Preparation and properties of Ge–Ga–La–S–AgI chalcogenide glass

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Abstract

Chalcogenide glasses of $65\text{GeS}_2-(25-x)\text{Ga}_2\text{S}_3-10\text{AgI}-x\text{La}_2\text{S}_3$ ($x=0, 1, 3$, and 5 mol%) were fabricated through the traditional melt-quenching method. The effects of addition of La_2S_3 on physical, thermal and optical properties of the glass system were investigated. The results showed that the fabricated glasses possess considerably high glass transition temperature, exhibit improved mechanical property and excellent infrared transmission. A redshift at the visible absorbing cut-off edge is observed with increasing of La_2S_3 content. The direct and indirect optical band gap values are also calculated. Raman spectra analysis indicated that the band at 265 cm^{-1} decreased in amplitude and a new peak at 230 cm^{-1} was detected manifesting the formation of La-S bond in the network. In addition, the mid-infrared emission at $3.74\text{ }\mu\text{m}$ of the glasses doped with Tm^{3+} ions was achieved. The results indicated that the glasses are promising materials for mid-infrared applications such as imaging, remote sensing and lasers.

Keywords: Chalcogenide glasses; La_2S_3 addition; Optical properties; Mid infrared emission

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1. Introduction

Chalcogenide glasses have been attracting widespread interest due to their superior properties, including extended infrared (IR) transparency, low phonon energy and high refractive index in contrast to those of oxide glass and fluoride glass hosts[1, 2]. These properties can be useful in applications such as thermal imaging, optical fibers for chemical and biological sensing, optical modulator and optical communications[1, 3, 4]. Particularly, by doping with rare-earth (RE) ions, chalcogenide glasses have the potential to be mid-IR fiber lasers and amplifiers considering their transparency at potential pump and emission wavelength[5-7].

However, despite the various desirable attractive properties of these glasses, the above applications are still limited by their poor mechanical properties and substantial inherent weaknesses. Several studies have reported that GeS₂-based chalcogenide glasses are more stable and have more mechanical properties in most cases than other sulfide glasses. The addition of gallium (Ga) into Ge–S glasses has been shown to cause significant changes in the structures and properties of the Ge–S glasses. According to Zhang Mingli et al.[8], the introduction of Ga₂S₃ into GeS₂ notably improved the mechanical property and the thermal stability of the glasses by increasing the glass transition temperature, density and microhardness. C. Julien et al.[9] also investigated the formation of Ga–Ga metal bonds as a possible alternative to compensate the sulfur deficiency in the network structure, drawing a conclusion that gallium sulphide formed more stable glasses with GeS₂ over a wide range of composition. Furthermore, the introduction of Ga to the host can also increase RE

emission to a certain extent for the same level of RE-dopant[10], because Ga^{3+} -adopted tetrahedral coordination has been hypothesized to encourage the complexation of RE ions at Ga^{3+} sites. This complexation is significant for the application of RE-ion-doped lasers or amplifiers. Meanwhile, La_2S_3 , as network modifiers in Ga_2S_3 , has been reported to be capable of forming stable glasses by breaking the unstable S–Ga dative bonds in a Ga_2S_3 crystalline phase. Jong Heo et al.[11] proposed that La^{3+} can be dissolved into the glass network as charge compensators for these non-bridging sulfurs, which appears to be the crucial factors for the increase of La^{3+} solubility. It has been further reported that GeS_2 – Ga_2S_3 – La_2S_3 glasses can include more than 10 cation mol% of rare-earth ions replacing La_2S_3 by the other rare-earth ions[12]. This indicated that La^{3+} had a facilitating effect on the solubility of rare-earth ions. Therefore, the introduction of Ga and La into Ge–S glasses is feasibly used to reform the structure of Ge–S glasses that facilitating the solubility of relatively large RE ions. In addition, approximately 520 nm is the cut-off wavelength of the electronic absorption of the GeS_2 – Ga_2S_3 – La_2S_3 glasses in the visible region, which is 100–200 nm shorter than those of conventional sulfide glasses such as As_2S_3 -based glasses[6]. Furthermore, the Ga_2S_3 – GeS_2 – La_2S_3 glass system has higher glass transition temperature and refractive index according to the report of K. Kadono et al.[13]. Although many studies have already investigated Ga_2S_3 – GeS_2 – La_2S_3 glasses, the substitution capacity of La_2S_3 to Ga_2S_3 and the dependence of glass structure on the physical, thermal and optical properties need to be further elucidated.

