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Investigation of the drawing region in the production of Ge-S-I optical fibers for infrared applications

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ABSTRACT

In the present work, series of Ge-S-I glass samples with 5, 10 and 15% of iodine and a concentration of germanium varying between 25 and 35% were prepared and their physical properties such as Tg, density, Visible and infrared light absorption were investigated. From the analysis of the properties close to the stoichiometric composition $(GeS_2)_xI_{100-x}$, we propose an equation of composition that takes into account the effect of iodine as a structure modifier. A great change is observed in the band-gap and Tg values, both of which follow the $(GeS_2)_x$—$(GeI_4)_{1-X}$ composition line. We report for the first time a study of the drawing ability of these glasses using a preform-to-fiber drawing technique, to obtain fibers with wide composition range. The results allow us to define a fiber drawing domain inside the glass forming region. We demonstrate that the fiber drawing region is located between two composition lines for which the Mean Coordination Number (MCN) values are 2.4 and 2.55. Attenuation losses measured at 1310 nm for some selected fibers range between 10.9 and 23.0 dB/m.

1. Introduction

Nowadays high purity As_2S_3 chalcogenide fibers with low loss are easily obtained by the double crucible method [1]. However, arsenic is considered toxic which makes them unsuitable materials for medical or environmental applications [1]. In the large family of chalcohalide glasses, Ge-S-I glasses combine high transparency from the visible around 500 nm to the infrared at 12 μm [2,3], a good solubility of rare earth elements [4], a good thermal and chemical stability [5], so they are potential candidates for lasers fibers and amplifiers in the mid-IR. The preparation and characterization of Ge-S-I glasses was reported for the first time in 1971 [5], however they were less studied than other chalcogenide glasses because of their optical quality. Nevertheless they recently received great interest with the development of a new method of synthesis and purification that enables preparation of glasses with higher levels of purity and lower temperature of synthesis [6], by thermal decomposition of $Ge_2S_3I_2$. Since then, much research has been done to determine more precisely their properties, but also their capability to be drawn into optical fibers by the investigation of their thermal stability [7]. The analysis of properties such Tg or band-gap (Eg) have shown that these glasses have extreme values in their properties which have been related to the stoichiometric composition GeS_2 [8], considering intrinsically iodine as a spectator, i.e. it does not have any interaction with germanium or sulfur. However, structural characterization by Raman spectroscopy indicated that the introduction of iodine induces the formation of GeI_zS_{4-z} structural units [9,10] (where z can take the values 1, 2, 3 and 4). Hence, the incorporation of iodine in the glass composition is expected to modify the extreme value' position. Therefore, a careful analysis of the properties around the stoichiometric composition is highly needed to get a better understanding of the iodine effect on the glass. Additionally, recent works have shown the potential of Ge-S-I glasses to be *co*-drawn with polymers to make multimaterial fibers [11], or the possibility of making them by new methods such as plasma-enhanced chemical vapor deposition [12]. Recently, Ge-S-I optical fibers with only two compositions could be obtained by the single crucible method [8], but no studies using the classical preform drawing technique have been reported so far.

In this work, we investigate the possibility of producing optical fibers with a wide range of Ge-S-I glass compositions using the classical preform-to-fiber drawing technique, to provide more information about the drawing region of this ternary system. For that purpose glasses with 5, 10 and 15 at.% of iodine and an atomic concentration of germanium varying between 25 and 35% have been prepared. In the first part of the paper we report and discuss the physical properties of the bulk samples such as Tg, density, refractive index, Visible and IR absorption spectra. We particularly studied the properties of the glasses at the border line

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$(GeS_2)_xI_{100-x}$ close to the extreme value of Tg, and we report new results that indicate a modification of this border position due to iodine incorporation. In the second part, based on our investigations of drawing tests of all the compositions we depict a ternary diagram in which we define a drawing domain inside the glass forming region. Optical losses of some glass composition optical fibers are also reported to demonstrate the potentiality of producing optical fibers.

2. Experimental

2.1. Glass and preform synthesis

Ge-S-I glasses were prepared by the melt-quenching technique starting from pure elements, germanium (5 N), sulfur (5 N) and iodine (3 N). Additional steps of purifications were made for some samples: distillation of sulfur and iodine, thermal stripping of germanium. The batches were loaded into a silica glass ampoule which was sealed under high vacuum (10^{-5} Torr), forming the synthesis tubes. The synthesis uses a slow heating ramp at 1 °C/min in the aim to avoid a quick rise of the pressure in the ampoule and its explosion, but also enable to continue the reaction of the precursors until the furnace riches the final temperature of 850 °C. Then the final reaction (melting of germanium mainly) and the homogenization of the melt takes place during 12 h. Synthesis tubes were then quenched in water at 650 °C, or in air (for glasses containing a large amount of sulfur). They were then annealed in a furnace at 10 °C below the Tg during 6 h to remove the internal stress and then slowly cooled to room temperature. Preforms in the form of rods with 10–12 mm of diameter and 80 mm of length were prepared for drawing single index fibers. Preforms were obtained directly in the silica glass ampoules after quenching, which is the reason of glass preforms shape. The surface of the preform is naturally polished by the inner surface of the ampoule during quenching. Slices of 1–2 mm of thickness were cut on the preform before drawing and polished with abrasive silicon carbide disc (grit 400 to 1200) for optical characterizations.

