Journal of Non-Crystalline Solids 459 (2017) 169–175

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

An experimental study of the effect of AgI on the optical and electrical properties of conductive glasses in the system AgI-$AgPO_3$-WO_3

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ARTICLE INFO

Article history:
Received 1 November 2016
Received in revised form 19 December 2016
Accepted 3 January 2017
Available online xxxx

Keywords:
Silver iodide
Tungsten oxide
Silver phosphate glass
Multifunctional glasses
Ionic conductivity

ABSTRACT

This study describes the preparation and characterization of AgI-$AgPO_3$-WO_3 glasses displaying unique optical and electrical properties for applications where simultaneous optical and electrical transmissions are required, especially in the field of electrophysiology. Glass samples were produced following the composition laws (45-x)AgI-(50 + x)$AgPO_3$-5WO_3 and (45-x)AgI-(45 + x)$AgPO_3$-10WO_3 with x = 0–45 mol%. Their features can be precisely tailored by adjusting the concentration of silver iodide. The determination of the vitreous domain within the AgI-$AgPO_3$-WO_3 pseudo-ternary diagram showed the main role played by $AgPO_3$ and WO_3 as glass-former. Raman spectroscopy has been performed to understand how AgI is incorporated into the phosphate glassy network which relies on chains of Q_2 tetrahedral units. The measured short cut-off wavelength increases from 418 nm up to 480 nm whereas the refractive index linearly increases from 1.70 up to 2.05 by increasing the AgI concentration from 0 to 45 mol%. The electrical conductivity of the glasses has been measured between 25 and 100 °C at 1 MHz AC frequency with values ranging from 10^{-5} S·cm^{-1} up to 10^{-2} S·cm^{-1} in accordance with the increasing AgI content. Taken together, the results presented in this study make these glassy materials promising candidate in the field of multifunctional optical fibers for electrophysiology applications.

1. Introduction

In the past few years, multimaterial fibers that concurrently display different functions have been extensively studied in the field of piezoelectricity, physical/chemical sensing and electrophysiology [1–8]. These fibers are usually made of different metals (e.g. tin), polymers (e.g. polymethylmethacrylate, polycarbonate) and glassy materials (e.g. semi-conducting $As_{40}Se_{50}Te_{10}Sn_5$ chalcogenide glass). Recently, we demonstrated that a new kind of fibers can ensure optical guidance and electrical transport by using silver iodide (AgI) based glasses [9]. Among the plethora of ion conducting glasses, AgI based glasses have been the most investigated for their ability to conduct electricity and are considered to be among the best electro-conductive glass systems [10–13]. AgI is a superionic compound that has been intensively studied for its unusual high electrical conductivity above 147 °C in its alpha phase [14,15]. Despite the fact that this phase can be stabilized in a glassy matrix at room temperature, it usually results in glasses with too poor mechanical properties to envisage their use in practical applications [16–19]. Nonetheless, AgI has been used in disordered materials to achieve high electrical conductivity. Indeed, the presence of iodide anions (I^-) leads to the formation of free volume inside the glassy matrix which in turn permits the silver ions to move more easily inside the open channels structure to conduct electricity [20–22]. The most studied AgI-containing glasses are those based on the xAgI-(1-x)$AgPO_3$ pseudo-binary system with x = 0–60 mol%. Ionic conductivity as high as 10^{-1} S·cm^{-1} has been reported for low frequencies at room temperature in this system [11]. Numerous studies carried out on the xAgI-(1-x)$AgPO_3$ glass system have shown a significant increase of the electrical conductivity with increasing AgI content [10–13]. However, to the best of our knowledge, no AgI-$AgPO_3$-M_yO_x system has been investigated with respect to the effect of silver iodide AgI on the optical, thermal and electrical properties except for the AgI-$AgPO_3$-Ag_2MoO_4 system [23]. Unfortunately, their very low softening temperature (i.e ≈ 100 °C) and their hygroscopic nature make them very difficult to use in practical applications. To circumvent this drawback we fabricated and characterized optically and electrically conductive glasses and optical fibers in the 45AgI-(55-x)$AgPO_3$-$x$$WO_3$ system, with x = 0–25 mol%, by maintaining constant the concentration of AgI and by varying the content of tungsten oxide (WO_3) [9]. This study evidenced improvement on the moisture resistance of the AgI-$AgPO_3$ materials with increasing the WO_3 content, because of the reticulating effect of W^{x+} ions, which is observed with high coordination transition metal oxides [24,25,26]. The phosphate glasses, especially AgI-$AgPO_3$, are susceptible to react with water by hydrolysis reactions. A heavy atom like tungsten can act as a Lewis acid and will interact with the oxygens of

