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Glass formation and properties of Ge-Ga-Te-ZnI₂ far infrared chalcogenide glasses

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ABSTRACT

In order to develop novel far infrared window material, a series of Ge-Ga-Te-ZnI₂ chalcogenide glasses were prepared by traditional melt-quenching method and its glass-forming region was determined also. Here, some measurements including X-Ray Diffraction (XRD), differential thermal analysis (DTA), UV-Vis-NIR absorption spectrum, and Infrared optical transmission spectra were carried out. The allowed indirect transition optical band gap was calculated according to the classical Tauc equation. The results show that with the addition of ZnI₂, the glass-forming ability and thermal stability are improved gradually. With the contents of ZnI₂ increased from 5 to 20 at%, continued blue-shifting occurs in the cutting-off absorption edge of short-wavelength and the values of indirect optical band gaps were observed with ranges from 0.596 to 0.626eV in these glasses. These

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GeTe_{4.3}-GaTe₃-ZnI₂ glasses show wide optical transmission and the infrared cut-off wavelengths are larger than 25μm, which implies that the Ge-Ga-Te-ZnI₂ chalcogenide glasses possess the potential of far-IR optical window applications.

Keywords: Chalcogenide glass; Far-infrared; Te-based

1. Introduction

In recent decades, tremendous interest has been focused on the exploration of out-space. The European Space Agency (ESA) Darwin mission aims to detect life signals in these exoplanets with directly analyzing extra solar earth-like planets [1]. The main biological markers of life are the molecules of water, ozone and carbon dioxide which have their infrared signatures in the 6, 10 and 15μm regions and development of IR optics operating in the 4-20μm regions is critical for space exploration [2]. Chalcogenide glasses are well known for their transparency in the infrared optical range and their ability to be drawn into fiber. Such optical fibers can transmit light wavelength ranging from 2 to 20μm, depending on the fiber glass compositions [3]. The transparency of a chalcogen based glass in the infrared region is determined by the multi-phonon absorption and it correlated to the chalcogen atomic weight, bond energy and so on [4]. For instance, the IR edge for the S based glasses is limited to 12μm(bulk glass)while for a Se based materials the edge is shifted towards 16μm [5]. To extend the transparency towards longer wavelength it is necessary to use Te, the heaviest chalcogen [6, 7]. However, there are still some problems for Te-based glasses preparation: first, tellurium has strong metallic character in comparison with S, Se, its glass-forming ability is relatively weak; second, the glass transition

temperature of Te-based chalcogenide glasses is low and thermal stability is poor; third, due to structure defects, traditional Te-based glasses are synthesized with Se or As, which will make infrared optical wavelength ($<16\mu\text{m}$) far less than the theoretical level ($20\mu\text{m}$) or environment-hazardous. In a word, the development of Te-based glasses is restricted by all these defects, so some basic elements of glass former or adjuster, such as Ga, Ge, I or others are needed.

Up to now, some advances of the Te based glasses and the applications in far-Infrared region have been reported. In the early stage, Tichy et al. [8] reported that the transparent range of Se-Te-I glasses could be extended from 2 to $21\mu\text{m}$ and these glasses could be attractive for further studies in connection with their possible applications in CO_2 lasers. Bureau and Danto [5] have reported the glass forming region in the Te-Ga-Ge ternary diagram, within which the most promising glass composition is $\text{Te}_{75}\text{Ga}_{10}\text{Ge}_{15}$. The IR transmitting range of $\text{Te}_{75}\text{Ga}_{10}\text{Ge}_{15}$ glass sample was from 2 to $25\mu\text{m}$, while there is an obvious absorption around $15\text{-}20\mu\text{m}$ band aroused by some impurities, and it is very difficult to be removed by ordinary purification processes. Recently, Lucas et al. [2] reported that Ge-Te-I system could form relatively stable glasses and exhibited good transmitting property in the range of $2\text{-}22\mu\text{m}$, but it does not resolve the volatilization problem of I_2 in evacuating process. However, it reveals that some halogen contained compound (such as heavy metal halides) may be a new candidate to improve Ge-Te-based chalcogenide glasses and to advance the chalcogenide glass for the application of infrared thermal imaging and bio-sensing. X. Wang et al. and G. Wang et al have make some attempts to add metal

halide into the Te-based chalcogenide glasses and got some interesting results, such as glasses in Ge-Te-AgI [9] and Ge-Te-ZnI₂ [10] systems, but there are still need to develop more new Te-based chalcogenide glass systems and improve the glass stability.

