

## THEORETICAL INVESTIGATION OF THE STRUCTURAL PROPERTIES OF Sb<sub>2</sub>S<sub>3</sub>-As<sub>2</sub>S<sub>3</sub> AND Sb<sub>2</sub>Te<sub>3</sub>-As<sub>2</sub>S<sub>3</sub> GLASSES

K. N'Dri<sup>a\*</sup>, J. Sei<sup>a</sup>, D. Houphouët-Boigny<sup>a</sup>, J. C Jumas<sup>b</sup>

<sup>a</sup>Laboratoire de Chimie des Matériaux Inorganiques, UFR-SSMT, Université de Cocody  
22 B.P 582 Abidjan 22 (Côte d'Ivoire).

<sup>b</sup>Laboratoire des Agrégats Moléculaires et des Matériaux Inorganiques, CNRS ESA 5072,  
Université Montpellier II, Place Eugène Bataillon, F-34095 Montpellier Cedex 5, France.

The general formulas of studied vitreous compositions of the Sb<sub>2</sub>S<sub>3</sub>-As<sub>2</sub>S<sub>3</sub> and Sb<sub>2</sub>Te<sub>3</sub>-As<sub>2</sub>S<sub>3</sub> systems are As<sub>0,4x</sub>Sb<sub>0,4(100-x)</sub>S<sub>60</sub> (10 ≤ x(mol.%As<sub>2</sub>S<sub>3</sub>) ≤ 100) and As<sub>0,4y</sub>Sb<sub>0,4(100-y)</sub>S<sub>0,6y</sub>Te<sub>0,6(100-y)</sub> (40 ≤ y(mol.%As<sub>2</sub>S<sub>3</sub>) ≤ 100), respectively. Glass-forming region of the Sb<sub>2</sub>S<sub>3</sub>-As<sub>2</sub>S<sub>3</sub> system is wider than that of the Sb<sub>2</sub>Te<sub>3</sub>-As<sub>2</sub>S<sub>3</sub> system. The Ordered Bond Network Model shows that all glasses of the above systems are stoichiometric vitreous compositions with only heteronuclear bonds: Sb<sub>2</sub>S<sub>3</sub>-As<sub>2</sub>S<sub>3</sub> glasses contain mainly Sb-S and As-S bonds while the Sb<sub>2</sub>Te<sub>3</sub>-As<sub>2</sub>S<sub>3</sub> system consists of S-Te, Sb-S and As-S bonds. For these vitreous compositions, the average coordination number (*Z*) determined by the constraints model is equal to 2.4. Glasses having contents of As<sub>2</sub>S<sub>3</sub> beyond 75 mol% (Sb<sub>2</sub>S<sub>3</sub>-As<sub>2</sub>S<sub>3</sub> system) and 90 mol% (Sb<sub>2</sub>Te<sub>3</sub>-As<sub>2</sub>S<sub>3</sub> system) are thermally more stable than their counterparts of each system because they exhibit only the glass transition temperature (*T<sub>g</sub>*) but not the crystallization temperature (*T<sub>c</sub><sup>h</sup>*).

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*Keywords:* Glass-forming region, chemical bonds, average coordination number, glass transition temperature, optical gap.

### 1. Introduction

Chalcogenide glasses are vitreous materials whose composition contains one or more chalcogen elements S, Se or Te, as well as elements of the groups IV and V of periodic classification. These glasses are interesting materials because of their technological applications [1] and commercial importance [2]. In this study, the glass-forming regions of Sb<sub>2</sub>S<sub>3</sub>-As<sub>2</sub>S<sub>3</sub> and Sb<sub>2</sub>Te<sub>3</sub>-As<sub>2</sub>S<sub>3</sub> systems, the nature of chemical bonds in their glasses determined by the Ordered Bond Network Model (OBNM) [3], the calculated average coordination number (*Z*) of antimony (Sb) and arsenic (As) atoms by the constraints model [4] and the stability of glasses quantified by numerical parameters  $K_{SP} = (T_x^h - T_g) / (T_c^h - T_x^h)$  [5] and  $K_{WO} = (T_x^h / T_m)$  [6] are discussed. The correlation between the glass transition temperature (*T<sub>g</sub>*), the optical gap (*E<sub>g</sub>*) and the average coordination number (*Z*) in each system was investigated in order to find the possible structural modifications in the Sb<sub>2</sub>S<sub>3</sub>-As<sub>2</sub>S<sub>3</sub> and Sb<sub>2</sub>Te<sub>3</sub>-As<sub>2</sub>S<sub>3</sub> glasses.

