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New chalcogenide glasses in the $\text{GeSe}_2\text{-Ga}_2\text{Se}_3\text{-In}_2\text{Se}_3$ and $\text{GeSe}_2\text{-Ga}_2\text{Se}_3\text{-PbSe}$ domains

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Abstract

Two new chalcogenide glassy domains were explored by substituting Ga for In or Pb in compositions from the $\text{GeSe}_2\text{-Ga}_2\text{Se}_3$ tie line in the Ge-Ga-Se ternary diagram. The thermal, optical and mechanical properties of these glasses were determined and the effect of the substitutions on these properties was assessed. It is shown that addition of lead tends to destabilize the glasses while the addition of indium tends to stabilize them. Both elements induce a systematic increase in the onset of transmission values and in the densities when substituted to gallium. The glasses synthesized represent good potential candidates for the production of glass-ceramics with photovoltaic or nonlinear properties.

Keywords

Chalcogenides; Glasses; Optical properties; Thermal properties; Mechanical properties

1. Introduction

Chalcogenide glasses show extended transparency in the infrared range in the second and third atmospheric transmission windows, located in the 3-5 μm and 8-12 μm regions, respectively [1]. Due to their viscoplastic properties, they can be shaped by molding and drawn into fibers at a temperature above their glass transition temperature [2-4]. For these reasons, these materials are currently used for a wide range of applications in the infrared range. These include thermal cameras optics [2, 5], nonlinear optics [6, 7] or fibers for chemical and biological sensing [3, 8]. Notably, glasses from the system Ge-Ga-Se such as the $80\text{GeSe}_2\text{-}20\text{Ga}_2\text{Se}_3$ composition are of particular interest as it has been shown that it can be crystallized in a controllable and reproducible way to produce infrared transparent glass-ceramics with enhanced mechanical properties [9, 10]. In this study, we investigated

the addition of indium ($M_{\text{In}}=114.8$ g/mol) and lead ($M_{\text{Pb}}=207.2$ g/mol) to glasses from the GeSe_2 - Ga_2Se_3 tie line in the Ge-Ga-Se ternary diagram. The glassy domains of the GeSe_2 - Ga_2Se_3 - In_2Se_3 and GeSe_2 - Ga_2Se_3 - PbSe pseudo-ternary systems have been determined. The influence of addition of Pb and In on the mechanical, optical and thermal properties of the glasses with compositions the $(100-x)(80\text{GeSe}_2-20\text{Ga}_2\text{Se}_3)-(x)\text{PbSe}$ and $80\text{GeSe}_2-(20-x)\text{Ga}_2\text{Se}_3-(x)\text{In}_2\text{Se}_3$ have been analyzed. Indium and lead can form crystalline phases with selenium, respectively In_2Se_3 and PbSe . Indium selenide crystals possess a high conductivity [11] and may show potential applications in optoelectronic device such as lasers, light emitting diodes (LEDs) and solar cells [12]. The PbSe crystalline phase possesses non-linear optical properties [13-16] and could also present an interest for photovoltaic applications [17, 18]. The work presented in this study focuses only on the exploration of the chalcogenide glass compositions containing indium or lead and their thermal, optical and mechanical properties. The crystallization study aiming at developing glass-ceramics containing In- or Pb-based crystalline phases will be part of a subsequent study.

2. Experimental procedure

The bulk glass samples from the systems GeSe_2 - Ga_2Se_3 - In_2Se_3 and GeSe_2 - Ga_2Se_3 - PbSe were prepared using the melt-quenching technique commonly used for chalcogenide glass synthesis. Pure raw 99.999% Ge, Se, Ga, and 99.9% In and Pb were introduced in stoichiometric quantities in a silica tube of 10 mm inner diameter, evacuated under vacuum for 2 hours and sealed. The sealed silica ampoule containing the elements was heated up at 750°C for 12 hours in a rocking furnace for homogenization. The melt was quenched in water before being annealed 10°C below T_g for 4 hours to minimize inner constraints. After annealing, the bulk materials were cut into slices of 2 mm thickness and polished before characterization.

The optical transmission of each glass was characterized in the 0.6 - 2 μm region using a Perkin Elmer Lambda 1050 UV-Vis spectrometer. A Bruker Vector 22 FTIR spectrophotometer was used to characterize the optical transmission in the 2 - 20 μm region.

