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Glass formation and properties of Ge–Ga–Te–ZnI_2 far infrared chalcohalide glasses

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ABSTRACT

In order to develop novel far infrared window material, a series of Ge–Ga–Te–ZnI_2 chalcohalide glasses were prepared by traditional melt-quenching method and their 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 ZnI_2, the glass-forming ability and thermal stability are improved gradually. With the contents of ZnI_2 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 0.626 eV in these glasses. These $GeTe_{4.3}$–$GaTe_3$–ZnI_2 glasses show wide optical transmission and the infrared cut-off wavelengths are larger than 25 μm, which implies that the Ge–Ga–Te–ZnI_2 chalcogenide glasses possess the potential of far-IR optical window applications.

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 explants 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 15 μm regions and development of IR optics operating in the 4–20 μm 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 from 2 to 20 μm, depending on the fiber glass composition [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 12 μm (bulk glass) while for a Se based materials the edge is shifted towards 16 μm [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 glass preparation: first, tellurium has strong metallic character in comparison with S, and 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 μm) far less than the theoretical level (20 μm) 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, Tichý et al. [8] reported that the transparent range of Se–Te–I glasses could be extended from 2 to 21 μm and these glasses could be attractive for further studies in connection with their possible applications in CO_2 lasers. Lucas and Danto [5] have reported the glass forming region in the Te–Ga–Ge ternary diagram, within which the most promising glass composition is $Te_{75}Ga_{10}Ge_{15}$. The IR transmitting range of $Te_{75}Ga_{10}Ge_{15}$ glass sample was from 2 to 25 μm, while there is an obvious absorption around 15–20 μm 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 exhibit good transmitting property in the range of 2–22 μm, 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 made 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–ZnI_2 [10] systems, but

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there is still a need to develop more new Te-based chalcohalide glass systems and improve the glass stability.

In the present work, with the help of heavy metal halide ZnI_2 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 ZnI_2 on the Ge–Ga–Te glasses were discussed systematically and the alkali halide shows much help to improve the stability against the 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–ZnI_2 glasses were prepared by traditional melt-quenching method. Elemental raw materials of high purity Ge (99.999%), Te (99.999%), Ga (99.999%), and ZnI_2 (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 15 h 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 1.5 mm thickness which were then polished for testing [10].

Densities were measured according to the Archimedes principle and the measurement 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 CuKα radiation (λ = 1.54056 Å) at 30 kV and 10 mA. 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 15 mg and an error of ±0.5 °C was observed in measuring the characteristic temperature. The visible absorption spectra of glass samples were recorded in the range of 1600–2500 nm using a Perkin-Elmer Lambda 950 UV–Vis–NIR spectrophotometer with a resolution of 1 nm. The IR transmission spectra of samples were obtained in the range of 4000–400 cm^{-1} using Nicolet 380 Fourier Infrared spectrophotometer. The resolution of the IR spectra was 1 cm^{-1}. The others of error without mention are about 0.1%.

3. Results and discussion

3.1. Glass-forming region

The glass-forming region of Ge–Ga–Te–ZnI_2, a pseudo-quaternary system is obtained by quenching 8 g melts in water and shown in Fig. 1. The investigated compositions in this system include Series A: $(GeTe_{4.3})_{60}(GaTe_3)_{40-x}(ZnI_2)_x$ (x = 0, 5, 10, 15 mol%), Series B: $(GeTe_{4.3})_{65+x}(GaTe_3)_{30-x}(ZnI_2)_{5+x}$ (x = 0, 5, 10, 15 mol%), and Series C: $(GaTe_3)_5(GeTe_{4.3})_{95-x}(ZnI_2)_x$ (x = 0, 5, 10, 15, 20 mol%). It presents a detailed distribution of glass-forming region about Ge–Ga–Te–ZnI_2. 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: $(GaTe_3)_5(GeTe_{4.3})_{95-x}(ZnI_2)_x$ (x = 5, 10, 15, 20 mol%) and the samples are

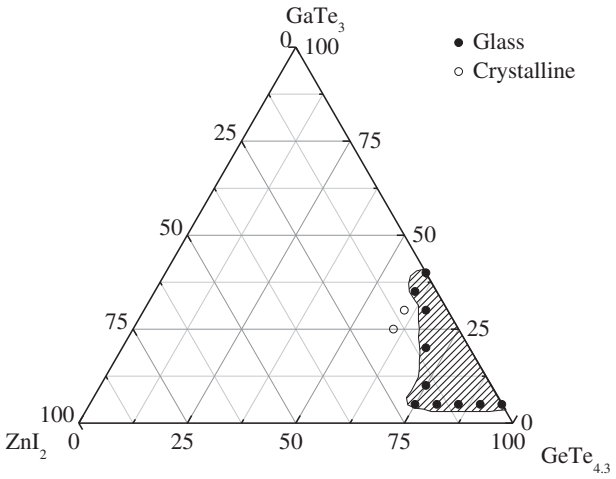

Fig. 1. Glass-forming region of Ge–Ga–Te–ZnI_2 system.

denoted 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 content of ZnI_2, the values of glass density increased accordingly, because 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).

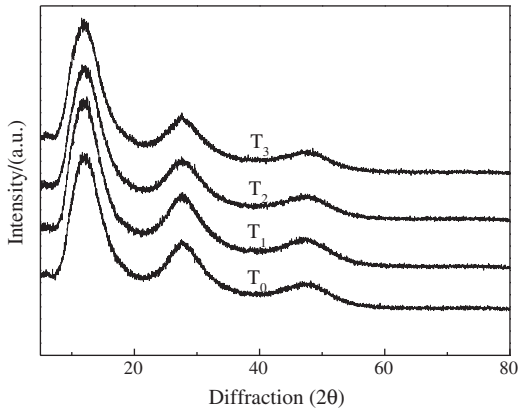

Fig. 2. XRD pattern of the powdered glass samples.