



Regular article

Influence of the selenium content on thermo-mechanical and optical properties of Ge–Ga–Sb–S chalcogenide glasses

Bin Ye^a, Shixun Dai^{a,*}, Rongping Wang^b, Guangming Tao^c, Peiqing Zhang^{a,b}, Xunsi Wang^a, Xiang Shen^a^a Laboratory of Infrared Materials and Devices, The Research Institute of Advanced Technologies, Ningbo University, Ningbo, Zhejiang 315211, China^b Laser Physics Centre, Research School of Physics and Engineering, Australian National University, Canberra ACT 0200, Australia^c CREOL, The College of Optics & Photonics, University of Central Florida, Orlando, FL 32816, United States

ARTICLE INFO

Article history:

Received 29 January 2016

Accepted 12 May 2016

Available online 13 May 2016

Keywords:

Chalcogenide glasses

Thermo-mechanical and optical properties

Infrared transmission region

ABSTRACT

A number of $\text{Ge}_{17}\text{Ga}_4\text{Sb}_{10}\text{S}_{69-x}\text{Se}_x$ ($x = 0, 15, 30, 45, 60$, and 69) chalcogenide glasses have been synthesized by a melt-quenching method to investigate the effect of the Se content on thermo-mechanical and optical properties of these glasses. While it was found that the glass transition temperature (T_g) decreases from 261 to 174 °C with increasing Se contents, crystallization temperature (T_c) peak only be observed in glasses with Se content of $x = 45$. It was evident from the measurements of structural and physical properties that changes of the glass network bring an apparent impact on the glass properties. Also, the substitution of Se for S in Ge–Ga–Sb glasses can significantly improve the thermal stability against crystallization and broaden the infrared transmission region.

© 2016 Published by Elsevier B.V.

1. Introduction

Chalcogenide glasses (ChGs) have promising applications in Infrared (IR) imaging lenses and optical devices, such as IR amplifiers and fiber laser [1–3]. Binary glasses such as As_2S_3 or As_2Se_3 have been widely used in these areas. However, some undesired properties of these glasses, like the relatively lower glass transition temperatures, low optical nonlinearity, and large photo darkening effect, make the research in new glass compositions with high transition temperatures (T_g), high crystallization temperature (T_x), and broad IR transparency window necessary. It is generally accepted that, the addition of four-coordinated Ge into the glass matrix can improve the crosslink of the different structure units, leading to high T_x , and the substitution of S by Se or Te can push the transmission edge to longer wavelength. Following this, some glass compositions like $\text{Ge}_{11.5}\text{As}_{24}\text{Se}_{64.5}$, $\text{Ge}_{10}\text{As}_{35}\text{Se}_{55}$ and GeAsSe have been demonstrated to possess excellent properties like high nonlinearity and photo stability [4]. However, Arsenic is toxic and environmentally unacceptable when As-based devices were discarded. One alternative element is Antimony. It has been found that the substitution of As by Sb can enhance the optical nonlinearity of the glasses because of more ionic nature of Sb compared with that of As.

We aimed at screening the best core and cladding glasses for optical fibers. One of the essential requirements is that the glasses

should have a better solubility of the rare earth elements. However, the formation of rare earth clusters has been verified to be one of the challenging issues achieving strong emission from the different energy level of rare earth elements. It has been demonstrated that, while doping with Ga, Ga–RE bonds can be formed and homogeneously distributed in the glass network. Sulfur-based ChGs, Ge–Ga–Sb–S, was found to exhibit high thermal, mechanical, and chemical stabilities [5], lower attenuation losses, low thermal expansion coefficient, high nonlinear refractive index n_2 (~78% of As_2S_3 for $\text{Ge}_{17}\text{Ga}_4\text{Sb}_{10}\text{S}_{69}$) [6], and a high rare-earth (RE) solubility [7]. These make the glasses promising as host matrix for potential mid-IR fiber lasers. Guery et al. [8] have systematically investigated the effect of the substitution of S by Se on the structure of $\text{Ge}_{28}\text{Sb}_{12}\text{S}_{60-x}\text{Se}_x$ glasses using Raman spectra and X-ray photoelectron spectra (XPS) [9]. Since both S and Se are two-coordinated, the replacement of S by Se has negligible effect on the topological order of the glasses although the strength of the chemical bonds changes. This is an advantage to choose the glasses with mixed S and Se doping as core and cladding materials since their physical properties can be tuned but the topological order can be maintained by changing S or Se content. The full investigation of optical properties in Ge–Sb–Se–S system is insufficient. Furthermore, we bring Ga into glass matrix for a better solubility of RE^{3+} ions [10].