In this work, the glass composition of $65\text{GeS}_2-(25-x)\text{Ga}_2\text{S}_3-10\text{AgI}-x\text{La}_2\text{S}_3$ ($x=0, 1, 3, \text{ and } 5 \text{ mol\%}$) was investigated. The aim of this paper is to investigate the effect of La_2S_3 addition on physical and optical properties of $\text{GeS}_2\text{--Ga}_2\text{S}_3\text{--AgI}$ glass substrate. Optical parameters such as optical band gaps are calculated. The produced samples were characterized using UV/VIS/NIR spectrophotometer, Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy and fluorescence spectrometer. In addition, the effects on the glass optical properties are elucidated in detail.

2. Experimental

2.1 Sample preparation

Bulk glasses were synthesized by traditional melt-quenching method. Elemental raw materials, which consist of approximately 10 g of high purity Ge (5N), Ga (5N), Tm (5N) and S (5N), and analytically pure AgI (4N) and La_2S_3 (4N), were thoroughly weighed and melted in evacuated quartz ampoules using a rocking furnace at temperature between 950 and 1000 °C for several hours. The composition of the prepared glasses were $65\text{GeS}_2-(25-x)\text{Ga}_2\text{S}_3-10\text{AgI}-x\text{La}_2\text{S}_3$ ($x=0, 1, 3, \text{ and } 5 \text{ mol\%}$), marked with G0, G1, G3, G5, respectively. The silica tubes containing the melts were quenched to room temperature in water, then immediately transferred to a preheated furnace to anneal at approximately 10 °C below the glass transition temperature for 6 h in order to minimize the inner tension induced by quenching. The specimens were cut into disks of about 9 mm in diameter and approximately 1.9 mm in thickness, and then polished at both sides for optical measurements.

2.2 Characterization

The **density** of the samples were measured at room temperature according to Archimedes principle using distilled water as an immersion liquid. A microhardness tester (Everone MH-3, Everone Enterprises. Ltd., Shanghai, China) was used with dwell time of 6 s and test load of 25 gt to measure the microhardness. IR variable angle spectroscopic ellipsometry (IR-VASE; J. A. Woollam Co., Lincoln, NE) was used to measure the linear refractive indices, in which the angles of incidence were 70° and 75°. The amorphous nature of the glasses was examined through X-ray diffraction (XRD) method with a power diffractometer (German Bruker D2) using Cu Ka radiation. The glass transition temperature was obtained through differential scanning calorimetry (DSC) measurement at the temperature range of 50–500 °C and at a heating rate of 10 °C per min using a TAQ2000 thermal analyzer. The Perkin–Elmer Lambda 950 UV/VIS/NIR spectrophotometer was used to analyze the visible absorption spectra of the glass samples. The recording of the IR transmission spectra employed a Nicolet 380 Fourier IR spectrophotometer within the range of 2–14 μm . Raman spectra were obtained using a Renishaw InVia Raman Spectrometer equipped with an Ar ion laser with excitation wavelength of 488 nm. The excitation power applied to the measurement is approximately 2.5 mW. The mid-IR emission spectra of Tm^{3+} -doped Ge–Ga–La–S–AgI samples were measured using a fluorescence spectrometer (Edinburgh, ENGLAND FLS980) equipped with a monochromator and a steady InSb detector cooled with liquid nitrogen. A semiconductor CW laser at 808 nm was used as the excitation source.

