Composition dependence of physical and optical properties in Ge-As-S chalcogenide glasses

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Abstract

The composition dependence of density (d), refractive index (n) and optical bandgap (E_g) of Ge-As-S chalcogenide glasses is investigated. It is shown that d correlates linearly with sulfur content but **relatively** poorly with the mean coordination number (MCN). It is also shown that n does not correlate directly with d , and instead a semi-empirical relation based on the molar refractivity (R) of Ge, As and S is derived, permitting to predict n from d with less than 1% error. A convenient method based on diffuse reflectance is proposed to measure E_g of Ge-As-S glasses with good accuracy. It is shown that the value of E_g is dominated by the S content. These findings make it convenient to tailor the physical and optical properties of glasses in Ge-As-S system.

Keywords: Chalcogenide glasses; Refractive index; Optical bandgap; Diffuse

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reflectance spectrum

1. Introduction

Chalcogenide glasses (ChG) are increasingly popular infrared (IR) optical materials because of their wide IR transparency windows, superior thermal and chemical stability, and low costs. Currently, IR lenses made of ChG are manufactured for thermal imaging systems [1,2] while chalcogenide fibers and planar waveguides are produced for IR light transmission [3,4], optical sensing [5-7], and nonlinear optics [8-10]. Among the physical parameters of ChG, the refractive index (n) may be the most important one as it is crucial for most optical designs. However, limited attention has been paid to the origin and control of this parameter in ChG. In this paper the composition dependence of n , optical bandgap (E_g) and density (d) in Ge-As-S ChG is investigated. We examine the co-dependence between the three parameters as well as the mean coordination number (MCN). MCN defines the average number of covalent bond per atoms, and is calculated by the sum of respective elemental concentration times their covalent coordination number [11]. A semi-empirical relation is proposed to predict n from d and a method based on diffuse reflectance is described to measure E_g . The Ge-As-S system was chosen for this investigation because it has a large glass forming domain, so that a large number of compositions with remarkably different structures and properties can be tested. In addition, Ge-As-S glasses are also expected to be relatively robust materials for nonlinear optics and IR gratings due to their superior mechanical property, relatively high power damage threshold, and tunable photosensitivity [12-14].

2. Experimental procedures

Ge-As-S glasses were synthesized by the melt-quenching technique [10]. High-purity Ge (5N), As (6N) and S (6N) elements were weighed in a glove box filled

with dry N₂, and loaded into a low-OH silica tube with an inner diameter of 15mm. Before weighing, the arsenic was thermally treated under vacuum ($<10^{-5}$ torr) for 1h to remove surface oxide impurities, and the sulfur was sublimated under vacuum to eliminate most carbon and hydrogen related impurities. The tube containing the raw materials was then evacuated ($<10^{-5}$ torr) and flame-sealed. After that, the mixture was homogenized at 800-850°C for more than 12h in a rocking furnace. In the end, the tube containing the melt was quenched in water and the formed glass was annealed near its glass transition temperature for 3 hours.

The amorphous nature of the samples was verified by X-ray diffraction (XRD) measurements (D2 Phaser, Bruker Corporation, Karlsruhe, Germany). The sample compositions were confirmed (within the experimental uncertainty of ± 1 mol%) using the energy-dispersive X-ray spectroscopy (EDS) feature of a scanning electron microscope (JSM-6510, JEOL, Tokyo, Japan). The d of the glasses were measured using the Archimede's method. A balance with an accuracy of 0.0001g was used. Each sample was measured 6 times, and the error of measured d was about ± 0.01 g/cm³. The E_g of the glasses were determined from their diffuse reflectance spectra (DRS), which were recorded on fine glass powders using a spectrophotometer (Lambda 950, Perkin-Elmer, Waltham, MA) equipped with a PbS integrating sphere. The ground glass powders were put onto standard sieves with different meshes. The powders passing through the meshes were used for the measurement. Each glass was measured 5 times, and the error of determined E_g was about ± 0.01 eV. The n of the glasses in the 1.7-20 μ m range were measured on single-side polished glass discs ($\varnothing 15$ mm) by an IR variable angle spectroscopic ellipsometer (IR-VASE, J. A. Woollam, Lincoln, NE). The Ge-As-S glasses have Brewster's angles of about 64-66.5°. To avoid sudden changes of the phase shift in the reflected lights, the angles of incidence were selected

outside of this range. In these measurements, they were selected at 70° and 77° . The spectral resolution was 16 cm^{-1} . Sellmeier equations, which are commonly used to show dispersion of n in chalcogenide glasses [7, 15], were used to fit the data. Each sample was measured more than 3 times, and the error of measured n was about ± 0.001 . All measurements were conducted at room temperature.