The vitreous domain has been simultaneously determined by XRD measurements and optical transmission measurements. It has been observed that the optical transmission measurements in the visible range are much more sensitive than XRD to the presence of small amounts of nanoparticles. In

fact, the scattering effects of the nanoparticles, even at low concentrations, induce a shift and a slight decrease of the optical transmission in the short wavelength range. This technique was thus used to estimate the glass-forming region of the glass systems. Materials showing partial crystallization were considered as being at the limit of the glass-forming region.

Differential Scanning Calorimetry (DSC) analyses were performed using a TA Instruments DSC Q20 calorimeter to measure the characteristic temperatures of the glasses. Bulk samples of ~10 mg were used with a heating ramp of 10°C/min. Hardness and toughness were determined using a Vickers micro-indenter (Matzuzawa WMT-7S) with a load of 100 g for 5 s. Young's modulus was obtained by measuring the ultrasound propagation speed in the glass. Density was measured using Archimedes' method of double weighing in air and water.

3. Results and discussions

Fig. 1. shows the glass-forming regions for the systems $\text{GeSe}_2\text{-Ga}_2\text{Se}_3\text{-PbSe}$ and $\text{GeSe}_2\text{-Ga}_2\text{Se}_3\text{-In}_2\text{Se}_3$. The thermal, optical and mechanical properties measured on the glasses synthesized are listed in Table 1 and Table 2, respectively. The glasses synthesized possess a Vickers hardness of about 200 Hv, a toughness of about $0.200 \text{ MPa}\cdot\text{m}^{1/2}$ and Young's modulus above 20 GPa. These values are comparable to those of the $80\text{GeSe}_2\text{-}20\text{Ga}_2\text{Se}_3$ glass, which possess a Vickers Hardness of 193 Hv, a toughness of $0.213 \text{ MPa}\cdot\text{m}^{1/2}$ and a Young's modulus of 22.7 GPa. These mechanical properties are relatively high for chalcogenide glasses. As a comparison, the GASIR[®] glass ($\text{Ge}_{22}\text{As}_{20}\text{Se}_{58}$), currently one of the most widely used chalcogenide glass for commercial infrared devices, presents a Vickers hardness of 170 Hv and a Young's Modulus of 17.89 GPa [19].

The effect of the addition of Pb and In on the thermal properties (glass transition temperature T_g , crystallization temperature T_x , and thermal stability coefficient $\Delta T = T_x - T_g$) of the $(100-x)(80\text{GeSe}_2\text{-}20\text{Ga}_2\text{Se}_3)\text{-(x)PbSe}$ and $80\text{GeSe}_2\text{-(}20\text{-x)Ga}_2\text{Se}_3\text{-(x)In}_2\text{Se}_3$ glasses is presented in Fig. 2-a and Fig. 2-b, respectively. The corresponding compositions in Table 1 and Table 2 are indicated on the figure between brackets.

The progressive introduction of Pb leads to a decrease of the glass transition temperature as well as a decrease of the crystallization temperature. The value of ΔT is decreased with increased Pb content, thus Pb tends to destabilize the glasses. Similar evolution of the thermal properties with lead content

has been reported for other chalcogenide glassy systems such as Ge-Se-Pb [20] and $\text{GeSe}_2\text{-Sb}_2\text{Se}_3\text{-PbSe}$ [21]. This behavior was attributed to the creation of the linear chains Pb-Se-Pb-Se, yielding a progressive depolymerization of the glassy network and a decrease of the glass transition temperature with higher Pb content [21, 22].

When Ga is substituted for In, the glass transition temperature is also decreased, but the crystallization temperature remains stable. The value of ΔT increases with increased In content, thus indium tends to stabilize the glasses. The bond energies differ for Ga and In when coordinated to Se. In fact, the bond energy of Ga-Se bonds (65 Kcal/mol [23]) is higher than that of In-Se bonds (61.5 Kcal/mol [24]). Increasing indium content decreases the average bond energy, thus decreases the network rigidity of the system and leads to lower glass transition temperatures [24].

The effect of the addition of Pb and In on the onset of transmission (λ_g) and on the density of the the $(100-x)(80\text{GeSe}_2\text{-}20\text{Ga}_2\text{Se}_3)\text{-}(x)\text{PbSe}$ and $80\text{GeSe}_2\text{-}(20-x)\text{Ga}_2\text{Se}_3\text{-}(x)\text{In}_2\text{Se}_3$ glasses is presented in Fig. 3-a and Fig. 3-b, respectively.

