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Novel NaI improved Ge-Ga-Te far-infrared chalcogenide glasses

Ci Cheng[1], Xunsi Wang[1*], Tiefeng Xu[1], Qingde Zhu[1], Lihong Sun[1], Zhanghao Pan[1], Qiuhua Nie[1], Peiqing Zhang[1], Yuehao Wu[1], Shixun Dai[1], Xiang Shen[1], Xianghua Zhang[2]

([1]*Laboratory of Infrared Material and Devices, The Research Institute of Advanced Technologies, Ningbo University, Ningbo, Zhejiang 315211, China*)

([2]*Laboratory of Glasses and Ceramics, UMR 6226 CNRS-University of Rennes 1, Rennes Cedex 135042, France*)

Abstract: In this study, a novel Te-based glass system was investigated. Some properties of Ge-Ga-Te-NaI chalcogenide glasses such as physical, thermal and optical transmitting were discussed. XRD patterns show this glass system with best amorphous state can dissolve NaI content as much as 35 at.%. And a lowest cut-off wavelength of glass samples is 1645nm which is the smallest wavelength among the reported Te-based glasses doping with alkali-halide. DSC curves indicate that all the glass samples have good thermal stabilities ($\Delta T>100$℃) and the highest ΔT value corresponding to $(Ge_{15}Ga_{10}Te_{75})_{85}(NaI)_{15}$ glass is 120℃ which is 8℃ greater than that of Ge-Ga-Te host glass. The infrared spectra manifest Ge-Ga-Te-NaI chalcogenide glasses have a wide infrared transmitting window between 1.6 μm and 25 μm. Consequently, Ge-Ga-Te-NaI glasses can be a candidate material for far infrared optic imaging and bio-sensing applications.

Keywords: chalcohalide glass; thermal property; infrared spectra

1. Introduction

To explore the existence of life in exoplanet, many projects have been carried out. Particularly, the Darwin project conducted by European Space Agency is the most popular among these projects[8]. This project aims at detecting CO_2 molecule which is produced by living organisms. At the same time, the detection of CO_2 gas content in the earth's atmosphere is also of interest in environmental science such as global warming. All this applications are located at the optical spectra of middle and far infared.

Chalcogenide glasses have attracted great attention in the infrared material and device filed due to its excellent infrared transmission characteristics over the past decades. Apart from oxygen element, chalcogenide glasses which contain sulfur, selenium or tellurium elements have many excellent features such as lower phonon energy, outstanding transmission properties, high linear and nonlinear refractive index and high photosensitivity etc. [1, 2] Compared to traditional silica based glasses, chalcogenide glasses have a larger transparency window which can cover from visible region to the far infrared depending on the glass composition [3-6]. Nevertheless, the transmission of sulfur- or selenium-based glasses is limited to 12 μm or 14 μm respectively. Thus, developing the glass fibers which transmission are up to 20 μm are necessary. However, S- and Se-based glass fibers are cannot meet the requirement because the very specific CO_2 broad absorption band is located around 15μm.Since the atomic mass of Te atom is larger than S and Se atoms, according to the principle of phonon vibration spectrum[7], the far infrared cut-off wavelength of Te-based glass is larger than S- and Se-based glasses. Hence, Te-based glasses can better meet the requirement of far infrared applications. So the only way is to prepare Te-based

* Corresponding author. Fax: +86 574 87600947.

E-mail address: xunsiwang@siom.ac.cn (X.Wang).

glasses and then drawn into fibers. Due to its strong metallic and low dimensionality of glass framework, traditional Te-based glasses such as Te-X (Cl, Br, I) have weak mechanical and low thermal characters. Thus, these glasses are not the candidate material for fibers. Then, the Ge-As-Te, the Ge-Te-I and the Ge-Ga-Te glass systems have investigated recently [9-11]. Although these glasses have better mechanical and thermal properties than Te-X glasses, they have many detects. The Ge-As-Te glasses contain the element of "As" that will pollute the environment seriously. The Ge-Te-I glasses are prone to volatilize because of I element contained. The maximum ΔT value (the difference between the glass transition temperature Tg and the glass onset crystallization temperature Tx) of Ge-Ga-Te glass is only 113℃, the ΔT value is still too small to ensure the glasses would not crystalize when they are drawn into optical fibers or shaped into lenses. Wang et al. proposed that halide doped into Te-based glasses can open up the glass network and then enlarge the glass formation, improve the chemical stability as well as the ability of anti-crystal[12]. Therefore, halide, which are not easily volatile, are added into Ge-Ga-Te glass may be able to improve the thermal properties of chalcogenide glasses[13]. So far, there is still no report about the investigation of NaI doped into Ge-Ga-Te glasses.

