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Structural characterization and compositional dependence of the optical properties of Ge–Ga–La–S chalcohalide glass system

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ABSTRACT

In this paper, chalcogenide glasses of $80GeS_2$–$(20-x)Ga_2S_3$–xLa_2S_3 ($x = 0, 1, 3, 5$ mol%) were synthesized through the traditional melt-quenching technique. The effects of La_2S_3 addition on the thermal, optical, and structural properties of Ge–Ga–S glasses were investigated. Results showed that the synthesized glasses possessed considerably high glass transition temperature, improved glass forming ability, high refractive index, and excellent infrared transmittance. A redshift at the visible absorbing cut-off edge lower than 500 nm was observed with increasing of La_2S_3 content. Direct and indirect optical band gap values were calculated. SEM result suggested that this glass system owned better glass forming ability and uniformity. Raman spectral analysis indicated that the introduction of La_2S_3 induced the dissociation of Ge–Ge metal bonds and transformed the [S_3Ge–GeS_3] structure to GeS_4 tetrahedrons. Consequently, the connectivity between tetrahedrons of the vitreous network was enhanced. This work suggests that La_2S_3 modified Ge–Ga–La–S glass is a promising material for infrared optical research.

1. Introduction

Chalcogenide glasses as a kind of promising candidate material for thermal imaging, infrared (IR) optics, biological sensors, and optical communications has many excellent properties, such as wide transparency window, high refractive index, and low phonon energy [1–3]. Particularly, the low phonon energy of chalcogenide glasses enables many mid-IR transitions of rare-earth ions (REIs) to be more active, which brings about the unique optoelectronic potential in the mid-IR spectral range [4,5]. However, despite the various attractive properties of these glasses, the above applications are still limited by their poor mechanical properties and substantial inherent weaknesses. Fortunately, the strong correlation between the optical and physical properties and the chemical composition of chalcogenide glasses makes improving their properties and technological applications by compositional modification feasible [6,7].

GeS_2–Ga_2S_3 chalcogenide glasses have already been certified to have eminent IR transparency, low phonon energy, and high chemical durability, which offers many advantages for potential application in optical modulators, efficient laser host materials, and fiber-optical amplifiers in the IR [8–11]. However, some difficulties arise in the fabrication process, and the pure GeS_2–Ga_2S_3 chalcogenide glasses are prone to crystallization. The introduction of small amounts of a fourth element into this glass system is an effective way to overcome this drawback [12,13]; moreover, flexible compositional modification can be carried out in this system. The lanthanum element exhibits excellent interactions with Ge, Ga, and S elements, which contributes to the improvement of glass forming ability, thermal stability, and optical properties of prepared glasses by its introduction to glass network [14,15]. Moreover, the addition of La_2S_3 into GeS_2–Ga_2S_3 glass as network modifiers can facilitate the formation of stabilized glass system by breaking the unstable S–Ga dative bonds in the original glass network. Kohei Kadono et al. also proposed that Ga_2S_3–GeS_2–La_2S_3 glasses notably improves the optical property and the thermal stability by increasing the large refractive index, glass transition temperature, and density [16]. La^{3+} can be dissolved into the glass network as charge compensators and make some modifications in the structure of glass, which is beneficial to the enhancement of capacity for resistance against crystallization [17,18]. Meanwhile, this behavior also promotes the increase of La^{3+} solubility and subsequently enhances the solubility of REIs by the substitution for La [19]. These

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properties are important not only for the infrared spectroscopic studies but also for practical applications, such as the fabrication of active fiber waveguide. Notably, the absorption cut-off for the shortwave length side of the Ga_2S_3–GeS_2–La_2S_3 glass is 100–200 nm shorter than those of conventional sulfide glass systems [20] such as Ga–Sb–S glass. This makes spectroscopic studies for visible region possible.

The aim of this research was to study the influences of La_2S_3 addition on the physical, thermal and optical properties of Ge–Ga–La–S glass. The fabricated samples were characterized using XRD, UV/VIS/NIR spectrophotometer, scanning electron microscope, and Raman spectroscopy. The effects on the glass optical properties were elucidated in detail, and the mechanism responsible for the enhancement of glass forming ability was explained.

2. Experimental

2.1. Sample preparation

Bulk glasses (10 g) with compositions $80GeS_2$–$(20-x)Ga_2S_3$–xLa_2S_3 ($x = 0$, 1, 3, 5 mol%) were synthesized by traditional melt-quenching technique according to the published procedures by us [18], labeled as G0, G1, G3, G5, respectively. Highly pure raw materials (Ge, Ga, and S at 99.999%, and La_2S_3 at 99.99%) were thoroughly weighed and melted in evacuated quartz ampoules using a rocking furnace at temperatures between 960 and 980 °C for several hours. The ampoules were agitated at regular intervals to produce homogeneous melts. At the end of the melting cycle, the melts were quenched to room temperature in cold water. Then, the cooled melts were immediately transferred to a preheated furnace for annealing at approximately 20 °C below the glass transition temperature for several hours to minimize the inner tension induced by quenching. The glass rod was taken out from the tube, cut into several disks at a diameter of 10 mm and a thickness of approximately 2 mm, and then polished at both sides for optical measurements.

