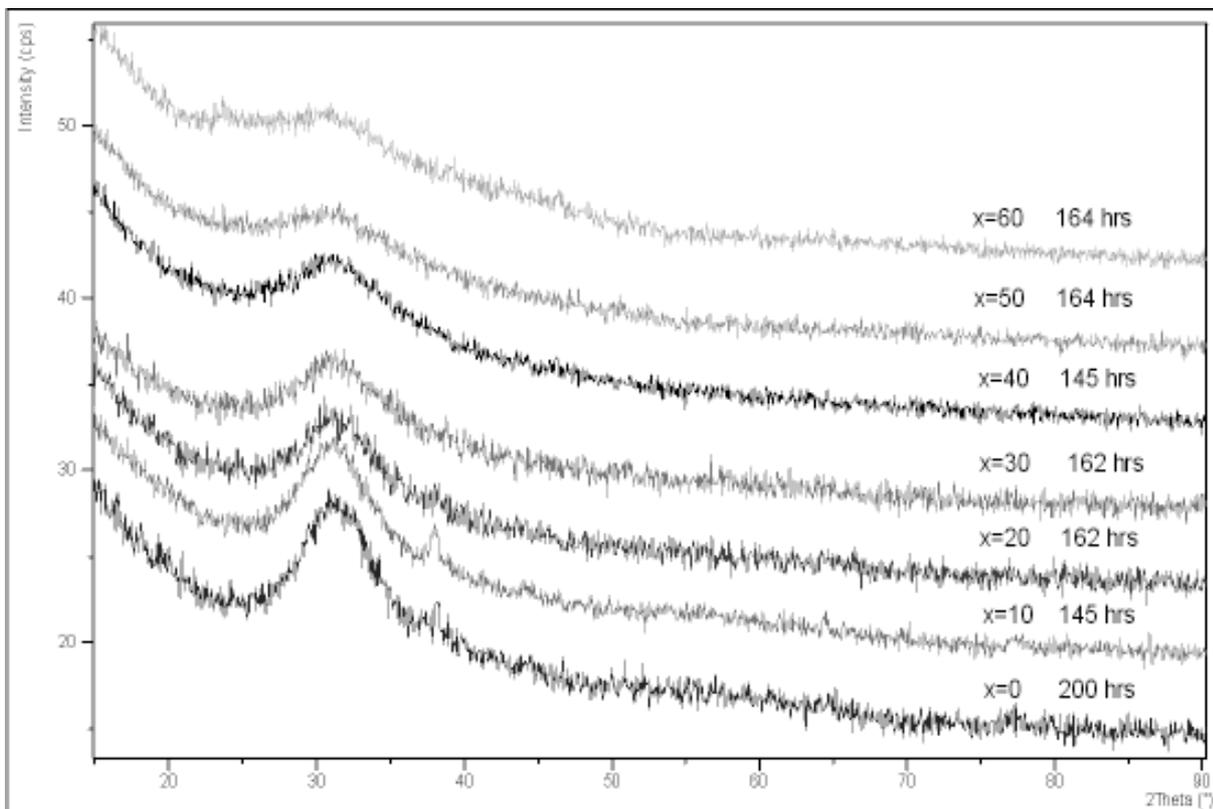


Fig. 2. The diffraction patterns of the $x\text{AgI}-0.2(100-x)(3\text{Ag}_2\text{O}-2\text{V}_2\text{O}_5)$, $x \in (0,60)$ family as a function of milling time. Fritsch Planetary Micro Mill Pulverisette 7 was used in preparation.

