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Mechano-insertion syntheses of molybdate silver ion conductors: Process traits and driving factors

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ABSTRACT

In this work we present traits of mechano-inserion technique employed in a formation process of AgI-Ag_2O-MoO_3 ion conductors. Our methodology adopted incorporation of external AgI amounts into ahead formed molybdate silver ion conducting glasses by means of ball-milling method. The primary glasses were formed using rapid quenching techniques with applied different cooling rates. The final synthesis of both components resulted in formation of new products: homogeneous or heterogeneous. We discuss the principles governing in the synthesis course in terms of processing method and starting materials. Correlation of XRD and MDSC results points to central factors driving the mechano-insertion process: alongside of mechanosynthesis parameters, the target chemical composition and structure of primary glass precondition the properties of yielded products.

1. Introduction

Since few decades silver ion conductors attract the attention of researchers as technologically applicable materials. Within group of solid electrolytes, Ag^+ conductors are considered as an operational component of electrochemical devices by virtue of a major encompassed by subgroup: superionic conductors [1–3]. Highly conducting properties have been observed in a range of materials: from homogeneous – amorphous and crystalline – to heterogeneous. Considering the number of released articles and published findings, the hallmark of the highest attentiveness, in terms of applications and physical properties, apparently belong to superionic glasses [4].

Most common fabrication method of superionic glasses is the high temperature route synthesis: the method implements melting of the constituents at elevated temperatures and rapid cooling of the melt [5–8]. On the other hand, since late 90', a novel technique of glass formation that could be conducted in room temperatures emerged – mechanosyntehsis [9,10]. In this synthesis method ingredients participate in ball-milling process executed in milling vials; ball-powder collisions of small amounts of ingredients entail agitation, reactions and lastly synthesis of the starting mixture [11–13].

The literature reports present a broad and extensive discussion on the influence of preparation methods and process parameters on final composition of formulated glasses. From this picture one can get the notion of certain limitations of the high temperature approaches. That is because rapid cooling methods provide only narrow range of parameters that may be manipulated: time, temperature, humidity conditions and rate of cooling, [14,15]. In contradiction mechanosynthesis method offers a set of easily controllable parameters in respect to the milling procedure. These are: milling speed, milling time, ball-to-powder mass ratio, presence of supporting agents and mill type [9–11]. The juxtaposition of advantages and constrains of both approaches gives an ambiguities impression on the effectiveness and performance of both synthesis means. It raises the issue, whether it is possible to formulate alike products within the first and later method. As the answer appears twofold and links to the structure of synthesized materials, it is worthy to pinpoint on the researcher's intention and adopt most suitable practices [14,16].

Nevertheless, the need and eagerness for seeking of novel materials and technical solutions pushes forward towards development of sophisticated tools and optimization of existing ones. These aim attention at achieving better results than for existing solutions. And from technical applications point of view, one of the most crucial attributes of ion conductors is the value of total ionic conductivity. At this point the seek for possibilities of total ionic conductivity enhancement arises.

In the light of above, one of the most interesting and worth exploring variation of feasible methods is the mechano-insertion operating pattern [10,17]. The process aims to formulate a product from primary material (A) enriched by supplementary component (B). The mechano-insertion occurs by cause of mechanical interactions of (A) and (B) components processing in a suitable milling vial. In a common

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variation, a glassy material stands for (A) whereas (B) material, inattentive to its structure crystalline or amorphous, is being incorporated to the glass in order to maintain an amorphous structure of the overall product.

The literature reports increased values of ionic conductivity for materials with higher AgI contents [18]. So, in regards to the ionic conductivity enhancement, the opportunity of glass treatment and thus "injection" of additional AgI amounts appears as very promising. Considering that (A) is an ion conducting glass and silver iodide plays the role of component (B), according to mechano-insertion pattern there is a possibility to incorporate pristine silver iodide into the glass matrix and thus provide a significant ionic conductivity enhancement. Such methodology may be remarkably useful for improvements of finished glasses.

In these terms, usage of mechano-insertion may lead towards developing novel materials exposing higher conductivity values. Therefore, we want emphasize some of the traits: this work aims to demonstrate the possibilities of superionic glasses formation with increased AgI contents obtained by means of mechano-insertion technique.

2. Experimental

Investigated materials were formed by means of: standard melt-quenching procedure (MQ), ultra-fast quenching method (UFQ), and mechano-insertion technique (MI). Prepared in suitable molar ratios batches were grounded with a mortar and a pestle. All operations were executed on laboratory benches in an open air without preheating, drying and any additional precautions against moisture.

As the MQ and UFQ techniques involve melting and rapid cooling of a melt, aligned procedures were adopted. An open vertical furnace was employed for heating operations. At first, the mixture was heated from room temperature to about 300 °C and stored until melting of the ingredients. Within that stage volatile products of the synthesis were released to the atmosphere. Then, the temperature was elevated up to about 750 °C. After stilling of the melt, what indicated the completion of the synthesis, the melt was additionally annealed for 15–20 min. In the last stage the melt was rapidly cooled. For MQ technique melted material was poured out between two stainless steel plates and quickly quenched. In result 0.5–0.9 mm thick glassy samples were formed. For UFQ method the melt was streamed between steel rotating twin rollers with speed of 90 rpm. The procedure was supported with additional nitrogen cooling system. Such approach resulted in formation of thin ribbons and flakes. Formed products were grounded into a powder form of separate batches.