Glasses with higher PbSe or In_2Se_3 contents show increased onset of transmission. In the case of Pb-based glasses, this increase may be due to a stronger metallic character of the Pb-Se bonds, as suggested by Parvanov et al. [25].

Studies report that an increase of the average bond energy of the system leads to an increase of the optical band gap energy (E_g , in eV) for chalcogenide glasses [23, 24]. The onset of transmission (in nm) is inversely proportional to E_g ($\lambda_g = 12400/E_g$), thus the decrease of the average bond energy in the $\text{GeSe}_2\text{-Ga}_2\text{Se}_3\text{-In}_2\text{Se}_3$ by progressive substitution of Ga for In leads to the increase of the onset of transmission value (λ_g) observed in Fig. 3b.

For all the glasses synthesized, the onset of transmission is above 690 nm, yielding glasses opaque to visible light and presenting a dark metallic aspect. However, all the glasses synthesized here are transmitting in the infrared above 800 nm and their transparency covers the 2nd and 3rd atmospheric windows, respectively 3-5 μm and 8-12 μm , which are of interest for the production of infrared optics [2]. The multiphonon cut-off remains dominated by the vibration energy of Se-Se bonds and stays constant at 16 μm whatever the PbSe and In_2Se_3 contents for these glasses.

Finally, the molecular weights of In ($M_{\text{In}} = 114.82 \text{ g/mol}$) and Pb ($M_{\text{Pb}}=207.2\text{g}\cdot\text{mol}^{-1}$) are greater than that of gallium ($M_{\text{Ga}} = 69.72 \text{ g/mol}$). Hence, the progressive substitution of Ga for In or for Pb leads to the increase of the density of the glasses as observed in Fig. 3.

4. Conclusion

In this study, two new chalcogenide glassy domains have been explored: $\text{GeSe}_2\text{-Ga}_2\text{Se}_3\text{-In}_2\text{Se}_3$ and $\text{GeSe}_2\text{-Ga}_2\text{Se}_3\text{-PbSe}$. The thermal, optical and mechanical properties of the glasses synthesized were determined and the effect of the addition of Pb and In on these properties was assessed. It was demonstrated that the addition of indium tends to stabilize the glasses while Pb destabilizes them. The progressive substitution of Ga for In or Pb yields increased values for the onset of transmission as well as higher density of the glasses. This work constitutes the first step toward the development of new families of chalcogenide glass-ceramics with properties potentially interesting for non-linear optics or photovoltaic by precipitating In-based or Pb-based crystalline phases. A ceramization study will have to be performed on the synthesized glasses to assess the ceramization behavior of these materials.

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Captions

Table 1: Thermal, optical and mechanical properties of the $\text{GeSe}_2\text{-Ga}_2\text{Se}_3\text{-PbSe}$ glasses

Table 2: Thermal, optical and mechanical properties of the $\text{GeSe}_2\text{-Ga}_2\text{Se}_3\text{-In}_2\text{Se}_3$ glasses

Figure 1: Glassy domains in the $\text{GeSe}_2\text{-Ga}_2\text{Se}_3\text{-MX}$ systems with a) $\text{MX} = \text{In}_2\text{Se}_3$ and b) $\text{MX}=\text{PbSe}$

Figure 2 : Evolution of the thermal properties of the a) $(100-x)(80\text{GeSe}_2\text{-}20\text{Ga}_2\text{Se}_3)\text{-}(x)\text{PbSe}$ glasses and b) $80\text{GeSe}_2\text{-}(20-x)\text{Ga}_2\text{Se}_3\text{-}(x)\text{In}_2\text{Se}_3$ glasses

Figure 3 : Evolution of the thermal properties of the a) $(100-x)(80\text{GeSe}_2\text{-}20\text{Ga}_2\text{Se}_3)\text{-}(x)\text{PbSe}$ glasses and b) $80\text{GeSe}_2\text{-}(20-x)\text{Ga}_2\text{Se}_3\text{-}(x)\text{In}_2\text{Se}_3$ glasses