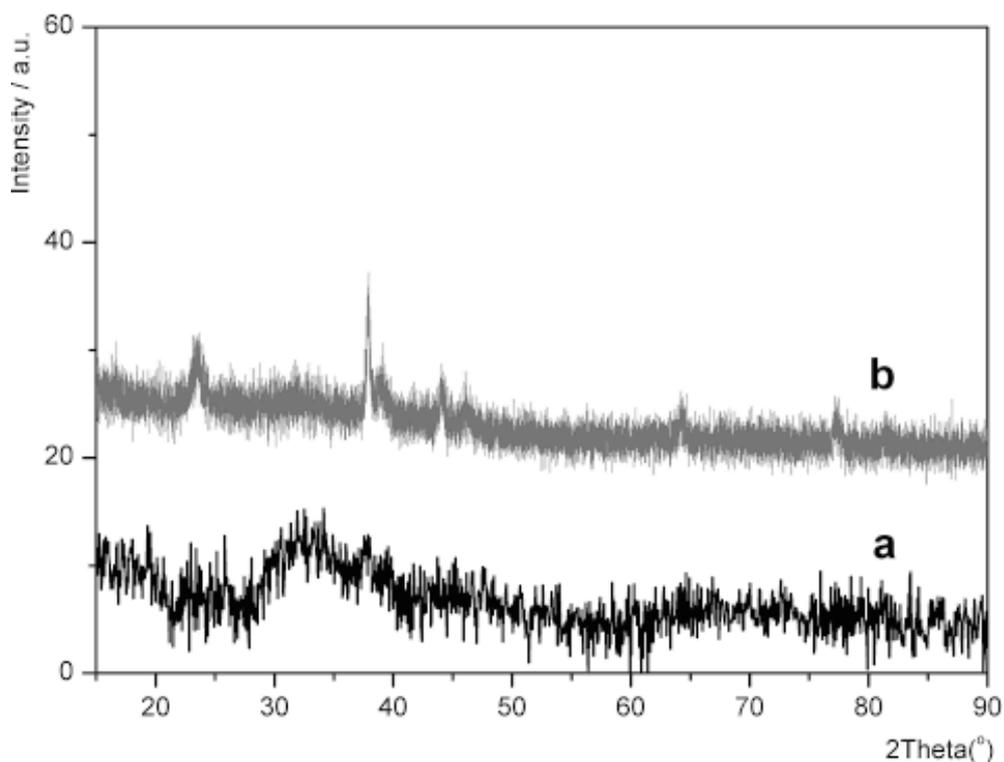


Fig. 3. The diffraction patterns of the 60AgI:30Ag₂O:10V₂O₅ material obtained by means of (a) Fritsch Planetary Micro Mill Pulverisette 7 for 140.5 hrs, (b) the home-made planetary mill for 186.5 hrs.

The work presents the results of investigation of materials obtained in the AgI-Ag₂O-M_xO_y (M_xO_y = V₂O₅, CrO₃) systems by means of mechanochemical synthesis. It is well known, that superionic, glassy materials of this systems are readily obtained by the classical preparation methods [18-20]. The attention is focused on kinetics of changes of the chemical composition of the mixed components during milling. As far as authors were aware such investigations had not been performed before.

2. EXPERIMENTAL

The silver chromate materials were prepared from reagent grade AgI, Ag₂O, and CrO₃ whereas the vanadate ones from AgI, Ag₂O, and V₂O₅. The appropriate amount of the starting chemicals were ground and preliminary mixed in a mortar. Then a batch, each 3 g, was placed in a grinding bowl (Si₃N₄ from Fritsch), 20 ml volume. Next three silicon nitride, 12 mm diameter balls were located inside it and finally the bowl with the reagents and the balls was filled with about 10 ml of acetone. Some at-

tempts to use dry substrates only, without acetone, failed to produce an amorphous material. Two kinds of mills were employed for preparation of the materials. The first one, a Fritsch Planetary Micro Mill pulverisette 7, was set up to work with the rotation speed about 500 rpm. The second mill, home-made but also of the planetary motion, could work with the speed about 250 rpm. Generally two milling schemes were applied. The long lasting continuous milling, usually exceeding hundred of hours, was used when aimed to prepare a highly amorphous material. The interrupted milling was employed when the interest was focused on influence of the milling time on the material. In this case, during each stop, some small, token sample of the milled materials was taken off, dried from acetone, measured and then it was given back to the bowl to continue the milling process.

The long lasting scheme was applied during preparation of two families of the vanadates, to those of the overall, nominal composition of the xAgI-0.25(100-x)(3Ag₂O-V₂O₅), x ∈ (0,85), maintaining the ratio [Ag₂O]/[V₂O₅]=3 and to the second one