In this letter, we concentrated on S and Se co-doped $\text{Ge}_{17}\text{Ga}_4\text{Sb}_{10}\text{S}_{69-x}\text{Se}_x$ (the ratio of Se “x” is in weight%) ChG system aiming to search for a glass with lower T_g and higher T_x , which is

* Corresponding author.

E-mail address: daishixun@nbu.edu.cn (S. Dai).

essential for both active and passive optical fiber drawing. The composition dependence of parameters, such as T_g , T_x , and optical band gap were investigated. The thermal and optical effects of the addition of Se on the $\text{Ga}_2\text{S}_3\text{--GeS}_2\text{--Sb}_2\text{S}_3\text{ChG}$ were discussed systematically based on DSC, UV–VIS–NIR and FTIR optical spectra.

2. Experimental

Bulk samples of $\text{Ge}_{17}\text{Ga}_4\text{Sb}_{10}\text{S}_{69-x}\text{Se}_x$ ($x = 0, 15, 30, 45, 60$, and 69) were prepared using a conventional melt-quenching technique with high purity (5 N) Ge, Ga, Sb, S and Se. Elements were carefully weighed with a precision of 0.1 mg to give a total sample mass of 10 g and then loaded into pre-cleaned quartz ampoules ($\Phi 10$ mm) that were then sealed under vacuum at a pressure of 2×10^{-3} Pa. The quartz ampoule containing the raw materials were heated at $T = 950^\circ\text{C}$ for 12 h in a rocking furnace which were specially fabricated to ensure the homogenization of the mixture. The melts of glasses were cooled rapidly to room temperature by strong wind before they were swiftly moved to a preheated furnace to anneal at 10°C below T_g for 6 h to minimize inner tension induced by the quenching step. Then, the glass rods were obtained by taking them out from the ampoules and finally cut into slices (2 mm) which were then polished to optical quality for the measurements discussed below, which were illustrated in Fig. 1.

All physical and optical measurements were carried out at room temperature. The amorphous nature of as-prepared samples was examined by the X-ray power Diffraction (XRD) method. The differential scanning calorimeter (DSC) (Q1000, TA Instruments, New Castle, DE) were conducted at a heating rate of 10 K/min under the protection of a flowing N_2 atmosphere. The absorbance and transmittance spectra of the samples were recorded by using an ultraviolet–visible–near-infrared (UV–VIS–NIR) spectrophotometer (PerkinElmer Lambda 950) in the range of 400–2500 nm. The IR transmission spectra of samples were obtained in the range of $4000\text{--}400\text{ cm}^{-1}$ using Nicolet 380 Fourier Infrared spectrophotometer. Raman spectra of samples were obtained using a Raman Spectrometer (Advantage Nir) with an excitation wavelength of 785 nm (semiconductor laser) and the power of 700 mW. The resolution of the Raman spectra was 1 cm^{-1} .

3. Results and discussion

3.1. X-ray diffraction investigations

Since these glasses are opaque in the visible spectrum except the one with $x = 0$, visual examination is impossible. In order to examine the amorphous state of these glasses, the XRD analysis was used. As presented in Fig. 2, the amorphous state of the glasses could be confirmed. As the content of Se increases, diffraction intensity of the crystallization peak has pronounced increased.

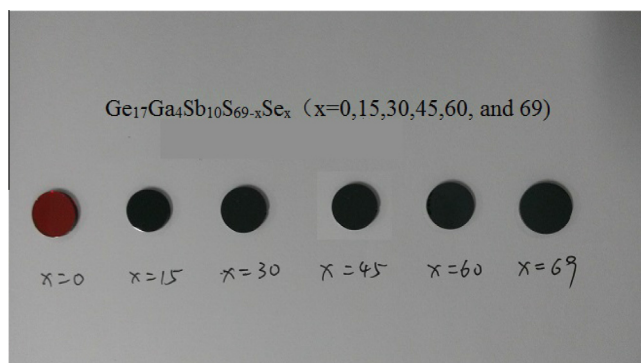


Fig. 1. The morphology of the samples.