In this study, we discussed a new family of Te-based chalcogenide glass. By adding different molecular weight of NaI content, some glass properties such as thermal and infrared transmission etc. were investigated. There is no other comprehensive report about the influence of NaI on the structure and chemical or physical properties about Ge-Ga-Te-NaI glasses. The optical and thermal properties were discussed by the help of Fourier Transform infrared spectroscopy (FTIR) and DSC instruments.

2. Experiments and Testing Methods

The raw materials Ge, Ga, Te with 5N purity and NaI (4N) were chosen to prepare for a series of Ge-Ga-Te based glass samples. The preparation method was adopted with conventional vaccum melt-quenching process. The raw materials were weighed accurately and then mixed into a silica tube which was sealed under the pressure of 1×10^{-3}Pa. The tubes were then placed in rocking furnaces and heated at 850h for 15 hours to homogenize the mixtures. After that, the temperature of furnaces decreased to 730 before ampoules quenched in ice water. Afterwards, the ampoules were annealed at 10℃ below Tg in the prepared furnaces. The glass rods were taken out from the silica tubes and then were cutted into discs. The thickness of these glass disk samples were recorded in the Table 2. Finally, the glass discs were polished for testing.

The densities of glass samples were calculated by the Archimedes' principle (with an accuracy of ±0.001 g/cm^3). In order to confirm the amorphous state, the X-ray powder diffraction apparatus by German Bruker D2 using CuKα radiation were performed. Glass transition temperature (Tg) and onset crystallization temperature (Tx) of glass samples were measured by Differential Scanning Calorimetry (DSC). The heating temperature is range from 50 to 350℃ with a heating rate of 10℃/min by a TAQ2000 thermal analyzer. The infrared transparency windows were obtained by using Nicolet 380 Fourier transforming infrared spectroscopy in the range of 4000-400 cm^{-1}. The visible to near infrared transmission spectra was acquired by means of Perkin-Elmer Lambda 950 spectrophotometer which the wavelength range is from 400 to 2500 nm. The Raman spectra were gathered using a Renishaw Raman microscope with an Ar+ ion laser in the range of 80–800 cm^{-1}. The spectral resolution was set to 1 cm^{-1}. All optical testing procedures were performed at room temperature.

3. Results and Discussions

3.1 Physical and thermal properties

A series of $(Ge_{15}Ga_{10}Te_{75})_{100-x}(NaI)_x$ glass samples were prepared successfully with x=0, 5, 10, 15, 20, 25, 30, 35. The densities of all glass samples are listed in Table 1. With content of NaI increasing, the densities of glass samples decreased from 5.735 $g \cdot cm^{-3}$ to 5.387 $g \cdot cm^{-3}$ gradually. As that the glass density is determined by the elemental relative atomic mass and the packing efficiency of atoms[14]. The relative atomic mass of NaI is 150, smaller than that of $GeTe_4$ (585) and $GaTe_3$ (454). With NaI doped into Ge-Ga-Te glass, $GeTe_4$ and $GaTe_3$ units reduced, and the packing efficiency of atoms was lower. Thus, the densities of $(Ge_{15}Ga_{10}Te_{75})_{100-x}(NaI)_x$ glass samples decreased along with NaI content increasing. On the contrary, the average molar volume increased. This can be calculated by the following formula (1).

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

where M_i is the molar mass of glass samples ($M_i = A_i B_i$, A_i : the molar concentration; B_i : the molecular weight of glass composition; ρ: the density of glass sample). The specific values are presented in Table 1.