### 2. Synthesis and characterization of glasses

Glasses of Sb<sub>2</sub>S<sub>3</sub>-As<sub>2</sub>S<sub>3</sub> and Sb<sub>2</sub>Te<sub>3</sub>-As<sub>2</sub>S<sub>3</sub> systems, whose formulas are As<sub>0,4x</sub>Sb<sub>0,4(100-x)</sub>S<sub>60</sub> (10 ≤ x(mol.%As<sub>2</sub>S<sub>3</sub>) ≤ 100) and As<sub>0,4y</sub>Sb<sub>0,4(100-y)</sub>S<sub>0,6y</sub>Te<sub>0,6(100-y)</sub> (40 ≤ y(mol.%As<sub>2</sub>S<sub>3</sub>) ≤ 100)

\* Corresponding author: ezekmk@yahoo.fr

respectively, were prepared by direct synthesis from pure starting elements such as arsenic (As), antimony (Sb), tellurium (Te) and sulphur (S). Quartz ampoules were filled with  $\sim 0.3$  g of the mixed elements and then evacuated to  $\sim 10^{-3}$  Torr, sealed and heated to  $900^\circ\text{C}$  at the rate of  $1^\circ\text{C}/\text{minute}$ . The ampoules were held at this temperature for 24 hours and quenched in ice-water. The glassy state in the quenched samples was confirmed by X-ray diffraction at room temperature using Cu-K $_{\alpha}$  radiation ( $\lambda=1.5405 \text{ \AA}$ ).

The thermal characteristics such as the glass transition temperature  $T_g$ , the onset crystallization temperature  $T_x^h$ , the peak crystallization temperature  $T_c^h$  and the melting temperature  $T_m$ , were measured by using DSC 121 Setaram apparatus at a heating rate of  $5^\circ\text{C}/\text{minute}$  in the studied temperature range (from  $25^\circ\text{C}$  to  $650^\circ\text{C}$ ). The thermal stability of  $\text{Sb}_2\text{S}_3\text{-As}_2\text{S}_3$  and  $\text{Sb}_2\text{Te}_3\text{-As}_2\text{S}_3$  glasses was estimated using  $K_{\text{SP}}$  and  $K_{\text{WO}}$  parameters defined above.

The absorption spectra of stabilized glasses (at temperatures lower than  $T_g$  during 24 hours) were carried out using a spectrophotometer Beckman Acta Miv with double beam operating at the ambient temperature between the ultraviolet and the infrared ( $0.2$  to  $2.5 \mu\text{m}$ ) regions. The optical gap ( $E_g$ ) values of the investigated glasses were got from the recorded spectra.

### 3. Results and discussions

#### 3.1. Chemical composition of glasses.

The chemical composition of the investigated glasses is indicated in Table 1.

Table 1. Chemical composition of  $\text{Sb}_2\text{S}_3\text{-As}_2\text{S}_3$  and  $\text{Sb}_2\text{Te}_3\text{-As}_2\text{S}_3$  glasses.

$\text{Sb}_2\text{S}_3\text{-As}_2\text{S}_3$ system		$\text{Sb}_2\text{Te}_3\text{-As}_2\text{S}_3$ system	
mol% $\text{As}_2\text{S}_3$	Chemical composition	mol% $\text{As}_2\text{S}_3$	Chemical composition
10	$\text{As}_4\text{Sb}_{36}\text{S}_{60}$	40	$\text{As}_{16}\text{Sb}_{24}\text{S}_{24}\text{Te}_{36}$
25	$\text{As}_{10}\text{Sb}_{30}\text{S}_{60}$	50	$\text{As}_{20}\text{Sb}_{20}\text{S}_{30}\text{Te}_{30}$
50	$\text{As}_{20}\text{Sb}_{20}\text{S}_{60}$	60	$\text{As}_{24}\text{Sb}_{16}\text{S}_{36}\text{Te}_{24}$
75	$\text{As}_{30}\text{Sb}_{10}\text{S}_{60}$	80	$\text{As}_{32}\text{Sb}_8\text{S}_{48}\text{Te}_{12}$
100	$\text{As}_{40}\text{S}_{60}$ or $\text{As}_2\text{S}_3$	90	$\text{As}_{36}\text{Sb}_4\text{S}_{54}\text{Te}_6$
		100	$\text{As}_{40}\text{S}_{60}$ or $\text{As}_2\text{S}_3$