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http://dx.doi.org/10.1016/j.jnoncrysol.2017.01.011
0022-3093/

the silver phosphate chains ($AgPO_3$), impeding their eventual reaction with water, increasing thus the glass density and chemical durability. We also proposed that the red shift in the optical transmission was due to the reaction between WO_3 and iodine (I_2). Typical targeted applications for these materials rely on the fabrication of multifunctional fibers for electrophysiological studies [1,27]. In such application, the prerequisite for the proposed fibers is the transmission of light and the conduction of electricity in order to optically excite the optogenetically modified nervous cells and subsequently probe the generated electric signal. Thus, the optical and electrical properties of the selected glassy materials have to be easily adjusted in order to meet the requirements of measurement parameters. First, the impedance magnitude has to range in the order of 10 MΩ to record the electrical activity of few cells. If the impedance is too low, the electrical activity is recorded on too many cells and the specificity is lost. Second, the excitement of optogenetically modified neurons at 488 nm wavelength requires that the glass transmits blue light. Therefore, a systematic study has been conducted to determine the best candidate exhibiting both efficient optical transmission in the visible spectrum and sufficiently low electrical resistance.

2. Materials and methods

2.1. Sample preparation

Tungsten(VI) oxide powder (99.9%) and ammonium phosphate monobasic (≥98.5%, *ReagentPlus*) were both obtained from Sigma Aldrich. Silver nitrate (99.9%, ACS grade) was obtained from Alfa Aesar. Silver iodide (≥99.9%) was obtained by a silver recycling method previously developed in our laboratory [28]. The $AgPO_3$ is synthesized by reaction of silver nitrate ($AgNO_3$) with ammonium phosphate monobasic ($NH_4H_2PO_4$) followed by successive temperature steps method. First, the mixture was loaded in an alumina crucible, heated to 300 °C at a rate of 2 °C·min^{-1} and kept at this temperature to allow a progressive degassing of the reaction. Then, the mixture was heated to 350 °C and kept at this temperature during 24 h to allow the two compounds to react completely together to form $AgPO_3$. The $AgPO_3$ was finally heated to 500 °C and kept at that temperature during 60 min to decrease its viscosity and facilitate its casting into a stainless steel mold at room temperature. Considering the purity of the starting materials $AgNO_3$ and $NH_4H_2PO_4$, we can reasonably believe that the obtained $AgPO_3$ has a minimum purity of 98.5%.

Glasses following the composition laws (45-x)AgI-(50 + x)$AgPO_3$-5WO_3 (AAW5) and (45-x)AgI-(45 + x)$AgPO_3$-10WO_3 (AAW10) with x varying from 0 to 45 mol% were prepared. Samples with a 10 mm diameter and 5 mm thickness were obtained by simple powder melting in crucible/pouring method at 1000 °C during 10 min [9]. The AgI provides the silver ions for the transport of electricity, the $AgPO_3$ is the glass matrix that enables the dissolution of high concentration of metallic ions and the WO_3 is used to increase the durability of the glasses. Each glass is then polished for the optical and electrical characterizations.

2.2. Optical and Raman spectroscopy characterizations

The optical transmission spectra were measured by using a UV-VIS-NIR Agilent Cary 5000 double beam spectrophotometer on polished 5 mm-thick samples. The linear refractive index has been measured by using the prism coupling technique (M-lines Metricon 2010) at 532, 633, 972, 1308 and 1538 nm with a precision of ±0.001.