Table 1 Physical and thermal parameters of $(Ge_{15}Ga_{10}Te_{75})_{100-x}(NaI)_x$ glass samples

X at.%	ρ $g \cdot cm^{-3}$	V_m $m^3 \cdot mol^{-1}$	Tg ℃	Tx ℃	ΔT ℃
0	5.735	19.869	172	284	112
5	5.512	21.000	177	285	108
10	5.492	21.405	171	288	117
15	5.467	21.832	168	288	120
20	5.446	22.248	171	284	113
25	5.420	22.687	173	283	110
30	5.402	23.096	176	281	105
35	5.387	23.495	176	278	102

3.2 Analysis of amorphous state

To verify the amorphous state of glass samples, XRD were performed on $(Ge_{15}Ga_{10}Te_{75})_{100-x}(NaI)_x$ glass samples. The XRD diffraction patterns are presented in Fig. 1. Here, all curves were smooth while peaks exhibited width and dispersion. All glass samples showed excellent amorphous properties. Ge-Ga-Te host glass can dissolve 35 at.% NaI contents eventually.

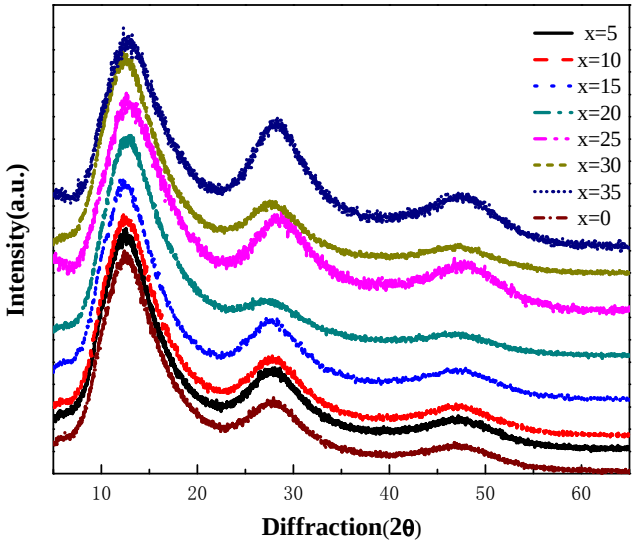


Fig. 1 XRD patterns of Ge-Ga-Te-NaI glass samples

3.3 Thermal properties

Thermal properties of these glass samples were tested by DSC instrument. DSC curves of all glass samples are showed in Fig. 2. The glass transition temperature Tg and the glass onset crystallization temperature Tx can be obtained from the curves. The difference between Tg and Tx is defined as ΔT which is always used to evaluated the thermal performance of glass samples. And the specific values of Tg, Tx and ΔT are recorded in Table 1. Here, $(Ge_{15}Ga_{10}Te_{75})_{85}(NaI)_{15}$ glass sample whose ΔT value is 120℃ possesses superior thermal properties than other glass samples. Compared to that of $Ge_{15}Ga_{10}Te_{75}$ glass, the ΔT value of $(Ge_{15}Ga_{10}Te_{75})_{85}(NaI)_{15}$ glass was increased by 8℃. This may be resulted from the effect of I atoms which trapped the metallic electrons from Te atoms and formed strong Te-I bonds. With Te-Te bonds reducing, the tendency of Te microcrystal formation decreased. Thus, the stability of the chalcogenide glasses against crystallization was improved. When the content of NaI is from 5 to 15 at.%, the ΔT of glass samples increased gradually. But, ΔT values decreased when NaI content surpassed 15 at.%, as that it is too much for resovalation in the $Ge_{15}Ga_{10}Te_{75}$ glass matrix. The variation tendency of Tg and Tx are shown in Fig. 3. As a consequence, it proves that a proper content of NaI doping into chalcogenide glasses can improve the thermal properties of matrix glass. What's more, the ΔT values of all glass samples are above 100℃. It indicates that $(Ge_{15}Ga_{10}Te_{75})_{100-x}(NaI)_x$ glasses keep good thermal characteristics which are potential for being drawn into fibers.