In the present work, with heavy metal halide ZnI₂ acting as glass modifier in the network of Ge-Ga-Te glass, a new pseudo-quaternary glass forming region was determined. With the help of DTA, UV-Vis-NIR absorption and FTIR optical spectra testing to the glass system, optical effects of alkali halide ZnI₂ on the Ge-Ga-Te glasses were discussed systematically and the alkali halide show much help to improve the stability against crystallization of Te-based chalcogenide glass. The present study will help to develop perfect optical materials suitable for optical applications in far-infrared spectral range.

2. Experimental

A systematic series of Ge-Ga-Te-ZnI₂ glasses were prepared by traditional melt-quenching method. Elemental raw materials of high purity Ge (99.999%), Te (99.999%), Ga (99.999%), and ZnI₂ (99.9%) were carefully weighed and transferred into quartz ampoules, which were then sealed under vacuum at a pressure of 2×10^{-3} Pa. The quartz ampoules containing the raw materials were heated at 850°C for 15h in rocking furnaces to ensure the mixture's homogenization. Then, the ampoules were quenched in water at room temperature, swiftly moved to a preheated furnace to anneal at the temperature, below 10°C of T_g for 5 h to minimize inner tension induced by a quenching step. After that, glass rods were obtained by taking them out from the

ampoules and finally cut into disks of about 1.5mm thickness which were then polished for testing [10].

Densities were measured according to the Archimedes principle and the accuracy was 0.001 g/cm^3 . All optical tests were carried out at room temperature. To identify the amorphous nature, X-ray diffraction (XRD) analysis was carried out with a powder diffractometer (BRUKER AXS GMBH) using $\text{CuK}\alpha$ radiation (36kV, 20mA). Differential thermal analysis (DTA) measurement was carried out in the temperature range 100–350°C at a heating speed of 10°C/min by a CRY-2 thermal analyzer for sample weights of approximately 15mg. The visible absorption spectra of glass samples were recorded in the range of 1600–2500nm using a Perkin-Elmer Lambda 950 UV–Vis–NIR spectrophotometer. The IR transmission spectra of samples were obtained in the range of $4000\text{--}400\text{cm}^{-1}$ using Nicolet 380 Fourier Infrared spectrophotometer.

3. Results and discussion

3.1 Glass-forming region

The glass-forming region of Ge-Ga-Te-ZnI₂, a pseudo-quaternary system is obtained by quenching 8g melts in water and shown in Fig.1. The investigated compositions in this system include Series A: $(\text{GeTe}_{4.3})_{60}(\text{GaTe}_3)_{40-x}(\text{ZnI}_2)_x$ ($x=0,5,10,15\text{mol}\%$), Series B: $(\text{GeTe}_{4.3})_{65+x}(\text{GaTe}_3)_{30-x}(\text{ZnI}_2)_{5+x}$ ($x=0,5,10,15\text{mol}\%$), Series C: $(\text{GaTe}_3)_5(\text{GeTe}_{4.3})_{95-x}(\text{ZnI}_2)_x$ ($x=0,5,10,15,20\text{mol}\%$). It presents a detailed distribution of glass-forming region about Ge-Ga-Te-ZnI₂. According to the three series, two main trends were observed, firstly the addition of I in the network appears

to help stabilizing the glass and acting as a non-bridging modifier; secondly, in the first series, an addition of ZnI_2 in concentrations higher than 10% will lead to a rapid crystallization.

3.2 X-ray diffraction investigations

Fig. 2 presents the XRD patterns of sample glasses: $(\text{GaTe}_3)_5-(\text{GeTe}_{4.3})_{95-x}-(\text{ZnI}_2)_x$ ($x=5, 10, 15, 20\text{mol } \%$) and the samples are identified as T_0 , T_1 , T_2 and T_3 . The results of X-ray diffraction investigation show that the glass samples under study keep amorphous states as it is shown in Fig. 2. The addition of ZnI_2 up to 20 mol% does not introduce any sharp peak. As there are no obvious crystalline phases appeared in the measured spectra by X-ray diffraction investigation, the amorphous nature of the synthesized glasses could be confirmed [11].

3.3 Physical properties

Table 1 lists the components and physical properties of the T_0 , T_1 , T_2 , and T_3 samples. The density (ρ) increased with the ZnI_2 content increasing, as the molar volume (V_m) decreased. The density is determined by the mean atom molar mass and packing efficiency in atoms. With the increasing of content ZnI_2 , the values of glass density increased accordingly, because of that ZnI_2 (larger atomic weight of 319) has a large polarization rate. That will also lead to the decrease of average molar volume; and then bring about the packing density and ratios of the glasses structure being promoted, in other words, the glass density increased linearly with the content of ZnI_2 .