2.2. Fiber drawing

Optical fibers with 130–180 μm of diameter were obtained using the preform-to-fiber drawing technique [13,14]. This process is the most used in the field of fiber optics production. The technic consist of holding the preform with a piece of rod and maintain it with a chuck mounted on a translation stage. The preform is fed into a furnace at the hot zone position to obtain a weight which drop from the preform. The fiber is then hand taken to the bottom of the tower to start the process. In our case the preform was fed into a furnace under continuous high purity argon gas flow (2 L.min^{-1}), heated above the glass transition temperature and stretched at a rate of 2–2.5 m/min. A polymer coating was deposited on the fiber before winding on a capstan and > 20 m of unclad fibers (single index) were obtained for compositions with a good ability to be drawn.

2.3. Material characterization

Glass transition temperatures were determined by differential scanning calorimetry (DSC) using a Netzsch DSC Pegasus 404F3 apparatus. Small pieces of glass loaded and sealed into Al pans, were heated at a rate of 10 °C min^{-1} up to 500 °C (accuracy ± 2 °C). The refractive indices of the samples were determined by measuring the Brewster angle at 935 nm by using a set-up (external reflectivity) developped by one of us [15] with a precision of ± 0.02. The density of each sample was measured according to the Archimedes' principles on a Precisa XT 220A weighing scale by immersing a glass chunk in diethyl phthalate at room temperature with an estimated error of 0.001 g/cm^3. The stoichiometry of the samples was controlled after synthesis using a C-AMECA-SX100 (Cameca, Gennevilliers, France) electron probe microanalyzer. The analysis was made by wavelength-dispersive spectroscopy (WDS) employing an electron microprobe (EPMA) with an accelerating voltage of 15 kV and a current of 20 nA. UV–Vis spectra [250–900] nm were recorded on a PerkinElmer Lambda 650 spectrometer. Infrared (IR) absorption spectra were recorded with a Nicolet iS50 FT-IR from Thermo Scientific, with a resolution of 4 cm^{-1} and 32 accumulations. Visible and Infrared absorption spectra were both normalized by the thickness of the samples which were measured with a mechanical profilometer with a precision of ± 2 μm. Fiber attenuation losses were measured by the cut-back technique on a homemade set-up using a source emitting at 1310 nm and a XLP12-3S-H2 thermopile detector (GENTEC). An objective 20 × with a N.A. of 0.32 was used for the injection of the beam into the fiber, and a three-axis sample holder was used to adjust the position of the fiber. The end of the fiber was put directly onto the surface of the detector to detect the output transmitted signal. The accuracy is estimated *ca* 0.1 dB/m.

3. Results and discussion

3.1. Bulk glasses

The values of Tg, density and refractive index for all the samples are gathered in Table 1. The compositions of some samples was verified after synthesis and showed a change that did not exceed 0.5 at.% regarding the theoretical compositions. We observe that when varying the concentration of germanium, the Tg of the samples from the series with 5, 10 or 15% of iodine, present a maximum around the $(GeS_2)_xI_{100-x}$ composition line (Fig. 1). Actually, the nonmonotonic behavior of the glass transition temperature with the germanium content of Ge-S-I glasses has been reported in the literature [8]. It has been shown that these glasses exhibit a maximum of Tg close to the $(GeS_2)_xI_{100-x}$ line (similar singularity for the band-gap). This behavior is consistent with

Table 1
Glass transition temperature (Tg), density, and refractive index of Ge-S-I glasses.

Compositions	Tg (°C) ± 2	Density (g/cm^3) ± 0.001	Refractive index (@ 935 nm) ± 0.02
$Ge_{25}S_{70}I_5$	275	2.752	2.03
$Ge_{33.9}S_{61.1}I_5$	391	2.960	2.09
$Ge_{35}S_{60}I_5$	381	2.995	2.09
$Ge_{25}S_{65}I_{10}$	255	2.889	2.01
$Ge_{30}S_{60}I_{10}$	340	2.914	2.02
$Ge_{31}S_{59}I_{10}$	375	2.934	2.00
$Ge_{31.7}S_{58.3}I_{10}$	385	2.953	2.02
$Ge_{32.33}S_{57.67}I_{10}$	344	3.033	2.02
$Ge_{33.5}S_{55.7}I_{10.8}$	325	3.088	2.05
$Ge_{35}S_{55}I_{10}$	310	3.090	2.08
$Ge_{25}S_{60}I_{15}$	210	3.004	1.97
$Ge_{30.83}S_{54.17}I_{15}$	355	3.0932	2.00
$Ge_{35}S_{50}I_{15}$	288	3.154	2.05