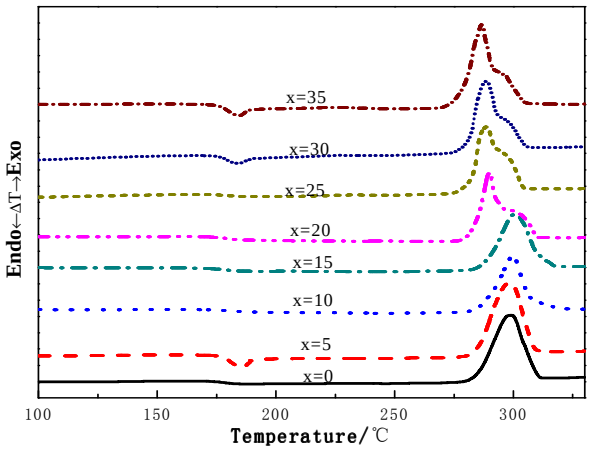


Fig. 2 The DSC curves of Ge-Ga-Te-NaI glass samples

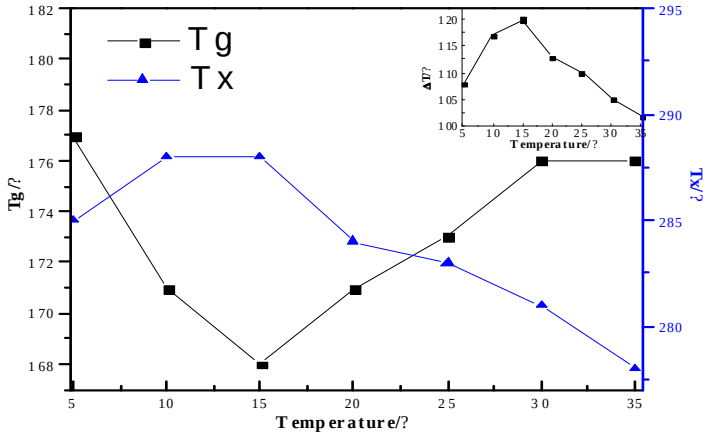


Fig. 3 Tg and Tx of Ge-Ga-Te-NaI glass samples

3.3 Raman spectra analysis

Structure comfirmation for the glass is one important aspect for glass researching. The spectrum signature of glass' matrix and net structure can be recoreded with Raman spectrometer. Raman spectra of Ge-Ga-Te-NaI glass samples are seen in Fig. 4. Here, some peaks appear in the curves. There are three strong vibration peaks located around 65cm^{-1},130cm^{-1},156cm^{-1} respectively. A very broad and low intensity vibration band locates near 220cm^{-1}. These vibration peaks or band are usually resulted from some bonds or atomic energy[15]. The first two vibration peaks are attributed to Ge-Te bonds while the peak at 155cm^{-1} is ascribed to the vibration of Te-Te bonds[15-17]. The last vibration band may be due to Ge-Ge bonds[18]. From Fig. 4, the intensity of vibration peaks at 65cm^{-1},130cm^{-1},220cm^{-1} were not affected with the increasing content of NaI. However, some subtle variations appeared at 155cm^{-1} with the adding NaI. When the value of x was between 5 and 15, the vibration intensity at 155 cm^{-1} decreased little by little. What's more, when the content of NaI is above 15 at.%, the vibration intensity enhanced gradually along with the content of NaI increasing. Some reasons can account for this phenomenon. The inherent

structure of glass network which is mainly consist of $GaTe_3$ triangle and $GeTe_4$ tetrahedra was modified when NaI was introduced into the Ge-Ga-Te host glass. As is well known to all, iodine atom is considered to be a network terminator because it can trap the metallic electrons from tellurium atoms. As a result, Te-Te chains were split by iodine atoms and then new Te-I covalent bonds formed. Therefore, the vibration intensity of Te-Te bonds decreased when some contents of NaI were co-doped into Ge-Ga-Te glass. However, when too much NaI contents co-doped, many dissociative Te atoms may appear in the network. Due to its strong metallic, these dissociative Te atoms combined together as a form of Te-chain. Hence, the Te-Te bonds increased and the peak intensity at 159cm^{-1} was strengthened.

