INFRARED REFLECTANCE INVESTIGATION OF THE STRUCTURE OF $xSb_2S_3.(1-x)As_2S_3$ GLASSES

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1. Introduction

Chalcogenide glasses have attracted much attention over the years in light of their technological applications, including infrared transmitting optical elements, acousto-optic and memory switching devices, and materials useful for image creation and storage [1]. In addition, new chalcogenide glass compositions exhibit superionic conducting properties very promising for electrochemical applications [2].

As_2S_3 is the most extensively studied chalcogenide glass mainly because of its ease of formation, its excellent IR transmission and its resistance to atmospheric conditions and chemicals [3]. Even though As and Sb belong to the same group of the Periodic table, As_2S_3 and Sb_2S_3 do not display the same glass-forming tendency. Glassy Sb_2S_3 is very difficult to form because of the high cooling rates required [4]. However, addition of As_2S_3 to Sb_2S_3 enhances greatly the glass-forming ability of the latter, and thus, glasses in the mixed system Sb_2S_3-As_2S_3 can be formed.

It is generally accepted that the three dimensional network of glassy As_2S_3 is built of trigonal pyramidal units, AsS_3, which are interconnected through As-S-As bridges [5-7]. There is also evidence that the intermediate range order of this glass involves two neighboring pyramids and their shared S-atom, with the correlation length being ~ 7Å [8]. The rearrangement of such coupled pyramids with respect to the neighbors has been used to explain properties such as the reversible photoinduced structural changes [8]. Correspondingly, it has been shown that the basic structural units of glassy Sb_2S_3 are the trigonal pyramids SbS_3 bonded to each other by S atoms [4]. It is of interest to note that the resulting network of glassy Sb_2S_3 exhibits lower degree of local disorder around Sb atoms than that of crystalline Sb_2S_3 [9].

Despite the general agreement on the structure of glasses X_2S_3 (X=As, Sb), the structure of glassy materials in the mixed system Sb_2S_3-As_2S_3 remains controversial. Thus, some authors based on the results of various spectroscopic

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techniques, such as EXAFS, XANES, IR and ^{121}Sb-Mossbauer, propose the random substitution of As by Sb and the creation of mixed As-S-Sb bridges [10-13]. On the other hand, others have interpreted the results of IR [14, 15], XRD [15], crystallization kinetics [16] and optical gap measurements [17] as suggestive of a glass structure consisting of heterogeneous phases of As_2S_3 and Sb_2S_3 with little or no interactions between them.

It is clear from the above that further work is required to help resolving existing controversies concerning the structure of these mixed chalcogenide glasses. In this paper we present a systematic infrared reflectance study of glass compositions $xSb_2S_3.(1-x)As_2S_3$ in a wide glass forming region, $0 \leq x \leq 0.75$. The purpose of this investigation is twofold; first, to identify the effect of Sb_2S_3 addition on the local glass structure, and second, to explore the possibility of formation of mixed As-S-Sb bridges.

2. Experimental

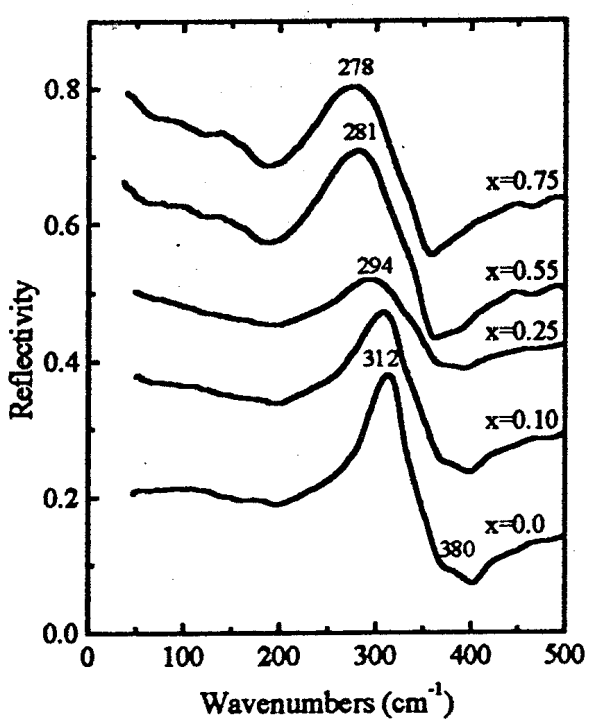
Glasses were prepared by melting stoichiometric mixtures of glassy As_2S_3 and polycrystalline Sb_2S_3 in evacuated (at 10^{-5} Torr) sealed silica ampoules. Melting was performed at 850 °C for *ca* 8 hrs in a rotating furnace in order to ensure homogeneity. Glasses were then obtained by water-quenching the silica tubes. This technique results in $xAs_2S_3.(1-x)Sb_2S_3$ glasses in a continuous glass forming region, $0 \leq x \leq 0.75$. The color of the obtained glasses varies from red to dark red upon increasing Sb_2S_3 content. The bulk glasses were polished to yield flat samples with good quality surfaces appropriate for infrared measurements. It is noted that glassy Sb_2S_3 could not be prepared in dimensions suitable for infrared reflectance measurements.

