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Ga-modified As_2Se_3–Te glasses for active applications in IR photonics

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ABSTRACT

Effect of Ga addition on physical properties of glassy As_2Se_3 alloys within $Ga_x(As_{0.4}Se_{0.6})_{100-x}$ system (x = 0–5) is studied for further improvement as rare earth ions matrix hosts. Following conventional synthesis conditions, it has been shown it is possible to introduce up to 3 at.% of Ga into As_2Se_3 matrix without any crystallization and up to 2 at.% of Ga without any changes in the properties of these alloys. The synthesized $Ga_x(As_{0.4}Se_{0.6})_{100-x}$ alloys with 4 and 5 at.% of Ga are partly crystallized by cubic Ga_2Se_3 crystallites. Tellurium has been introduced in the selected $Ga_2(As_{0.4}Se_{0.6})_{98}$ glass following the $Ga_2(As_{0.4}Se_{0.6})_{98-y}Te_y$ cut-section to lower phonon energy and enhance quantum efficiency of the incorporated rare earth ions. The $Ga_2(As_{0.4}Se_{0.6})_{88}Te_{10}$ glass composition is the richest in Ga and Te, keeping its vitreous state without any crystallization. It has been successfully doped with 500 and 1000 ppmw Pr^{3+} and drawn into optical fiber possessing low attenuation in mid-IR region. Emission in mid-IR was efficiently recorded by pumping Pr^{3+}: $Ga_2(As_{0.4}Se_{0.6})_{88}Te_{10}$ glasses at 2 μm.

1. Introduction

The chalcogenide glasses (ChG) are known to be one of most versatile functional candidates for active application in IR photonics [1–4]. These special glassy-like media possess an excellent transparency from visible to far IR, gaining a great potential for advanced sensors including ones developed for *in-situ* mid-IR monitoring of biochemical reactions [1–4] and far-IR waveguides for atmospheric and space telecommunication windows [2–3]. To a great extent, this unique IR transmittance is increased by shifting from sulphide to selenide and to mixed selenide–telluride ChG presenting characteristic phonon energies less that 300–350 cm^{-1} [4].

Once doped with rare earth ions, such as Pr^{3+} or Dy^{3+}, these ChG significantly improve their functionality due to numerous radiative transitions emitting in the near and mid-IR range up to 10 μm [5–17]. Thus, such rare earth doped glasses can be used to fabricate optical fiber providing sources working in the mid-infrared. However, because of very low rare earth ions solubility in pure ChG matrices, the search of new efficient candidates for rare earth hosting is highly required. This problem can be solved by introducing Ga (or alternatively In) in the ChG [5,6,18], permitting the dissolution of higher rate of rare earth. To ensure high rare earth ions emission, the ratio between added Ga (In) atoms and rare earth ions should be at least 10:1 [5,6]. However, Ga additions significantly restrict the glass-forming ability of known ChG systems, mainly due to uncontrolled processes of phase separation, crystallite nucleation and growth of different Ga_2Se_3 polymorphs [19–22].

In this work, material engineering strategy will be comprehensively conducted through two stages starting from stoichiometric glassy arsenic triselenide As_2Se_3, (1) searching an optimized chemical–technological solution for Ga-doped As_2Se_3 glass and, (2) transition to Ga-contained As_2Se_3–Te glass with maximal amount of added Te to lower the phonon energy of the matrix. The most promising glass composition containing both Ga and Te was selected for doping it by Pr^{3+} ions which is known to emit a broad signal in the 4–5 μm spectral domain.