The molar volume of a given composition is calculated using the following

formula [12]:

$$V_m = \frac{\sum_i M_i}{\rho} \quad (1)$$

where M_i denotes the molar mass of the glass, $M_i = A_i B_i$, (A_i : the molar concentration, B_i : the molecular weight of the component).

3.4 Thermal properties

Fig. 3 shows the DTA curves for the glass samples, Table 1 lists the results of the DTA measurement. Here, the glass transition temperature (T_g) and onset crystallization temperature (T_x) were measured for the samples. The common stability criterion of $\Delta T = T_x - T_g$ is used to evaluate the thermal stability of these glasses [13]. As shown in Table 1, the T_g values stay nearly constant (150-152 °C), but little difference with ZnI_2 concentration increasing, just as that first increase from 150 to 152 and then decrease to 151 °C. This can probably be ascribed to that the iodine atom can form covalent bonds with tellurium by trapping the metallic electrons and decreasing the tendency to formation of tellurium microcrystals [9, 14]. So the connectivity of glass network is improved and glass forming ability is enhanced consequently. Then, with too much ZnI_2 co-doped, the T_g decreased, as that can be ascribed to the decreasing of glass network connectivity with excessive halogens introduced to break off much glass network structure of short-range order.[15]. In all, the values of T_g first increase and then decrease with the addition of ZnI_2 .

3.5 Analysis of near infrared absorption spectra and optical band gap

The Vis–NIR absorption and transmission spectra of the glass samples were shown in Fig. 4. In short wavelength absorption areas, the optical cut-off edges of electric absorption appear blue shifts obviously with the increasing of the ZnI_2 contents. This can be ascribed to that the addition of I with higher electronegativity in the glass network leads to enlargement of the width of the forbidden band [16]. Besides, the Zn^{2+} cation compensates the negative charge of Te-non-bridging atoms [10]. It is clearly demonstrated that this phenomenon generates a blue-shift of the short-wavelength cut-off edge. So it reduces the delocalization of the electrons in the

glass.

The absorption coefficient is given by the following quadratic equation, which is often called the Tauc law[17]:

$$\alpha(\omega) \cdot h\omega = B(h\omega - E_{\text{opt}})^m \quad (2)$$

Where E_{opt} is the Tauc optical band gap, α is the absorption coefficient determined as $\alpha=2.303A/d$ (A — optical density, d — thickness of the samples), h is plank constant, ω is the incident light angular frequency and m is a parameter depending on the transition type of the absorption edge. The m is equal to 1/2 and 2 for direct allowed and indirect allowed transition. B is a constant that depends on the electronic transition probability, which is expressed as:

$$B = \frac{(4\pi / c)\sigma_0}{n_0\Delta E} \quad (3)$$

Where ΔE is the located-state tail width and σ_0 the minimum metallic conductivity.

Fig. 5 shows the indirect allowed band gap of the four glass samples. The relationship between optical gap and content of heavy metal halide is illustrated in the inserted upper left figures. By extrapolating the linear portion of the curves to zero value of absorption, the value of the indirect optical band gap of the Ge–Ga–Te–ZnI₂ glass system is determined, as show in Table 1. The obtained value of E_{opt} revealed that the indirect optical gap increased with the ZnI₂ content increasing. That may be explained as the increase of the average bond energies of the system. Pauling proposed that single covalent bond energy of heteronuclear bonds $D(A-B)$ are calculated using the following formula [18]:

$$D(A-B) = [D(A-A) * D(B-B)]^{0.5} + 30(\chi_A - \chi_B)^2 \quad (4)$$

Where χ_A and χ_B are the electronegativities of the atoms A and B, $D(A-A)$ and $D(B-B)$ are the bond energies of A—A and B—B bonds, respectively. The values of chemical bond energies are show in Table 1.

In Ge-Ga-Te-ZnI₂ glass system, ZnI₂ enters into the Ge–Ga-Te glass network and forms the Zn-Te and Te-I bonds, which thus lead to the decreasing of the concentration of Te-Te bonds [19]. Since the bond energy of Zn-Te (155.2kJ/mol) and Te-I (148.1kJ/mol) are higher than that of Te-Te bonds (142.3kJ/mol), the average bond energy of the system increases, which results in the increase of the optical band gap.

