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Synthesis and characterization of chalcogenide glasses from the system Ga–Ge–Sb–S and preparation of a single-mode fiber at 1.55 μm

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Abstract

The aim of this work is to study different compositions in the Ga–Ge–Sb–S system for the definition of two compositions compatible with the elaboration of a single-mode fiber at the 1.55 μm telecom wavelength. The variations of the glass transition temperature (T_g), the dilatation coefficient (α) and the refractive index (n) have been studied for two glasses series: Ga_x-$Ge_{25-x}Sb_{10}S_{65}$ (series 1), $Ga_5Ge_{25-x}Sb_{10}S_{60+x}$ (series 2). This study has lead to the choice of the $Ga_4Ge_{21}Sb_{10}S_{65}$ composition as clad glass for the preparation of the single-mode fiber and $Ga_5Ge_{20}Sb_{10}S_{65}$ composition as the core. The discrepancies for the studied parameters between the core and clad compositions are the following: $\Delta\alpha < 2\%$, $\Delta T_g < 3\%$ and $\Delta n = 5 \times 10^{-3}$. Finally a single-mode fiber has been prepared by the rod in tube technique.

Keywords: A. Chalcogenides; A. Glasses; A. Optical materials; D. Optical properties

1. Introduction

Chalcogenide glasses are based on sulfur, selenium or tellurium and the addition of other elements, such as arsenic, germanium, antimony, gallium, etc. These materials have numerous potential applications especially in the telecommunication field due to their high non-linear optical properties [1–4]. Third order non-linear optical materials are thus extensively investigated for telecommunications applications, such as high speed all optical communications, signal regeneration, ultra fast switching [5–10], but also for other applications in the field of infrared sources, such as Raman sources for example [12,13]. One of the interests of chalcogenide glasses is to associate high non-linear properties, from 100 to 1000 times the non-linear refractive index of silica [8–11], with a transmission which extends far in the infrared from 0.5–l to 12–18 μm depending on the composition. For numerous applications in the field of telecommunications, it will be important to obtain single-mode fibers at 1.55 μm. Such fibers have been studied in

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different chalcogenide glasses systems: As–Se [14], Ge–Ga–S–As [15] or Ge–Se [16]. In the Ga–Ge–S–Sb system, original single-mode fibers have been obtained by the realization of a holey fiber [17]. The aim of this study of the Ga–Ge–S–Sb glass system is the elaboration of a classical step index single-mode fiber. For that purpose, we have studied different physical parameters, the glass transition temperature (T_g), the dilatation coefficient (a) and the refractive index (n) for two series of glasses: $Ga_xGe_{25-x}Sb_{10}S_{65}$ (series 1) and $Ga_5Ge_{25-x}Sb_{10}S_{60+x}$ (series 2). Then, two compositions have been selected as the core and the clad glass. Finally, a double index fiber has been prepared by the rod in tube technique.

2. Experimental

2.1. Glasses synthesis

Glasses used in optical devices need a meticulous synthesis. The chalcogenide glasses are prepared in a silica tube under vacuum (10^{-5} mbar) and high purity raw materials are used for their preparation (5N). The starting materials are placed into different tubes and sulfur is especially purified by multiple distillations to eliminate water and carbon which are indeed present. After purification, the required amounts of the different elements are placed in the same silica tube. This tube is finally sealed under vaccum giving a silica ampoule of typically 10 mm in diameter for 10 cm long, in which the glass batch is melted. For that purpose, the ampoule is placed in a tipping furnace and is progressively heated from room temperature to the refining temperature of 850 °C at the heating rate of 1.5 °C/min. The melt is homogenized at 850 °C for 24 h, slowly cooled at 650 °C and maintained at this temperature during 2 h in order to obtain the condensation of the vapors present in the ampoule and their mixing to the melt. The batch is then quenched in water at a cooling rate close to 50 °C/min to allow the glass formation and to avoid any crystallization process. After that, the vitreous sample is annealed for 4 h at its glass temperature in order to relax the internal mechanical stress induced by the quenching, and then it is slowly cooled to room temperature.