	GeSe₂ <i>mol %</i>	Ga₂Se₃ <i>mol %</i>	PbSe <i>mol %</i>	T_g <i>± 2°C</i>	T_x <i>± 2°C</i>	ΔT <i>± 4°C</i>	λ_g <i>± 2 nm</i>	H_v <i>± 1 Kg.mm²</i>	K_{1c} <i>± 0.005 Mpa.√m</i>	E <i>± 0.3 GPa</i>	ρ <i>± 0.03 Kg/m³</i>
	90	5	5	365	430/456	65	711	206	0.200	20.2	4.43
	80	10	10	334	447	113	722	203	0.201	22.0	4.56
(1)	80	20	0	370	460	90	690	193	0.213	22.7	4.39
	75	5	20	322	389	67	797	200	0.214	22.9	4.95
(2)	75	18.75	6.25	355	465	110	707	206	0.190	20.6	4.63
	70	10	20	325	399	74	754	204	0.171	20.2	4.96
	70	20	10	330	450	120	726	212	0.181	22.7	4.57
(3)	66.67	16.67	16.67	347	438	91	749	204	0.186	21.2	4.93
(4)	60	15	25	328	405	77	785	200	0.190	20.6	5.31
	60	30	10	355	418/454	63	745	199	0.211	21.6	4.64
	60	20	20	330	418	88	719	200	0.195	21.0	4.95
	60	10	30	311	387	76	783	-	-	-	-

Table 1

	GeSe₂ mol %	Ga₂Se₃ mol %	In₂Se₃ mol %	T_g ± 2°C	T_x ± 2°C	ΔT ± 4°C	λ_g ± 2 nm	H_v ± 1 Kg.mm ²	K_{Ic} ± 0.005 Mpa.√m	E ± 0.3 GPa	ρ ± 0.03 Kg/m ³
	90	10	0	373	477	104	679	200	0.245	19.9	4.20
	85	15	0	360	466	106	693	202	0.225	20.8	4.36
(1)	80	20	0	370	460	90	690	193	0.213	22.7	4.39
	75	25	0	366	437	71	708	-	-	21.4	-
	90	0	10	340	440	100	710	194	0.218	18.7	4.39
	85	0	15	331	439	108	723	193	0.221	20.8	4.43
(8)	80	0	20	328	446	118	736	189	0.210	22.0	4.58
	75	0	25	325	441	116	745	188	0.171	22.3	4.68
	70	0	30	321	438	117	757	-	-	22.7	4.71
	90	5	5	361	482	121	709	196	0.223	19.2	3.97
(7)	80	5	15	330	459	129	734	192	0.209	22.0	4.55
(6)	80	10	10	342	460	118	723	197	0.219	21.2	4.49
(5)	80	15	5	357	469	112	710	204	0.223	23.1	4.43
	75	5	20	333	460	127	736	194	0.204	21.8	4.64
	75	6.25	18.75	329	458	129	738	192	0.189	21.7	4.56
	75	18.75	6.25	356	462	106	702	197	0.191	21.2	4.49
	70	20	10	349	461	112	729	207	0.205	22.2	4.52
	70	25	5	360	447	87	720	207	0.204	22.8	4.45
	65	10	25	328	459	131	769	203	0.193	24.2	4.70
	65	25	10	352	435	83	723	213	0.169	20.7	4.53
	60	10	30	323	432	109	756	198	0.207	24.5	4.72
	60	15	25	328	454	126	761	-	-	19.7	4.65