The MI syntheses were carried out by means of *Fritsch Pulverisette P7* planetary ball mill. The as prepared reagent batches of overall mass 3.5 g were located in suitable 45 ml Si_3N_4 vials. Three Si_3N_4 balls were used in order to maintain the ball-to-powder mass ratio equal to 10:1 [9]. The mill operated at 600 rpm rotation speed for 6 h in a constant work mode without supporting grinding mediums.

The structure of as-received materials was investigated by means of X-ray powder diffraction (XRD) employing Phillips X'Pert Pro diffractometer set up in a Bragg-Brentano configuration with filtered Cu Kα radiation. Presented thermal studies root in results provided by modulated differential scanning calorimetry method (MDSC). For this cause the Thermal Analysis TA Q2000 calorimeter was employed. The device operated in a heat-flow mode within a temperature range from 0 °C to 220 °C; the modulated component of temperature oscillated with amplitude of 1 °C and 3 °C period. The errors values provided for the measured quantities were determined according to the guidance of the manufacturer of TA Q2000. These include random errors measured as the standard deviation of the average value of determined quantities relevant to the: glass transition temperature determination onset points and enthalpy integration area bounded by inflection points of heat flow signal.

3. Results

3.1. Primary components: MQ and UFQ glasses

The rapid quenching techniques MQ and UFQ were employed for production of relevant (A) glasses. For further studies we selected two compositions: 30AgI-35Ag_2O-35MoO_3 and 40AgI-30Ag_2O-30MoO_3, thus four separate materials batches were formed. All products were examined by means of XRD method. As no visible bragg peaks were visible, XRD results confirmed the amorphous structure of these samples.

In order to investigate differences between formed materials we employed the MDSC method. Fig. 1 and Fig. 2 collect heat flow signals of 30AgI-35Ag_2O-35MoO_3 and 40AgI-30Ag_2O-30MoO_3 samples respectively – the a) traces denote materials formed by MQ method and b) stands for signals assigned to UFQ products. Two lines are visible for each figure: solid lines denote values of reversible heat flow part, whereas the dashed ones represent nonreversible components.

For the 30AgI-35Ag_2O-35MoO_3 (Fig. 1 a)) glasses the traces assigned to reversible part of heat flow reveal visible drop in the 95 °C–100 °C temperature range. Subsequent exothermal processes peak at 137 °C and 162 °C for the melt-quenched material, whereas for ultra-fast quenched material the maxima appear at 136 °C and 156 °C. In case of 40AgI-30Ag_2O-30MoO_3 (Fig. 2 a)) glasses the primary drop is also visible, however it is was recorded in 80 °C–95 °C range. At higher temperatures only one exothermal event was detected: the maximum is located at 134 °C for MQ material and at 126 °C for UFQ material.

Lines designating non-reversible component of heat flow present different profile. For 30AgI-35Ag_2O-35MoO_3 glasses (Fig. 1 b)) as first thermal event a broad low-intensity maxima is visible in temperature ranges of 70 °C–95 °C and 80 °C–95 °C for MQ and UFQ respectively. Consequently an endothermal process was recorded for both glasses: 95 °C–107 °C for the melt-quenched and 95 °C–105 °C for the ultra-fast quenched. In elevated temperatures both samples revealed

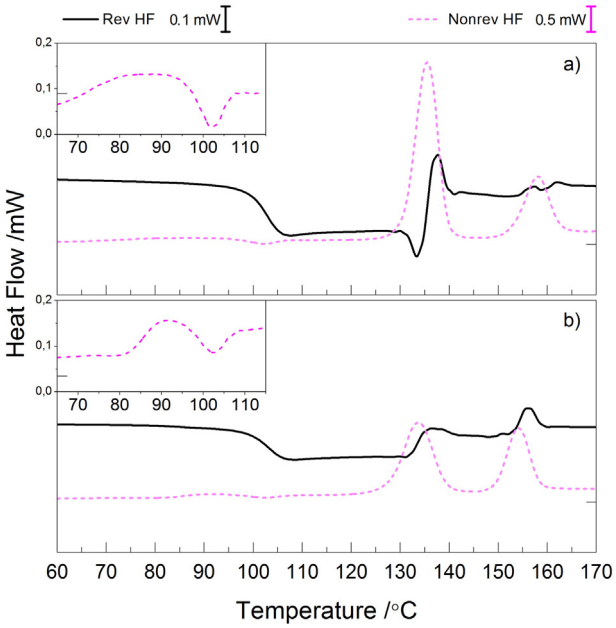

Fig. 1. MDSC scans of 30AgI-35Ag_2O-35MoO_3 glasses formed by means of a) melt-quenching and b) ultra-fast quenching techniques. Solid line denotes reversible component of heat-flow signal whereas dashed line represents non-reversible part. Inset figures present magnified sections of non-reversing traces in temperature ranges adjacent to glass transitions.