Studies of Sb_2S_3-As_2S_3 glasses by quenching methods and Raman spectroscopy

K. N'dri[*], B. M. Dally, C. Vamoussa, D. Houphouët-Boigny
Laboratoire de Constitution et Réaction de la Matière (LCRM)-Groupe de Chimie des Matériaux Inorganiques, UFR-SSMT, Université Félix Houphouët-Boigny de Cocody, 22 B. P 582 Abidjan 22 (Côte d'Ivoire)

Glasses of Sb_2S_3-As_2S_3 system with nominal composition of $As_{0,4x}Sb_{0,4(100-x)}S_{60}$ (where x= 10, 25, 50, 75 and 100 mol% As_2S_3) were investigated by different quenching methods and Raman spectroscopy. All studied samples were in the vitreous state. The average coordination number (Z), being equal to 2.4, has indicated that the numbers of neighbors of non-chalcogens (As and Sb) and chalcogens (S and Te) atoms were respectively 3 and 2. These coordination numbers were conditions fulfilled by the atoms to obtain vitreous materials. The vibrations of the SbS_3 and AsS_3 structural units dominated the Raman spectra of the studied Sb_2S_3-As_2S_3 glasses.

1. Introduction

The glass-forming region of Sb_2S_3-As_2S_3 system is located between 10 and 100 mol% As_2S_3 [1]. The optical and thermal properties of the glasses belonging to this system have been studied [1-7]. Glass-forming ability and glass stability have been studied by using the thermal temperatures such as the glass transition temperature (T_g), the onset crystallization temperature (T_x) and the melting temperature (T_f) [8]. It has been shown the dependence of electronegativity difference (Δx), atomic size parameter (δ) and width of supercooled liquid region (ΔT_x) of Sb_2S_3-As_2S_3 glasses on As_2S_3 content [9]

In this contribution, we investigate the effect of different quenching methods on the nature of the obtained materials in Sb_2S_3-As_2S_3 system. For Sb_2S_3-As_2S_3 glasses whose glass transition temperature is known, the average coordination number of each constituent in all vitreous samples is calculated by using Tanaka's equation. This can enable us to know the average coordination number adopted by the constituents in the vitreous state of the studied Sb_2S_3-As_2S_3 glasses. The structural study concerning these materials is also investigated by Raman spectroscopy in order to identify the type of structural units in the glasses belonging to Sb_2S_3-As_2S_3 system.

2. Glasses preparation

Mixtures of pure (>99.99%) elements with the nominal composition of $As_{0,4x}Sb_{0,4(100-x)}S_{60}$ (where x= 10, 25, 50, 75 and 100 mol% As_2S_3) were prepared by direct synthesis from pure starting elements such as As, Sb, S and Te. Quartz ampoules were filled with the mixed elements and then evacuated to $\sim 10^{-3}$ torr, sealed and heated to 900°C at the rate of 1°C/min. The tubes were held at this temperature for 24 hours. Three quenching methods were used to prepare Sb_2S_3-As_2S_3 glasses. The tubes containing 10%, 25%, 50%, 75% and 100% As_2S_3 were quenched rapidly in ice water. Those having As_2S_3 contents equal 50%, 75% and 100% were slowly quenched in the heating apparatus. Samples with As_2S_3 contents equal to 10% and 25% As_2S_3 were rapidly quenched in

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[*] Corresponding author: ezekmk@yahoo.fr

water at room temperature. Powder X-Ray Diffraction (XRD) was used to show the vitreous state of the samples by recording their patterns using a Philips PW 1050 X-ray diffractometer (with Cu-Kα radiation λ=1.54185Å) and 2θ range from 10 to 60°. The scanning in 2θ steps is 0.04° and the integration time is 3.5s/point.

Raman spectra of Sb_2S_3-As_2S_3 glasses obtained by rapid quenching method in ice water were recorded at room temperature in the range 100-800 cm^{-1} using Horiba Jobin Yvon–LabRAM ARAMIS spectrometer equipped with near infrared laser excitation equal to 785 nm. This laser excitation has been used as a monochromatic luminous source. The spectral resolution of the Raman spectrometer was 1 cm^{-1}. The acquisition time of Raman spectra concerning all studied Sb_2S_3-As_2S_3 glasses was 120 s.