The obtained glass rods are cut into small peaces of various thicknesses for the measurements of their dilatation coefficient and of their optical properties. They are especially polished with two parallel sides for the characterizations of the transmissions and of the refractive indices.

2.2. Fibers drawing

The elaboration of the single-mode step index chalcogenide fibers has needed several steps. The first one is the drawing of a single index stick of core glass with an external diameter of 2 mm by the stretching of a 12 mm diameter rod of a core glass on a drawing tower. Then, in order to obtain a step index optical fiber presenting a ratio between the core and the clad diameters suitable for a single-mode behavior we have used the rod in tube technique. The small rod of the core glass (2 mm diameter) is introduced in a clad tube obtained by rotational casting presented an inner diameter of around 4 mm for an outer diameter near 12 mm. Both are again stretched as a small rod of 2 mm external diameter. This stick is placed in a second tube of the clad glass to obtain the final perform. This perform is finally drawn to obtain the single-mode fiber which presents an outer diameter around 150–300 μm with a diameter of the core near 5–10 μm depending on the desired characteristics of the fiber.

2.3. Glasses and fibers characterizations

The samples have been analyzed by X-ray diffraction and no crystallization has been observed in glasses. Those analyses permit to confirm the glassy state.

The glass temperature (T_g) and the crystallization temperature (T_x) are measured for the different samples using a TA Instrument differential scanning calorimeter DSC 2010, with a heating rate of 10 °C/min between room temperature and 350 °C.

The refractive index of the different vitreous compositions have been determined by a Metricon device using a TeO_2 prism. It has been measured at three different wavelengths, 632, 1300 and 1540 nm. The absolute precision obtained on the refractive index with this system is 5×10^{-4}.

The transmission of the fibers has been analyzed with a BRUKER FTIR spectrophotometer for the infrared wavelengths range 2–20 μm by the cut back technique. Measurements have also been performed at the precise

telecommunication wavelength of 1550 nm on the fibers. The profile of the propagated beam in the double index fibers has been also realized at 1550 nm with the help of an IR camera used in the near field capture mode.

3. Results

3.1. Bulk glasses

In order to obtain the necessary linear refractive index variation between the core and the clad of the fiber, we have studied different glass compositions compatible with the structure of a core–clad single-mode fiber. Two series of compositions have been characterized. We have also measured the glass transition temperature (T_g) and the dilatation coefficient (α) for the different compositions. Indeed, for the elaboration of a double index fiber the core and the clad glasses must have similar T_g and similar dilatation coefficients.

In Figs. 1 and 2, we have reported the glass transition temperatures (T_g) and the dilatation coefficients (α) of the two vitreous series $Ga_xGe_{25-x}Sb_{10}S_{65}$ series 1 and $Ga_5Ge_{25-x}Sb_{10}S_{60+x}$ series 2. Fig. 3 gives the refractive index for the different glass compositions in the series 1 $Ga_xGe_{25-x}Sb_{10}S_{65}$ (Fig. 3a) and 2 $Ga_5Ge_{25-x}Sb_{10}S_{60+x}$ (Fig. 3b), respectively, at the three wavelengths 632, 1300 and 1540 nm. All these results are also reported in Table 1, where the real composition of the glasses measured by EDS with 1% of error is given. The differences between the nominal composition and the real composition are explained by the synthesis of high optical quality glasses. However, these differences are reproducible.

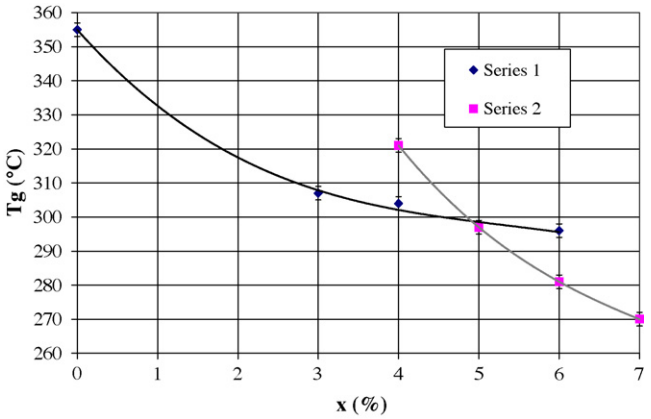

Fig. 1. Glass transition temperatures (T_g) of the two series: $Ga_xGe_{25-x}Sb_{10}S_{65}$ (series l) and $Ga_5Ge_{25-x}Sb_{10}S_{60+x}$ (series 2).