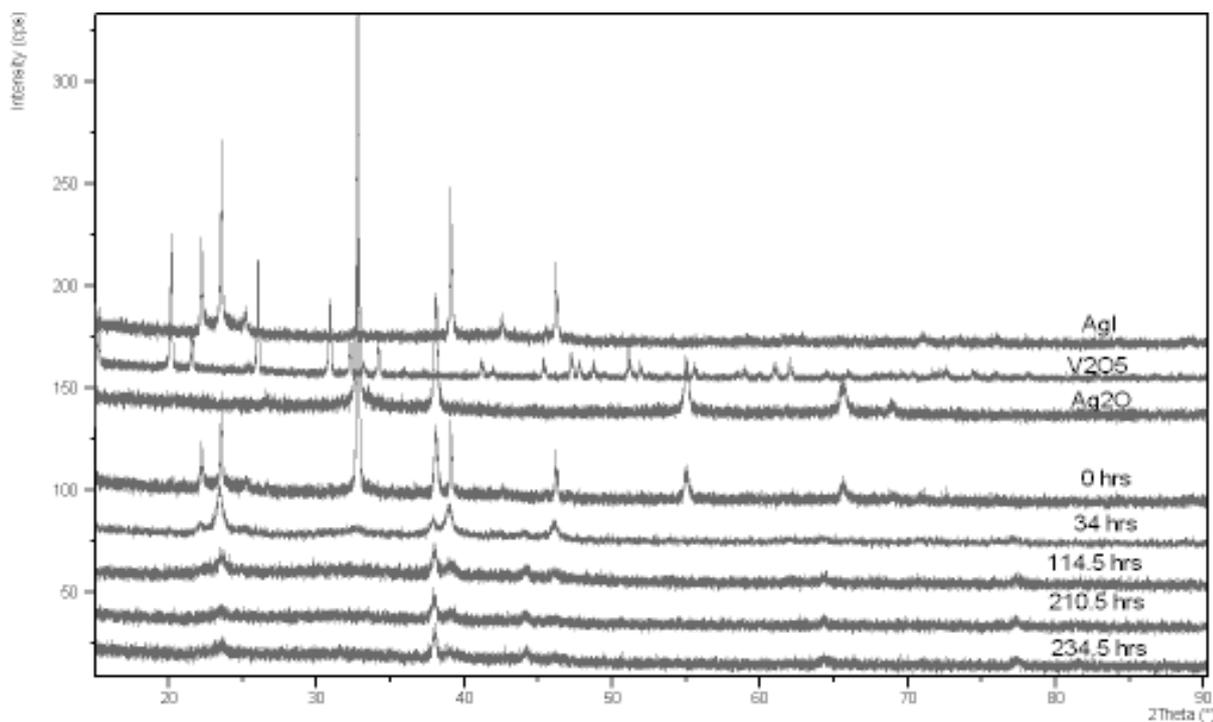


Fig. 4. The X-ray diffraction patterns of the material of the 60AgI:30Ag₂O:10V₂O₅ nominal composition as a function of milling time. The home-made planetary mill was employed in preparation. The XRD patterns of AgI, Ag₂O and V₂O₅ compositions used in synthesis are included for comparison.

described by the formula of the $x\text{AgI}-0.2(100-x)(3\text{Ag}_2\text{O}-2\text{V}_2\text{O}_5)$, $x \in (0,60)$, for which $[\text{Ag}_2\text{O}]/[\text{V}_2\text{O}_5]=3/2$. Selected composition of the 60AgI-30Ag₂O-10V₂O₅, the 50AgI-25Ag₂O-25CrO₃, and the 75AgI-15Ag₂O-15CrO₃ were subjected to the interrupted milling.

X-ray diffraction patterns (XRD) were collected at room temperature using Cu K_α radiation on a Philips X'Pert Pro diffractometer set in the Bragg-Brentano geometry. Analysis of the XRD data was carried out employing Philips X'Pert High Score, Philips X'Pert Plus and PCPDFWIN program (PDF-2 version of ICDD software).

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

3. RESULTS AND DISCUSSION

Fig. 1 presents the XRD patterns collected for the vanadate materials, which overall chemical compositions expresses the formula of the $x\text{AgI}-0.25(100-x)(3\text{Ag}_2\text{O}-\text{V}_2\text{O}_5)$, $x \in (0,85)$. The investigated materials were milled in the Fritsch mill for

time longer than 100 hours. The patterns described by $x \in (0,40)$ exhibit the presence of the broad X-ray lines characteristic for Ag₂O, which intensity decreases with x . For the range of $x \in (40,70)$, the patterns show no trace of diffraction lines exposing instead a very broad 'halo' peak, typical for glassy materials. But when the total concentration of silver iodide is high ($x \in (70,85)$) the diffraction lines appear again on the patterns, those are identified as due to crystalline β/γ-AgI phase. It is worthy to note, that equivalent materials for $x \in (40,70)$, prepared by high temperature quenching of the melt are partially crystalline [18,22].