3. Results

In order to systematically investigate composition dependence of n , d and E_g in Ge-As-S glass system, four groups of glasses with distinctive features were prepared: (i) $\text{Ge}_{0.1}\text{As}_x\text{S}_{0.9-x}$, $x=0.1, 0.2, 0.28$ and 0.35 ; (ii) $\text{Ge}_x\text{As}_{0.1}\text{S}_{0.9-x}$, $x=0.05, 0.1, 0.15, 0.2, 0.25, 0.3$ and 0.35 ; (iii) $\text{Ge}_x\text{As}_{0.2}\text{S}_{0.8-x}$, $x=0.1, 0.15, 0.2, 0.25$, and 0.3 ; and (iv) $\text{Ge}_x\text{As}_x\text{S}_{1-2x}$, $x=0.1, 0.15, 0.182, 0.2$ and 0.25 . These compositions cover a quite large part of the glass forming domain (see Fig.1) [16] and therefore are good representatives in this glass system. Table 1 lists the values of n , d and E_g of the Ge-As-S glasses. The n of the $\text{Ge}_{0.1}\text{As}_{0.35}\text{S}_{0.55}$ glass was not measured because it had inferior thermal stability and was difficult to form a homogeneous glass with a diameter large enough for the measurement. The d follows a remarkably linear dependence on S content regardless of the Ge/As ratio (see Fig.2a). This is consistent with the lower molar mass of S in comparison to Ge and As. While d broadly increase with increasing MCN the correlation is relatively poor (see Fig.2b). For example, $\text{Ge}_{0.1}\text{As}_{0.2}\text{S}_{0.7}$ glass (MCN=2.4) has higher d than $\text{Ge}_{0.2}\text{As}_{0.1}\text{S}_{0.7}$ glass (MCN=2.5); and $\text{Ge}_{0.25}\text{As}_{0.1}\text{S}_{0.65}$ glass (MCN=2.6) shows lower d than $\text{Ge}_{0.1}\text{As}_{0.28}\text{S}_{0.62}$ glass (MCN=2.48). Similarly n broadly increases with increasing d as would be expected from the concomitant increase in electronic density but the correlation is poor as shown in Fig. 2c. No apparent correlation is found between the n and MCN.

Fig.1 Glass forming domain of Ge-As-S system and 17 compositions synthesized in this study

Table 1. Mean coordination numbers (MCN), densities (d), optical bandgaps (E_g), measured (n_{mea}) and calculated (n_{cal}) refractive indices at 6 μm , and the deviations of n_{cal} from n_{mea} for Ge-As-S glasses.

Composition	MCN	d ($\pm 0.01 \text{ g/cm}^3$)	E_g ($\pm 0.01 \text{ eV}$)	n_{mea} (± 0.001)	n_{cal}	Deviation (%)
Ge _{0.1} As _{0.1} S _{0.8}	2.3	2.52	2.72	2.087	2.082	-0.24
Ge _{0.1} As _{0.2} S _{0.7}	2.4	2.82	2.57	2.195	2.188	-0.32
Ge _{0.1} As _{0.28} S _{0.62}	2.48	3.07	2.47	2.279	2.283	0.18
Ge _{0.1} As _{0.35} S _{0.55}	2.55	3.15	2.46	-	-	-
Ge _{0.05} As _{0.1} S _{0.85}	2.2	2.37	2.72	2.059	2.044	-0.73
Ge _{0.15} As _{0.1} S _{0.75}	2.4	2.65	2.70	2.099	2.107	0.381
Ge _{0.2} As _{0.1} S _{0.7}	2.5	2.79	2.71	2.130	2.139	0.42
Ge _{0.25} As _{0.1} S _{0.65}	2.6	2.89	2.79	2.129	2.145	0.75
Ge _{0.3} As _{0.1} S _{0.6}	2.7	2.99	2.50	2.155	2.153	-0.09
Ge _{0.35} As _{0.1} S _{0.55}	2.8	3.20	2.37	2.239	2.231	-0.36
Ge _{0.15} As _{0.2} S _{0.65}	2.5	2.96	2.61	2.217	2.220	0.14
Ge _{0.25} As _{0.2} S _{0.55}	2.7	3.14	2.35	2.220	2.221	0.05
Ge _{0.3} As _{0.2} S _{0.5}	2.8	3.32	2.23	2.307	2.284	-0.99
Ge _{0.15} As _{0.15} S _{0.7}	2.45	2.81	2.65	2.163	2.166	0.14
Ge _{0.182} As _{0.182} S _{0.636}	2.546	2.97	2.61	2.197	2.204	0.32
Ge _{0.2} As _{0.2} S _{0.6}	2.6	2.99	2.54	2.164	2.180	0.74
Ge _{0.25} As _{0.25} S _{0.5}	2.75	3.32	2.12	2.298	2.298	0

Fig.2. Correlations between parameters of Ge-As-S glasses: (a) A linear plot of density vs S concentration; (b) the variation of density with MCN; (c) the variation of refractive index with density.

