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Optical and thermo-mechanical properties of new Ge-Ga-Se-AgI glasses

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In this paper, the introduction of silver by incorporation of AgI in the family of chalcogenide glasses transparent from the visible range to 16 µm has been reported. A large glass forming region belonging to the $GeSe_2$-Ga_2Se_3-AgI and able to accept more than 50 mol. % of AgI was discovered. Pure glasses, slightly transparent in the visible range up to 16 µm have been synthesized. A systematic study of thermo-mechanical and optical properties was performed. The possibility of shaping and drawing these glasses give them a great interest in ion exchange experiments to achieve gradient of the refractive index.

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1. Introduction

Chalcogenide and chalco-halides glasses are known to be a low cost alternative solution to mono-crystalline germanium usually used for infrared applications. In fact, chalcogenide glasses present an excellent IR transmission and the possibility to be shaped by molding. Furthermore, many applications for chalcogenide glasses based on selenium, such as lenses for thermal imaging [1-2], optical fibers [3-4] or planar waveguides [5-6] are largely studied thanks to their wide range of optical transmission from 0.7 to 16 µm. However, mechanical properties such as resistance to thermal shocks are the weak point of chalcogenide glasses. In order to improve mechanical characteristics by generating nanocrystal inside the glassy matrix, the $GeSe_2$-Ga_2Se_3-MX (M: alkali, X: Halide) systems have been recently investigated [7, 8]. These new glasses are the first chalcogenide glasses based on selenium transparent in the visible range up to 16µm. Their transmission in the visible depend on the alkali halide content.

Previously, the addition of silver in chalcogenide glasses (Ag_2S, Ag_2Se, AgI) has been investigated for their ionic conductivity properties in the GeS_2-Ga_2S_3, As-Se or GeTe-As_2Se_3 systems [9-11]. The feasibility of making waveguides by ion-exchange technique was largely reported in soda-lime glasses [12-13], but few papers report this technique in chalcogenide glasses [14]. It is well known that the exchange of Ag^+ and the alkali cations present in the glass or in a molten salt bath induces a progressive change of the refractive index on the glass surface. Following these approaches and using the recent advances in the $GeSe_2$-Ga_2Se_3-MX systems [15], we decided to investigate the possibility of introducing silver iodine in this glassy matrix. In this paper, the synthesis and thermo-mechanical properties of these new chalco-halide glasses belonging to the $GeSe_2$-Ga_2Se_3-AgI system are reported.

2. Experimental

2.1. Glass synthesis

Glasses are prepared by the classical melting mixture of highly pure raw materials (Ge, Ga, Se: 99.999% and AgI: 99.9%) in a sealed silica ampoule under vacuum (10^{-3} Pa). The sealed ampoule of 9 mm inner diameter is placed in a rocking furnace. The raw materials are heated up from 20 °C to 850 °C with a rate of 2 °C/min and are maintained at this temperature for 12h. The silica tube is quenched in water at room temperature, then annealed at T_g for 3 hours to minimize inner constraints and finally slowly cooled down to room temperature. Glass rods were cut into slices of 2 mm thick and polished for different measurements.

2.2. Samples characterization

The glass forming region has been determined by X-Rays diffraction and optical microscopy.

The transmission range was characterized with a CARY5 double beam spectrophotometer (Varian) in the short wavelengths range while a BRUKER Vector 22 spectrophotometer operating in the 2 – 25 µm was used for the mid and far infrared spectra. In order to determine the characteristic temperatures of glasses such as glass transition temperature (T_g) and crystallization temperature (T_x), a differential scanning calorimeter (DSC2910 TA Instruments) was used under Ar atmosphere with a rate of 10 °C/min from 20 °C to 500 °C.

Samples with a thickness of 4 to 6 mm were polished for dilatation experiments. The thermal expansion coefficient was measured with a TMA 2940 Calorimeter (TA Instruments) using a heating rate of 2°C/min from 20 °C to 200 °C. Density, *d*, was measured using the Archimedes technique which consists in comparing the difference of the glass weight in air and in a solvent. A

Metler Toledo XS64 balance was used with distilled water as solvent. Micro-hardness tests were performed using a Vickers indenter (Matsuzawa VMT-7S) with a load of 100g during 5s.