3. Results

3.1. Effect of quenching methods on the X-ray diffraction patterns

Figs. 1 to 5 below show the patterns of Sb_2S_3-As_2S_3 glasses having the same chemical composition and prepared by different quenching methods indicated above.
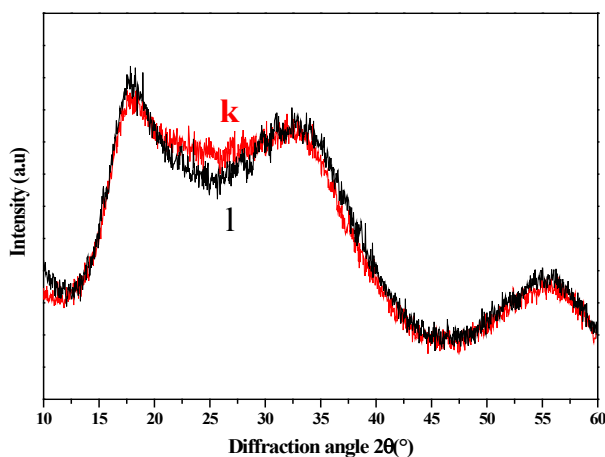

Fig. 1. X-Ray diffraction patterns of rapidly quenched in ice water (k) and slowly cooled in heating apparatus (l) of As_2S_3 glasses.
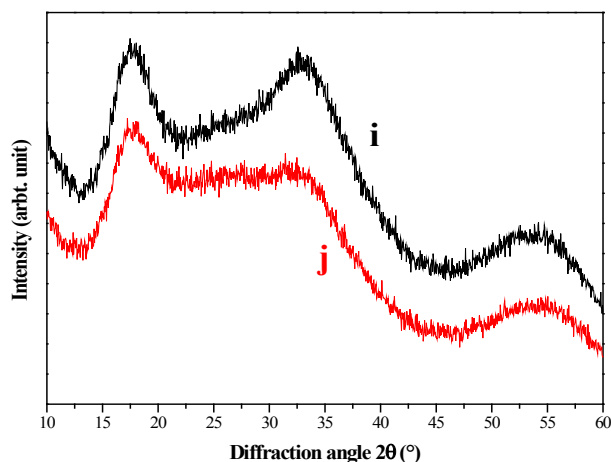

Fig. 2. X-Ray diffraction patterns of rapidly quenched in ice water (j) and slowly cooled in heating apparatus (i) of $25\%Sb_2S_3$-$75\%As_2S_3$ glasses.
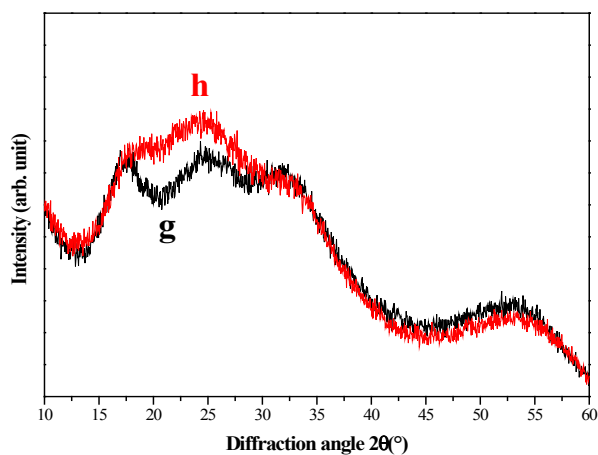
Fig. 3. X-Ray diffraction patterns of rapidly quenched in ice water (h) and slowly cooled in heating apparatus (g) of 50%Sb$_2$S$_3$-50%As$_2$S$_3$ glasses.

Fig. 4. X-Ray diffraction patterns of rapidly quenched in ice water (d) and rapidly quenched at room temperature (c) of 75%Sb$_2$S$_3$-25%As$_2$S$_3$ glasses.

