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远红外 Ge-Ga-Te-Ag 硫系玻璃性能研究

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摘 要:采用传统的熔融-淬冷法制备了一系列的$(Ge_{15}Ga_{10}Te_{75})_{100-x}(Ag)_x$硫系玻璃样品.通过 X 射线衍射、差式扫描量热法、傅里叶红外光谱仪等测试了玻璃样品的热学及光学性能.结果表明该玻璃具有良好的非晶态特性和热稳定性,玻璃开始析晶温度和玻璃转变温度的差值都超过了 100℃.随着 Ag 含量的增加,玻璃的吸收截止边产生了红移.通过提纯,Ge-Ga-Te-Ag 玻璃在 1.8~20 μm 有着较宽且平坦的红外光学窗口.Ge-Ga-Te-Ag 玻璃组分的优良性质使其在红外领域具有广阔的应用前景.

关键词:远红外;光学性质;热稳定性;硫系玻璃;红外光学窗口

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Research on Properties of Far Infrared Ge-Ga-Te-Ag Chalcogenide Glasses

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Abstract: A traditional melt-quenching method was adopted to prepare a series of $(Ge_{15}Ga_{10}Te_{75})_{100-x}(Ag)_x$ chalcogenide glass samples. The thermal and optical parameters were measured by X-ray diffraction, differential scanning calorimetry and Fourier transform infrared spectroscopy, etc. The results show that these glasses have well amorphous nature and good thermal stability. The differences between the glass onset crystallization temperature and the glass transition temperature are all beyond 100℃. With the addition of silver, the absorption cut-off edge has a red shift. The Ge-Ga-Te-Ag glasses have wide and flat infrared optical windows between 1.8 and 20 μm after a purification method. Therefore, all these properties indicate that Ge-Ga-Te-Ag glasses are potential candidate for far infrared applications.

Key words: Far infrared; Optical properties; Thermal stability; Chalcogenide glass; Infrared optical windows

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0 Introduction

Far infrared applications such as bio-sensing and optic imaging have motivated scientists great interest about the investigation of chalcogenide glasses. As is known to all, chalcogenide glasses are famous for its wide transparency window in infrared[1]. Sulfur- and Selenium-based glasses are good glass formers but the infrared transmitting cut-off wavelengths of their glass fibers are limited to 8 μm and 11 μm respectively[2-3]. However, numerous chemical molecules have its absorption bands beyond 11 μm, such as the main absorption band of CO_2 molecules locating at 15 μm especially. Therefore, developing glass fibers with infrared cut-off wavelength above 20 μm is imminent.

Te-based chalcogenide glass has a wider infrared transparency window than that of S- or Se-based glasses. The infrared transmitting cut-off wavelengths of Te-based glasses are usually above 25 μm. Thus, developing Te-based glasses can match well for the far infrared applications. However, Te-based glasses cannot form easily because of the strong metallic of Te atoms. To solve this problem, Lucas and Zhang reported that halogen atoms can spilt Te chains and form the Te-X (Cl, Br, I) glasse[4]. Nevertheless, these glass materials have weak mechanical and low thermal properties. Thus, the Te-X glasses can't meet the requirements of far infrared applications. So other adjuster ions, such as Ga, Ge, are needed to form Te-based glasses.

Recently, investigations about Te-based glasses have breakthroughs. The Ge-Te-I (known as GTI glasses), the Ge-As-Te (known as GAT glasses) and the Ge-Ga-Te (known as GGT glasses) have been investigated[5-8]. The thermal stability and optical properties of these chalcogenide glasses are superior to the Te-X glasses because of the higher dimensionality of their network provided by $GeTe_4$ tetrahedral or $GaTe_3$ triangle structural units. However, these glasses have some defects. The GTI glasses would volatilize during the process of being drawn into fibers because of the element of I contained. Due to the presence of As, the GAT glasses are poisonous to environment. The ΔT (difference between the glass onset crystallization temperature T_x and the glass transition temperature T_g) values of GGT glasses are still too small to guarantee any devitrification problem when the glasses are shaped into lenses or fibers. Ramesh et al and He et al reported that silver doping into chalcogenide glasses can make the glass structure more stable and improve the glass forming ability, respectively[9-10]. However, no comprehensive study of the influence of silver on the thermal and optical properties of Ge-Ga-Te glass system has been reported.

In this work, a novel Te-based chalcogenide glass system was investigated. The object is to enlarge glass formation and obtain vitreous materials with an Infrared (IR) cut-off edge beyond 20 μm. The amorphous state and thermal stability were measured by X-Ray Diffraction (XRD) and Differential Scanning calorimetry (DSC) instruments.