3.6 IR transmission spectra

As shown in Fig. 6, the most fascinating and original feature of these novel glasses is their ultra wide transparency window. The transmission of the studied glass samples extends to far IR (cut-off edge beyond 25 μ m) and shows stable to ZnI₂ co-doping. The quick drop in transmittance between 20 and 25 μ m sourced from the functions of hybrid multi-phonons, which can be divided into two or more order of the fundamental phonon mode or lateral optical mode coupling [20]. With increasing of the ZnI₂ content transmission of the studied glass samples decreases, which could be explained as follows. The metal halide ZnI₂ with high polarization rate can enter into the glass network, which will lead to increasing the refractive index [21] and emission cross-section. Some absorption bands in IR region are shown in Fig. 6. The strong absorption peak is located at 13 μ m, which can be ascribed to the Ge–O covalent bonds vibration[22]. The heavy metal halide ZnI₂ is easy to deliquescence

and introduces the impurities such as H_2O . As the content of ZnI_2 increases, the Ge–O absorption band is gradually strengthened. An absorption peak is observed near $15\mu\text{m}$, which might be attributed to harmonic intrinsic vibrations of Ga-containing structural units[23]. Thus, in order to reduce the impurity content, the glass purification process should be considered.

4. Conclusions

This study reports on the synthesis of Ge-Te-Ga- ZnI_2 bulk optical glasses. The introduction of heavy metal halide makes the glasses much easier to prepare and more stable against crystallization. X-ray diffraction investigations reveal the amorphous nature of the synthesized glass samples. With the increasing of ZnI_2 content, the density of the glasses increases while the molar volume of the glasses decreases. Meanwhile, the Zn–Te and Te-I bonds are formed, and that will decrease the concentration of Te-Te bonds, and increase the band gap instead. The present Te-based glasses have a wide optical transparency window ranging from 1.9 to $25\mu\text{m}$ and therefore will enable the development of a new generation of infrared systems.

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Tables

Table1

The physicals, thermal properties of the Ge-Ga-Te-ZnI₂ glass samples and values of bond energy of various possible bonds.

Sample	ZnI ₂ /mol%	Density/g·cm ⁻³	V _m /cm ³ ·mol ⁻¹	T _g /°C	T _x /°C	△T/°C	E _{opt} /eV ^a
T ₀	5	5.584	21.480	150	227	77	0.596
T ₁	10	5.600	20.874	151	232	82	0.610
T ₂	15	5.656	20.130	152	235	84	0.618
T ₃	20	5.708	19.420	151	241	90	0.626
Band	Ge-Ge	Ge-Te	Ga-Te	Te-Te	Ge-I	Zn-Te	Te-I
Bond energy(kJ/mol)	205.3	171.3	162.8	142.3	186.9	155.2	148.1

*a: Indirect optical band gap.

Figures

Fig 1. Glass-forming region of Ge–Ga–Te–ZnI₂ system.

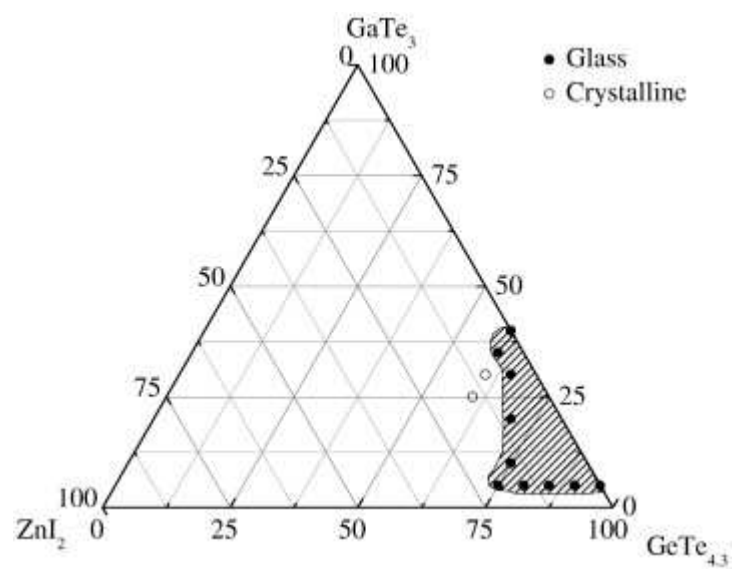


Fig 2. XRD pattern of the powdered glass samples.