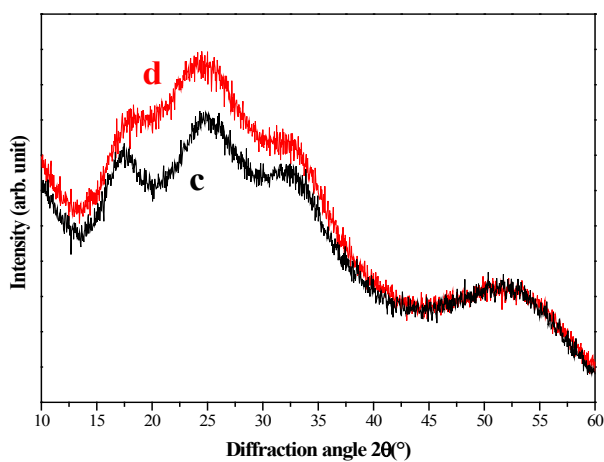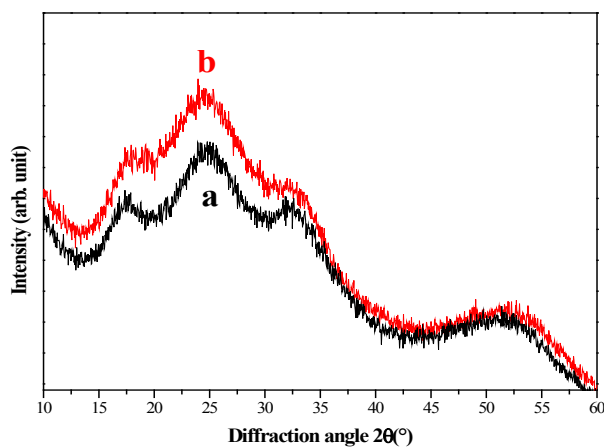*Fig. 5. X-Ray diffraction patterns of rapidly-quenched in ice water (b) and rapidly quenched at room temperature (a) of 90%Sb$_2$S$_3$-10%As$_2$S$_3$ glasses.*

The obtained X-ray diffraction patterns in each case are characterized by three halo diffusion peaks when As_2S_3 content is beyond 50 mol% (figs. 1 and 2) and four halo diffusion peaks for samples having As_2S_3 content below 50 mol% (figs. 3, 4 and 5). For each sample prepared by different quenching methods, the halo diffusion peaks of the diffraction patterns seem to appear at the same values of 2θ as indicated by the above figures.

In the case of glass $As_{40}S_{60}$, the X-ray diffractions patterns are practically the same because they are superimposable (fig.1). For $25\%Sb_2S_3$-$75\%As_2S_3$ glass, the diffractograms are slightly shifted one of the other (fig. 2). This shift is observed for $50\%Sb_2S_3$-$50\%As_2S_3$ (fig. 3), $75\%Sb_2S_3$-$25\%As_2S_3$ (fig. 4) and $90\%Sb_2S_3$-$10\%As_2S_3$ (fig. 5) glasses for 2θ values smaller than $35°$.

3.2. Average coordination number (Z) of glasses by Tanaka's equation

The average coordination number (Z) of a material can be defined as the average of the coordination number of each constituent of this material. It has been proposed by Plillips [10-11] and it measures the connectivity of the materials. For Sb_2S_3-As_2S_3 glasses whose thermal characteristics are known, calculation of their average coordination number (Z) is made by using the equation of Tanaka [12] which connects the vitreous transition temperature (Tg) to the average coordination number (Z). Tanaka's equation expression can be written as follow:

$$T_g = \exp(1{,}6\,Z + 2{,}3) \tag{1}$$

From the above expression, the relation used to calculate Z is:

$$Z = -1{,}4375 + 0{,}625\,LnT_g \tag{2}$$

Table 1 below indicates different values of vitreous transition temperature (T_g) and average coordination number (Z) belonging to the studied binary glasses of Sb_2S_3-As_2S_3 system obtained by rapid quenching method.

Table 1. Vitreous transition temperature (Tg)[1] and average coordination number (Z) of Sb_2S_3-As_2S_3 glasses.

As_2S_3 mol%	Chemical formula	T_g (K) [1]	Z
10	$As_{04}Sb_{36}S_{60}$	493	2,44
25	$As_{10}Sb_{30}S_{60}$	491	2,44
50	$As_{20}Sb_{20}S_{60}$	487	2,43
75	$As_{30}Sb_{10}S_{60}$	485	2,43
100	$As_{40}S_{60}$	487	2,43

The above table indicates that values of the average coordination number (Z) vary slightly on the Sb_2S_3-As_2S_3 system. The variation being very weak, the average coordination number (Z) is constant in the various considered cases and is close to 2.4 calculated numerically by K. N'Dri and D. Houphouet-Boigny [13] for glasses of this binary system.