1 Experimental

Elemental raw materials of Ge (99.999%), Ga (99.999%), Te (99.999%) and Ag (99.9%) were accurately weighed and transferred into silica tubes which were then sealed under vacuum. The ampoules were then placed in rocking furnaces for 15 h at 950℃ to homogenize the mixture. Afterwards, the temperature was decreased to 700℃ before tubes were quenching in water and then placed in a preheated furnace at 10℃ below T_g. Then, glass rods were released from the tubes and were then cut into discs. Finally, these discs were polished for testing.

Densities of glass samples were measured according to the Archimedes' principle with an accuracy of ±0.001 g/cm^3. To confirm the amorphous state, XRD using German Bruker D2 with CuKα radiation and Scanning Electron Microscopy (SEM) were performed on powder for each composition samples. Thermal analyses were carried out by a TAQ2000 thermal analyzer with a temperature range from 80 to 350℃ at a heating rate of 10℃/min. The visible to near infrared transmission spectra were obtained through Perkin-Elmer Lambda 950 spectrophotometer. The IR transparency windows were acquired with Nicolet 380 Fourier Transform Infrared (FTIR) spectroscopy in the range of 400～4 000 cm^{-1}. The Raman spectra of glass samples were studied through a Renishaw InVia Raman microscope with an Ar+ ion laser in the range of 80～600 cm^{-1}. All optical tests were performed at room temperature.

2 Results and discussions

2.1 XRD investigations

A series of $(Ge_{15}Ga_{10}Te_{75})_{100-x}(Ag)_x$ ($x=0, 5, 10, 15, 20, 25, 30, 35, 40, 45$) were prepared. XRD patterns of Ge-Ga-Te-Ag glass samples are shown in Fig. 1. Here, all curves are smooth and no obvious crystalline phases are observed in the patterns. Fig. 2 is a SEM picture for Ge-Ga-Te-Ag glass samples. The

surfaces of these glass samples were nearly homogeneous and no obvious micro-crystals and phase-separated units occurred. The results indicate that all glass samples have amorphous state and the Ge-Ga-Te glass matrix can dissolve the content of Ag as much as 45 at.%. With the addition of Ag atoms, the connectivity of glass was improved and the glass formation was enlarged.

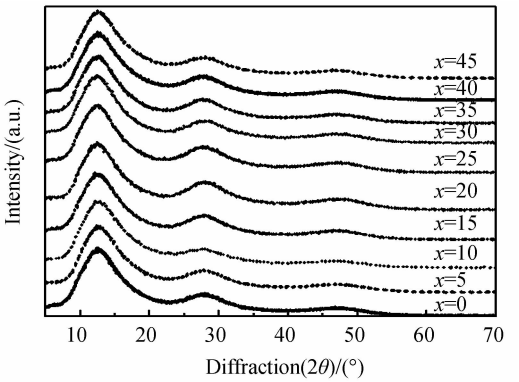

Fig. 1 XRD patterns of Ge-Ga-Te-Ag glass samples

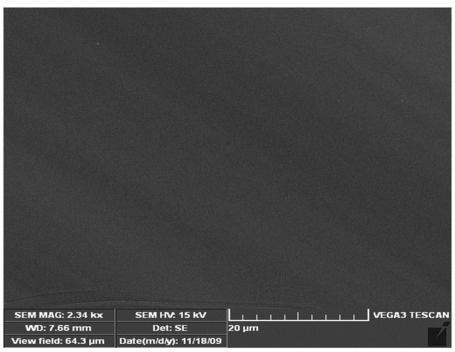

Fig. 2 SEM image for the typical glass sample: $(Ge_{15}Ga_{10}Te_{75})_{55}(Ag)_{45}$

2.2 Physical properties

Table 1 shows some physical parameters of Ge-Ga-Te-Ag glass samples. With the increasing content of Ag, the density decreased from 5.576 g·cm^{-3} to 5.125 g·cm^{-3} gradually. This may be attributed to that density is determined by the elemental relative atomic mass and the packing efficiency of atoms[11]. The relative atomic mass of Ag (108) is smaller than that of $GeTe_4$ (585) and $GaTe_3$ (454). The $GeTe_4$ and $GaTe_3$ units reduced with the addition of Ag. Therefore, the density decreased gradually with the addition of Ag. The molar volume is inversely proportional to the density that results in the increase of the molar volume. The relationships between molar volume and density can be described by

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

where M_i is the molar mass of glass sample, $M = A_i B_i$, A_i is the molar concentration, B_i is the molecular weight of the component, ρ is the density of glass sample.