The Raman spectra were obtained with a Renishaw inVia spectrometer coupled to a Leica DM2700 microscope in the frequency range of 300–1200 cm^{-1} with an uncertainty of ±2 cm^{-1}. The excitation light source was a vertically polarized He-Ne laser with a wavelength of 633 nm and a power of 17 mW. The laser beam was focused on glasses surface with a 50× long working distance objective. No photoinduced effect was observed after laser expositions.

2.3. Electrical conductivity characterizations

The electrical characterizations of the bulk glasses were performed using a 1260 Solartron impedance analyzer at 1 MHz frequency, with an applied voltage of 100 mV and an accuracy of 0.1%. The 5 mm-thick glass samples were disposed between two platinum electrodes embedded in a vertical resistive split furnace for temperature dependent measurements. The 2-point conductivity method was used with a 4-terminal measuring device that eliminates lead or parasite resistances on the electrodes. To allow better contact between the platinum electrodes and the glass samples, silver paint was applied on both contact surfaces of the glasses. The silver paint used is colloidal silver from Pelco with a sheet resistance of 0.02–0.05 Ω/sq/mil. It is important to note that the silver paste is a colloid which is basically made of silver Ag^0 particles and not of silver ions Ag^+. Thus, it is very unlikely that the particles will diffuse inside the glass since they are too large (1–16 μm). Electrical conductivity measurements were performed as a function of temperature, from 25 °C up to 100 °C for each sample.

2.4. DSC and density characterizations

Differential scanning calorimetric (DSC) measurements were performed using a Netzsch DSC Pegasus 404F3 apparatus on small glass pieces with a mass of (20 ± 5) mg into sealed Al pans at a heating rate of 10 °C·min^{-1} up to a temperature of 600 °C. The glass samples density was measured according to the Archimedes' principle by using a Mettler Toledo XSE204 balance (precision: ±0.1 mg) with distilled water as buoyant liquid.

3. Results and discussion

3.1. Glass forming range

To represent the glass forming ability in the AgI-$AgPO_3$-WO_3 and the $AgPO_3$-WO_3 systems, we plotted multiple compositions series into a ternary diagram (Fig. 1), which is the first one reported to date with these systems in the conditions of preparation described in the materials and methods section. As one can see, a large glass forming domain can be achieved allowing multiple compositions of glass. We first

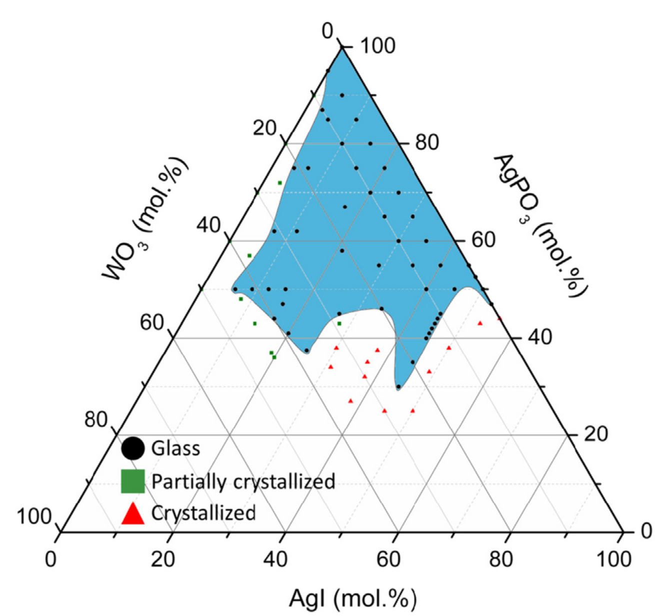

Fig. 1. AgI-$AgPO_3$-WO_3 pseudo-ternary diagram with the glass forming region (blue area). The green squares and the red triangles represent partially crystallized and crystallized glasses respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)