2. Experimental

The samples preparation procedure was based on the conventional melt-quenching route [23]. The studied samples were prepared from high-purity commercial elemental precursors Ga

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(7 N), As (5 N), Se (5 N), Te (6 N) and Pr_2Se_3 (3 N), the As, Se and Te being specially purified by distillation with low evaporation rate to remove impurities such as oxygen, water, silica and carbon. The appropriate amounts of initial elements with total weight close to 30 g were introduced into a silica tube of 10 mm in diameter. The ampoule was sealed under vacuum and heated to 900 °C in a rocking furnace for 10 h followed by quenching into water from 700 °C. To remove mechanical strains induced by quenching, the samples were then annealed during 5 h at the temperature of 10 °C below their glass transition temperature. The obtained rods were cut into disks of ~2 mm in thickness and polished to high optical quality.

Thermal characteristics of each sample were determined by differential scanning calorimetry (DSC) with TA Instruments Q20 and samples of 5–10 mg under 10 °C/min heating rate. The glass transition (T_g) and crystallization (T_x) temperatures were taken as onset points at the endothermic heat flow peaks with a resulting accuracy no worse than ±2 °C.

X-ray diffractometer PANalytical X'Pert Pro (Cu Kα radiation with $\lambda = 1.5418$ Å) was used to check the amorphous nature of the prepared alloys. The X-ray diffraction (XRD) patterns were collected on bulk samples at room temperature in the angular range from 5° to 90°2θ. The measurements of atomic density were performed at room temperature using the Archimedes displacement technique with distilled water, the accuracy being ±0.005 g cm^{-3}. The optical transmission spectra of the samples in the range of 0.6–2.5 μm were registered using UV/Vis/NIR spectrophotometer PerkinElmer LAMBDA 950 operating with 2 nm resolution, while IR transmission spectra in the range of 1.5–25 μm were measured using Bruker Tensor 37 spectrometer with 2 cm^{-1} resolution.

The single-core fibers were drawn by "rod" method using specially designed drawing tower under helium atmosphere [24]. The fibers of 20–40 m in length were drawn into a diameter of 400 μm at a rate of 1–1.5 m/min.

The conventional cutback technique was employed to measure the optical losses in fibers. The initial length of the measured fibers was about 2 m. After several cuttings, the fiber length was reduced to about 0.5 m. The light attenuation $\alpha(dB/m)$ was calculated from the difference of two measurements on different fiber length. Five measurements at different fiber lengths subsequently shortened after corresponding cuttings were performed to ensure high accuracy of averaged resulting attenuation.

The emission around 5 μm was recorded by means of a home-made Tm:YAG laser used for pumping Pr^{3+}:$Ga_2(As_{0.4}Se_{0.6})_{88}Te_{10}$ glasses (500 and 1000 ppmw of Pr^{3+}) at 2.01 μm. The mid-IR light focused on the monochromator slit with a CaF_2 lens was detected by a cooled InSb detector. Fluorescence decays were obtained considering $^3F_2$ excitation by using the same cooled InSb detector and 2.01 μm laser modulated by a mechanical chopper with 1 μs pulses width and 5% duty-cycle. Decay curves of the Pr^{3+} emission were recorded at 2.4 μm and 4.7 μm by a digital oscilloscope.

3. Results and discussion

3.1. The Ga–As_2Se_3 system

The Se-based materials such as binary As–Se with the As_2Se_3 stoichiometry are typical formers of transparent glasses in the region up to 18 μm [25]. Consequently, the first step of this work was to study the network-forming ability of Ga-doped As_2Se_3-based glasses within $Ga_x(As_{0.4}Se_{0.6})_{100-x}$ system (x = 0, 1, 2, 3, 4, 5; Table 1).

The results of XRD measurements shown in Fig. 1 testify that glasses containing 0–3 at.% of Ga are fully amorphous with character wide-stretched halos around ~18, 32 and 55°2θ. Small

Table 1
Characteristic temperatures T_g and T_x, criterion of stability $\Delta T = T_x - T_g$, and density of studied glasses.