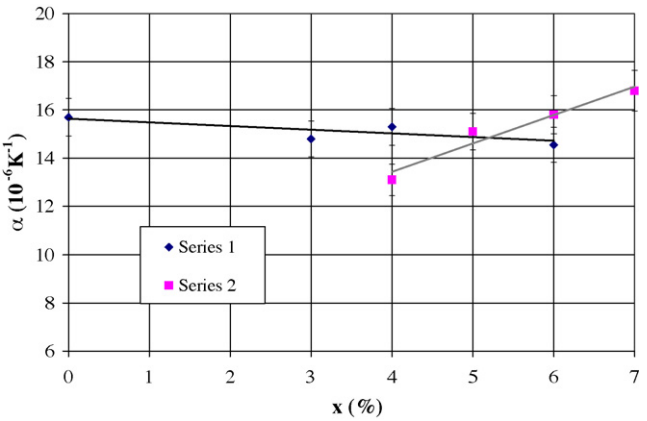

Fig. 2. Thermal dilatation coefficients (α) of the two series: $Ga_xGe_{25-x}Sb_{10}S_{65}$ (series 1) and $Ga_5Ge_{25-x}Sb_{10}S_{60+x}$ (series 2).

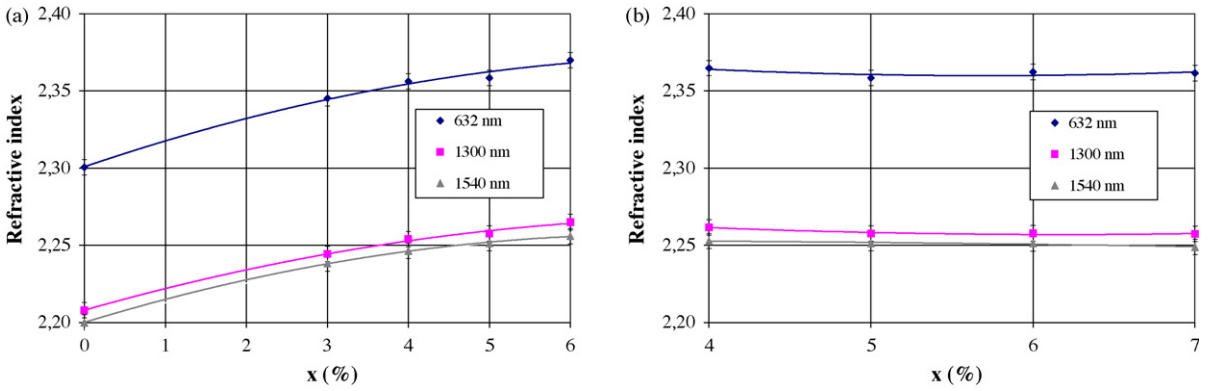

Fig. 3. Evolution of the refractive index in the system (a) $Ga_xGe_{25-x}Sb_{10}S_{65}$ (series 1), (b) $Ga_5Ge_{25-x}Sb_{10}S_{60+x}$ (series 2), at 632, 1300 and 1540 nm.