3. Results and Discussion

3.1 X-ray diffraction analysis

Fig. 1 presents the XRD patterns of the prepared glasses. This analysis with regard to signal accumulation shows that each sample nearly has a single-phase composition. The absence of sharp peaks corresponding to the formation of any crystalline phases from the spectra confirms the typical amorphous nature of the materials formed[14]. With the increase in the La_2S_3 content and in the diffraction angle, the glass samples exhibit representative envelope pattern belonging to amorphous material, which indicates that the glass system has a better glass formation ability.

3.2 Physical and thermal properties

Table 1 summarizes certain physical, thermal, and optical parameters of the Ge–Ga–La–S–AgI glasses. The glass samples have a notably high glass transition temperature (T_g), which increases from 357 °C in the host glass to 378 °C in the glass with the introduction of 5 mole fraction of La_2S_3 . Meanwhile, the density, microhardness, and refractive index at 1.55 μm of the optical communication window all increased with the increased La_2S_3 content, indicating a considerable improvement in the thermal stability and mechanical capacity of the glass system. These results indicate potential applications in all-optical devices.

In most cases, the increase in T_g has been associated with an increase in the rigidity between the short range order structures in the glass, an overall increase in the bond strengths between the various network-forming atoms in the structure, or both[15]. The increase in T_g demonstrates that the bond strength of the glass network could be

strengthened to a certain extent by the addition of La_2S_3 . The density (ρ) and refractive index both increase with the substitution of Ga component with La. This could be due to the higher atomic weight of lanthanum (La) in contrast to gallium (Ga), and the higher polarizability of La^{3+} ions in contrast to Ge^{4+} and Ga^{3+} ions. The polarizabilities of La^{3+} , Ge^{4+} , and Ga^{3+} are 1.04, 0.143, and 0.198, respectively[16]. According to Kazuya Shirao[17], the polarizability of ions is directly correlated with the refractive index of the material. The introduction of La_2S_3 and the La^{3+} as charge compensators in the network structure increase the packing density of the glass structure.

3.3 Absorption spectra and optical band gap

Fig. 2 shows the absorption spectra of the studied glasses. The absorption spectra indicates that the visible cut-off edge of the glasses exhibit an evident redshift to **the longer wavelength**. The absorption of the cut-off edge is between 515 nm and 554 nm when the content of La_2S_3 in the $\text{GeS}_2\text{--Ga}_2\text{S}_3\text{--AgI}$ glass substrate is increased. The short-wave absorption edge of the glasses is attributed to the electrical transition between the valence bands and the conduction bands[18]. The higher polarizability of La^{3+} than Ga^{3+} is directly correlated to the decrease in the electronic potential of the valence band because of the polarization effect. This phenomenon caused the decreased energy difference between the conduction band and the valence band of the glass host. Thus, the required excitation energy of the electronic transition is decreased, thus sufficiently demonstrating the short-wave cutoff wavelength for longer periods[19].

Optical measurements are productive instruments for the band structure and the width of the energy band gap of amorphous materials. The optical band gap is expressed by the Tauc law[20]:

$$\alpha(\omega)h\omega=B(h\omega-E_{opt})^m$$

where B is a constant depending on the transition probability, α is the absorption coefficient and is calculated using the expression $\alpha=2.303A/d$ (A is the optical density and d is thickness of the glass sample), ω is the incident light angular frequency, E_{opt} is the width of the band gap, namely, the optical energy gap, and m is an index characterizing the transition process in the glass. The variable m takes the values of 1/2 and 2 in most cases for directly allowed and indirectly transitions, respectively.

