Journal of Non-Crystalline Solids xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

Ge-free chalcogenide glasses based on Ga-Sb-Se and their stabilization by iodine incorporation

Alicia Lecomte, Virginie Nazabal, David Le Coq, Laurent Calvez*

Equipe Verres et Céramiques, UMR-CNRS 6226 Institut des Sciences Chimiques de Rennes, Université de Rennes 1, 263 Avenue Général Leclerc, Rennes 35042, France

ARTICLE INFO

Keywords:
Chalcogenide glass
Glassy domain
Optical materials
Thermal analysis
Optical properties

ABSTRACT

In this paper, we report the existence of new bulk chalcogenide glasses free of germanium and transparent up to 18 μm. The investigation of the Ga-Sb-Se ternary diagram has allowed bringing out the presence of a small glassy domain mainly formed for compositions with low contents of Ga. Thermal, optical and mechanical characteristics of these glasses have been studied. In order to enhance the low stability against crystallization pure iodine was successfully added. At last, structural analysis by Raman spectroscopy was performed to point out the iodine addition effect.

1. Introduction

The civilian and defense applications of transparent chalcogenide glasses are mainly devoted to night vision because of their large window of transparency recovering the second (3–5 μm) and third (8–14 μm) atmospheric window [1].

For now, most of the marketable chalcogenide glasses used for night vision applications are made of germanium and selenium combined with gallium or antimony. Germanium is from far the most expensive compounds constituting these glasses. Some other glasses based on As_2Se_3 are also available but they suffer from their high photosensibility, crystallizing or strongly ageing under light. It is then of a paramount interest to develop new glass compositions free of germanium to give a better competitiveness toward monocrystalline germanium or polycrystalline ZnSe.

In this paper, new bulk glasses belonging to the Ga-Sb-Se binary system are described. In fact, the possibility to obtain nano-amorphous domain was demonstrated on several glass compositions by using ultrafast laser heating and quenching for making phase change memory materials [2]. However, never bulk glasses belonging to this domain were synthesized by the conventional melt-quenching method in silica tubes.

More recently, Jiao et al. and Yang et al. [3,4] worked on the analogous sulfide system showing a good ability to form glass with gallium and antimony entities. The substitution of sulfur by selenium is known to strongly broaden the transmission window in the infrared range permitting to take the full benefit of the third atmospheric window ranging from 8 to 14 μm.

2. Experimental

Glasses in the Ga-Sb-Se system were synthesized by melting the constituent elements (Ga, Sb, Se of 99.999%) under vacuum in a sealed silica tube of 8 mm and 10 mm as inner and outer diameter, respectively. The ampoule was heated up in a rocking furnace at 950 °C for 12 h and then the temperature was reduced to 870 °C for 2 h before being quenched in iced water. The sample was annealed 10 °C below Tg for 5 h to minimize the inner stresses induced by the water quenching. The glass was finally slowly cooled down to room temperature. Special cares were taken for the iodine-based sample syntheses using pure iodine (5N) as starting element because of its high vapor tension under vacuum. The procedure described by Zhu et al. has been carefully reproduced by maintaining the silicon tube in liquid nitrogen during pumping under vacuum [5].

The amorphous or crystalline state of synthesized Ga-Sb-Se samples allowing delimiting the glass-forming domain in this system has been determined using X-Ray Diffraction analysis on ground base samples. These experiments were carried out at room temperature with a Phillips PW3710 diffractometer equipped with a copper anode (λ = 1.5406 Å). The scattering intensities were measured over an angular range of $10^\circ \leq 2\theta \leq 80^\circ$ with a step-size of $\Delta(2\theta) = 0.02^\circ$ and a count time of 2 s/step.

The transmission measurements were performed with a double beam CARY spectrometer in the visible to calculate the optical band-gap. By convention, the optical band-gap has been calculated and obtained at 10 cm^{-1}.according to the Beer-Lambert law.

The infrared transparency has been checked using a Bomem Fourier transform infrared spectrometer from 2 to 25 μm.

* Corresponding author.
E-mail address: laurent.calvez@univ-rennes1.fr (L. Calvez).

https://doi.org/10.1016/j.jnoncrysol.2017.11.046
Received 28 September 2017; Received in revised form 23 November 2017; Accepted 26 November 2017

Scanning Electronic Microscope (SEM, JEOL IT 300) coupled with Energy Dispersive Spectrometer was used to analyze the glass composition and to verify the good accordance between the theoretical and experimental compositions especially when volatile iodine was incorporated.

Differential Scanning Calorimetry experiments (DSC 2010 TA Q20) were performed to measure the glass transition temperature (Tg) and the crystallization temperature (Tx), corresponding to the onset points. The experiments were led from room temperature up to 400 °C using a heating rate of 10 °C/min.

Hardness and toughness were determined using a Vickers micro indenter MATZUZAWA, with a charge of 50 g for 5 s. The reported value is an average of ten measurements.

Raman acquisitions were made with the HR 800–785 nm optical density D2 with a laser wavelength at 785 nm.

The thermal expansion coefficient (α) was determined by the means of a TMA 2840CE TA Instrument at 0.2 N from 20 °C up to 120 °C with a ramp of 2 °C/min.

The glass density was measured using the classical Archimedes technique in distilled water. The obtained value for each composition is an average of five measurements.