4. Discussion

4.1 Refractive index and density

The correlation between d and n is indeed more complex and must account for the molar refractivity of the sample. The n of a glass mainly depends on the electric polarizability (p) of constituent elements and the glass density (d) [17]. The p represents the relative tendency of the electron cloud of an atom to be distorted from its normal shape by an external electric field. A glass consisting of atoms with larger radius, which are more likely to be polarized, tends to exhibit a higher n . The n of a glass could be estimated from the p and d using the following equation [17]:

$$\sum_i p_i x_i = K \times \frac{n^2 - 1}{n^2 + 2} \times \frac{M_{mol}}{d} \quad (1)$$

where x_i is the molar percentage of the constituent element with the electric polarizability of p_i ; K is a constant, and M_{mol} is the molar mass of the glass. Eq.(1) can also be expressed by:

$$\sum_i R_i x_i = \frac{n^2 - 1}{n^2 + 2} \times V_{mol} \quad (2)$$

where $R_i = p_i/K$, is the molar refractivity and $V_{mol}=M_{mol}/d$ is the molar volume. The refractive index n can then be calculated from the density d using Eq.(3) granted the values of R_i for each constituent elements are known.

$$n^2 = \frac{2 \sum_i R_i x_i + V_{mol}}{V_{mol} - \sum_i R_i x_i} \quad (3)$$

The molar refractivity R_i of Ge, As and S elements were evaluated by the least-squares fitting method using the measured n and d of the investigated glasses and Eq.(2). The optimal average values of molar refractivity for each elements are $R_{Ge}=10.07$, $R_{As}=11.78$, and $R_S=7.82 \text{ cm}^3/\text{mol}$ for glasses in the Ge-As-S system. In

order to assess the divergence of Eq.(3) for the determination of n using these molar refractivity values, the calculated refracted index values n_{cal} of each glass were compiled and compared with the measured values n_{mea} as shown in Table 1. The correlation plot between n_{mea} and n_{cal} shown in Fig. 3 indicates an excellent match and the deviation of n_{cal} from n_{mea} is below 1%. It is therefore expected that the refractive index of any glass composition in the Ge-As-S system can be predicted using Eq.(3) from its density. It is worth mentioning that the molar refractivity of Ge, As and S were determined empirically for n values at 6 μm , hence the n_{cal} values determined from Eq.(3) should be only valid at that wavelength. This is important because the refractive index dispersion of sulfide glasses is significant [10, 18].

Fig.3. Correlation between the measure n and the calculated n using Eq.(3).

4.2 Optical bandgap

E_g of a glass is usually obtained by conducting a Tauc plot [19] on the absorption spectrum measured using a spectrophotometer. According to Tauc, electronic transitions from delocalized states in the valence band to delocalized states of the

conduction bands lead to the optical absorption behavior in the region $\alpha > 10^4 \text{cm}^{-1}$ (α is the absorption coefficient). To conduct a valid Tauc plot, the values of α as low as $\sim 10^4 \text{cm}^{-1}$ are required. The value of E_g is then obtained from extrapolation of the $(\alpha h\nu)^{1/2}$ vs $h\nu$ plot where $h\nu$ is the photon energy. However, a number of amorphous semiconductors do not follow a quadratic energy dependence [20] and a more common approach is to define E_g as the photon energy for which α reach some fixed value in the Tauc region, usually 10^4cm^{-1} [19, 20] or 10^3cm^{-1} [21]. For a 1mm-thick bulk glass, the detection limit of a spectrophotometer is typically $\alpha < 100 \text{cm}^{-1}$. To reach the Tauc plot region, the sample thickness used for the measurement has to be less than $10 \mu\text{m}$. Because of this, useful data are usually collected on thin films. However, it is difficult to prepare chalcogenide films (e.g. Ge-As-S, Ge-Sb-S, Ge-Sb-Se) with accurate nominal compositions, and therefore a number of researchers used thin bulk samples [22-24] for the measurements. The E_g determined this way turned out to be smaller than those obtained on corresponding films. It is not surprising because the Tauc linear extrapolation carried out to obtain E_g on bulk samples were not really conducted in the Tauc plot region, but in a region with much smaller α .

DRS provide another approach to obtain E_g of a glass. Based on DRS of glass powders, the Kubelka-Munk function $F(R)$ [25, 26] can be calculated according to Eq.

