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New chalcogenide glasses in the CdTe–AgI–As_2Te_3 system

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ABSTRACT

Chalcogenide glasses in the pseudo-ternary CdTe–AgI–As_2Te_3 system were synthesized and the glass-forming range was determined. The maximum content of CdTe in this glass system was found to be equal to 15 mol.%. The macroscopic characterizations of samples have consisted in Differential Scanning Calorimetry, density, and X-ray diffraction measurements. The cadmium telluride addition does not generate any significant change in the glass transition temperature but the resistance of binary AgI–As_2Te_3 glasses towards crystallisation is estimated to be decreasing on the base of $\Delta T = T_x - T_g$ parameter. The total electrical conductivity σ was measured by complex impedance spectroscopy. First, the CdTe additions in the $(AgI)_{0.5}(As_2Te_3)_{0.5}$ host glass, $(CdTe)_x(AgI)_{0.5-x/2}(As_2Te_3)_{0.5-x/2}$ lead to a conductivity decrease at $x \leq 0.05$. Then, the behaviour is reversed at $0.05 \leq x \leq 0.15$. The obtained results are discussed by comparison with the equivalent selenide system.

1. Introduction

The scientific interest in chalcogenide and chalcohalide glasses arises from their numerous applications in scientific and technological field. They are suitable model materials to verify theories of glass formation, network rigidity, ionic and electronic transport in disordered systems ([1–4] and references therein). In addition, chalcogenide glasses show large non-linear properties and high transparency in the near- and mid-infrared region making them very suitable for many optical applications including optical fibres [5], waveguides [6], and solar cells [7]. Also the reversible photo structural changes taking place within the amorphous phase [8] and/or the photo-induced phase transition occurring between the amorphous and crystalline phases [9] allow wide range applications in optical memories and optical data storage [10]. From an analytical point of view, their potential application as chemical sensors has been widely demonstrated both in biological and environment fields. The bio-optic sensor can be designed in fibre to spectroscopically detect the cell response to various toxic agents [11,12]. The in situ monitoring in real time of pollutants in wastewater has also been demonstrated using chalcogenide optical fibres [13]. Membranes based upon chalcogenide glasses were used in ion-selective electrodes (ISE) for detection of heavy metals and toxic anions in solutions [14–16].

In this paper, the glass-forming region of the pseudo-ternary CdTe–AgI–As_2Te_3 system is determined for the first time. Glasses of the binary AgI–As_2Te_3 system were also synthesized over a wide composition range up to 65 mol.% of AgI in accordance to previous work [17], in order to study and well understand the effect of both AgI and CdTe additions. The new pseudo-ternary chalcogenide glasses, which are very promising material for membrane of ISE, are investigated from physical, thermal, and conductivity point of view. As_2Te_3 is one of the highest conductivity components of glasses with a hole conductivity and AgI is one of the best cationic conductors. The incorporation of AgI, crystalline compound with extraordinarily high ionic conductivity, into As_2Te_3 glass matrix reveals a mixed electronic–ionic behaviour of conductivity [17]. The conductive electronic process predominates over the ionic process, thus revealing a major difference from the super ionic conductor AgI–As_2Se_3 binary glass system [18,19]. The CdTe additions in the binary system, necessary in case of ISE applications dedicated to the Cd^{2+} heavy metal, are also expected to generate changes in the total conductivity behaviour. The results are investigated on the base of three different A, B, and C series corresponding to the specific compositions $(CdTe)_x(AgI)_{0.5-x/2}(As_2Te_3)_{0.5-x/2}$ with $0.0 \leq x \leq 0.2$, $(CdTe)_{0.1}(AgI)_y(As_2Te_3)_{0.9-y}$ with $0.0 \leq y \leq 0.7$, and $(AgI)_y(As_2Te_3)_{1.0-y}$ with $0.0 \leq y \leq 0.7$, respectively. Finally, analogies and differences with the equivalent selenide system recently published [20–22] are discussed.

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2. Experimental

2.1. Glass preparation

All investigated samples were prepared using the appropriate proportions of AgI, CdTe, and As_2Te_3 precursors. The synthesis of AgI was carried out by precipitation in the absence of light by adding 6×10^{-2} M KI solution to 5.9×10^{-2} M $AgNO_3$ solution. After 3 h, the remaining liquid was decanted and the silver iodide precipitate was rinsed with distilled water several times. The precipitate was left overnight in water under agitation with magnetic stirrer, then filtered and dried at 110–120 °C. Commercial CdTe pieces (99.99% pure, Alfa) were employed for synthesis of the samples without additional purification. High purity (6 N, Cerac) As and Te pieces were used for the preparation of As_2Te_3. Te (CERAC, 99.999%) is beforehand treated by hydrochloric acid and thoroughly rinsed by absolute ethanol and distilled water, and introduced in the experimental set-up. As is introduced into the set-up and the high vapour pressure contaminants such as oxides are removed by evaporation (T = 290 °C) under vacuum. Both elements are then gathered and the resulting melt is homogenised in a rocking furnace at 800 °C for 24 h. The purified precursors were then weighted in correct proportions to get a sample of 3 g. Then, they were put under vacuum (10^{-6} mbar) in a cleaned silica tube (with a inner diameter of 8 mm and a thickness of 1 mm), heated slowly in a rocking furnace to 850 °C for 24 h, and cooled down to 650 °C before quenching in cold water.

2.2. Density, XRD and DSC measurements

The measurement of the sample density d was performed by a hydrostatic method using the toluene as immersion fluid and the germanium as standard (5.323 g cm^{-3}). A Sartorius YDK 01-0D density kit was used for the measurements, the sample mass in air varied between 0.4 and 1 g.