Sample	Composition	Density (g/cm^3)	T_g (°C)	T_x (°C)	ΔT (°C)
G0	$As_{40}Se_{60}$	4.619	184	–	–
G1	$Ga_1(As_{0.4}Se_{0.6})_{99}$	4.629	182	–	–
G2	$Ga_2(As_{0.4}Se_{0.6})_{98}$	4.635	182	307	125
G3	$Ga_3(As_{0.4}Se_{0.6})_{97}$	4.631	180	283	103
G4	$Ga_4(As_{0.4}Se_{0.6})_{96}$	4.642	182	277	95
G5	$Ga_5(As_{0.4}Se_{0.6})_{95}$	4.662	180	276	96
T10	$Ga_2(As_{0.4}Se_{0.6})_{88}Te_{10}$	4.791	151	267	116
T15	$Ga_2(As_{0.4}Se_{0.6})_{83}Te_{15}$	4.860	149	265	116
T20	$Ga_2(As_{0.4}Se_{0.6})_{78}Te_{20}$	4.940	132	239	107
T30	$Ga_2(As_{0.4}Se_{0.6})_{68}Te_{30}$	5.069	115	264	149
RE1	$Ga_2(As_{0.4}Se_{0.6})_{88}Te_{10}$ + 500 ppmw Pr	4.778	160	273	113
RE2	$Ga_2(As_{0.4}Se_{0.6})_{88}Te_{10}$ + 1000 ppmw Pr	4.787	160	279	119

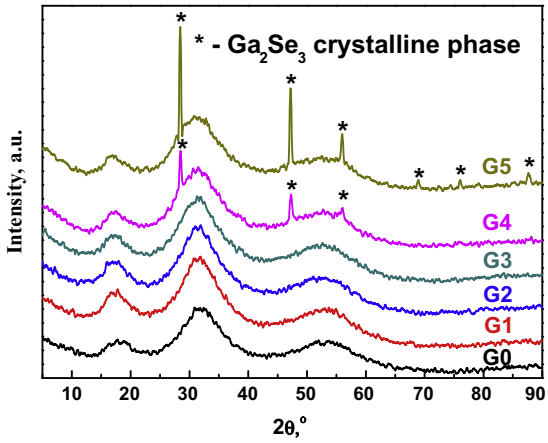

Fig. 1. Experimental XRD patterns of G0–G5 samples.

crystallization occurs in the $Ga_4(As_{0.4}Se_{0.6})_{96}$ sample (as shown by the XRD peaks near 28, 47 and 56°2θ), and more pronounced effect of crystallization is observed in $Ga_5(As_{0.4}Se_{0.6})_{95}$ sample (XRD peaks centered near 28, 47, 56, 68.5, 76 and 87.5°2θ). In these two cases, the extracted crystalline phase can be preferentially attributed to one of cubic Ga_2Se_3 polymorphs with a space group of $F\bar{4}3m$, as recently observed in Ga doped $As_{30}Se_{50}Te_{20}$ glasses [21,22].

The optical transmission spectra of these ChG in Vis/NIR 0.6–2.5 μm and IR 2–25 μm ranges are shown in Fig. 2a and b, respectively. The observed long-wave shift of transmission edge with Ga addition testifies in a favor of decreased optical band-gap in the studied alloys. It should be noted that the maximum transmission rate for samples containing 0–2 at.% of Ga is on the same level, showing their good homogeneity and close values of refractive index. On the other hand, the decrease in optical transparency is observed in $Ga_3(As_{0.4}Se_{0.6})_{97}$ sample in the NIR region (up to 4 μm) due to appearance of scattering centers caused by phase separation processes. Concentration of such heterogeneities is quite low in this alloy, so no crystallization peaks are observed in the XRD pattern. This assumption is fully confirmed for Ga-enriched alloys. Fig. 2b shows significant transparency decrease in the region up to 6 μm and in the full IR region for the samples with 4 and 5 at.% of Ga, respectively. These changes can be explained by Rayleigh scattering losses due to heterogeneities (Ga_2Se_3 crystallites) of nanometer sizes in the NIR region together with Mie