(4)

$$F(R) = \frac{(1-R)^2}{2R} \quad (4)$$

where R is the reflectance in acquired DRS. The $F(R)$ is proportional to the absorption coefficient of the glass α [25, 26], hence E_g could be determined based on calculated $F(R)$. However, the effective absorption length is unknown in a reflection experiment so that the absolute value of α cannot be obtained. Instead we define E_g as the photon

energy for which $F(R)$ reach some fixed value in the Tauc region determined by calibrating the method with a standard glass with similar electric band structure and known value of E_g . In this experiment we calibrated the absorbance using DRS of As_2S_3 glass powders with a size of $\sim 15 \mu\text{m}$. It is well known that As_2S_3 glass has an E_g of $\sim 2.40 \text{ eV}$ [27, 28]. As an example, Fig.4a presents a diffuse reflectance spectrum of As_2S_3 fine glass powders with a size of $\sim 15 \mu\text{m}$, and Fig.4b displays the absorption spectra derived from the DRS. For comparison, transmission or absorption spectra of As_2S_3 bulk glasses with different thickness are also included in the figures. Figures 4a and 4b indicate that the transmission or absorption spectra of bulk glasses get cut-off far above the wavelength ($\sim 516\text{nm}$) corresponding to the E_g , making it impossible to collect absorption data in the 10^4 cm^{-1} range required for E_g determination. In comparison, the DRS or derived absorption spectra of powders provide measurable data around 516 nm, making it possible to define a fixed DRS absorption value for the determination of E_g from these data. In order to determine this fixed DRS absorption value we used the known E_g value of our As_2S_3 standard glass. The value of E_g (2.40 eV) corresponds to a DRS absorbance of ~ 3.93 (Fig.4b). If all DRS are collected in the same conditions (e.g. same size of glass powders, same testing condition), the same absorbance value can yield a systematic value of E_g . Using the same DRS absorbance value of 3.93, E_g of the Ge-As-S glasses (see table 1) were determined based on DRS of powders measured in the same condition.

Fig.4 (a) Diffuse reflectance spectrum of As_2S_3 glass powders with a size of $\sim 15 \mu\text{m}$, and transmission spectra (TS) of As_2S_3 glass discs; (b) Absorption spectra of As_2S_3 glasses derived from corresponding data in (a).

E_g of a glass depends on the average electron affinity of anions, the average bonding energy and the average polarization energy of ions in the glass [17, 29]. Although some investigations on chalcogenide glasses [19, 28] indicated that a glass with smaller E_g was more likely to show a higher n , especially n increased with decreasing E_g when a chalcogenide glass was subjected to photodarkening, we did not find clear correlation between n and E_g in the Ge-As-S glasses. It is not surprising because the influencing factors of n and E_g are significantly different, although both of them are related to the electric polarizability of constituent elements in the glasses.

Instead we find a broad correlation between the bandgap and the sulfur content as depicted in Fig. 5. This is consistent with the expected dependence on the optical

bandgap value on the molar bond energy [19]. Indeed the corresponding bond energies are $E_{S-S}=280$ kJ/mol, $E_{Ge-S}=265$ kJ/mol, $E_{As-S}=260$ kJ/mol, $E_{As-As}=200$ kJ/mol and $E_{Ge-Ge}=185$ kJ/mol. It is therefore expected that sulfur rich glass will have higher molar bond energies while sulfur-deficient glasses containing homopolar metal bonds will have lower molar bond energies and consequently lower bandgap values. This is also consistent with the fact that Ge-As-S glasses exhibit chemical order so that homopolar metal bonds only appear in sulfur deficient glasses [30]. In addition, sulfur has a notably higher electron affinity (200 kJ/mol) than Ge (116 kJ/mol) and As (78 kJ/mol) which also contributes to the increase in bandgap energy with increasing sulfur content.

Fig.5 Correlation between bandgap E_g and sulfur content in Ge-As-S glasses.

5. Conclusion

It is shown that the density of Ge-As-S glasses is linearly correlated with the sulfur content but is not well correlated to the *MCN* or the refractive index n . Instead a relation based on the molar reflectivity of Ge, As and S and the glass density is shown to predict the refractive index with an error below 1%. The estimated values of molar reflectivity for Ge, As and S elements are 10.07, 11.78, and 7.82 cm³/mol,

respectively. It is also shown that a reasonable optical bandgap E_g of a glass could be determined from DRS of the glass powders. The E_g of Ge-As-S glasses is found to decrease with decreasing sulfur content. Following these findings, refractive index, density and optical bandgap of a glass in Ge-As-S system could be tailored intentionally.

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