Table 1 Physical properties of $(Ge_{15}Ga_{10}Te_{75})_{100-x}(Ag)_x$ glass samples

x/%	Thickness d/cm	Density ρ/(g·cm^{-3})	V_m/(cm^3·mol^{-1})
5	0.126	5.576	20.382
10	0.125	5.511	20.569
15	0.151	5.472	20.661
20	0.155	5.416	20.820
25	0.163	5.361	20.978
30	0.162	5.307	21.135
35	0.177	5.275	21.207
40	0.174	5.202	21.448
45	0.156	5.125	21.712

2.3 Raman spectra analysis

Fig. 3 shows the Raman spectra of glass samples. Here, three distinct vibration peaks which located at 65 cm^{-1}, 126 cm^{-1}, 155 cm^{-1} respectively appeared. In addition, a weak band located around 220 cm^{-1}. These vibration peaks are caused by some bonds or energy units. The first two vibration peaks are resulted from Ge-Te bonds[12-13]. The vibration peaks at 155 cm^{-1} is attributed to Te-Te bonds while the last vibration band is ascribed to Ge-Ge bonds[13-14]. With the increasing content of Ag, the amplitude of absorption peaks at 65 cm^{-1}, 126 cm^{-1}, 220 cm^{-1} have no obvious change. However, the intensity of absorption peak at 155 cm^{-1} has some changes. With the values of x ranged from 5 to 15, the intensity of the vibration peak at 155 cm^{-1} decreased gradually. On the contrary, the intensity of this vibration peak increased when x exceeded 15. Some reasons may be in charge of this phenomenon. With the addition of Ag, Te-Te chains were spilt and Te-Ag bonds formed. As a result, the intensity of absorption peak at 155 cm^{-1} decreased with Te-Te bonds reducing. However, too much silver ($x > 15$) doping into the glass matrix resulted in the disruption of glass network. The

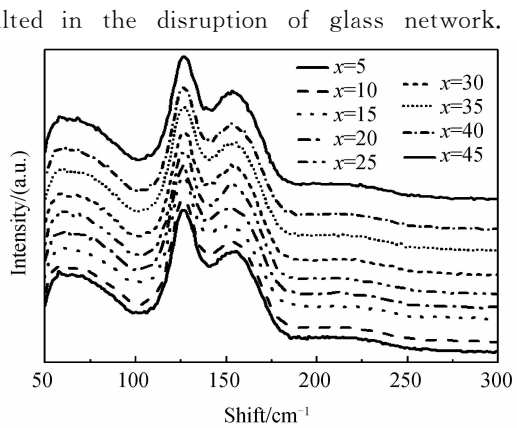

Fig. 3 Raman spectra of Ge-Ga-Te-Ag glass samples

redundant silver existed in the parent glass as a micro-inclusion. Meanwhile, many dissociative Te atoms combined together. Eventually, the intensity of vibration peak at 159 cm^{-1} strengthened.

2.4 Thermal properties

Fig. 4 shows the DSC curves of glass samples. From these curves, the glass transition temperature (T_g) and the glass onset crystallization temperature (T_x) of studied glasses were confirmed. The specific values are listed in Table 2. Here, the values of T_g ranged from 170 to 178℃, and the values of ΔT ranged from 102 to 114℃. When x varies from 5 to 15, the values of ΔT increase from 105 to 114℃. However, the values of ΔT decreased when x exceeded 15. This may be ascribed to the network structure of Ge-Ga-Te glass which was destroyed with the addition of Ag. A bit of silver content destroyed the original stable structure of Ge-Ga-Te glass. Under such situation, ΔT values of Ge-Ga-Te-Ag decreased when x ranged from 0 to 5. The thermal stability of glass improved because of the decrease of Te-Te bonds from the Raman spectra. When x was above 15, the Te-Te bonds increased. Due to strong metallic of Te, the thermal stability of glass deteriorated and the values of ΔT decreased.

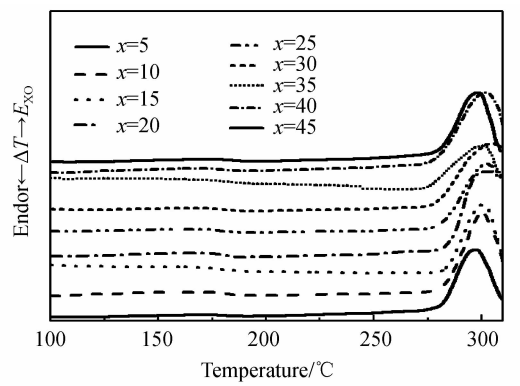

Fig. 4 DSC curves of Ge-Ga-Te-Ag glass samples

Table 2 Thermal parameters of Ge-Ga-Te-Ag glass samples

x/%	T_g/℃	T_x/℃	ΔT/℃	Cut-off λ/nm
0	172	284	112	1 789
5	177	282	105	1 703
10	176	284	108	1 717
15	170	284	114	1 731
20	175	285	110	1 740
25	174	282	108	1 750
30	175	280	105	1 756
35	173	276	103	1 763
40	176	279	103	1 772
45	178	280	102	1 793

2.5 Analysis of near infrared absorption spectra

The near infrared absorption spectra are shown in Fig. 5. From the insert picture, the absorption cut-off wavelength shifted to the long wavelength region with the increase of silver content. The specific values are listed in Table 2. The cut-off edge of short wavelength is usually limited by the stimulation of valence electrons from forbidden band to conduction band. With high polarizability Ag doping into glass, the width of forbidden band became narrower. In consequence, a red shift of cut-off edge occurred.