In the  $\text{Sb}_2\text{S}_3\text{-As}_2\text{S}_3$  system the atomic percentage of arsenic (As) increases from 4 % to 40 %. The one of antimony (Sb) decreases from 36 % to 0 %. For sulphur (S) atom, the atomic percentage remains equal to 60 %. As replaces Sb, the number of As-S bonds increases at the expense of Sb-S. In the  $\text{Sb}_2\text{Te}_3\text{-As}_2\text{S}_3$  system, the atomic percentages of As and S increase respectively from 16 % to 40 % and from 24 % to 60 %. Those of Sb and tellurium (Te) decrease from 24 % to 0 % and from 36 % to 0 %, respectively. As replaces Sb and Te is substituted by S. It is suggested that the number of As-S bonds increases at the expense of Sb-Te.

#### 3.2. Glass-forming regions

The domain of glass formation in the  $\text{Sb}_2\text{S}_3\text{-As}_2\text{S}_3$  system extends from 10 to 100 mol %  $\text{As}_2\text{S}_3$ .  $\text{Sb}_2\text{S}_3$ -rich compositions having contents lower than 10 mol %  $\text{As}_2\text{S}_3$  do not form glasses. The maximal solubility of  $\text{Sb}_2\text{S}_3$  in the glasses is 90 mol %. The glass-forming region of  $\text{Sb}_2\text{S}_3\text{-As}_2\text{S}_3$  system obtained in this study is wider (from 10 to 100 mol %  $\text{As}_2\text{S}_3$ ) than the one obtained on the same system [7-8] which is extended from 25 to 100 mol %  $\text{As}_2\text{S}_3$ . The glass-forming region of  $\text{Sb}_2\text{Te}_3\text{-As}_2\text{S}_3$  system is between 40 and 100 mol %  $\text{As}_2\text{S}_3$ .  $\text{Sb}_2\text{Te}_3$ -rich compositions having contents less than 40 mol %  $\text{As}_2\text{S}_3$  are crystalline. The maximum solubility of  $\text{Sb}_2\text{Te}_3$  in the  $\text{Sb}_2\text{Te}_3\text{-As}_2\text{S}_3$  glasses is 60 mol %.

By comparing the domains of glass formation obtained in the two binary systems one observes that glass-forming region is reduced when one passes from  $\text{Sb}_2\text{S}_3\text{-As}_2\text{S}_3$  system to  $\text{Sb}_2\text{Te}_3\text{-As}_2\text{S}_3$  system. The substitution of sulphur (low atomic mass equal to 32.1 g/mol) by tellurium (high atomic mass equal to 127.6 g/mol) involves the reduction of glass-forming region. The glass-forming ability of sulphur is higher than that of tellurium. This is in agreement with A. R. Hilton [9]. According to [9], the glass-forming tendency decreases in the order:  $\text{S} > \text{Se} > \text{Te}$  and  $\text{P} > \text{As} > \text{Sb}$ .

From the above considerations, an analysis concerning the glass-forming ability of  $\text{As}_2\text{S}_3$ ,  $\text{Sb}_2\text{S}_3$  and  $\text{Sb}_2\text{Te}_3$  compounds can be done. In the  $\text{As}_2\text{S}_3$  compound, the environment of arsenic atoms is given by a trigonal pyramid  $\text{AsS}_3$  (three sulphur atoms located at 2.28 Å from arsenic atom) and its structural arrangement is two-dimensional (2D) with covalent As-S bonds. Glassy  $\text{As}_2\text{S}_3$  is easily synthesized [10]. For the  $\text{Sb}_2\text{S}_3$  compound the coordination number for antimony atoms is larger than 3 when they form bonds with sulphur atoms. The average coordination number for antimony is greater than the topological threshold for glasses (2.4) [11]. This is in agreement with the results of a  $\text{Sb}_2\text{S}_3$  study where antimony is on two crystallographic sites [12]: one is of the pyramidal type  $\text{SbS}_3$  with bond lengths between 2.52 and 2.54 Å and the other is the square-based pyramid type  $\text{SbS}_5$  with bond lengths between 2.46 and 2.85 Å. The structural arrangement of  $\text{Sb}_2\text{S}_3$  is one-dimensional (1D) with Sb-S bonds less covalent than the As-S bonds. The preparation of  $\text{Sb}_2\text{S}_3$  glass requires high cooling rates [10]. Sb in the  $\text{Sb}_2\text{Te}_3$  compound is found on poorly deformed octahedral sites constituted by three tellurium atoms located at 2.98 Å and three others at 3.17 Å.  $\text{Sb}_2\text{Te}_3$  is a semi-metal with a compact three-dimensional (3D) structure. It does not form glass with usual hardening. It can be concluded that the glass-forming ability of  $\text{As}_2\text{S}_3$ ,  $\text{Sb}_2\text{S}_3$  and  $\text{Sb}_2\text{Te}_3$  compounds is due to the structural arrangement resulting from the condensation of coordination polyhedra (constituent elements) of the framework.