The amorphous nature of the samples was verified at room temperature by X-ray diffraction, XRD, technique using a Bruker D8 Advance diffractometer equipped with a copper anode (λ = 1.5406 Å). The scattering intensities were measured over an angular range of $4^\circ \leq 2\theta \leq 100^\circ$ with a step-size of $\Delta(2\theta) = 0.02^\circ$ and a count time of 2 s per step. The Bragg peaks in diffraction patterns of glassy/crystalline samples were identified and indexed using the JCPDS database.

Differential Scanning Calorimetry analyses using a Seiko SSC 5200 instrument were performed to determine the glass transition (T_g), crystallisation (T_x), and melting (T_m) temperatures of the samples. The samples of 10–15 mg were hermetically sealed in a standard aluminium pan and were heated at a rate of 10 K min^{-1} from 20 to 400 °C under high purity nitrogen gas.

2.3. Impedance measurements

Total electrical conductivity of the samples was measured using a Hewlett Packard 4194A impedance meter. The impedance modulus Z and the phase angle θ were obtained in the frequency range from 100 Hz to 15 MHz from room temperature up to 378 K, corresponding to a temperature below T_g for all the glass samples. The quenched samples, prepared as rectangular plates, were polished using SiC powder. The sample sides were ground parallel and gold was deposited on opposite sides to form electrodes, meaning that the electrochemical cell for conductivity measurements was Au|glass|Au. The typical sample thickness was 1.0 mm (±0.2 mm) and their areas were about 7 mm^2 (±1 mm^2). The temperature dependence on the conductivity was studied in several cycles, each consisting of a heating step followed by a cooling step, in order to investigate a possible hysteresis that was found to be insignificant.

3. Results and discussion

3.1. The glass-forming region

The glass-forming region of the pseudo-ternary system CdTe–AgI–As_2Te_3 obtained in our conditions of synthesis is presented in Fig. 1. This domain is located around the binary As_2Te_3–AgI line, in the As_2Te_3 side where glassy compositions are observed from pure As_2Te_3 until 65 mol.% of AgI. Whatever the binary composition in As_2Te_3–AgI system, the solubility of CdTe remains below 16 mol.%. The XRD patterns of two different series are shown in Fig. 2. The series A, corresponding to the formula $(CdTe)_x(AgI)_{0.5-x/2}(As_2Te_3)_{0.5-x/2}$ with $0.0 \leq x \leq 0.2$, exhibits only broad features characteristic of glassy and amorphous materials for $x \leq 0.15$. Narrow Bragg peaks appear and grow up in intensity with further increasing x. Similar DRX patterns were obtained for the series B, corresponding to the formula $(CdTe)_{0.1}(AgI)_y(As_2Te_3)_{0.9-y}$, allowing to estimate the limit of the glass formation for $0.1 \leq y \leq 0.6$ in our conditions of glass synthesis.

Cadmium solubility in chalcogenide glasses is usually low and this metal is often considered as a modifier and crystallisation agent [23]. The limited glass-forming range in the CdTe–AgI–As_2Te_3 system is not an exception to this rule. Besides, it is quite similar to the equivalent pseudoternary CdSe–AgI–As_2Se_3 system, even if the maximum solubility of CdX in the binary AgI–As_2X_3, X = Se or Te is higher for the selenide system [20]. For example, in the series A, the maximum of CdTe is 15 mol.% whilst in the equivalent selenide series, this maximum is 20 mol.%.

The observed crystalline phases in samples were all identified as Ag_2CdI_4 either the β and β' hexagonal or the γ tetragonal forms. The reactions leading to the formation of these crystalline phases could be the result of a possible exchange reaction taking place in the glass-forming melt:

$$CdTe + 2AgI \leftrightarrow CdI_2 + Ag_2Te \quad (1)$$

$$CdI_2 + 2AgI \leftrightarrow Ag_2CdI_4 \quad (2)$$

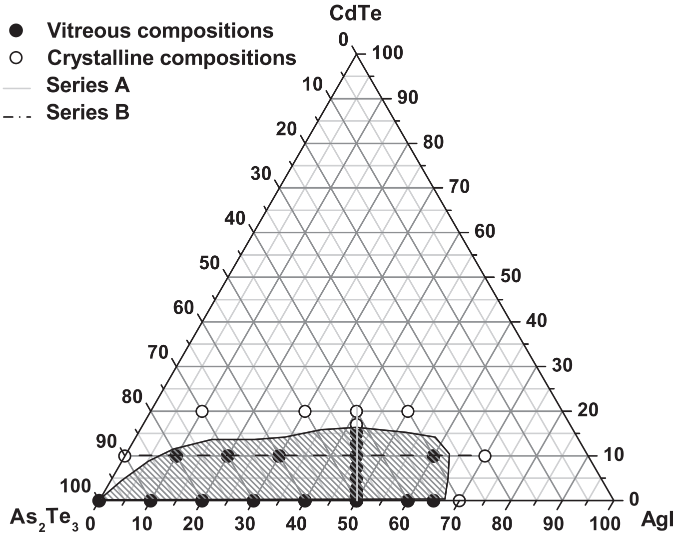

Fig. 1. Glass-forming region in the CdTe–AgI–As_2Te_3 pseudo-ternary system. The three series more particularly investigated are: Series A: $(CdTe)_x(AgI)_{0.5-x/2}(As_2Te_3)_{0.5-x/2}$, series B: $(CdTe)_{0.1}(AgI)_y(As_2Te_3)_{0.9-y}$, and series C: $(AgI)_y(As_2Te_3)_{1-y}$ (the bottom axis).