3.3. Raman study of Sb_2S_3-As_2S_3 glasses

Fig. 6 depicts the Raman spectra of Sb_2S_3-As_2S_3 glasses as a function of Sb_2S_3 content (x) when it increases from 0 to 90 mol %.
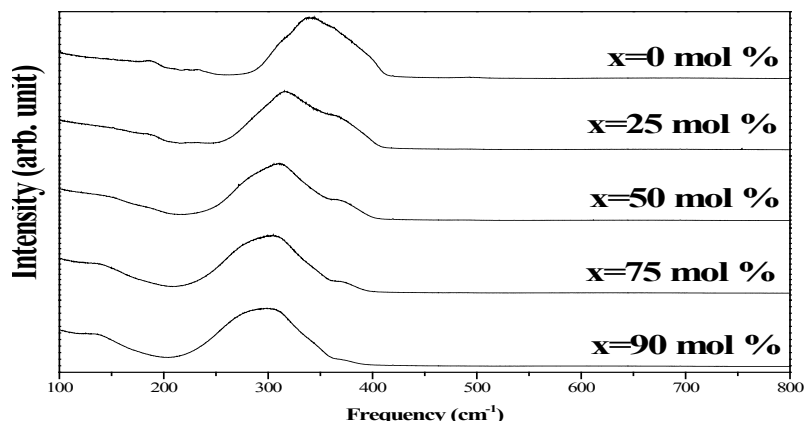
Fig. 6. Raman spectra of Sb$_2$S$_3$-As$_2$S$_3$ glasses as a function of mol % (x) of Sb$_2$S$_3$.

For frequencies between 100 cm^{-1} and 250 cm^{-1}, bands with weak intensities are observed on the Raman spectra of the compositions with Sb$_2$S$_3$ contents equal to 0 mol% (fig. 7) and 25 mol% (fig. 8) and they disappear beyond 25 mol % Sb$_2$S$_3$. These bands, centered at around 186, 221 and 237 cm^{-1}, are in agreement with D. Georgiev et al [14]. There are also two bands (with low intensity) appearing at around 500 cm^{-1} and 686 cm^{-1} respectively (figs. 7 and 8). These bands which appear for higher frequencies are not observed for other glasses of Sb$_2$S$_3$-As$_2$S$_3$ system.
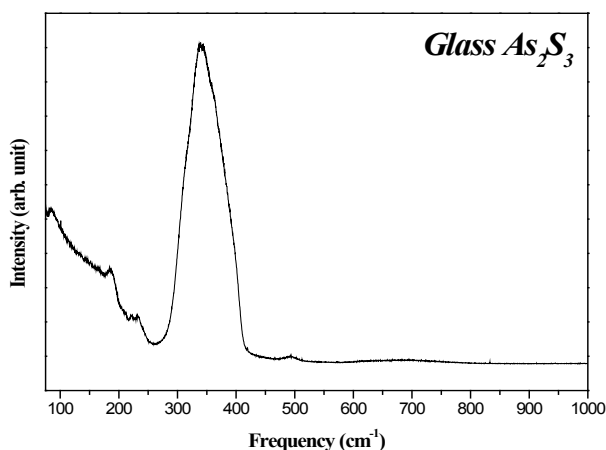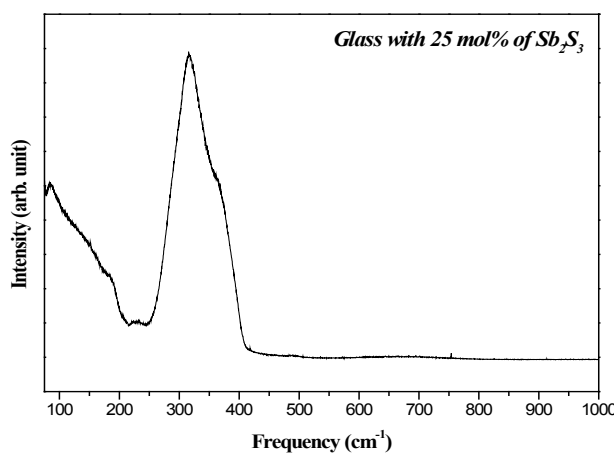

Fig. 7. Raman spectrum of As$_2$S$_3$ glass.

Fig. 8. Raman spectrum of 25%Sb$_2$S$_3$-75%As$_2$S$_3$ glass.

In the 250-400 cm^{-1} region (for glasses with Sb_2S_3 contents equal to 0 and 25 mol%) and in that of 200-400 cm^{-1} (for glasses containing 50, 75 and 90 mol% Sb_2S_3), each of all studied spectra presents an asymmetric dominant feature which is broadened due to the increasing of Sb_2S_3 content from 0 mol% to 90 mol%. This dominant feature has a shoulder (between 360 cm^{-1} and 400 cm^{-1}) whose intensity decreases with increasing of Sb_2S_3 content. Schulte et al [15] have observed a shoulder localized between 380 cm^{-1} to 400 cm^{-1}.