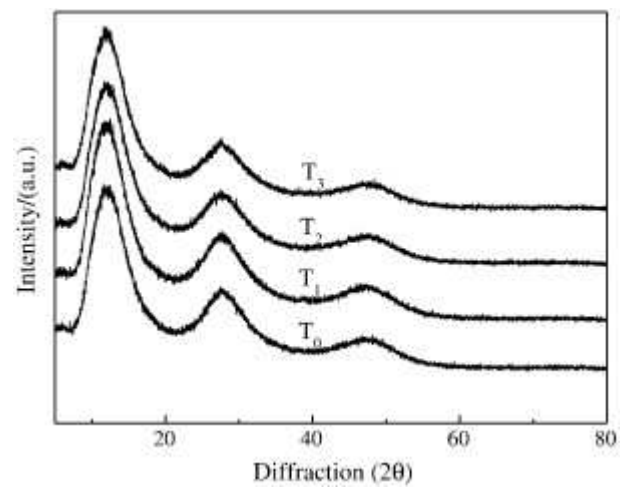


Fig 3. DTA curve of Ge-Ga-Te-ZnI₂ glass samples.

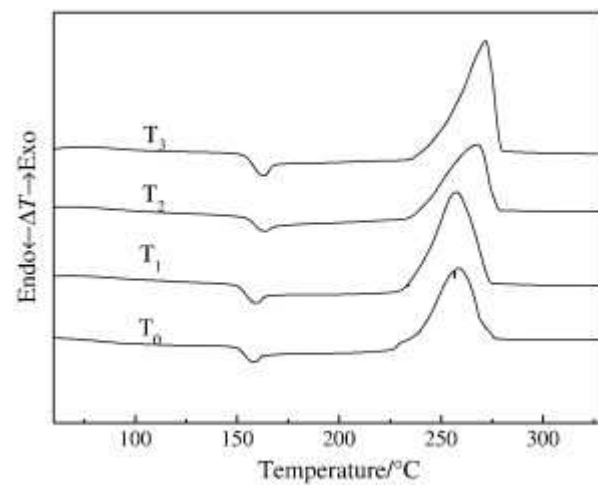


Fig 4. Absorption spectra of glass samples (inset figure is Vis-IR transmission spectra corresponding).

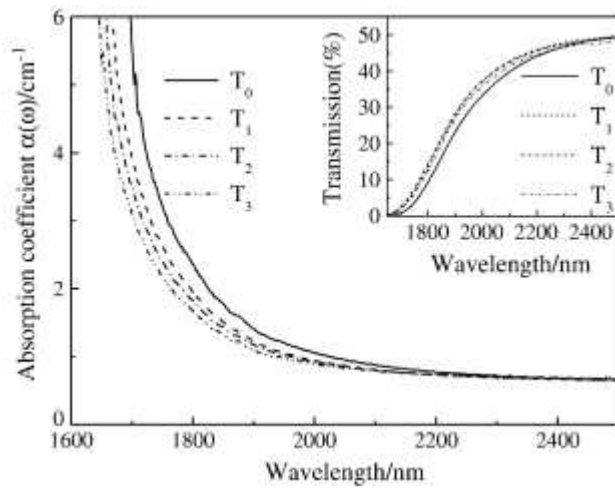


Fig 5. Relationship between $(ah\omega)^{1/2}$ and $h\omega$ for glass samples (inset figure is the relationship between indirect optical gap: E_{opt} and ZnI_2 contents).

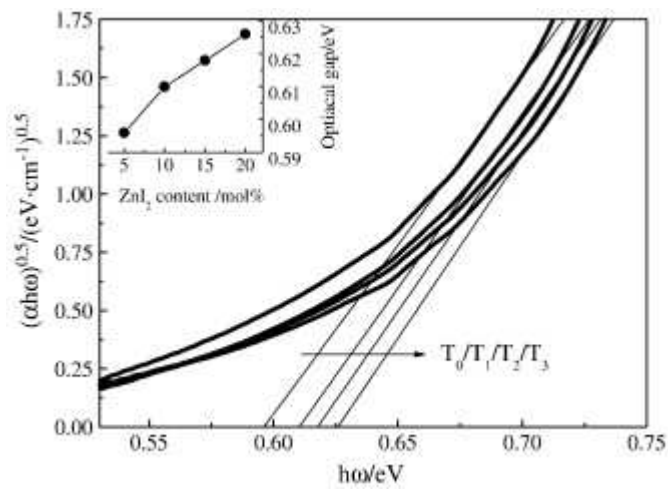


Fig 6. Infrared transmission spectra of Ge-Ga-Te- ZnI_2 glass samples.

