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Far infrared transmission study of the ternary system Sb_2S_3–As_2S_3–Tl_2S

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Abstract

The local environment of metal (arsenic and antimony) atoms in amorphous samples of the ternary system As_2S_3–Sb_2S_3–Tl_2S has been studied by far infrared transmission spectroscopy. Variations in shape and position of observed bands are attributed to changes in the nature of the coordination patterns of the arsenic and antimony atoms. The variations reveal the different influences of the glass forming arsenic sulfide and antimony sulfide and the glass modifying thallium sulfide on the respective host matrices. The results presented here confirm the hypotheses established previously on the basis of studies of this system by EXAFS at the arsenic K-edge and by XAS at the sulfur K- and antimony L_{III}-edges.

Keywords: Amorphous alloys; As–Sb–Tl–S alloys; Infrared transmission spectroscopy; Local environment

1. Introduction

A study of the structure of amorphous semiconductors is important in understanding their specific physical properties as well as their applications in electronic devices.

Optical investigations such as Raman scattering and infrared reflection and absorption are especially useful in obtaining information on the local structure of disordered solids. Thus, infrared transmission spectroscopy is one of the most widely used techniques for the characterization of the local structure [1–16]. For amorphous materials, however, the results of several different techniques must be compared in order to establish a structural model.

In our previous papers [17–19], we reported on a study of the ternary system Sb_2S_3–As_2S_3–Tl_2S by means of EXAFS at the arsenic K-edge [17] and XAS at the sulfur K- [18] and antimony L_{III}-edges [19]. The study of this system is of particular interest owing to its wide domain of glass formation. Our previous studies [17–19] revealed the possibility of varying considerably the structural features of the glasses belonging to this system by changing their stoichiometry. The structural variety is due to the strongly different properties of the three basic binary sulfides. Sb_2S_3 and As_2S_3 are both glass forming compounds, while Tl_2S is a glass modifying compound. Arsenic usually obeys the "8-N" rule, which means that its coordination number is determined by the number of electrons needed to complete its valence shell. Arsenic is therefore found in a pyramidal AsS_3E-type environment [17] (with E the "lone pair" of 4s electrons not involved in chemical bonds). Antimony does not obey this rule and can be found in several different environments, usually described as SbS_xE with $x = 3$, 4 or 5.

Studies at the As K- and Sb L_{III}-edges have already provided an insight into the structural modifications that can be achieved by each of the three basic compounds. It was shown that the binary system Sb_2S_3–As_2S_3 is characterized by a random substitution of arsenic by antimony, in agreement with a model proposed earlier by Bychkov et al. [20]. Thal-

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lium sulfide was found to crack the As–S–As bridges present in the As_2S_3 host matrix and to lead to terminal As–S bonds, which confirms the results of Heo et al. [15]. The influence of Tl_2S on the Sb_2S_3 host matrix lies in an increase of the fraction of SbS_3E units and a reduction of the number of SbS_4E- and SbS_5E-type coordinations. This picture is altered when all three sulfides are present simultaneously. Adding Sb_2S_3 to an already Tl_2S-doped As_2S_3 matrix reduces the number of terminal As–S bonds by virtue of the formation of As–S–Sb bridges with SbS_4E and SbS_5E units. Introduction of As_2S_3 into an Sb_2S_3 matrix already containing Tl_2S gives rise to a higher fraction of SbS_4E and SbS_5E units.

The aim of this paper is to complete the investigation of the Sb_2S_3–As_2S_3–Tl_2S system by a far infrared transmission study, which is expected to confirm the results of the preceding work [17–19].

2. Experimental

The amorphous samples were synthesized in two steps. First the binary sulfides Sb_2S_3, As_2S_3 and Tl_2S were prepared by direct reaction from stoichiometric mixtures of the elements in evacuated tubes ($p = 10^{-3}$ Pa). Then, mixtures of these binary sulfides were heated in evacuated tubes up to about 1173 K for 1 h under permanent shaking and then quenched in a mixture of water, ice, and salt. Finally, the glasses were kept for two days at a temperature 50 K below that of their respective glass transition temperature in order to stabilize the glasses. This procedure minimizes mechanical strain caused by quenching.