3. Results

3.1. Glass formation and thermo-mechanical properties

The extended glass-forming region of $GeSe_2$-Ga_2Se_3-AgI pseudo ternary system is shown in Fig. 1.

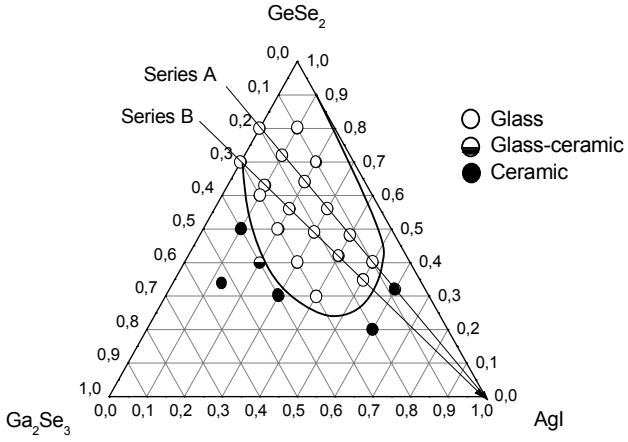

Fig. 1. Glass-forming region of the $GeSe_2$ -$_{Ga2Se3}$-AgI system.

As we can see, this pseudo ternary system presents a very wide glass forming region as more than 50 mol. % of AgI can be introduced in the $GeSe_2$-Ga_2Se_3 system. Two series of compositions belonging to the $GeSe_2$-Ga_2Se_3-AgI system have been studied. The series A is based on the $(80GeSe_2\text{-}20Ga_2Se_3)_{100-x}AgI_x$ glass composition with x = 0, 10, 20, 30, 40, 50 and the series B based on the $(70GeSe_2\text{-}30Ga_2Se_3)_{100-x}AgI_x$ glass composition with x = 0, 10, 20, 30, 40, 50. Glasses of the first and the second series are respectively numbered from 1 to 6 and 7 to 12. The thermo-mechanical properties are reported in the Table 1.

The obtained bulk glasses have good thermal stability and are all slightly transparent in the visible region presenting a dark-red color. For the series A and B, glass transition temperatures vary from 351 to 227 °C and from 370 to 225 °C as observed in the Table 1. Also, micro-hardness is both decreasing for series A and B when AgI is added in the base glass, respectively from 193 kg/mm² to 110 kg/mm² and from 199 kg/mm² to 127.4 kg/mm². Thermal expansion coefficient increases proportionally with the amount of AgI from 13.3×10^{-6} K^{-1} to 22.9×10^{-6} K^{-1} for series A and from 12.5×10^{-6} K^{-1} to 22×10^{-6} K^{-1} for series B. While glasses containing a higher quantity of Ga_2Se_3 (series B) has better mechanical properties, they also present a lower stability against crystallization. Furthermore, the incorporation of about 10 to 30 mol. % of AgI leads to the increase of ΔT between T_x and T_g, meaning a better thermal stability of glasses against crystallisation.

Table 1. Thermo-mechanical properties of $GeSe_2$-Ga_2Se_3-AgI glasses.

Glass number	Composition $GeSe_2$-Ga_2Se_3-AgI	Tg(°C)	Tx(°C)	Tx - Tg (°C)	α (10^{-6} K^{-1})	ρ (g/cm^3)	Hv (kg/mm²)
	$GeSe_2/Ga_2Se_3$ = 4						
1	80-20-0	351	434	83	13.3	4.357	193.2
2	72-18-10	338	463	125	13.8	4.486	183.6
3	64-16-20	312	432	120	15.7	4.628	173.7
4	56-14-30	277	402	125	16.7	4.764	157.1
5	48-12-40	262	406	144	19	4.928	143
6	40-10-50	227	303	76	22.9	5.072	110.1
	GeSe2/Ga2Se3 = 2.33						
7	70-30-0	370	471	101	12.5	4.412	199.2
8	63-27-10	344	430	86	14.4	4.548	195.3
9	56-24-20	327	418	91	16	4.624	181
10	49-21-30	290	400	110	18.4	4.793	166.7
11	42-18-40	266	371	105	19	4.923	145.6
12	35-15-50	225	317	92	22	5.091	127.4