Table 2

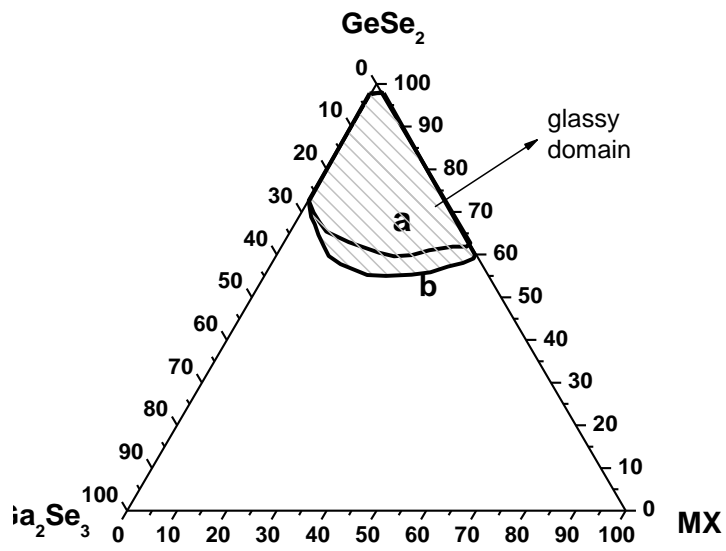


Figure 1

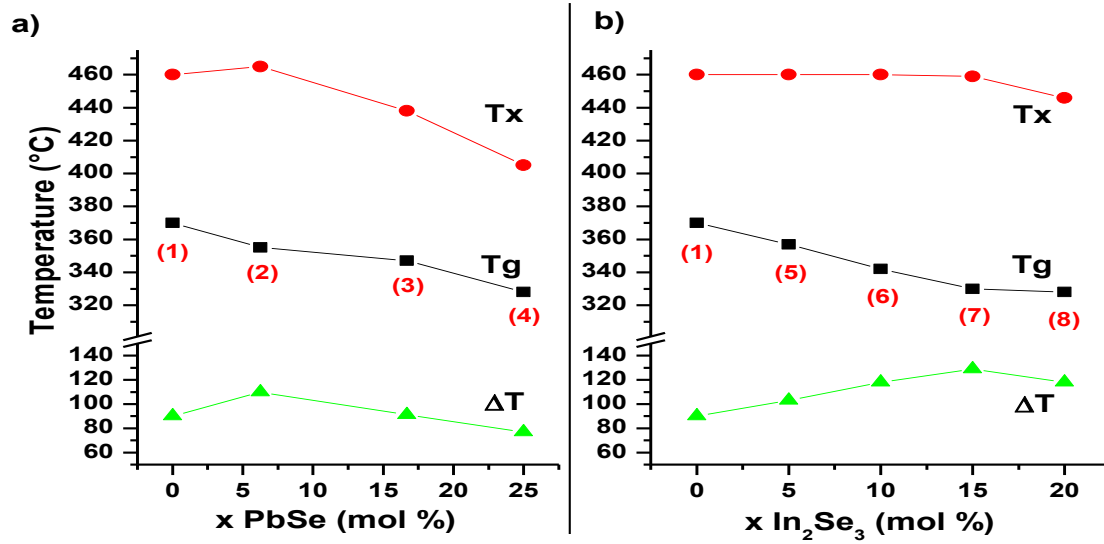


Figure 2

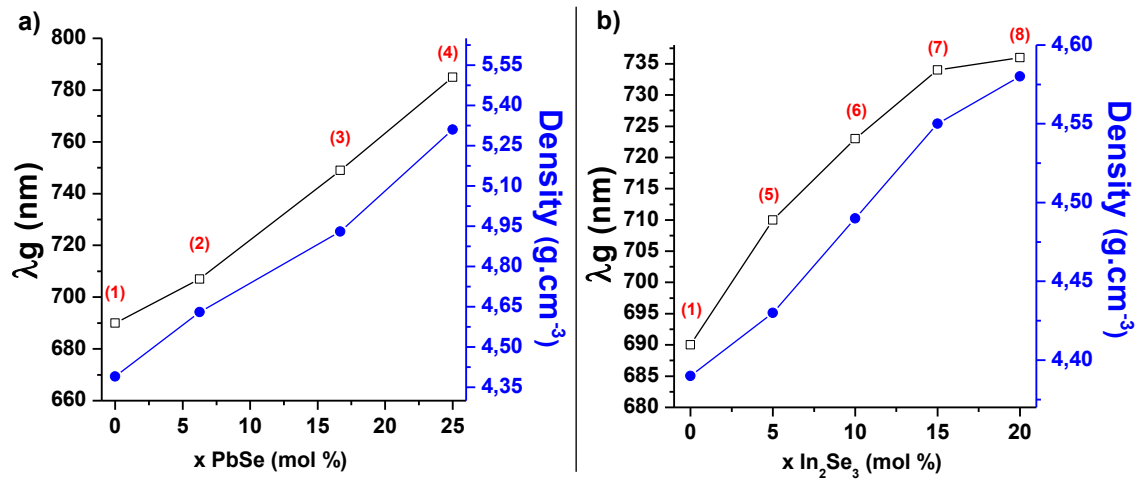


Figure 3