Infrared spectra were recorded in the reflectance mode at near normal incidence (11° off-normal) on a Fourier-transform vacuum spectrometer (Bruker 113v), using of a high reflectivity Al mirror as reference. A Hg source, a DTGS detector with polyethylene window and five mylar beam splitters with variable thickness (3.5-50 μ) were used in the far infrared region in order to measure continuous spectra in the range 30-700 cm^{-1}. Each spectrum represents the average of 200 scans with 2 cm^{-1} resolution. The measured reflectivity spectra were analyzed through the Kramers-Kronig inversion technique to obtain the absorption coefficient spectra, as well as the optical and dielectric constants, as described in details elsewhere [18, 19].

3. Results and Discussion

Infrared reflection spectra of $xSb_2S_3.(1-x)As_2S_3$ glasses, with Sb_2S_3 contents spanning the entire glass forming region, are presented in Fig. 1. The presented reflectivity spectra are in good agreement with those reported earlier by Kato et al. in the range $0 \leq x \leq 0.60$ [14]. The spectrum of pure As_2S_3 glass (x=0) is characterized by a strong

band at 312 cm^{-1}, a weak feature at 380 cm^{-1} and a weak and broad band at *ca* 100 cm^{-1}. Addition of Sb_2S_3 to As_2S_3 induces systematic spectral changes. Thus, increasing x results in the broadening of the main reflection band and its shifting to lower frequencies (278 cm^{-1} for x=0.75), followed by the progressive weakening of the 380 cm^{-1} feature.



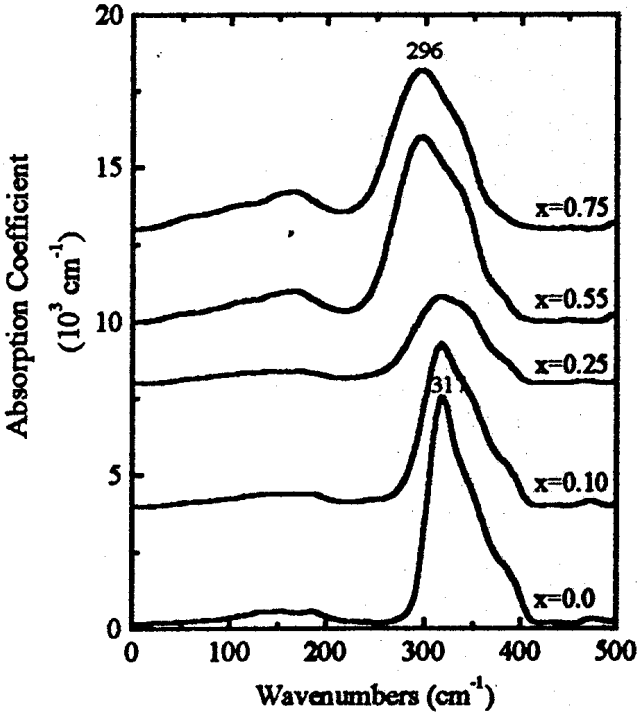


Figure 1(left). Infrared reflection spectra of $xSb_2S_3.(1-x)As_2S_3$ glasses. For x>0, the spectra have been off-set by 0.175, 0.35, 0.35 and 0.5, respectively, to facilitate comparison.