### 3.3. Chemical bond determination

Ordered Bond Network Model suggests that the formation of the heteropolar bonds is favoured over the homopolar bonds. And they are formed in decreasing order of their energies. Each atom is then coordinated by (8-N) atoms where N is the number of valence electrons. In this case, glass is made of the structural units which are the most stable chemical components of the system. The nature of chemical bonds in the glasses can be determined by using the parameter (R) which represents the ratio of covalent bonding possibilities of chalcogen atoms to covalent bonding possibilities of non chalcogen atoms [13]. The value of  $R=1$  represents the case of the existence of only heteronuclear bonds in a given system, which indicates the existence of a chemical threshold. The  $R_1$  and  $R_2$  parameters of  $\text{Sb}_2\text{S}_3\text{-As}_2\text{S}_3$  and  $\text{Sb}_2\text{Te}_3\text{-As}_2\text{S}_3$  glasses can be calculated by using, respectively, the equations below:

$$R_1 = 2z(\text{S}) / (3z(\text{As}) + 3z(\text{Sb})) \quad (1)$$

$$R_2 = (2z(\text{S}) + 2z(\text{Te})) / (3z(\text{As}) + 3z(\text{Sb})) \quad (2)$$

where  $z(\text{S})$ ,  $z(\text{Te})$ ,  $z(\text{As})$  and  $z(\text{Sb})$  are the atomic fractions of S, Te, As and Sb by considering table 1 formulas, respectively. The atomic coordination number is 2 for chalcogens (S, Te) and 3 for non-chalcogens (As, Sb).

The calculation of  $R_1$  and  $R_2$  for each studied glass gives a value equal to 1. This means that all glasses can be then regarded as stoichiometric compositions in which only the heteropolar bonds are present. Stoichiometric glasses were found in  $\text{As}_2\text{S}_3\text{-GeS}_2$  and  $\text{Sb}_2\text{S}_3\text{-GeS}_2$  systems [14].

The bond energies  $D_{A-B}$  for heteronuclear bonds are calculated on the basis of the relation postulated by Pauling [15]:

$$D_{A-B} = (D_{A-A} \times D_{B-B})^{1/2} + 30(X_A - X_B)^2 \text{ (kcal/mole)} \quad (3)$$

where,  $D_{A-B}$  and  $D_{B-B}$  are energies of the homonuclear bonds and  $X_A$  and  $X_B$  are the electronegativity values of the atoms involved. The values of the energies of the homopolar

bonds S-S, Te-Te, As-As and Sb-Sb are 212.762 kJ/mole, 137.94 kJ/mole, 134.18 kJ /mole and 126.24 kJ /mole, respectively. The electronegativities according to Pauling are: As = 2.18; Sb=2.05; S=2.58 and Te=2.10. The relative probability of chemical bonds formation can be calculated by the Boltzmann factors  $\exp(-E/RT) = \exp(D/RT)$ , where D is the bond energy, R the gas constant and T the reaction temperature (at which the samples were prepared during their synthesis) in Kelvins ( $T = 900+273.15=1173.15$  K).

The orders of bond energies and the relative probabilities listed in Tables 2 and 3 indicate that the stronger the chemical bond is, the larger is its forming probability. According to the Ordered Bond Network Model, the chemical bonds in the  $Sb_2S_3$ - $As_2S_3$  glasses must be formed in the order of Sb-S > As-S >> As-Sb. When there is excess Sb and As atoms, the chemical bond As-Sb can be formed. The order established above indicates that the prior formation of the energetic bonds Sb-S leads to pyramidal type structural units: based on  $SbS_3$ . The remaining sulphur will bind to arsenic to give trigonal pyramids units  $AsS_3$  by satisfying the 8-N rule where N is the number of valence electrons. The presence of the structural configurations  $SbS_3$  and  $AsS_3$  in the  $Sb_2S_3$ - $As_2S_3$  glasses was already confirmed by infrared and Raman spectroscopy [16]. This study has shown that these structural units ( $SbS_3$  and  $AsS_3$ ) are connected through sulphur atoms.