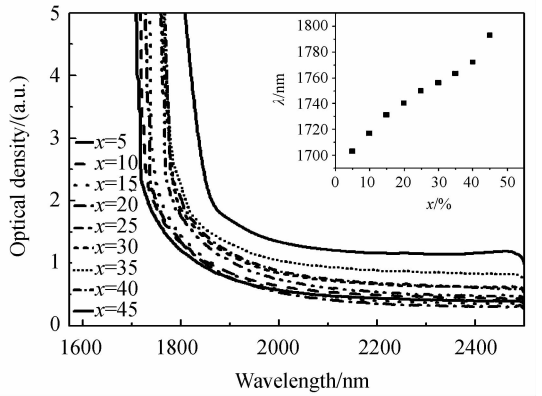

Fig. 5 Near IR absorption spectra of glass samples (relationships between cut-off edge wavelength and silver content are shown in the inset image)

2.6 Analysis of infrared spectra

As shown in Fig. 6, all glass samples had wide and flat infrared spectra. The highest transmission corresponding to $(Ge_{15}Ga_{10}Te_{75})_{85}(Ag)_{15}$ was up to 52% without any purification. Meanwhile, long cut-off wavelengths of glass samples were beyond 25 μm. However, when x was 45, the transmission of this glass sample decreased remarkably. This may be ascribed to that too much silver doping into Ge-Ga-Te glass made it difficult to form glass and some impurities were introduced. The difference of the transmission ratio is sourced from the thickness variation and different polishing methods for glass samples. Some absorption peaks appeared in the spectra. The peak at 9.9 μm is produced by Si-O bonds while the absorption band at 15 ~ 20 μm results from Ge-O or Ga-O bonds[15-17]. The rapidly drop in transmittance between

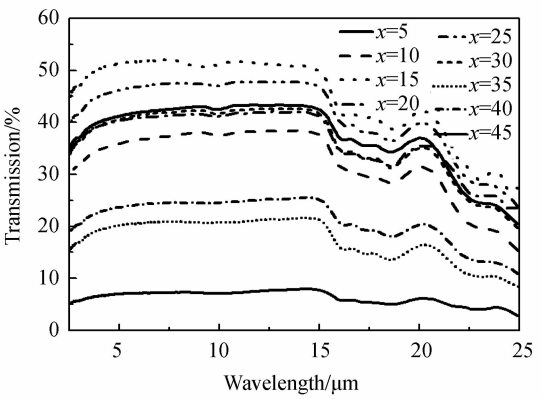

Fig. 6 Infrared transmission spectra of glass samples

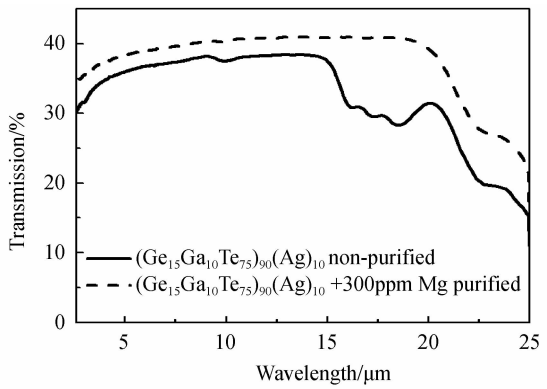

Fig. 7 Infrared spectra of $(Ge_{15}Ga_{10}Te_{75})_{90}(Ag)_{10}$ glasses

20 and 25 μm is ascribed to the function of multi-phonons[7]. To solve the elimination of impurities, a distillation method with 300 ppm Mg under vacuum was performed. The transmission spectra of glasses before and after purification are shown in Fig. 7. Here, we just list a typical glass sample $(Ge_{15}Ga_{10}Te_{75})_{90}(Ag)_{10}$. Here, the infrared spectrum is flat from 2.5 to 20 μm without any absorption peaks after purification.

3 Conclusions

A series of Ge-Ga-Te-Ag glasses were prepared and investigated. This glass system has good thermal properties and the highest ΔT is 114℃. With the increase of Ag, the absorption cut-off wavelength shifts to the long region. All glass samples have wide transmission windows from 1.8 to 20 μm. The excellent properties make these glasses good candidate for potential infrared applications.

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