Similar investigations were carried out for the other vanadate family prepared in the same manner and described by the overall expression of the $x\text{AgI}-0.2(100-x)(3\text{Ag}_2\text{O}-2\text{V}_2\text{O}_5)$, $x \in (0,60)$. On the all patterns recorded for that family the 'halo' peak is clearly seen (Fig. 2). However for the $x \in (0,20)$, i.e. low AgI concentration, some trace of a peak is noticeable, which 2Theta position corresponds to the Ag₂O [200] diffraction line. The patterns for the higher AgI contents show no diffraction peaks.

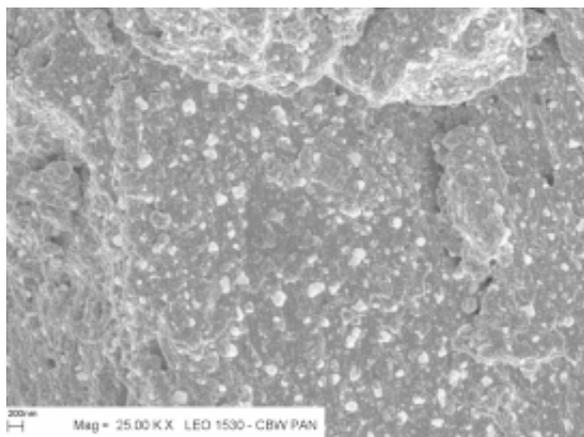


Fig. 5. The SEM image of the 60AgI:30Ag₂O:10V₂O₅ material milled for 210 hrs in the home-made planetary mill.

The selected material of the 60AgI:30Ag₂O:10V₂O₅ overall composition was prepared by long lasting continuous milling under two different conditions. Part of the material was milled in Fritsch mill, which rotated with the speed about 500 rpm for 140.5 hrs, whereas the other one was milled in the home-made planetary milling device with the speed about 250 rpm for 186.5 hrs. Fig. 3 presents the resultant X-ray patterns recorded after preparation. One can notice, that high milling speed produces a completely amorphous material, whereas low speed milling, even longer lasting, results only in formation of the partially crystalline material. Impact of the milling speed on efficiency of reactions and processes was observed for various metallic glasses and alloys [5].

The same 60AgI:30Ag₂O:10V₂O₅ material was used in investigation aimed to study the influence of the milling time on formation of the amorphous phase. The home-made mill was employed during preparation and the interrupted milling scheme was applied. Fig. 4 presents some selected diffraction patterns recorded at different milling time. Even preliminary mixing and grinding influence the microstructure of the substrate mixture, as one can conclude analyzing the X-ray pattern for 0 h milling. The lines assigned to V₂O₅ are almost invisible on the pattern of the as-prepared mixture. During milling the diffraction lines decreased and after 210 hrs of milling some very weak lines overlapping the halo peak could be observed. The de-

tected peaks coincide with the β -AgI [002] for 23.47 deg and the [200] Ag₂O [200] for 37.80deg lines suggesting presence, at least, of two crystalline phases in the milled material. On the contrary, the FE-SEM investigations seem to indicate only one additional phase. Fig. 5 presents the exemplary micrograph of the milled material. In the continuous matrix only one type of some small oval inclusions, about 100 nm diameter each, is visible.

Further, more detailed analysis of the patterns related to the early stage of the milling reveals other interesting features of the materials appearing in a course of the reaction. When the normalized intensities of the β -AgI and Ag₂O peaks are plotted against the milling time, one can see that the lines attributed to silver oxide become weaker faster than those related to AgI. Fig. 6 presents the selected case of the kinetics of the γ -AgI [002] and the Ag₂O [002] peaks.

The formation of amorphous chromate materials by means of the mechanochemical route was studied employing the family of materials described by the $x\text{AgI} \cdot 0.5(100-x)(\text{Ag}_2\text{O} \cdot \text{CrO}_3)$, $x=50$ and 70 . Figs. 7 and 8 show respectively the diffraction patterns of the 50AgI:25Ag₂O:25CrO₃ and 70AgI:15Ag₂O:15CrO₃ materials obtained by means of the home-made planetary mill in a function of the milling time. The XRD patterns of the original AgI, Ag₂O and CrO₃ chemicals used in the synthesis are also included for comparison. In the case of the 50AgI:25Ag₂O:25CrO₃, after 138 h of milling, an amorphous material is formed, as a smooth shape of the recorded pattern indicates. On the contrary, the long lasting milling applied to the 70AgI:15Ag₂O:15CrO₃ produce the material which the X-ray pattern demonstrates, apart from the intense 'halo', some broad, low intensity peaks related to AgI. The result indicates the presence of the crystalline silver iodide remnants in the processed material and it suggests incomplete amorphisation of the starting mixture.