Figure 2 (right). Absorption coefficient spectra of $xSb_2S_3.(1-x)As_2S_3$ glasses. Spectra of glasses $0.1 \leq x \leq 0.75$ have been off-set by 4, 8, 10 and 13 (10^3 cm^{-1}), respectively, to facilitate comparison.

Corresponding changes are observed in the absorption coefficient spectra of these glasses displayed in Fig. 2. The dominant high frequency absorption profile (250-400 cm^{-1}) becomes broader and shifts to lower frequencies upon increasing xSb_2S_3. Also, the absorption envelope below 200 cm^{-1} acquires intensity with x and peaks eventually at *ca* 150 cm^{-1} for x=0.75.

In order to understand the structural origin of these spectral changes with increasing x further analysis of the infrared spectra is required. In particular, we focus attention on understanding the evolution of the complex profile 250-450 cm^{-1}. This is because absorptions due to stretching vibrations of As-S and Sb-S bands are expected in this frequency range. Thus, we have attempted to deconvolute the high frequency envelope, to assign the resulting component bands and to understand their composition dependence. For this purpose we apply in this work a least-squares-fitting program and

a deconvolution procedure employed previously to study binary and ternary glasses (18-21). In this approach, we use the minimum number of component bands that gives a reasonable agreement between experimental and calculated spectra. The functional form, the frequencies, bandwidths and intensities of component bands are parameters adjustable by the program. The steps of the spectral analysis followed here are described below.

We have started the spectral analysis by considering first the spectrum of the As_2S_3 glass (x=0). The profile of the 250-400 cm^{-1} absorption envelope of this glass suggests the existence of at least three component bands (Fig. 2). Indeed, a good fit was obtained with three Gaussian bands, as shown in Fig. 3. The three components, designated by 1As, 2As and 3As, have frequencies 317, 348 and 380 cm^{-1}, respectively. The assignment of these bands can be made on the basis of the molecular model, proposed for the interpretation of the vibrational spectra of As_2X_3 (X=S, Se, Te) glasses [5], and found useful to treat the vibrational spectra of binary glasses such as Li_2S-As_2S_3 [22]. This model considers the modes of vibrationally decoupled AsX_3 pyramids and As-X-As water-like bridging bonds [5]. Thus, in terms of the molecular model, the stronger band at 317 cm^{-1} (1As) is assigned to the asymmetric stretching mode, $\nu_3(E)$, of AsS_3 pyramids, while the one at 348 cm^{-1} (2As) to the symmetric stretching mode, ν_1 (A_1), of the AsS_3 pyramidal units. Besides those modes, AsS_3 pyramids exhibit two bending modes, $\nu_4(E)$ and $\nu_2(A_1)$, which are also infrared active [5] and contribute to the weak absorption in the 100-200 cm^{-1} frequency range. The high frequency component at 380 cm^{-1} (3As) is attributed to the asymmetric stretching vibration of As-S-As bridges, ν_{as}(As-S-As). These assignments are consistent with the Raman spectrum of glassy As_2S_3, which shows strong scattering at 343 cm^{-1} (ν_1), a weaker feature at 312 cm^{-1} (ν_3) and a shoulder at 373 cm^{-1} (ν_{as}(As-S-As)) [6].

The infrared spectrum of a glassy Sb_2S_3 film shows the strongest band at 285 cm^{-1} and a weaker feature at 330 cm^{-1} [23]. Bernier et al. [24] reported the corresponding bands of amorphous Sb_2S_3 dispersed in paraffin at 293 cm^{-1} and 332 cm^{-1}. In analogy with As_2S_3, these bands can be attributed to the ν_3 (~290 cm^{-1}) and ν_1 (330 cm^{-1}) modes of SbS_3 pyramidal units. This suggests that consideration of SbS_3 pyramids is sufficient to explain the infrared spectra of glassy Sb_2S_3 in agreement with Ref. [6]. With the above information in mind, and on the basis of the results of deconvolution of the spectrum of As_2S_3 (x=0), we tried to deconvolute the spectra of mixed Sb_2S_3-As_2S_3 glasses (x>0). As input we used the frequencies and bandwidths of bands 1As, 2As, 3As, as determined for x=0, plus two additional bands at *ca* 290 and 330 cm^{-1} to account for the presence of the Sb_2S_3 components. With these five bands we could fit the 250-450 cm^{-1} spectra quite satisfactorily. Using this approach, we found that in all cases the intensity of the 2As band is equal or even higher than that of the 1As band. There is no reason to believe that the symmetric stretching mode, ν_1 (2As), of AsS_3 pyramids, which is the strongest band in the Raman spectrum of the As_2S_3 glass [6], acquires additional intensity in the infrared spectra of the mixed glasses. Thus, we take this result as suggesting the presence of an additional band close to 2As. When the spectra of mixed glasses were fitted with the input presented above and the consideration of a sixth component at *ca* 350 cm^{-1}, then the relative