Table 2. Bond energy D and relative probability of heteronuclear bonds at 900°C in  $Sb_2S_3$ - $As_2S_3$  glasses

Bond	Bond energy D (kJ/mole) <sup>a</sup>	Relative probability
Sb-S	199.1	1
As-S	189.02	0.355
As-Sb	132.26	$1.053 \times 10^{-4}$

<sup>a</sup>Probability of the Sb-S bond was taken as unity

Table 3. Bond energy D and relative probability of heteronuclear bonds at 900°C in  $Sb_2Te_3$ - $As_2S_3$  glasses.

Bond	Bond energy D (kJ/mole)	Relative probability
S-Te	200.26	1
Sb-S	199.11	0.893
As-S	189.02	0.3174
As-Te	136.86	$1.50 \times 10^{-3}$
Sb-Te	132.276	$9.40 \times 10^{-4}$
As-Sb	132.263	$9.40 \times 10^{-4}$

<sup>a</sup>Probability of the S-Te bond was taken as unity

In the  $Sb_2Te_3$ - $As_2S_3$  system, the chemical bonds can be formed in the following order: S-Te > Sb-S > As-S >> As-Te > Sb-Te = As-Sb (Table 3). The As-Te, Sb-Te and As-Sb bonds will be formed when there are excess of Te, As and Sb atoms. The energetic S-Te bonds are probably used to connect the structural units  $SbS_3$  and  $AsS_3$  announced beforehand in the case of  $Sb_2S_3$ - $As_2S_3$  glasses and which would be found in  $Sb_2Te_3$ - $As_2S_3$  glasses.

On the basis of the above discussion, one can deduce that the network structure of  $Sb_2S_3$ - $As_2S_3$  glasses mainly consists of the strongest Sb-S and As-S bonds, whereas the structure of  $Sb_2Te_3$ - $As_2S_3$  glasses mainly consists of the strongest S-Te, Sb-S and As-S bonds.

A quantitative criterion for predicting which types of materials are likely to be good glass formers has been proposed by Phillips [4, 17], who used a topological viewpoint in which connectivity is measured by the average coordination number Z. One implication of this result is that alloys such as  $a-As_2Se_3$ , which have  $Z=2.4$ , have the ideal network rigidity to optimise both the bond lengths and the bond angles. They should thus be excellent glass formers, i.e. yield amorphous structures after quenching from the melt at a relatively modest rate. The average coordination number Z of the central atom of the coordination polyhedrons of  $Sb_2S_3$ - $As_2S_3$  and  $Sb_2Te_3$ - $As_2S_3$  glasses can be obtained starting from the coordination numbers of the As, Sb, S and



Table 5. Values of thermal characteristics ( $T_g$ ,  $T_x^h$ ,  $T_c^h$  and  $T_m$ ), stability parameters ( $K_{SP}$  and  $K_{WO}$ ) and the optical gap ( $E_g$ ) of  $Sb_2Te_3$ - $As_2S_3$  glasses.

% $As_2S_3$	$T_g$ (K)	$T_x^h$ (K)	$T_c^h$ (K)	$T_m$ (K)	$K_{SP}$	$K_{WO}$	$E_g$ (eV)
50	440	466	474	557	0.473	0.837	0.82
60	443	471	481	559	0.632	0.843	0.88
80	458	497	520	580	1.958	0.857	1.04
90	462	---	---	---	---	---	1.31
100	487	---	---	---	---	---	2.15

---: Absence of thermal properties ( $T_c^h$  and  $T_m$ ) from DSC curves and values of stability parameters ( $K_{SP}$  and  $K_{WO}$ ) cannot be calculated.