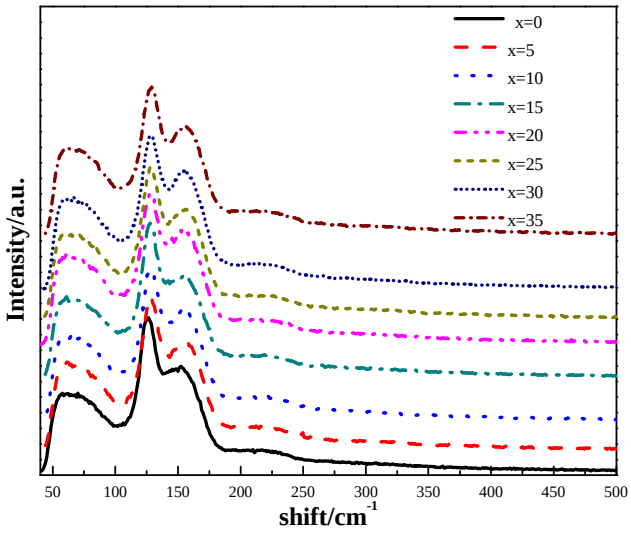


Fig. 4 The Raman graph of Ge-Ga-Te-NaI glass samples

3.4 Near infrared absorption spectra and optical band gap analysis

Fig. 5 shows the near infrared absorption spectra of Ge-GaTe-NaI glass samples. From the insert figure, the relationships between cut-off edge wavelength and NaI content are clear at a glance. When the content of NaI increased from 5 at.% to 15 at.%, the cut-off wavelength of these glasses shifts to the long-wavelength region. However, cut-off wavelength may shift to short-wavelength region as soon as x exceeds 15. This may due to the electronegativity I^- doping into Ge-Ga-Te glass and new Te-I bonds formed. With the co-doping of NaI content, which was named as x (varing from5 at.% to 15 at.%), doping into glass, Te-Te chains were spilt from the glass network structure. Since the bond energy of Te-I (198kJ/mol) is lower than that of Te-Te bonds (235kJ/mol), the average bond energy of glass system decreased. Thus, cut-off wavelength had a red shift[19]. However, when x>15 at.%, from Raman spectra, the intensity of Te-Te bonds strengthened. It indicated that Te-Te bonds increased. So the average bond energy of glass system increased. As a result, cut-off wavelength had a blue shift. Eventually, the cut-off wavelengths of glass samples are located between 1645nm and 1772nm. The lowest cut-off wavelength of glass samples is 1645nm which is the smallest cut-off wavelength among the reported Te-based glasses doping alkali-halide[20, 21]. The specific values of cut-off wavelength are listed in Table 2.

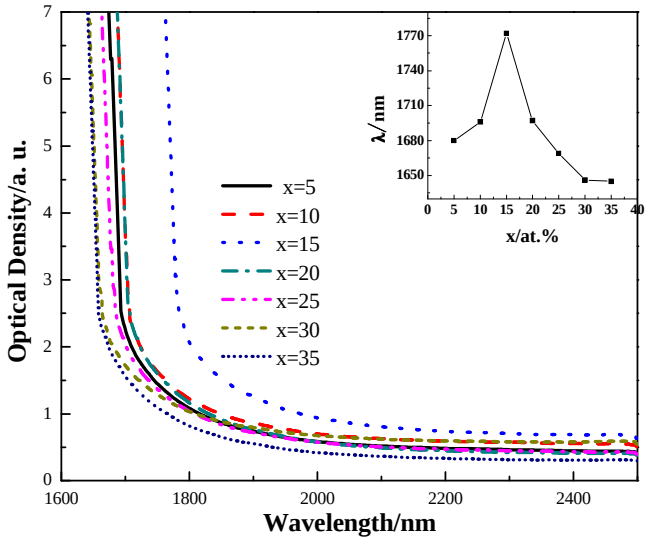


Fig. 5 Vis-IR absorption spectra of Ge-Ga-Te-NaI glass samples.Cut-off wavelengths with NaI increasing are shown in the insert figure)

The relationship between the absorption coefficient and the optical band-gap is given by the following equation:

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

where $\alpha(\omega)$ is the absorption coefficient, and it can be calculated by the function α=2.303A/d (A is the optical density of glass sample; d is the thickness of testing glass sample); ħ is Plank constant, ω is the incident light angular frequency, m is a parameter which determines the transition type of absorption edge. For amorphous materials, the direct allowed transition and indirect allowed transition are corresponding to m=1/2 and m=2 separately. B is a constant about local state in the band gap. It can be calculated by the following equation:

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

here, c is the light speed in vacuum, σ_0 is the electrical conductivity of absolute zero, n_0 is the static refractive index, ΔE is the local state tail width. Fig. 6 is corresponding to direct band gap, and the concrete values are listed in Table 2. The insert figure demonstrate that the optical gap decreased firstly with x values from 5 to 15. However, the optical gap increased when x values exceeded 15. All this results fit well with the appearance of cut-off wavelength shift from red to blue on turn..

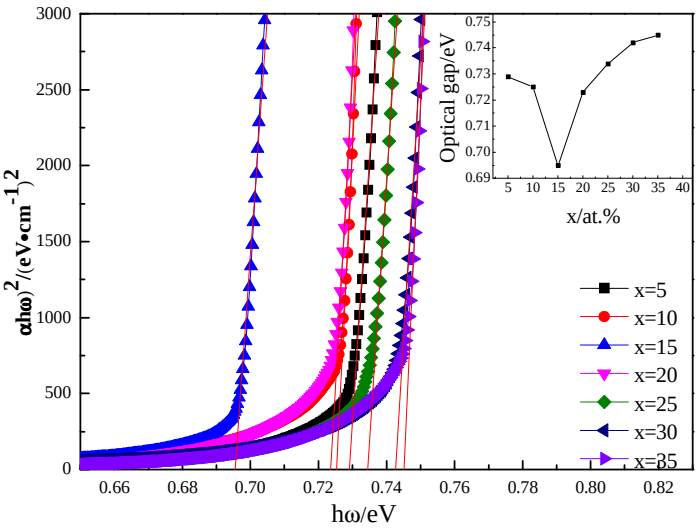


Fig. 6 The relationship between $(\alpha \bullet \hbar\omega)^2$ and $\hbar\omega$ for glass samples (relationships between direct band gap and NaI content are shown in the insert figure)

Table 2 Cut-off wavelength and direct band gap of Ge-Ga-Te-NaI glass samples

x/at.%	Thickness/mm	Cut-off λ(nm)	Direct-E_{opt}/(eV)
5	1.71	1680	0.729
10	1.51	1696	0.725
15	2.17	1772	0.695
20	1.46	1697	0.723
25	1.73	1669	0.734
30	1.55	1646	0.742
35	1.41	1645	0.745

3.5 Infrared spectra analysis

The infrared transmission spectra of Ge-Ga-Te-NaI glass samples are shown in Fig. 7. All glass samples had a wide optical transmitting window from 2.5 μm to 25μm. $(Ge_{15}Ga_{10}Te_{75})_{70}(NaI)_{30}$ glass sample has the highest transmission ratio which can reach up to 52%. The transmission of all glass samples plunged when wavelength was above 20 μm. This is attributed to the multi-phonon absorption which is produced by the Ge-Te bonds[11]. Some typical absorptions peaks existed in all curves. Two slight absorption peaks were respectively located at 6.3 μm and 9.8 μm. The first and second absorption peaks are separately attributed to H_2O molecule [22]and Si-O bonds[12] . Moreover, a wide absorption band was located between 15 μm and 20 μm. The absorption band at 15-20 μm may be ascribed to some oxygen contamination such as Ga-O or Ge-O bonds[23, 24]. To eliminate the absorption peaks which are caused by impurities especially oxygen impurities, some purification process need to be taken into account. Due to its excellent thermal property, $(Ge_{15}Ga_{10}Te_{75})_{85}(NaI)_{15}$ glass sample was chosen for the purification experiment. In the beginning, 300 ppm Mg co-doped into Te raw materials and then they were distilled into a Ge, Ga, NaI contained ampoule. Next, the steps were the same with traditional melt-quenching method. The spectra of $(Ge_{15}Ga_{10}Te_{75})_{85}(NaI)_{15}$ glass sample are presented in Fig. 8. In contrast to the unpurified glass sample, the purified $(Ge_{15}Ga_{10}Te_{75})_{85}(NaI)_{15}$ glass had a

ulti-wide and ulti-flat optical transmitting window. Consequently, this purification method is considered to be a fine approach to reduce the content of impurities and eliminate the harmful effects resulted from the impurities.