intensities of the resulted 1As and 2As components were similar to that in the spectrum of x=0. Typical results of deconvolution are shown in Figure 3. Following the assignments for glassy Sb_2S_3, bands 1Sb and 2Sb are attributed to ν_3 and ν_1 modes of SbS_3 pyramids in the mixed network. The origin of the component denoted by 3Sb/As in Fig.3 will be discussed below.

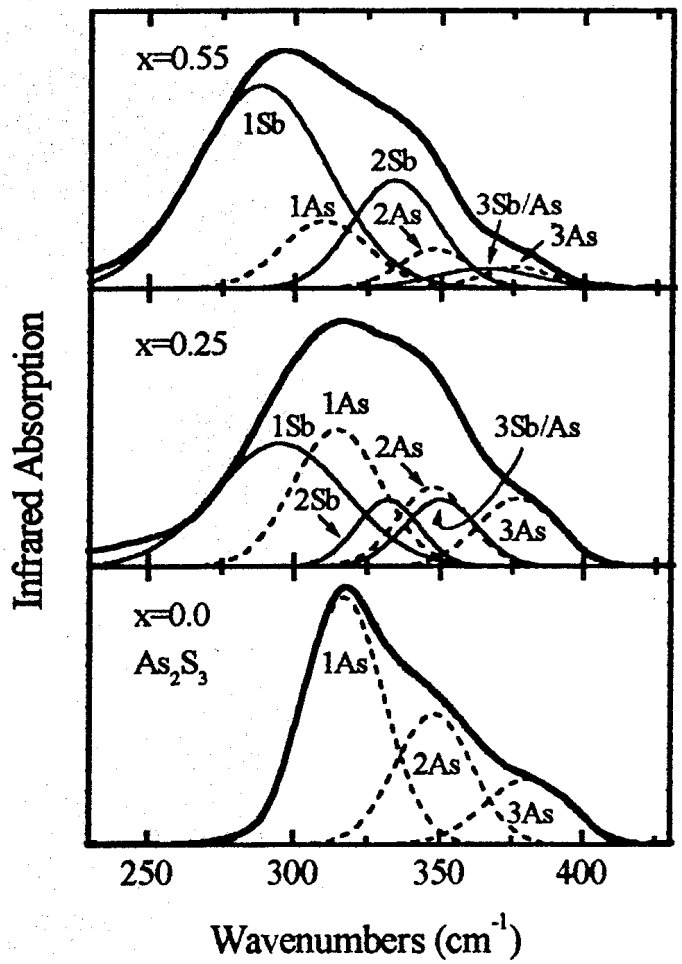
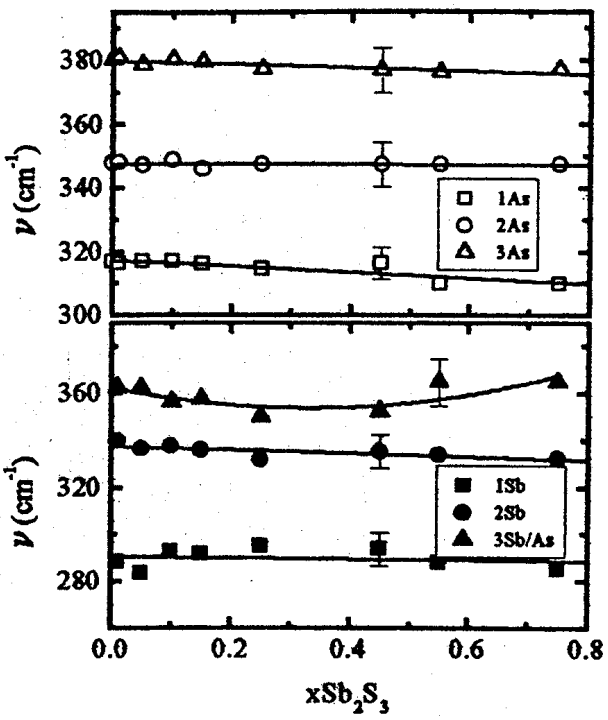