Table 1
Optical and thermal properties of several compositions in the $Ga_xGe_{25-x}Sb_{10}S_{65}$ and $Ga_5Ge_{25-x}Sb_{10}S_{60+x}$ systems (series 1 and 2)

Glass	x	Index +/− 5×10^{-4}			T_g (°C) +/− 2 °C	α (10^{-6} K^{-1}) +/− 5%	Composition (at%) +/− 1%			
		632 nm	1300 nm	1540 nm			Ge	Ga	Sb	S
$Ga_xGe_{25-x}Sb_{10}S_{65}$ (series 1)										
$Ge_{25}Sb_{10}S_{65}$	0	2.3006	2.2079	2.2000	355	15.7	26.8	0	10.3	62.9
$Ge_{22}Sb_{10}S_{65}Ga_3$	3	2.3453	2.2444	2.2382	307	14.8	24	2.6	10.4	63
$Ge_{21}Sb_{10}S_{65}Ga_4$	4	2.3562	2.2540	2.2464	304	15.3	23	3.7	10.3	63
$Ge_{20}Sb_{10}S_{65}Ga_5$	5	2.3584	2.2576	2.2514	297	15.1	22	4.8	10.4	62.9
$Ge_{19}Sb_{10}Se_5Ga_6$	6	2.3700	2.265	2.256	296	14.5	21	5.7	10.3	62.9
$Ga_5Ge_{25-x}Sb_{10}S_{60+x}$ (series 2)										
$Ge_{21}Sb_{10}Sg_4Ga_5$	4	2.3648	2.2617	2.2528	321	13.1	23	4.8	10.2	62
$Ge_{20}Sb_{10}S_{65}Ga_5$	5	2.3584	2.2576	2.2514	297	15.1	22	4.8	10.4	62.9
$Ge_{19}Sb_{10}S_{66}Ga_5$	6	2.3623	2.2578	2.2512	281	15.8	21.2	4.5	10.2	62.2
$Ge_{18}Sb_{10}S_{67}Ga_5$	7	2.3616	2.2574	2.2489	270	16.8	20.2	4.8	10.3	64.7

In the series 1, the glass transition temperatures (T_g) are varying between 360 and 290 °C when the concentration of gallium is varying from 0 to 6% (at). In this system, the thermal dilatation coefficient (α) shows no significant variation. In the series 2, the variation of the T_g and α are more important. The T_g are varying between 320 and 270 °C and α between 13×10^{-6} and 17×10^{-6} K^{-1} depending on the composition.

The glass compositions studies will permit to select the core and the clad glasses since the two different glasses must present similar thermal properties (T_g and α).

3.2. Fibers

The two glasses selected for the elaboration of the single-mode step index chalcogenide fiber are the following: the $Ga_5Ge_{20}Sb_{10}S_{65}$ glass has been selected to be the core composition and the $Ga_4Ge_{21}Sb_{10}S_{65}$ glass is the clad glass. Table 2 gives the characteristics of the corresponding fiber. In this case, we must realized a fiber with a core diameter under $2a_{max} = 8$ μm.

Table 2
Optical and thermal properties of the core and clad glass selected compositions in the Ga–Ge–Sb–S system

Compositions	T_g (°C) ± 2 °C	α (10^{-6} K^{-1}) ± 5%	n (λ = 1.550 μm) ± 5×10^{-4}	NA	a_{max} (μm) (λ = 1.55 μm)
$Ga_{(x)}Ge_{(25-x)}Sb_{10}S_{65}$					
$x = 5$, core	304	15.3	2.2514	0.15	4
$x = 4$, clad	297	15.1	2.2464		

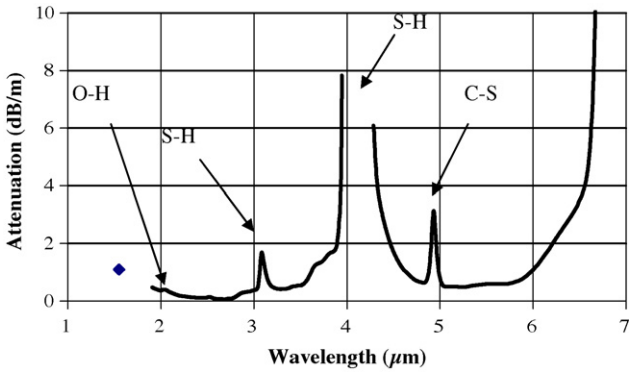

Fig. 4. Attenuation curve of a monoindex fiber from the $Ga_5Ge_{25}Sb_{10}S_{65}$ glass.