The frequency corresponding to the maximum of the asymmetric dominant feature is displaced from 343.6 cm^{-1} (0% Sb_2S_3) to 291.14 cm^{-1} (90% Sb_2S_3) with the increasing of Sb_2S_3 content. This displacement was observed by M. A. El Idrissi Raghni et al [16]. The frequency of the centered band at 291.14 cm^{-1} (90% Sb_2S_3) is close to 290 cm^{-1} and 293 cm^{-1} observed respectively by M. Rubish [17] and I. D. Turianitsa [18] on the Raman spectra of Sb_2S_3 glasses.

4. Discussions

In spite of different quenching methods used to prepare the samples, all the obtained materials are in the vitreous state because their patterns are characteristic of non-crystalline solids. So the different quenching methods employed in this study can't change the state of the samples. The appearance of the halo diffusion peaks on the X-ray diffraction patterns of glasses at the same values of 2θ can enable us to suggest that the basic structural units of the glasses are preserved.

The calculated value of the average coordination number (Z) equal to 2.4 by using Tanaka's relation indicates that all the studied samples have a layer structure. And the coordination numbers (or the number of neighbors) of non-chalcogens (As and Sb) and chalcogens (S and Te) atoms are respectively equal to 3 and 2. These atoms respect the 8-N rule. Coordination numbers such 3 and 2 are among factors which must be fulfilled by the atoms to obtain vitreous materials in Sb_2S_3-As_2S_3 system.

The centered bands at 186, 221 and 237 cm^{-1} for As_2S_3 glass (also the glass containing 25 mol % of Sb_2S_3) are attributed to As-As bonds in As_4S_4 molecule. The absence of these bands for Sb_2S_3 content above 25 mol% implies the absence of these bonds for frequencies between 100 and 250 cm^{-1}.

The shoulder appearing between 360 and 400 cm^{-1} is caused by the interactions between AsS_3 structural units according to R. Golovchak et al [19]. The decreasing of its intensity with the increasing of Sb_2S_3 content indicates the decreasing of the interactions between AsS_3 structural units because the population of AsS_3 units diminishes at the expensive of SbS_3 units.

The decreasing concerning the frequency of the maximum for dominant feature from 343.6 cm^{-1} (0% Sb_2S_3) to 291.14 cm^{-1} (90% Sb_2S_3) can be explained by the progressive replacement of pyramidal SbS_3 units at the expensive of those of AsS_3 when Sb_2S_3 content increases. The frequency 343.60 cm^{-1} is assigned to the symmetric As-S stretching vibration in the AsS_3 structural units according to R. M. Holomb and V. M. Mitsa [20], G. Lukovsky and R. Martin [21]. The frequency 291.14 cm^{-1} corresponds to the vibration frequency of Sb-S bonds in SbS_3 units. In this case, the vibration frequencies of the structural SbS_3 and AsS_3 units are in the 200-400 cm^{-1} region including that located between 220 and 335 cm^{-1} reported by S. Kharbish et al [22]. The bands of the two types of structural units such as SbS_3 and AsS_3 overlap and form the asymmetric dominant feature.

The band appearing at around 500 cm^{-1} is related to the vibration mode frequency of S-S homopolar bonds in As-S-S-As fragments according to R. Golovchak et al [19] or in S_2As-S-S-AsS_2 unities according to F. Kyriasis et S. N. Yannopoulos [23] in As_2S_3 glass (figure 7) and in the glass containing 25 mol% Sb_2S_3 (figure 8). The broad band (with low intensity) in 600-800 cm^{-1} region and having a maximum around 686 cm^{-1} represents the resonance in the glasses known in molecular systems as Raman resonance effect [24].

5. Conclusions

It has been shown that glasses can be obtained in Sb_2S_3-As_2S_3 system by using different quenching methods. The basic structural units of the glasses are preserved.

The calculated value of the average coordination number (Z) equal to 2.4 by using Tanaka's relation indicates that the number of neighbors of non-chalcogens (As and Sb) and chalcogens (S and Te) atoms are respectively equal to 3 and 2. Coordination numbers equal to 3 and 2 are conditions which must be fulfilled by the atoms to obtain vitreous materials in Sb_2S_3-As_2S_3 system.

It has been shown that Raman spectra of Sb_2S_3-As_2S_3 glasses are dominated by an asymmetric main band which is composed of the structural units such as SbS_3 and AsS_3 derivative respectively from Sb_2S_3 and As_2S_3 compounds.

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262

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