3. Results and discussion

3.1. Glass forming domain

The boundary of glassy domains directly linked to the small frontier between a glass and a glass-ceramic slightly crystallized is often still subject to discussion. In this study, only samples presenting both a high transparency in the infrared range and no crystallization signature in XRD patterns have been considered as glasses. In other words, samples presenting scatterings in the near IR but fully transparent in the mid-IR, constitute the boarder of the glassy domain, even if no crystalline signature is observed by XRD (crystals proportions < 5%). Fig. 1 shows the vitreous domain in the Ga-Sb-Se system obtained by taking into account the previous considerations. It can be noticed that the Ga content ranges from 4 to 12 at.%. Moreover, the minimum rate of Se is 50 at.% and no glass composition is found if this rate is higher than 62.5 at.%. Next, the minimum and the maximum of Sb content are

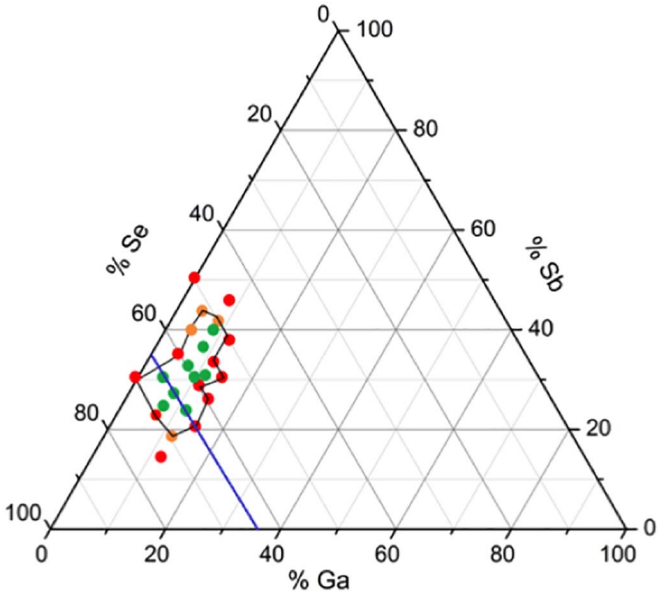

Fig. 1. Ga-Sb-Se ternary diagram obtained by melt-quenching in sealed silica tubes. Red dots are crystallized, orange are glass-ceramics, and green dots are glasses. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Thermal properties including Tg, Tx and ΔT = Tx − Tg (T ± 2 °C) for glass samples belonging to the ternary system Ga-Sb-Se.

Composition	Name	Tg	Tx	ΔT
		°C	°C	°C
$Ga_4Sb_{31}Se_{65}$	GSS-1	168	216	48
$Ga_8Sb_{24}Se_{68}$	GSS-2	180	233	53
$Ga_8Sb_{27}Se_{65}$	GSS-3	175	252	77
$Ga_8Sb_{32}Se_{60}$	GSS-4	227	292	65
$Ga_8Sb_{37}Se_{55}$	GSS-5	212	305	93
$Ga_8Sb_{40}Se_{52}$	GSS-6	211	293	82
$Ga_{10}Sb_{30}Se_{60}$	GSS-7	236	304	68
$Ga_{12}Sb_{23}Se_{65}$	GSS-8	180	257	77
$Ga_{12}Sb_{31}Se_{57}$	GSS-9	230	300	70

20 at.% and 40 at.%, respectively. Finally, the glass domain is mainly elongated according to the Se axis and poorly spread out. For a better reading, the series of samples has been named as “GSS-X” (Table 1).

3.2. Thermo-mechanical properties

Glass stability against crystallization has been calculated according to ΔT, which corresponds to the difference between the onset crystallization temperature (Tx) and the glass transition temperature (Tg). All the as-made glasses have ΔT below than 100 °C, which indicates a low stability against crystallization. This parameter is of paramount importance in order to make IR optics by molding at higher temperature than Tg, usually Tg + 50 °C for shaping lenses and Tg + 100 °C for drawing fibers.

Moreover, glass transition temperatures are rather low compared to Ge-Sb-Se glasses (about 250 °C) and Ge-Ga-Se glasses (about 350 °C) [6–8], showing a low reticulation of the glassy network. Although it can be assumed that Se and Sb are two-fold and three-fold coordinated, respectively, the coordination of Ga can remain unclear [9]. In fact, many studies have [4,6,7,9,15] demonstrated that high concentration of Selenium elicits Se−Se chains according to the composition giving a higher flexibility to the network. The higher coordination number of Ga and Sb (tetrahedral and pyramidal coordination for Ga and Sb with Se, respectively) in vitreous system induces a breaking of the Se−Se chains and consequently a higher reticulation of the glass network. It leads to a more rigid network with higher thermo-mechanical properties.

In the present study, the substitution of Se by Ga is characterized by an increase of Tg (see for ex: GSS-1 and GSS-9, 185 °C vs 230 °C, respectively) whilst the substitution of Sb by Ga tends to slightly decrease Tg (See for ex: GSS-1 and GSS-8, 185 °C vs 180 °C). If we consider that the total coordination number is the main responsible of the Tg evolution, the first case can be easily explained. Unexpectedly, in the second case, the explanation based on a tetrahedral coordination of the Ga should also give higher Tg when Sb is substituted by Ga. Nevertheless, another Tg comparison between $Ga_{10}Sb_{30}Se_{60}$ (Tg = 230 °C) and $Ge_{10}Sb_{30}Se_{60}$ (Tg = 277 °C) [10], one can assume that the coordination number of Ga could be 3 rather than 4 since the germanium coordinate number is well-known to be 4, and the glass based on Ge exhibits a higher Tg.

Then, studies have been focused on glasses containing 65 at.% of Se (blue line in Fig. 1). The results of thermal and mechanical properties are listed in Table 2.

From this low reticulation of the glass network follows rather low Vickers hardness ranging from 130 to 158 Hv and a large range of relatively high thermal expansion extending from 12 to 23 $\mu m \cdot m^{-1} \cdot °C$. As already demonstrated by Calvez et al. in the Ge-Ga-Se system, increasing amount of Gallium leads to a glass bleaching whatever the Sb/Se ratio [8].