Figure 3. Examples of deconvolution of the higher-frequency envelope 250-450 cm^{-1} (thick lines) of the infrared spectra of $xSb_2S_3.(1-x)As_2S_3$ glasses. The simulated spectra are shown by dotted lines.

The frequencies of the component bands are plotted in Figure 4 versus mole fraction of Sb_2S_3. Besides the frequency of band 3Sb/As the rest of them do not display a great variation with composition, suggesting that the structure of the basic building units, i.e. pyramids AsS_3 and SbS_3, is retained in the mixed glasses. Nevertheless, closer examination reveals some systematic trends with x which deserve our attention. First, it is of interest to note that the difference ν_1(2As)-ν_3(1As) increases with x, while ν_1(2Sb)-ν_3(1Sb) decreases with x. It was demonstrated by Giehler [6] that the frequency difference ν_1-ν_3 of pyramidal XY_3 units depends mainly on the value of the pyramidal angle, Y-X-Y. In particular, ν_1-ν_3 increases when the angle Y-X-Y decreases. On this basis, the observations made above indicate that the pyramidal angle for both pyramids, AsS_3 and SbS_3, decreases in the mixed glass with respect to

the values they have in pure As_2S_3 and Sb_2S_3 glasses. Second, it is observed that the frequency of the 3As band, ν_{as}(As-S-As), decreases with xSb_2S_3. The implication of



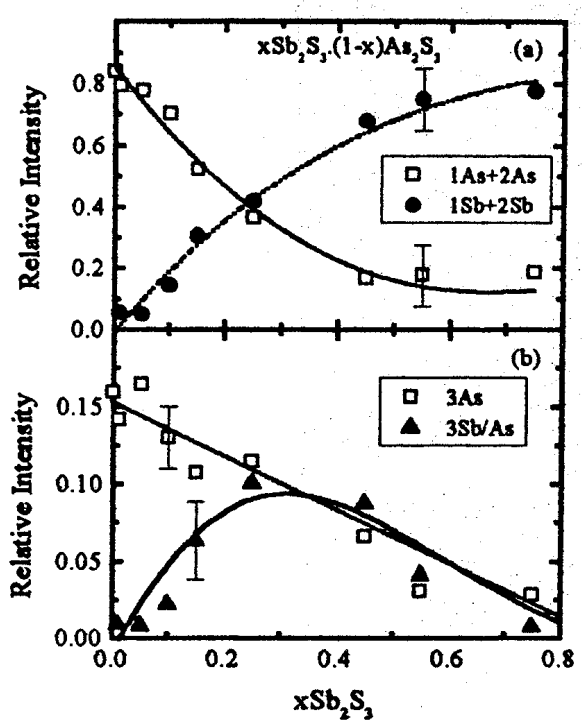


Figure 4 (left). Composition dependence of the frequencies of the component bands resulted from the deconvolution of the 250-450 cm^{-1} absorption envelope (see fig. 3) of xSb_2S_3. $(1-x)As_2S_3$ glasses. Lines are least-squares fitting.
Figure 5 (right). Relative intensities of component bands versus Sb_2S_3 content. Lines are drawn to guide the eye. For details see text.

this trend can be understood in terms of the following formula which gives the frequency of the asymmetric stretching vibration of X-Y-X bridges [25]:

$$\nu^2_{as} = \left(\frac{1}{4\pi^2 c^2}\right)\left[\frac{1}{m_X} + \frac{2}{m_Y}\sin^2\alpha\right]k_r \qquad (1)$$

where m_X, m_Y are the masses of atoms X and Y, respectively, k_r is the force constant of bond X-Y, 2α is the angle X-Y-X and c is the speed of light. If the force constant of the bond As-S does not change upon mixing, then the observed trend of ν_{as}(As-S-As) (3As) suggests, in term of Eq. (1), the decrease of the As-S-As angle upon increasing xSb_2S_3. The variation with x of the frequency of the 3Sb/As band is considered below in connection with the composition dependence of its relative intensity.

