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Novel Ge–Ga–Te–CsBr glass system with ultrahigh resolvability of halide



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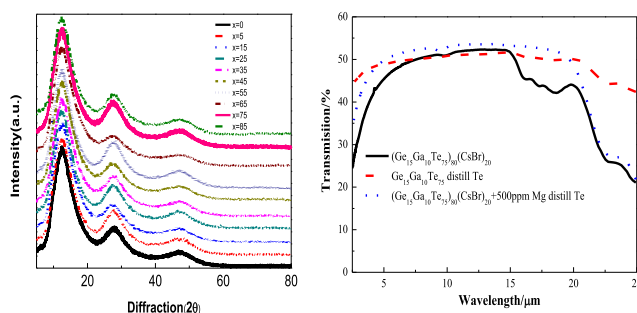
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HIGHLIGHTS

- Ge–Ga–Te host glass can dissolve the content of CsBr as much as 85 at.%.
- The ΔT values of $(\text{Ge}_{15}\text{Ga}_{10}\text{Te}_{75})_{65}(\text{CsBr})_{35}$ glass sample can reach to 119 °C.
- The infrared cut-off wavelength could reach up to 25 μm .
- The absorption peaks in the infrared transmission spectra disappeared through a purifying method.

GRAPHICAL ABSTRACT



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ABSTRACT

CO_2 molecule, one of the main molecules to create new life, should be probed accurately to detect the existence of life in exoplanets. The primary signature of CO_2 molecule is approximately 15 μm , and traditional S- and Se-based glass fibers are unsuitable. Thus, Te-based glass is the only ideal candidate glass for far-infrared detection. In this study, a new kind of Te-based chalcogenide glass system was discovered with relatively stable and large optical band gap. A traditional melt-quenching method was adopted to prepare a series of $(\text{Ge}_{15}\text{Ga}_{10}\text{Te}_{75})_{100-x}(\text{CsBr})_x$ chalcogenide glass samples. Experiment results indicate that the glass-forming ability and thermal properties of glass samples were improved when CsBr was added in the host of Ge–Ga–Te glass. Ge–Ga–Te glass could remarkably dissolve CsBr content as much as 85 at.%, which is the highest halide content in all reports for Te-based chalcogenide glasses. Moreover, ΔT values of these glass samples were all above 100 °C. The glass sample $(\text{Ge}_{15}\text{Ga}_{10}\text{Te}_{75})_{65}(\text{CsBr})_{35}$ with ΔT of 119 °C was the largest, which was 7 °C larger than that of $\text{Ge}_{15}\text{Ga}_{10}\text{Te}_{75}$ host glass. The infrared transmission spectra of these glasses show that the far-infrared cut-off wavelengths of $(\text{Ge}_{15}\text{Ga}_{10}\text{Te}_{75})_{100-x}(\text{CsBr})_x$ chalcogenide glasses were all beyond 25 μm . In conclusion, $(\text{Ge}_{15}\text{Ga}_{10}\text{Te}_{75})_{100-x}(\text{CsBr})_x$ chalcogenide glasses are potential materials for far-infrared optical application.

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Introduction

In recent years, chalcogenide glasses have attracted increasing attention in infrared technology fields, particularly in high

nonlinearity, infrared fingerprints, and life detection [1–3]. Among these projects, the Darwin Mission and the Terrestrial Planet Finder conducted by the European Space Agency and the National Aeronautics and Space Administration, respectively, are the most impressive [3,4]. These projects aim to demonstrate whether life exists in exoplanet. H_2O , CO_2 , and O_3 are the three main molecules to create new life. Detecting these molecules

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needs IR optical devices with excellent infrared transparency. The infrared cut-off wavelengths of S- and Se-based glass fibers are only up to 8 and 10 μm , respectively. However, the main signature of CO_2 molecule is approximately 15 μm [5]. Hence, current infrared transparencies of these glasses are not sufficiently wide to match with CO_2 molecular signature at 15 μm . Thus, a glass with wider infrared transparency is necessary. According to phonon vibration spectrum analysis [6], heavy atoms are needed for long cut-off wavelength. Te-based glasses have wider infrared transparency and longer cut-off wavelength than S- and Se-based glasses because the atom mass of Te-based glasses is larger than those of the other two glasses. In addition, the cut-off wavelength of Te-based glass in the long wavelength area is above 20 μm . Given the wide optical windows and low loss in 6–20 μm range, Te-based chalcogenide glasses are suitable material for far-infrared application, particularly in some gas detections, such as the greenhouse gas CO_2 with absorption peaks at 4.3 and 15 μm [7,8] and poisonous gas benzene with absorption peak at 14.8 μm [9]. However, these glasses possess many disadvantages. First, Te cannot form stable glass alone because of its strong metallic property. Second, traditional Te–X (F, Cl, Br, I) glasses have low transition temperature; most of these glasses cannot reach more than 100 $^\circ\text{C}$. Its low optical band gap also limits its transmission in near IR (<2 μm), which is currently well developed. Moreover, the interstructure of traditional Te-based glasses possesses numerous inherent glass network defects, and these defects can result in high intrinsic loss. To solve these limitations, many scientists have exerted effort to develop suitable Te-based chalcogenide glasses. Aldon et al. [10] reported that Ge–As–Te glasses have stable structure and good formability. However, the element of As is poisonous to the environment. Wilhelm et al. [3] demonstrated that Ge–Te–I glasses possess a wide infrared transparency window and its cut-off wavelength is more than 25 μm . However, this glass is prone to volatilization because I element is contained. Danto et al. [5] proposed that the GeTe_4 binary glass system doping Ga can open the GeTe_4 tetrahedral network structure and split the Te–Te chains; $\text{Ge}_{15}\text{Ga}_{10}\text{Te}_{75}$ is also superior among these glasses. However, the values of ΔT of $\text{Ge}_{15}\text{Ga}_{10}\text{Te}_{75}$ glass is only 113 $^\circ\text{C}$, and it is still too small to guarantee any devitrification problem when shaping the glasses either by moulding or by drawing optical fibers. Wang et al. discovered that doping halide to Te-based glass can improve the thermal stability and decrease the optical loss of glass [11,12]. However, the highest content of halide in the Te-based glasses is limited to 30 at.%.