There are no sharp peaks and crystalline phases observed in the measured spectra by XRD measurements. The results show a perfect solubility of Se in the investigated $\text{Ge}_{17}\text{Ga}_4\text{Sb}_{10}\text{S}_{69-x}\text{Se}_x$ ($x = 0, 15, 30, 45, 60$, and 69) glass samples.

3.2. Physical and thermal properties

To be used as the gain material of mid-infrared optical fiber laser, the mechanical and thermal stability is of crucial importance. The results of all DSC measurements and the physical parameters for the glasses in the $\text{Ge}_{17}\text{Ga}_4\text{Sb}_{10}\text{S}_{69-x}\text{Se}_x$ system are listed in Table 1. We can see that the density of the system glasses increases with the increase of Se content. It can be explained by that the density mainly depends on atomic mass of the glasses, but it is also closely related to the molecular size of the glass structural unit which is also called the degree of accumulation, and their relationship shows [11] as:

$$d = \frac{M}{V_M} \quad (1)$$

The atomic mass of Se ($M_{\text{Se}} = 78.96$) is greater than the atomic mass of sulfur ($M_{\text{S}} = 32.065$). Therefore, as sulfur is gradually replaced by selenium, the density of the glasses increases (from 3.160 to 4.672). In addition, the hardness of the glasses increases with the increase of Se content. The results show that the mechanical property of the glasses system can be improved when sulfur is replaced by selenium. As a result, the novel glass system is much more suitable for drawing as optical fiber.

The DSC curve of the glass samples of the Ge–Ga–Sb–S–Se system are showed in Fig. 3. Table 1 lists the results of all DSC measurements. The common stability criterion of $\Delta T = T_x - T_g$ [12] and the weight stability criterion of $H_w = \Delta T/T_g$ [13] are used to evaluate the thermal stability of these glasses. The thermal stability of the glass system against crystallization is often reported in terms of the difference between T_x and T_g . The higher the value of ΔT , the greater the thermal stability and hence the easier the glass formation [14]. The glass transition temperature (T_g) decreases with the increasing of Se content from 251 to 174°C between $x = 0$ and $x = 45$, then increases to 191°C ($x = 69$). The onset crystallization temperature (T_x) can't be observed obviously except the one $x = 45$ at 330°C , which we can see in Fig. 2. This indicates the superb stability of the investigated glasses against crystallization, as characterized by possessing a difference in $T_x - T_g$ larger than 200°C . Therefore, the thermal stability against crystallization is improved with the addition of Se.

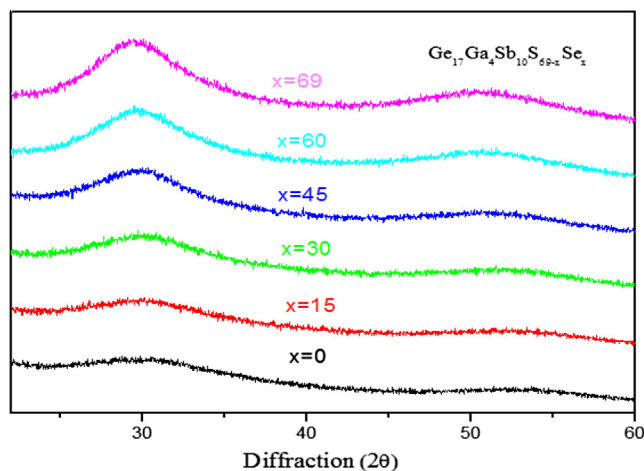


Fig. 2. XRD patterns of $\text{Ge}_{17}\text{Ga}_4\text{Sb}_{10}\text{S}_{69-x}\text{Se}_x$ ($x = 0, 15, 30, 45, 60, 69$) glass samples.

Download English Version:

<https://daneshyari.com/en/article/1783949>

Download Persian Version:

<https://daneshyari.com/article/1783949>

[Daneshyari.com](https://daneshyari.com)