X-ray diffraction with Cu Kα radiation revealed that all samples were amorphous. The diffraction patterns showed no sharp or intense Bragg reflection, but several scattering fringes. Additionally, the thermal properties of the samples, like the glass transition temperature T_g, crystallization temperature T_c, and melting temperature T_m, were measured by differential thermal analysis, which also proved that the synthesis led to amorphous compounds. The uniformity and homogeneity of the amorphous compounds were also checked by electron microscopy.

3. Background

Far infrared transmission measurements were carried out in vacuum with a Bomem DA8 Fourier transform spectrometer in the spectral range 200–700 cm^{-1}.

This spectrometer is equipped with a global source, a mylar (3 μm) beamsplitter and a DTGS detector. Each spectrum is the sum of 150 runs over the whole spectral range with a spectral resolution of 3 cm^{-1}. The samples were prepared using the polyethylene pellet method.

Vitreous compounds are usually described as being composed of a large number of smallest molecular units, arranged in a more or less disordered manner. In vitreous compounds, the assignment of an observed infrared absorption frequency to a corresponding vibrational mode depends, therefore, on the choice of this molecular unit. In vitreous compounds like As_2S_3 and Sb_2S_3, the molecular unit usually selected is the pyramidal XS_3E (X = As or Sb) unit. In addition, it is assumed that the XS_3E coordination patterns are not strongly linked to each other. To take account of these interactions, it is possible to introduce an X–S–X unit (sulfur bridges) similar to the hydrogen bridges between water molecules. The pyramidal XS_3E-type environment has a C_{3v} symmetry. It has four vibrational modes (Fig. 1): two symmetric modes, stretching ν_1 (A_1) and bond bending ν_2 (A_1); and two antisymmetric modes (doubly degenerate), stretching ν_3 (E) and bond bending ν_4 (E).

In an amorphous solid, it can be argued that all vibrational modes should be both infrared and Raman active due to a breakdown of selection rules. This may well apply to amorphous Si and Ge, but does not apply to vitreous As_2S_3 and Sb_2S_3. The dominant infrared (ν_3) and Raman (ν_1) modes occur at different frequencies, corresponding respectively to the antisymmetric and symmetric stretching modes of the pyramidal unit. Owing to the weak intermolecular coupling, these modes retain their inherent symmetry and are only observed in their respective spectra.

For the fundamental molecular AsS_3E unit of the vitreous compound As_2S_3, the set of bibliographic data is in agreement with the assignment of the observed infrared absorption frequencies to the stretching modes ν_1 and ν_3. The frequency of the

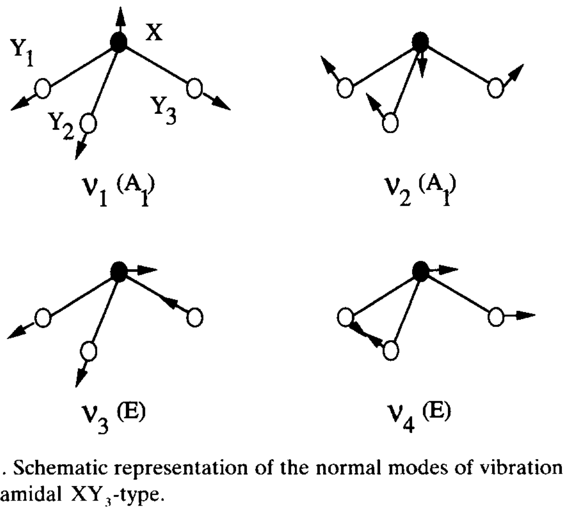

Fig. 1. Schematic representation of the normal modes of vibration of a pyramidal XY_3-type.