Fig. 3 and Fig. 4 depict the plots of $(\alpha(\omega)h\omega)^{1/2}$ and $(\alpha(\omega)h\omega)^2$ as a function of $h\omega$ in eV for both indirectly allowed and directly allowed transition. The optical band gap E_{opt} is obtained by extrapolating the linear portion of the curve to the photon energy $h\omega$ axis. The values of the indirect optical band gap of the glass system are determined in the range from 2.2274 eV to 2.3155 eV as shown in Table 2, which decrease with the increase of La_2S_3 content. In addition, the variation in the regularity of the values of the direct optical band gap is coincidental with those of the indirect optical band gap, as shown in the inset of Fig. 3 and Fig. 4. This behavior of the band gap might be related to the electronegativity of the elements in the glass component. In chalcogenide glasses, the valence band is composed of lone pair electrons, while the conduction band is composed of empty orbitals. The addition of atoms with lower electronegativity into the glass matrix increases the energy of the lone pair electrons,

thus increasing the width of the valence band[21]. The electronegativity values of La and Ga are 1.11 and 1.81, respectively. Thus, with the increase in content of La_2S_3 , a portion of Ga is substituted by La thus increasing the width of the valence band. However, the conduction band is nearly not affected. Consequently, E_{opt} decreases with the increase of La_2S_3 content.

3.4 Raman scattering investigations

Raman spectroscopy measurement is used in the present study to investigate the network structure of the glasses. Fig. 5 shows the spectra results of the glasses, which indicate the influence of La_2S_3 on the properties and structural changes of the glasses. The vibrations at 125, 148, and 190 cm^{-1} are associated with the symmetrical bending vibration of the $[\text{GeS}_4]$ and the $[\text{GaS}_4]$ units, the asymmetrical bending vibration of the $[\text{GeS}_4]$ and the $[\text{GaS}_4]$ tetrahedrons, and the vibration of the $[\text{GeS}_{4-n/2}\text{I}_n]$ structural units[[22, 23], respectively. The amplitudes of the last two vibrations are marginable and are modified to the least extent with the increase of La_2S_3 . The shoulders, approximately 372 and 395 cm^{-1} , are related to the vibration of the edge-shared GeS_4 and the asymmetrical stretching vibration of $[\text{GeS}_4]$ and $[\text{GaS}_4]$ structure[24], respectively. By increasing La_2S_3 content, intensity of the shoulders are increased and the connection between tetrahedra is increased. This is in agree with glass transition temperature. As we know, with increasing the connectivity of glass network, glass transition temperature is increased. Meanwhile, the band at 428 cm^{-1} originates from the asymmetric stretching vibration of two tetrahedra connected through a bridging sulfur atom, specifically, $[\text{S}_3\text{Ge-S-GeS}_3]$ structural units[25].

Notably in the spectra, the peak centered at around 265 cm^{-1} decreases with introduction of a marginal amount of La_2S_3 . It is attributed to the vibration of the metal–metal bonds of a certain $[\text{S}_3\text{Ge}(\text{Ga})-(\text{Ga})\text{GeS}_3]$ ethane-like unit[26]. Because of the lower strength of the Ge–S bonds[27] and lower electronegativity between Ge and S in contrast to the Ga–S bonds, this band is prevailing relative to the $[\text{S}_3\text{Ge}-\text{GeS}_3]$ bonds. However, the addition of La_2S_3 to the glass causes the dissociation of Ge–Ge metal bonds. The sulfur in the La_2S_3 compensates for the sulfur insufficiency because the formation of the GaS_4 from Ga_2S_3 unit requires a considerable amount of sulfur, and thus transforms the $[\text{S}_3\text{Ge}-\text{GeS}_3]$ bonds to GeS_4 units. This result manifests the decline in amplitude of the band at 265 cm^{-1} . Second, the band width of the peak at 340 cm^{-1} increases. The increase in width is facilitated by the high proximity of the symmetrical stretching vibration of $[\text{GeS}_4]$ structure to that of the $[\text{GaS}_4]$ unit[28]. Lastly, the slow growth of the peak is at approximately 230 cm^{-1} , which originated from the vibration of the La–S bonds[29]. Overall, the addition of La_2S_3 caused certain changes in the structure of the $\text{GeS}_2\text{--Ga}_2\text{S}_3\text{--AgI}$ glass system. The structural units constituting the backbone of the network structure are the corner-shared GaS_4 and the GeS_4 tetrahedra which are connected through a bridging sulfur. According to the results, by increasing La_2S_3 content, connectivity of glass network is increased. La^{3+} ions functions between the networks as charge compensators. Notably, La_2S_3 disrupts the Ge–Ge metal bonds to form corner-shared tetrahedra with non-bridging sulfurs and increase backbone of the glass.