The diffraction patterns recorded as a function of the milling time, for both investigated compositions, show some characteristic changes. Initially strong AgI and Ag₂O peaks become weaker and broader with the time. Similarly, like it was observed for the vanadates, the Ag₂O lines decreased faster than the silver iodide ones (Fig. 9).

So summarising, the presented investigations concern to the different, from the chemical point of view, materials, which were subjected to the similar mechanochemical treatment. The changes in their microstructure taking place during milling show common, for both group of the materials, features

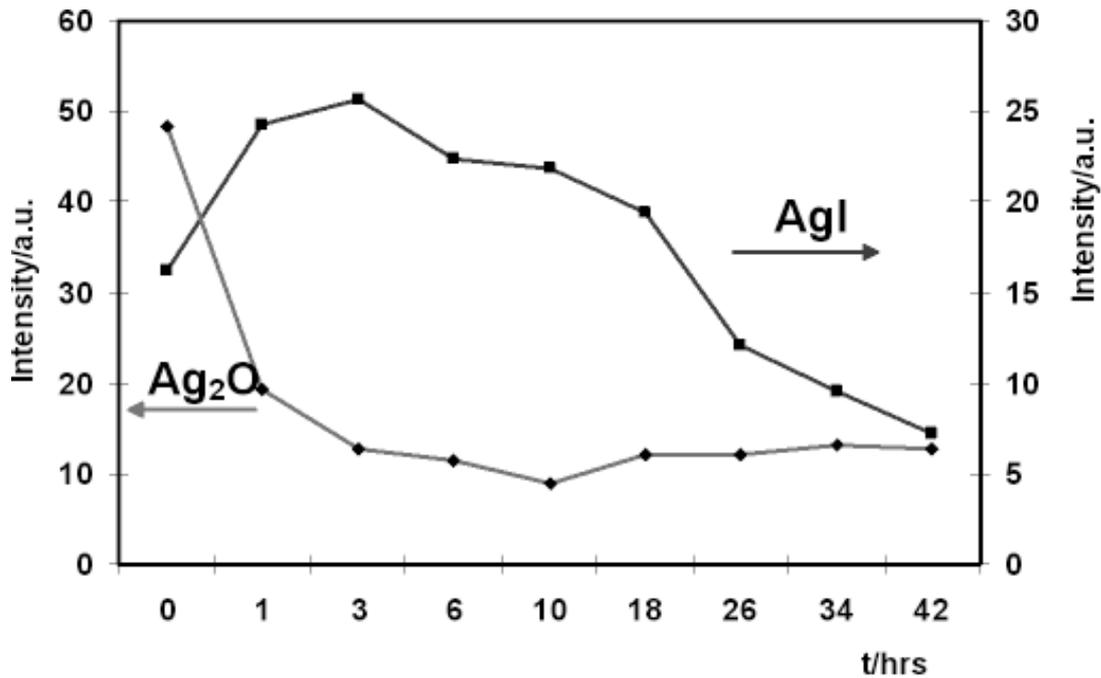


Fig. 6. The intensity of the (002) γ -AgI and the (002) Ag_2O peaks in the diffraction pattern of the material of the 60AgI-30 Ag_2O -10 V_2O_5 nominal composition as a function of the milling time in the home-made planetary mill.