Previously, Ge-Se-AgI glasses were investigated; the presence of AgI micro-crystals was observed in the glassy matrix by X-Ray diffraction [16]. The X-Ray diffraction diagram presented in the Fig. 2 show a perfect solubility of AgI in the $40GeSe_2$-$10Ga_2Se_3$-50AgI glass composition.

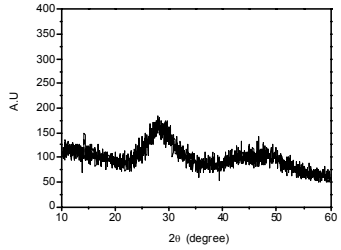

Fig. 2. RX diagram for the $40GeSe_2$-$10Ga_2Se_3$-50AgI composition.

3.2. Optical properties

Near infrared absorption curves are shown in Fig. 3. One can observe a small shift of the beginning of transmission in the visible spectra with the incorporation of AgI from 690 nm to 655 nm for both series. The band-gap position of glasses 1 and 4 is presented in the Table 2, compared with the band-gap of the glass with CsI.

Table 2. Band-gap position for the $80GeSe_2$-$20Ga_2Se_3$ base glass, base glass + 30% AgI, and base glass + 30% CsI [15].

Glass composition	$\lambda_{bandgap}$ (nm)
$80GeSe_2$-$20Ga_2Se_3$	690
$56GeSe_2$-$14Ga_2Se_3$-30AgI	659
$56GeSe_2$-$14Ga_2Se_3$-30CsI	605

A shift of the beginning of transmission of about 20 nm between the base glass and a glass containing 30% mol. of AgI is observed, whereas it reaches 85 nm with 30 mol. % CsI.

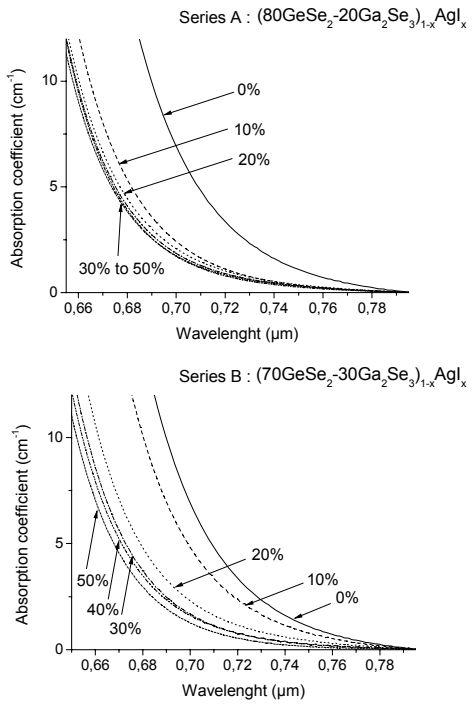

Fig. 3. Visible and near-infrared absorption of the $GeSe_2$-Ga_2Se_3-AgI glasses.

The beginning of transmission is shifted toward shorter wavelengths with increasing content of AgI. Nevertheless, the evolution of the band-gap is less important when more than 30 mol. % of AgI is introduced in the base glass. In the middle and far infrared, one can notice the presence of absorption bands. First, bands at 2.9 µm and 6.3 µm are respectively due to OH and H_2O impurities. The absorption band situated at 12.5 µm corresponds to the vibration of Ge-O bonds, and the absorption peak at 9.8 µm can be assigned to Si-O [17]. Despite of the purity of raw materials, we can see many absorption peaks which can be eliminated by the addition of a pure reductor metal like magnesium. The pure glass was synthesized with the addition of 1000 ppm of pure metallic Mg. The selenium is pre-heated at 240 °C for 2 hours in order to eliminate the SeO_2 formed during its storage. During the heat treatment magnesium reacts with oxygen impurities forming MgO which IR signature is not observable in the 2-18 µm range. As shown in the Fig. 4, all absorption bands due to oxide are greatly reduced in the pure glass.