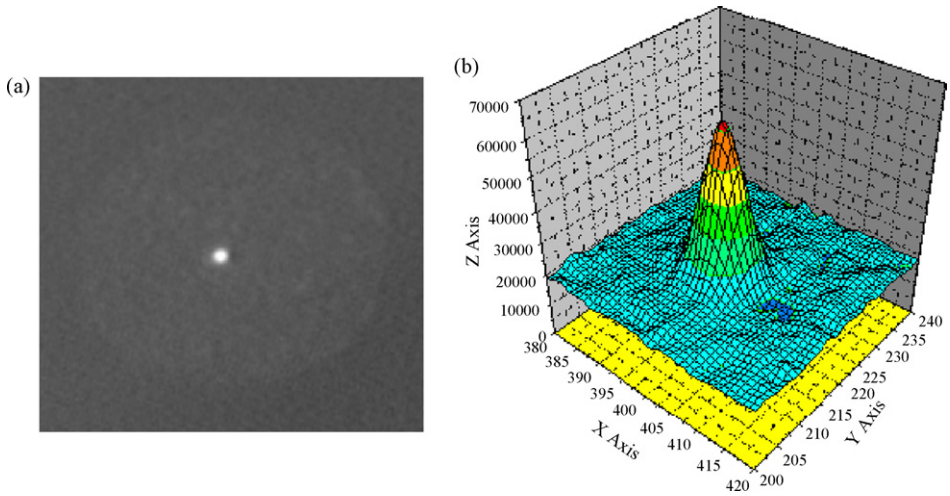

Fig. 5. Near field image at 1.55 μm of the double index fiber (a) and mode profile of the fiber (b).

Before the elaboration of the double index fibers composed from two different glasses we have drawn a single index fiber to control the quality of the glasses and to measure the optical losses. Fig. 4 gives the attenuation curve of the $Ga_5Ge_{25}Sb_{10}S_{65}$ monoindex fiber between 2 and 8 μm. The minimum of losses is near 0.1 dB/m at 2.8 μm. Absorption bands are observed at 4.0 and 3.1 μm due to S–H chemical bonds, at 2.1 μm due to OH bonds and finally at 4,95 μm due to the presence of C–S bonds. The losses above 6 μm are induced by the multiphonon absorption. The characterization of this fiber at 1.55 μm using a laser diode gives optical losses near 1.1 dB/m.

A rod from the same batch that the previous fiber is placed in a tube of the clad composition ($Ga_4Ge_{21}Sb_{10}S_{65}$) and is stretched. The operation is realized twice. The final fiber presents an outer diameter near 195 μm and a core diameter of 6 μm. The profile of the propagated beam in this fiber has been measured at 1550 nm with a near IR camera and is reported in Fig. 5a and b.

4. Discussion

Table 1 presents the results obtained for the characterization of the two series of glasses $Ga_xGe_{25-x}Sb_{10}S_{65}$ series 1 and $Ga_5Ge_{25-x}Sb_{10}S_{60+x}$ series 2. The compositions of the glasses obtained from energy dispersive spectroscopy (EDS) analysis are also indicated. One can see a variation between the nominal composition and the real composition obtained from EDS. The main reason for that is the variation of the sulfur content of the glass due to the great volatility of sulfur during the synthesis, and especially during the sulfur distillation process. This leads to a lack of sulfur in the final composition. But this fact is reproducible with the thermal treatment applied during the synthesis.

The glass composition studies permit to select the core and the clad glasses. Indeed, these two different glasses must present similar thermal properties (T_g and α) while the refractive index of the core (n_{core}) must be greater than the refractive index of the clad (n_{clad}) to obtain the guiding of the light beam in the core of the fiber. Moreover, to obtain a single-mode fiber, the radius of the core has to be below a_{max}, depending on n_{core} and n_{clad}, according to the formulas (1) and (2) [18].

$$a_{max} = \frac{2.405\lambda}{2\pi NA} \quad (1)$$

with

$$NA = \sqrt{n_{core}^2 - n_{clad}^2} \quad (2)$$

Then, the composition variation between the core and the clad glasses imposed by the necessary refractive index difference must remain compatible with the drawing process. For that purpose and to avoid the crack of the perform during heating or cooling due to a mechanical stress the glass temperatures and dilatation coefficients must be close to each other.