Figure 5 shows the composition dependence of the relative intensities of the component bands in the 250-450 cm^{-1} envelope. The intensities of bands 1As and 2As, as well as those of 1Sb and 2Sb, have been considered together (Fig. 5(a)), since they both originate from intramolecular vibrations of the XS_3 pyramids (X=As, Sb). The

relative intensity of bands attributed to AsS_3 pyramids decreases monotonically with xSb_2S_3, while the relative intensity of bands assigned to SbS_3 pyramids increases, as expected. It is noted though that the intensity of bands 1Sb+2Sb relative to that of 1As+2As is considerably higher than would be expected from the mole fraction of Sb_2S_3 alone. The observed differences can be explained if we consider the changes of dipole moment involved in the vibrations of the X-S bonds. Indeed, it has been shown that the effective charge involved in Sb-S bonding is considerably higher than that involved in As-S bonding [6, 14].

The relative intensity of band 3As, characteristic of As-S-As bridges, decreases monotonically with x (Fig. 5(b)). This is consistent with a progressive destruction of such bridges as the As_2S_3 content in the mixed system decreases. The relative intensity of band 3Sb/As displays a non-linear dependence on x, passing through a maximum value at $x\cong0.35$ (Fig. 5(b)). Since the probability for creating mixed As-S-Sb bridges would be maximized at $x\cong0.5$, the composition dependence of the relative intensity of 3Sb/As band is suggesting its assignment to ν_{as}(As-S-Sb).

According to Eq. (1), ν_{as}(As-S-Sb) would depend on an effective force constant, k_{eff}, and on an effective bond angle, As-S-Sb, both of which could be composition dependent. As shown previously [6] $k_{As\text{-}S}>k_{Sb\text{-}S}$, therefore k_{eff} is expected to decrease with x. On the other hand, the bridging angle, X-S-X, was estimated to be 99.5° in the As_2S_3 glass and 100.7° in Sb_2S_3 glass [4]. Thus, the effective angle As-S-Sb would increase with x. The combined effect of both factors could lead, according to Eq. (1), to a minimum value of ν_{as}(As-S-Sb) with composition. The composition dependence of the frequency of the 3Sb/As band (Fig. 4) is in accord with the proposed assignment.

The infrared results discussed above are supportive of the models proposing the random substitution of As by Sb, rather than the formation of heterogeneous As_2S_3 and Sb_2S_3 phases connected at the interfaces via mixed As-S-Sb bridges. If the latter proposition were true then one would expect that at least the intramolecular vibrations of XS_3 pyramids, in the two different microphases, would be independent of composition. However, this was not observed in the present work. In particular, the systematic variations with x of especially the ν_1 and ν_3 modes of the pyramids (Fig. 4), is indicating considerable neighboring of the AsS_3 and SbS_3 pyramids.

4. Conclusions

The structure of glasses in the mixed system $xSb_2S_3.(1\text{-}x)As_2S_3$ has been investigated in a wide composition range ($0\leq x\leq0.75$) employing infrared reflectance spectroscopy. The high frequency profiles (250-400 cm^{-1}) of the absorption coefficient spectra were deconvoluted into component bands in order to study the composition dependence of the glass structure. The main components of the deconvoluted spectra were understood on the basis of the intramolecular vibrations of trigonal AsS_3 and SbS_3 pyramids. While the structure of such pyramids is basically retained, it was found that the pyramidal S-X-S angle (X=As, Sb) decreases upon mixing. The destruction of As-S-As

bridges with increasing Sb_2S_3 content was found to be accompanied by the creation of mixed As-S-Sb bridges with their relative abundance showing maximum value at *ca* x=0.35. It was concluded that the composition dependence of the frequencies and relative intensities of the component bands found in this work is suggestive of a considerable mixing of AsS_3 and SbS_3 pyramids, rather than of the formation of separate As_2S_3 and Sb_2S_3 microphases.

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