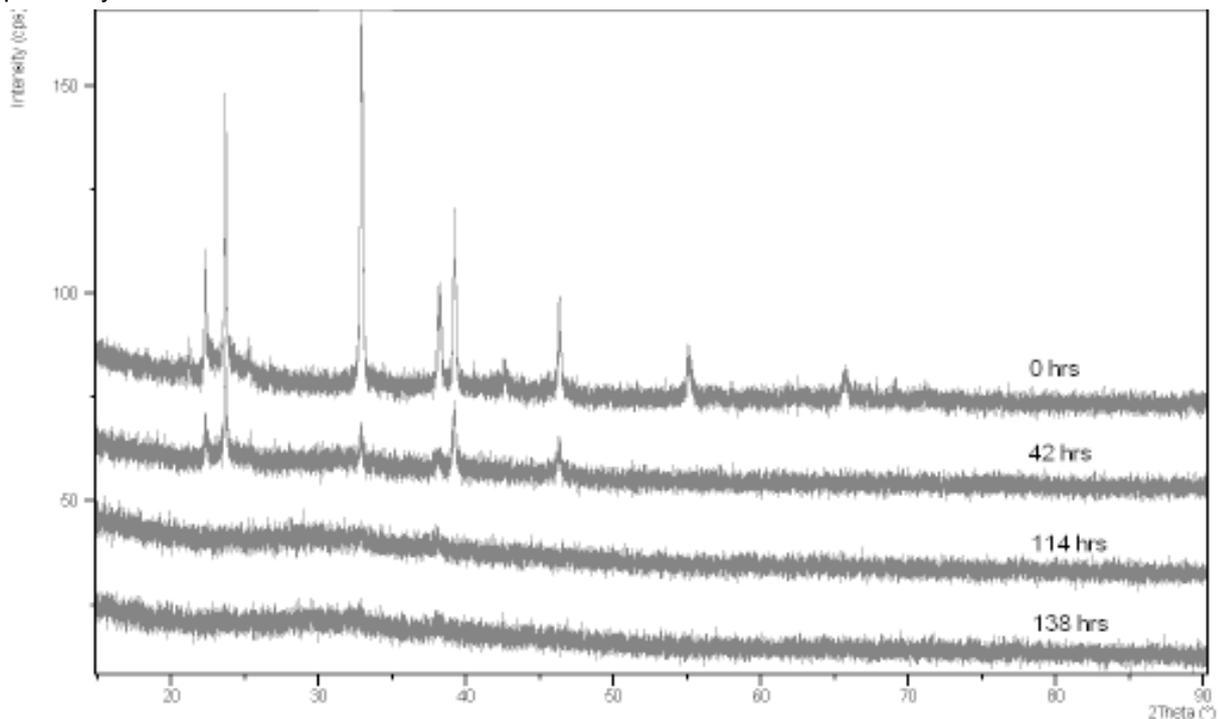


Fig. 7. The diffraction patterns of the material of the 50AgI:25 Ag_2O :25 CrO_3 nominal composition as a function of the milling time in the home-made planetary mill.

and the most striking evidence relates to the unequal rate of the decrease of the AgI and Ag_2O X-ray diffraction lines. The observed decrease asso-

ciated with the parallel broadening of the lines reflects an obvious fact, that the concentration of the AgI and Ag_2O crystalline phases decreases in the