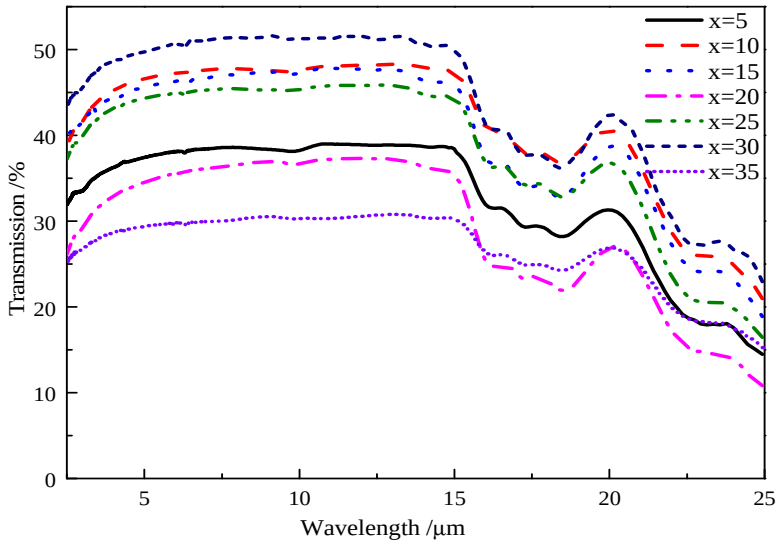


Fig. 7 Infrared transmission spectra of glass samples $((Ge_{15}Ga_{10}Te_{75})_{100-x}(CsBr)_x)$

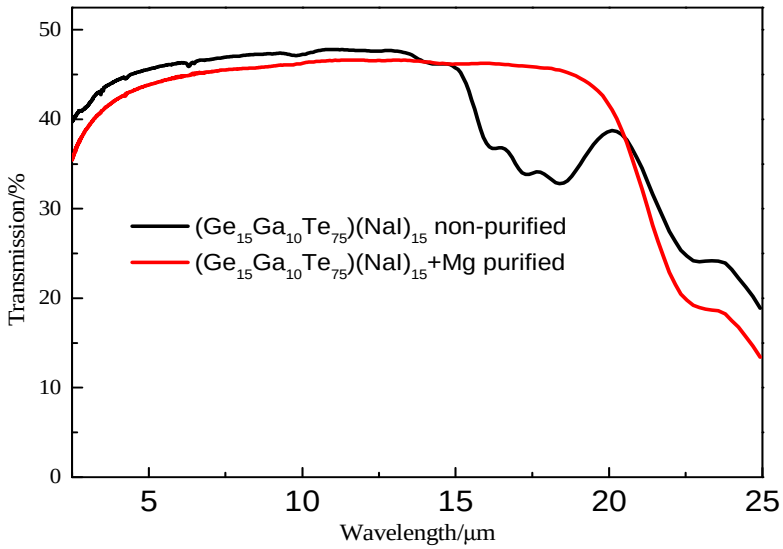


Fig. 8 Infrared spectra of $(Ge_{15}Ga_{10}Te_{75})_{80}(CsBr)_{20}$ glasses

4. Conclusion

In this study, a series of Ge-Ga-Te-NaI chalcogenide glasses were prepared and investigated. All glass samples have a wide infrared window and their infrared cut-off wavelengths are all above 25 μm. This glass system possesses good thermal characteristic because ΔT values of all glass samples are greater than 100℃. Especially, the glass of $(Ge_{15}Ga_{10}Te_{75})_{85}(NaI)_{15}$ has the highestΔT among other glass samples. What's more, it is 8℃ greater than that of Ge-Ga-Te glass.

The XRD patterns indicate that as much as 35 at.% NaI content can be added into Ge-Ga-Te host glass and improve the glasses efficiently. The maximum direct band gap value is 0.745eV. As a result, these excellent properties make the Ge-Ga-Te-NaI glasses potential materials for bio-optic sensors and ultra-wide spectrum infrared optical applications.

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