3.5 Transmission spectra and mid-IR emission

Fig. 6 shows the IR transmission spectra of the glass samples. The short-wavelength absorption edge (defined in the present study as the wavelength in which the absorption coefficient is 10 cm^{-1}) of the Ge–Ga–La–S–AgI glasses is distinctly located at approximately $2.47 \text{ }\mu\text{m}$. The cut-off edge with long wavelength corresponding to the multi-phonon processes is approximately $11.5 \text{ }\mu\text{m}$. With increasing concentrations of La_2S_3 , the transparency region sufficiently retained the transmission in the IR properties, and the maximum average transmission percentages are between 62% and 73%. The decrease in the maximum transmission could be due to the heterogeneity in the glass. In the transmission spectra, absorption bands are visible and situated on approximately $3.0 \text{ }\mu\text{m}$, $3.9 \text{ }\mu\text{m}$, $4.9 \text{ }\mu\text{m}$, and $6.6 \text{ }\mu\text{m}$, corresponding to the impurity absorption of $-\text{OH}$, $\text{S}-\text{H}$, $\text{Ge}-\text{H}$, and $\text{H}-\text{O}-\text{H}$ and H_2O [5], respectively (as observed in the spectra). On the one hand, the water on the surface of the raw materials introduced caused the formation of impurities during the glass preparation process. On the other hand, water and oxygen in the atmosphere are inevitable. The impurities can be dissolved through further distillation and purification process.

Considering the low phonon energy and the beneficial properties of Ge–Ga–La–S–AgI glass system, the glass has considerable potential for RE-doped glassy matrix materials, which can emit mid-IR lights. We investigated luminescence characteristics of Ge–Ga–La–S–AgI glasses with different La_2S_3 content, and we observed that higher content of La_2S_3 in the glass system can induce stronger mid-IR

emission of Tm^{3+} ions. Fig. 7 indicates the mid-IR luminescence spectra of 1 mol% Tm^{3+} -doped $65\text{GeS}_2-(25-x)\text{Ga}_2\text{S}_3-x\text{La}_2\text{S}_3-10\text{AgI}-1\text{Tm}$ ($x=1, 3$, and 5 mol%) glasses were stimulated by 808 nm laser. Strong and broad mid-infrared emission band centered at approximately $3.74\text{ }\mu\text{m}$ because of the $^3\text{H}_5 \rightarrow ^3\text{F}_4$ transition was observed, which coincides with an atmospheric transmission for potential remote-sensing applications. Evidently, more addition of La_2S_3 into the glass causes higher increases in emission intensity. This may be attributed to the lower non-radiative decay rate caused by lower phonon energy with the introduction of La_2S_3 , while causes the efficient population of $^3\text{H}_5$ level and the intensified fluorescence in return[30]. This behavior demonstrated that increasing Tm ions substituted of La_2S_3 with the increasing content of the latter. La^{3+} ions exist between the glass networks playing the role of a glass modifier to compensate the excess negative charge of the $[\text{GaS}_4]$ units. Tm^{3+} ions may also occupy the same positions of La^{3+} because Tm ions belong to the rare earth ions of La system with similar atomic radius and electron configuration. When Tm^{3+} ions occupy the site of La ions in the glass network, it is not easy for them to be gathered together but separated on the La ions site. Then the clustering effect was weakened and the emission efficiency was enhanced owing to the reduced cross relaxation between rare earth ions in the host. Therefore, the increased substitution of Tm^{3+} ions for La^{3+} gave rise to the increased infrared emission intensity of Tm^{3+} ions in Ge-Ga-La-S glasses making the doped glasses are potential as gain materials for mid-IR amplifiers or lasers.