In the case of the series 2 ($Ga_5Ge_{25-x}Sb_{10}S_{60+x}$), the substitution of Ge by sulfur leads to a small decreasing of the refractive index at 1300 and 1540 nm, around a maximum of 4×10^{-3} for a variation of 3% on the germanium and sulfur contents (Table 1 and Fig. 3). This indicates that this substitution has a little effect on the polarisability of the glass, when replacing sulfur atoms with two electronic lone pairs by germanium atoms four-fold coordinated but presenting electrons on higher energy levels. In the same time, the effect on T_g and α is important, since for the same maximum of composition variation (3%), T_g shows a decreasing of 50 °C (Table 1 and Fig. 1) and α is varying by around 3×10^{-6} K^{-1} (Table 1 and Fig. 2). These results indicate that this series is not well adapted to the definition of a core–clad compositions couple.

In the case of series 1 ($Ga_xGe_{25-x}Sb_{10}S_{65}$), the effect of the substitution of Ge by Ga on the refractive index is much more important since n is increasing by around 5.6–5.7 $\times 10^{-2}$ at 1540 and 1300 nm when replacing 6% of germanium by gallium (Table 1 and Fig. 3). In the same time, the T_g presents a strong diminution (around 50 °C) when replacing 3% of germanium by gallium in a gallium free composition, but shows then a slow decreasing (10 °C) when adding 3% more gallium (Table 1 and Fig. 1). What is more, the dilatation coefficient α in this series exhibits a slow decreasing with the increasing of gallium, around 1×10^{-6} K^{-1}, for a maximum composition variation of 6% (Table 1 and Fig. 2). Thus, this series is much more adapted to the definition of a core/clad couple of compositions, since we have the combination of a sharp variation of the refractive index with a small variation of T_g and α for germanium/gallium substitution between 3 and 6%. Finally, we have chosen as core and clad compositions the following, respectively, $Ga_5Ge_{10}Sb_{10}S_{65}$ and $Ga_4Ge_{21}Sb_{10}S_{65}$. The refractive index difference is thus 5 10^{-3}, for a T_g variation of 7 °C and a very similar dilatation coefficient around 15.2×10^{-6} K^{-1} (Table 2).

The core–clad fiber has been prepared as described in the previous section. The opto-geometrical parameters (Table 2) of the fiber are those of a single-mode one (core diameter 8 μm) and the near field image and mode profile at 1550 nm are presented Fig. 5. The Gaussian type of the beam and the mode diameter of 6–7 μm confirm the single-mode operation of the fiber. The losses at 1550 nm of the fiber have also been estimated. They exhibit an unexpected very high value of around 80 dB/m to be compared with the 1.1 dB/m losses at 1.55 μm of the single index core fiber with a minimum losses of 0.1 dB/m at 2.8 μm. We assume for the moment a bad interface between the core and the clad glass due perhaps to a pollution by water to explain for these high losses.

5. Conclusion

We have studied different compositions in the Ga–Ge–Sb–S system for the definition of two glasses compatible with the elaboration of a single-mode fiber at 1550 nm. The substitution of germanium by gallium is adapted to a sharp variation of the refractive index with limited evolution of the glass temperature and of the dilatation coefficient. The choice of the core composition $Ga_5Ge_{20}Sb_{10}S_{65}$ and clad composition $Ga_4Ge_{21}Sb_{10}S_{65}$ leads thus to the following parameters: $\Delta\alpha < 2\%$, $\Delta T_g < 3\%$ and $\Delta n = 5 \times 10^{-3}$. A step index optical fiber has been prepared by the rod in tube technique from these two compositions with a core diameter of 6 μm. The mode profile analysis confirms the single-mode operation at 1550 nm.

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