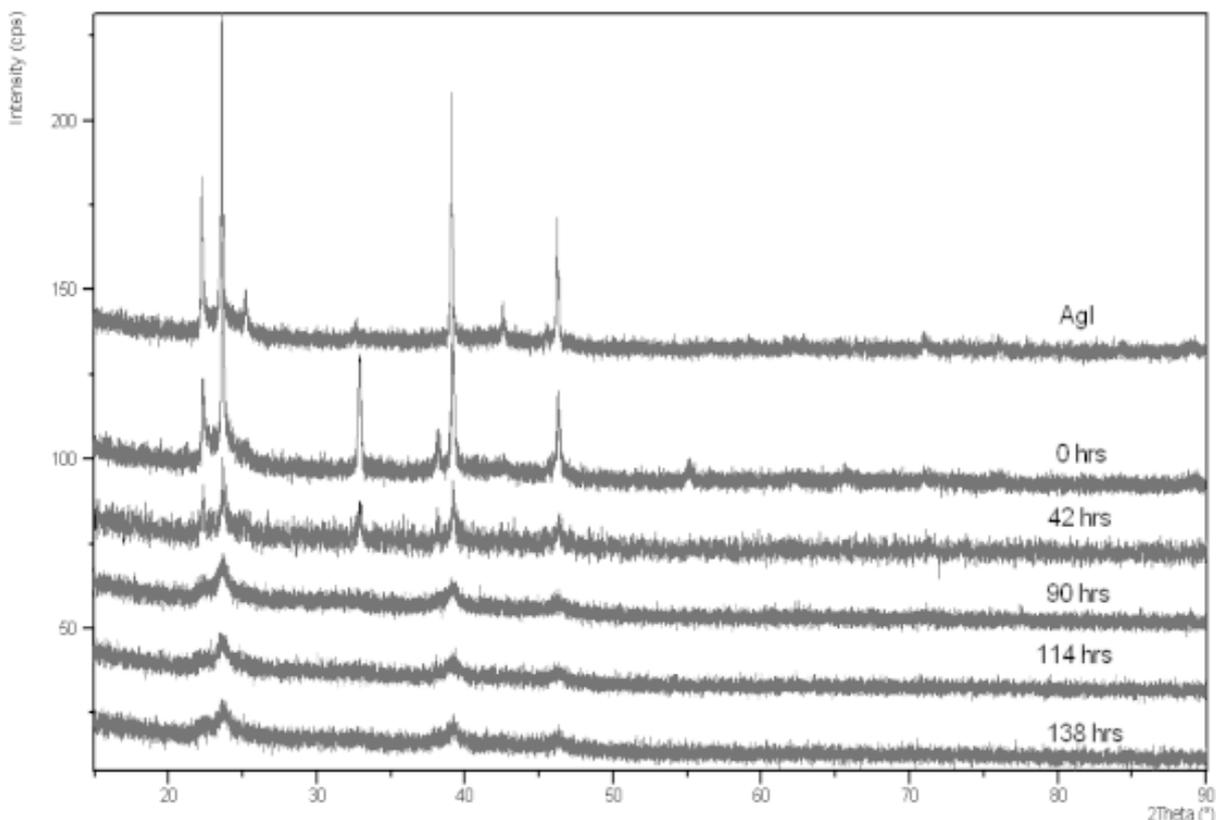


Fig. 8. The diffraction patterns of the material of the 70AgI:15Ag₂O:15CrO₃ nominal composition obtained as a function of the milling time in the home-made planetary mill.

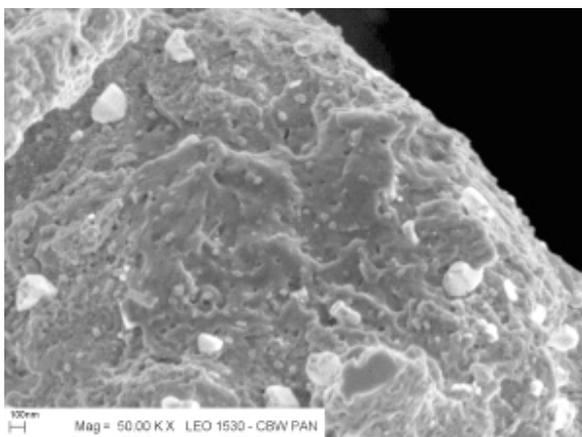


Fig. 9. The SEM image of the 50AgI:25Ag₂O:25CrO₃ material milled for 114.5 hrs in the home-made planetary mill.

material, when it milled and simultaneously grains constituting the material become smaller in size. It is obvious, that the milling is responsible for the crystallite destruction but the fundamental question is what, in fact, the milling causes in a mixture of the constituents. It is rather improbable that the

milling itself could destroy a crystal structure of the Ag₂O and AgI only, without implementing other, more serious changes in the mixture. As our other investigations of the binary mixtures of Ag₂O and CrO₃ or V₂O₅ showed, even long lasting, high speed milling did not produced the amorphous phase, apart from some special examples, like the 40Ag₂O:60CrO₃. The diffraction lines were always visible in patterns of the binaries and the peaks were more broader, which pointed out only a diminishing powder size. The alternative explanation of the obtained experimental evidences could be some chemical reaction, stimulated by the milling and accompanying a mechanical crushing of the crystalline grains. If such suggested process produced some new crystalline phases, it would be reflected in the relevant X-ray diffraction patterns as a growth of a new set of peaks at the expense of the initial one. Because our observations evidently show the peak decrease and no new diffraction lines, then the mechanism of the reaction should be more complex. The process seems to