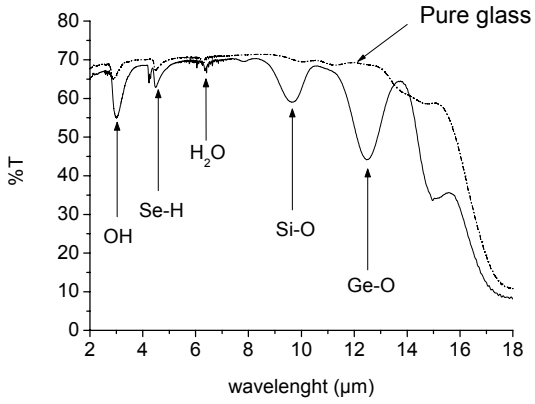

Fig. 4. Infrared transmission spectra of $(GeSe2)_{72}$-$(Ga2Se3)_{18}$-AgI_{10} glass without Mg and with 1000 ppm Mg.

4. Discussion

In previous works, glasses belonging to the $GeSe_2$-Ga_2Se_3-MX systems (MX: alkali-halides) were studied. It appears that more extended vitreous domains are obtained with larger radius and lower electronegative halide (I>Br>Cl) and bigger alkali radius (Cs>Rb>K>Na). In this study 50 mol. % of AgI can be introduced in the glassy matrix while only 40 mol. % of CsI can be incorporated in the $GeSe_2$-Ga_2Se_3-CsI system [15]. However, Cs^+ ionic radius (16.9 nm) is bigger than Ag^+ ionic radius (12.6 nm). As described elsewhere, halides act as network modifiers opening the $GeSe_2$ and Ga_2Se_3 tetrahedral and pseudo tetrahedral structures of these glasses. The cations compensates the negative charge of Se- non-bridging atoms. It is clearly demonstrated that this phenomenon generates a shift of the beginning of transmission towards the short wavelengths [8]. The effect of electronegative halide increases the energy gap (eV) between σ and σ* energy level of free selenium electron pairs. The strong difference of the beginning of transmission in glasses containing metal-halide instead of alkali-halide could be explained by the difference of electronegativity of alkaline and Ag^+. We suppose the creation of higher energy levels between the valence and the conduction band by introducing Ag. Consequently, the effect of halide on the

beginning of transmission would be partially compensated by these energy levels decreasing the energy band-gap.

Changes in mechanical properties occur with increasing AgI amount. In fact, the incorporation of metal-halide provokes the decrease of the glass network reticulation due to non bridging anions linked to Ge or Ga. Therefore, both glass transition temperature and micro-hardness are linearly decreasing with the addition of AgI. The increasing content of halides with a high ionic radius like I^- leads to an enlargement of the dilatation coefficient. However, glasses containing 50% mol. AgI present the same value of thermal expansion coefficient with glasses containing only 20% mol. of alkali-halide like CsI [15]. Consequently, resistance to thermal shocks will be better between two samples having the same molar composition. This phenomenon is mainly due to the small ionic radius of Ag^+.

5. Conclusions

In this paper, we have reported the synthesis of new chalcogenide glasses belonging to the $GeSe_2$-Ga_2Se_3-AgI system. A large glass forming region was discovered as more than 50% mol of AgI can be introduced in the $GeSe_2$-Ga_2Se_3 pseudo binary system. It is shown that pure glasses slightly transparent in the visible range to 16µm can be produced. Furthermore, the introduction of AgI instead of alkali halide induces an increase in mechanical properties such as hardness and resistance to thermal shocks. Moreover, thermal stability against crystallization can be controlled according to the incorporated amount of AgI. These new glasses present interesting properties to perform ion exchange experiments in order to produce waveguide or fibers with refractive index gradient.

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