2.2. Characterization techniques

The amorphous nature of the glasses was confirmed using X-ray diffraction (XRD) method with a power diffractometer (German Bruker D2) using Cu Ka radiation with resolution of 0.0203 2θ. The IR variable angle spectroscopic ellipsometry (IR-VASE; J. A. Woollam Co., Lincoln, NE) was used to measure the linear refractive indices using the spectral resolution of 18 nm, in which the angles of incidence were 70° and 75° and the sample is polished at single side. The glass transition temperature (T_g) for approximately 10 mg of glass sample of each composition was obtained through differential scanning calorimetry (DSC) measurement (TAQ2000) with temperature accuracy of ±1 °C at a temperature range of 50–580 °C. The upper temperature limit was set at 580 °C due to the restrictions of the aluminum pan in the experiment equipment. The heating rate was set at 10 °C per minute and Ar nitrogen gas was used for purging. The spectrophotometer (Perkin–Elmer Lambda 950 UV/VIS/NIR) was used to analyze the visible and near-infrared absorption spectra of the glass samples with spectral resolution of 2 nm. The acquisition of the IR transmission spectra employed a Fourier IR spectrophotometer (Nicolet 380) within a range of 2–14 μm using the spectral resolution of 12 nm. Raman spectra were obtained using a Raman Spectrometer (Renishaw InVia) equipped with an Ar ion laser with an excitation wavelength of 488 nm using the spectral resolution of 1.79 cm^{-1}. The excitation power applied to the measurement was approximately 2.5 mW. Surface morphology and chemical compositions of the glasses were investigated by scanning electron microscope (SEM) (Tescan, CZECH, and "VEGA3SB-EasyProbe") and energy dispersive spectroscopy (EDS) operated at 15 kV, respectively. All measurements were taken at room temperature. All the technology measurements could be well reproducible through appropriate means.

3. Results and discussion

3.1. X-ray diffraction analysis

Fig. 1 shows the XRD patterns of the prepared glasses. The patterns exhibited three broad, diffuse scattering halos derived from the polymeric nature of the glass materials, confirming a long-range structural disorder characteristic of the amorphous network of chalcogenide glasses. The absence of sharp peaks corresponding to the formation of any crystalline phases from the spectra also confirmed the typical amorphous nature of the materials formed. Regardless of the differences in chemical composition with increasing La_2S_3 content, all the studied samples exhibited the representative envelope pattern belonging to amorphous material, indicating that the glass system exhibited better glass-forming ability.

3.2. Physical and thermal properties

DSC curves of the samples are shown in Fig. 2, and the characteristic temperatures of T_g, T_x (the onset temperature of crystallization), and T_p (the peak crystallization temperature) are listed in Table 1. Besides, Table 1 summarizes certain physical and thermal parameters of the prepared glasses. Clearly, all the listed parameters increased as La concentration increased; thus, La certainly plays a very important role in these variations. The glass transition temperature of Ge–Ga–La–S glass system is up to 447 °C which is much higher than that (about 240 °C) of Ga–Sb–S glass [21]. The common thermal stability factor of ΔT (T_x-T_g) [22] and the weight stability criterion of H_w ($\Delta T/T_g$) [23] were used to assess the thermal stability of these glasses. In general, ΔT is >100 °C suggests that the glass is more thermally stable. Furthermore, higher ΔT values corresponded with greater thermal stability and hence easier glass formation. In our previous research [24], we didn't deliberate the values of ΔT and H_w, only T_g, which was not sufficient to testify the improved thermal stability. However, as shown in Table 1, with the incorporation of La into the GeS_2–Ga_2S_3 glass could effectively enhance the thermal stability of the glass system against crystallization, especially when $x = 5$, whereby the absence of

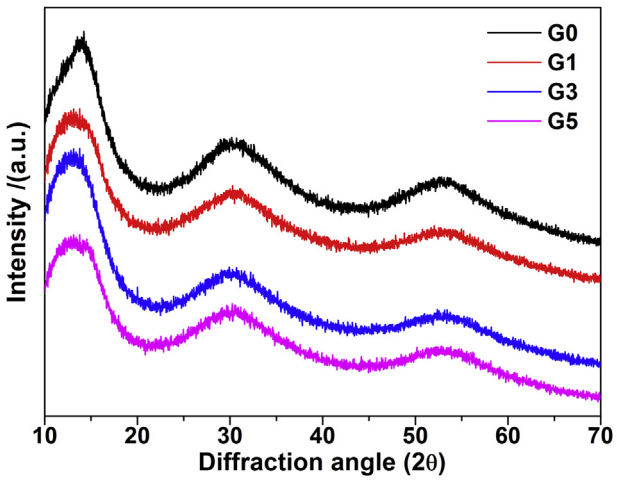

Fig. 1. XRD patterns of $80GeS_2$–$(20-x)Ga_2S_3$–xLa_2S_3 ($x = 0$, 1, 3 and 5 mol%) glasses.