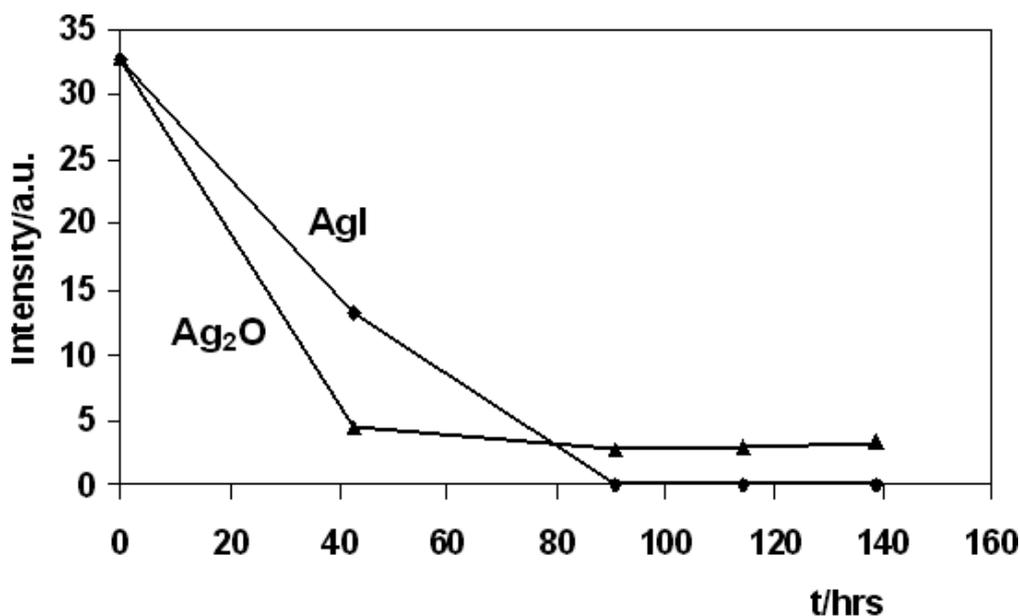


Fig. 10. The intensity of (002) γ -AgI and (002) Ag₂O peaks in the diffraction pattern of the material of the 50AgI:25Ag₂O:25CrO₃ nominal composition as a function of the milling time in the home-made planetary mill.

do not proceed in a single step. If it would be so, then all peaks would change at the same rate. The faster lessening of silver oxide indicates then, that the silver oxide reacts first and only reasonable option is its reaction with V₂O₅ or CrO₃, the compounds well known as glass formers [21]. Next, the newly formed intermediate product participates in a subsequent reaction with AgI. In consequence, its total concentration in the mixture is low, therefore the XRD investigations, requiring a relatively high threshold concentration of a foreign crystalline phase to be detected, fail, when they are employed to detect new phases in the milled materials. However, the subsequent reaction does not produce a crystalline phase but it should form an amorphous one. Ubiquitous ‘halo’ peaks visible always in the patterns of milled materials advocate for such mechanism. During this reaction the intermediate products gradually incorporate silver iodide molecules. So, the process could be considered as equivalent to solid state dissolution, in which the intermediate products are treated as a solvent and the AgI as a solute.

The presented model of the reaction enables a qualitative explanation of the experimentally observed differences between decrease rates of the AgI and the Ag₂O concentration during milling of the materials. If one assumes, that the process of

the silver iodide dissolution is slower in respect to the synthesis rate of the intermediate product, then during reactions, in a unit time, more Ag₂O molecules will be used and transformed than those of the AgI. When the initial silver iodide concentration in the mixture is higher than solubility limit, the unreacted AgI will remain in the amorphous phase, like it is observed for the case of long milled xAgI-0.25(100-x)(3Ag₂O-V₂O₅), $x \in (70,85)$ and the 70AgI:15Ag₂O:15CrO₃.

The discussed mechanism shares many common features with glass formation mechanism of the silver ion conducting superionic glasses, which are prepared via high temperature routes. It is well known, that when silver iodide is added, glasses are easily formed, even for low quenching rates [23]. A numerous experimental evidences highlight the importance of silver iodide in the glass formation. This compound preserves a disorder in the glass structure [23]. In case of the ball-milling, one should take into account, that this process takes place under severe, non-equilibrium conditions, which means, that locally in the milled mixture could be high temperature and pressure, although the mixture as a whole stays at normal conditions. In consequence, these factors could create locally favourable conditions, a melt-glass like, which pro-

mote formation of the amorphous phase according to the suggested mechanism.

4. CONCLUSIONS

The investigations show, that the mechanosynthesis could be a useful, competitive and also alternative method of preparation of the amorphous silver ion conducting superionic materials in respect to the classical, high temperature routes, allowing to synthesize new materials, unobtainable otherwise.

The milling speed, apart from the milling time, seems to be a key factor for the effectiveness of the process leading to formation of the amorphous chromate and vanadate materials.

The model of the synthesis process has been suggested. During initial stages of milling the Ag₂O and chromium or vanadium oxides react together forming some new phases. Then this intermediate products act as a solid solvent dissolving a silver iodide component of the mixture.

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