4. Conclusion

A series of $65\text{GeS}_2-(25-x)\text{Ga}_2\text{S}_3-10\text{AgI}-x\text{La}_2\text{S}_3$ ($x=0, 1, 3$, and $5\text{mol}\%$) chalcogenide glasses were synthesized. Addition of La_2S_3 into the glasses causes to increase the density, hardness and refractive index in all the samples. The glasses demonstrated eminent transparency in the range of $2.47\text{ }\mu\text{m}$ to $11.5\text{ }\mu\text{m}$ and obtained the comparatively high glass transition temperature up to $378\text{ }^\circ\text{C}$. Raman spectra analysis demonstrated that La_2S_3 causes the dissociation of Ge–Ge metal bonds and converts $[\text{S}_3\text{Ge}-\text{GeS}_3]$ type connection to $[\text{GeS}_4]$ units with non-bridging sulfurs. La^{3+} plays a crucial role as a charge compensator for these non-bridging sulfurs in the investigated glass. In addition, Tm^{3+} ions in the $\text{GeS}_2-\text{Ga}_2\text{S}_3-\text{AgI}-\text{La}_2\text{S}_3$ glass system display significant mid-IR luminescence at approximately $3.74\text{ }\mu\text{m}$. Thus, the RE-doped glasses are promising gain materials for mid-IR amplifiers or laser devices.

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Fig. 1. XRD patterns of Ge–Ga–La–S–AgI glass samples.

Fig. 2. Absorption spectra of 65GeS₂–(25–*x*)Ga₂S₃–10AgI–*x*La₂S₃ glasses (*x*=0, 1, 3, 5 mol%).

Fig. 3. Relationship between $(\alpha h\omega)^{1/2}$ and $h\omega$ in glass samples. The inset is the value of indirect optic gap (E_{opt}) dependence of La₂S₃ contents.

Fig. 4. Relationship between $(\alpha h\omega)^2$ and $h\omega$ for glass samples. The inset is the value of direct optic gap (E_{opt}) dependence of La_2S_3 contents.

Fig. 5. Raman spectra of Ge-Ga-La-S-AgI glass samples with variation in La_2S_3 content.
Infrared transmission spectra of the glass samples.

Fig. 6. Infrared transmission spectra of the glass samples.

Fig. 7. Mid-infrared emission spectra of Tm^{3+} in $65\text{GeS}_2-(25-x)\text{Ga}_2\text{S}_3-x\text{La}_2\text{S}_3-10\text{AgI}-1\text{Tm}$ ($x= 1, 3$, and 5 mol%) glasses under the excitation of 808 nm laser source. The insert shows the energy levels of Tm^{3+} ions with their possible transitions.

Table 1
Thermal and physical properties of the prepared glasses.

Sample	$T_g(^{\circ}\text{C})$	$\rho(\text{g}/\text{cm}^3)$	$H_v(\text{kg}/\text{mm}^2)$	Refractive index
G0	357	3.251	192	2.135
G1	360	3.252	196	2.138
G3	366	3.333	212	2.167
G5	378	3.357	218	2.198

Table 2
Derived characteristic parameters for the studied glasses.

Sample	$\lambda_{\text{vis}}(\text{nm})$	$E_{\text{opt-dir}}(\text{eV})^a$	$E_{\text{opt-indir}}(\text{eV})^b$
G0	515	2.4087	2.3155
G1	535	2.3745	2.2715
G3	539	2.3673	2.2652
G5	554	2.3332	2.2274

^a Direct optical band gap.

^b Indirect optical band gap.