In this study, an extensive investigation was developed to study the effect of alkali-halide on Ge–Ga–Te host glass. High content of CsBr was added to the Ge–Ga–Te glass system to enlarge the formation of Te-based glass. The optical and thermal properties of this glass were then analyzed by Fourier transform infrared spectroscopy (FTIR) and spectrophotometry. To date, no reports exist about the influence of CsBr on the structure and chemical or physical properties of Ge–Ga–Te–CsBr glasses.

Materials and methods

$(\text{Ge}_{15}\text{Ga}_{10}\text{Te}_{75})_{100-x}(\text{CsBr})_x$ glass samples were prepared by conventional melt-quenching methods. The specific glass compositions are listed in Table 1. High purities of 99.999% Ge, 99.999% Ga, 99.999% Te, and 99.999% CsBr were selected as raw materials. The weighed raw materials were mixed into a quartz tube, which was prewashed with deionized water. The tubes were then sealed with oxy-acetylene flame under a pressure of 1×10^{-3} Pa and heated in rocking furnaces with specific heating curve. Afterward, the quartz tubes were quenched in ice water and then annealed at 10 $^\circ\text{C}$ below T_g in a prepared furnace. The glass rods were removed

Table 1
Physical and thermal parameters of $(\text{Ge}_{15}\text{Ga}_{10}\text{Te}_{75})_{100-x}(\text{CsBr})_x$ glass samples.

x (at.%)	Thickness (cm)	ρ (g cm^{-3})	V_m ($\text{cm}^3 \text{mol}^{-1}$)	T_g ($^\circ\text{C}$)	T_x ($^\circ\text{C}$)	ΔT ($^\circ\text{C}$)
0	0.180	5.735	19.869	172	284	112
5	0.185	5.667	20.982	171	285	114
15	0.191	5.658	22.766	168	284	116
25	0.200	5.555	24.971	173	286	113
35	0.177	5.549	26.783	172	291	119
45	0.199	5.459	29.039	169	283	114
55	0.200	5.437	30.978	175	281	106
65	0.229	5.412	32.951	175	280	105
75	0.229	5.399	34.865	177	278	101
85	0.205	5.331	37.168	179	279	100

and cut into discs. A polishing procedure on the discs is indispensable to test the properties of these glasses precisely.

The Archimedes' principle was used to measure the density of glass samples (with an accuracy of $\pm 0.001 \text{ g/cm}^3$). XRD diffraction patterns of glass samples were tested through German Bruker D2 X-ray diffraction apparatus. Vis-near-infrared spectra of glass samples were acquired using a Perkin-Elmer Lambda 950 spectrophotometer in the range of 400–2500 nm. The infrared transmission spectra were obtained with Nicolet 380 FTIR in a spectral range of 400–4000 cm^{-1} . Glass transition temperature (T_g) and onset crystallization temperature (T_x) were determined with differential scanning calorimetry (DSC) measurements at 50 and 350 $^\circ\text{C}$ with a heating rate of 10 $^\circ\text{C}/\text{min}$ via a TAQ2000 thermal analyzer. Raman spectra of glass samples were gathered in the range of 80–800 cm^{-1} by using a Renishaw Raman microscope with an Ar⁺ ion laser that operates at a wavelength of 488 nm. The spectral resolution was set to 1 cm^{-1} . All of these optical tests were performed at room temperature.

Results and discussion

Physical properties

A series of $(\text{Ge}_{15}\text{Ga}_{10}\text{Te}_{75})_{100-x}(\text{CsBr})_x$ ($x = 0, 5, 10, 15, 20, 25, 35, 45, 55, 65, 75, 85$) glasses were prepared. These glasses are completely opaque and black in the visible region, and the physical parameters of these glasses are listed in Table 1. The densities of these glasses gradually decreased with increasing CsBr content because the glass density is generally determined by the elemental relative atomic mass. The relative molecular mass of CsBr was smaller than those of GeTe_4 and GaTe_3 . The recruitment and increase of CsBr resulted in reduced GeTe_4 and GaTe_3 contents. Consequently, the densities of these glasses gradually decreased, and the average molar volume increased. The average molar volume of the glass sample can be achieved using Formula (1):

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

where M_i is the molar mass of glass sample ($M_i = A_i B_i$, A_i , molar concentration; B_i , molecular weight of glass composition; ρ , density of glass samples).

XRD analysis

XRD was conducted to verify the amorphous state of the samples. The XRD patterns of $(\text{Ge}_{15}\text{Ga}_{10}\text{Te}_{75})_{100-x}(\text{CsBr})_x$ glass samples are presented in Fig. 1. The peak shapes in these diffraction curves exhibited dispersion and width. The XRD results indicated that these glass samples possessed an amorphous state. $\text{Ge}_{15}\text{Ga}_{10}\text{Te}_{75}$ glass could remarkably dissolve as much as 85 at.% content of alkali-halide CsBr. Thus, its glass-forming ability is strong.

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