DeNeufville and Rockstad [22] proposed and established the empirical relation between  $T_g$ ,  $E_g$  and  $Z$ . They showed that these parameters can be connected by the relation:

$$T_g \approx T_g^0 + \beta(Z-2)E_{04} \quad (6)$$

$T_g$  is the glass transition temperature,  $T_g^0$  is the extrapolated value of  $T_g$  obtained when  $E_{04}$  is equal to 0.  $\beta$  is a linear proportionality constant for value of  $Z$  (the average coordination number).  $E_{04}$  is the energy at which the optical absorption coefficient is  $10^4 \text{ cm}^{-1}$  and is the measure of the optical gap  $E_g$ . The equations of correlation between  $T_g$ ,  $E_g$  and  $Z$  of  $Sb_2S_3$ - $As_2S_3$  and  $Sb_2Te_3$ - $As_2S_3$  systems are obtained by applying (6):

$$T_g \approx 520.8 - 15.72 E_g \quad \text{for } Sb_2S_3\text{-}As_2S_3 \quad (7)$$

$$T_g \approx 413.8 + 34.05 E_g \quad \text{for } Sb_2Te_3\text{-}As_2S_3 \quad (8)$$

Fig. 1 indicates the  $T_g$ - $E_g$ - $Z$  correlation. The contrary evolution of  $E_g$  and  $T_g$  on the  $Sb_2S_3$ - $As_2S_3$  system and the increase in  $E_g$  and  $T_g$  on the  $Sb_2Te_3$ - $As_2S_3$  system enable to suggest that the physical characteristics  $T_g$  and  $E_g$  are not dominated by the structural units of studied glasses because  $T_g$  and  $E_g$  don't vary with  $Z=2.4$ . One can deduce that glasses of  $Sb_2S_3$ - $As_2S_3$  and  $Sb_2Te_3$ - $As_2S_3$  systems are effectively formed by the structural units  $SbS_3$  and  $AsS_3$  which do not change in each system.

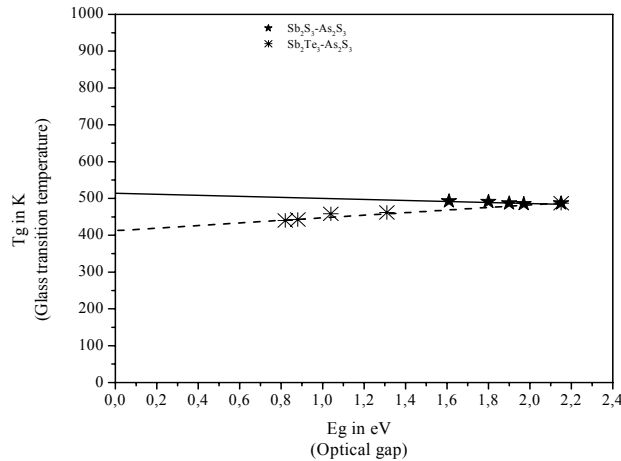


Fig. 1. The glass transition temperature  $T_g$  as a function of the optical gap  $E_g$  for  $Sb_2S_3$ - $As_2S_3$  and  $Sb_2Te_3$ - $As_2S_3$  glasses with fixed value of the average coordination number  $Z=2.4$ .

#### 4. Conclusions

The X-ray diffraction at room temperature is used to confirm the vitreous state of the investigated samples in the  $\text{Sb}_2\text{S}_3\text{-As}_2\text{S}_3$  and  $\text{Sb}_2\text{Te}_3\text{-As}_2\text{S}_3$  systems. This study shows that the substitution of sulphur by tellurium reduces the domain of glass formation because the glass-forming region becomes smaller when one passes from  $\text{Sb}_2\text{S}_3\text{-As}_2\text{S}_3$  system to  $\text{Sb}_2\text{Te}_3\text{-As}_2\text{S}_3$  system. The theoretical study by means of Ordered Bond Network Model indicates that, the studied glasses of the above systems are stoichiometric because of the existence of only heteronuclear bonds in these materials. Thus,  $\text{Sb}_2\text{S}_3\text{-As}_2\text{S}_3$  and  $\text{Sb}_2\text{Te}_3\text{-As}_2\text{S}_3$  glasses are made up mainly of Sb-S and As-S bonds and S-Te, Sb-S and As-S bonds, respectively. The calculated average coordination number ( $Z$ ) of all studied glasses by using the constraints model is 2.4. This implies that no structural phase transition occurs in the glasses. The correlation between  $T_g$ ,  $E_g$  and  $Z$  indicates that these thermal and optical properties are not dominated by the structural units ( $\text{SbS}_3$  and  $\text{AsS}_3$ ) because  $T_g$  and  $E_g$  do not vary with  $Z=2.4$ .

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