(Raman active) symmetric stretching mode ν_1 is 340 cm^{-1}. The frequency of the (infrared active) antisymmetric stretching mode ν_3 is 310 cm^{-1}. We can cite the work of Lucovsky et al. [2] who interpreted the frequencies of the four vibrational modes of the pyramidal AsS_3E-type coordination by reference to a pyramidal $AsCl_3E$ coordination pattern. Indeed, the frequency of classical oscillators is, in general, given by $\nu = (2\pi)^{-1}(K/M)^{1/2}$, where K is the force constant and M the mass of the oscillator. The molecular model states that the vibrational frequencies of a certain molecule can be calculated from the known frequencies of a molecule with a similar structure, i.e. by scaling the mass ratio and the force constant ratio. Consequently, the frequencies of principal modes of the pyramidal AsS_3E units can be derived from the known frequencies of the principal modes of the pyramidal $AsCl_3E$ units. Using the ratio of the frequencies of the vibrational mode ν_1 (Raman active) of two coordination patterns, Lucovsky et al. [2] determined the frequencies 162, 310, and 133 cm^{-1} for the vibrational modes ν_2, ν_3 and ν_4 respectively.

For the pyramidal molecular SbS_3E unit of the vitreous compound Sb_2S_3, the set of bibliographic data does not agree with the assignment of the frequency of stretching modes ν_1' and ν_3'. Kato et al. [8] determined the frequencies ν_1' and ν_3' for vitreous compounds of the system Sb_2S_3–As_2S_3 by infrared and Raman spectroscopy. Raman spectroscopy gave a frequency ν_1' of 297 cm^{-1} and extrapolation of the infrared data gave a frequency ν_3' of 270 cm^{-1}. Sun et al. [14] investigated vitreous compounds of the system Sb_2S_3–AgI. The infrared transmission spectrum of the vitreous compound Sb_2S_3 showed a strong band at 275 cm^{-1} which they attributed to the stretching mode ν_3' of the pyramidal SbS_3E unit. Barnier et al. [16] have studied the vitreous compounds of the system GaS_2–Sb_2S_3. The infrared transmission spectrum obtained for the vitreous compound Sb_2S_3 has two large bands, one of medium intensity observed at 154 cm^{-1} and another of very strong intensity at 293 cm^{-1}, and two shoulders (136 and 332 cm^{-1}). They attributed these various frequencies to the four vibrational modes of the pyramidal SbS_3E units ($\nu_1' = 332$ cm^{-1}, $\nu_2' = 154$ cm^{-1}, $\nu_3' = 293$ cm^{-1} and $\nu_4' = 136$ cm^{-1}).

This research should permit the determination of the frequency of the stretching mode ν_3' of the pyramidal SbS_3E units.

4. Results and discussion

In this section we will present and discuss the results obtained for amorphous samples and also for several crystalline compounds of the system Sb_2S_3–As_2S_3–Tl_2S, for which precise crystallographic data are available. The left panel of Fig. 2 shows the positions of the crystalline compounds studied here within the Sb_2S_3–As_2S_3–Tl_2S phase diagram, where the shaded area represents the domain of glass formation. The right panel shows the positions of the amorphous compounds with their numbering used throughout this paper. The exact composition of the amorphous samples is given in Table 1.

4.1. Binary system Sb_2S_3–As_2S_3

The far infrared transmission spectra of the vitreous compounds of the binary system Sb_2S_3–As_2S_3 are shown in Fig. 3.

The infrared transmission spectrum of the vitreous compound As_2S_3 (Fig. 3A) consists principally of a wide band (labeled A) of strong intensity at about 310 cm^{-1} and a shoulder (labeled B) at about 380 cm^{-1}.

The band A is attributed to the stretching mode ν_3 of the pyramidal AsS_3E unit, in agreement with a previous study. The shoulder B has been attributed by Kato et al. [8] to the sum of the two frequencies 348 and 386 cm^{-1} found in the spectrum of crystalline As_2S_3 [21–22]. In crystalline arsenic sulfide, arsenic is found in a pyramidal AsS_3E unit with bridging As–S

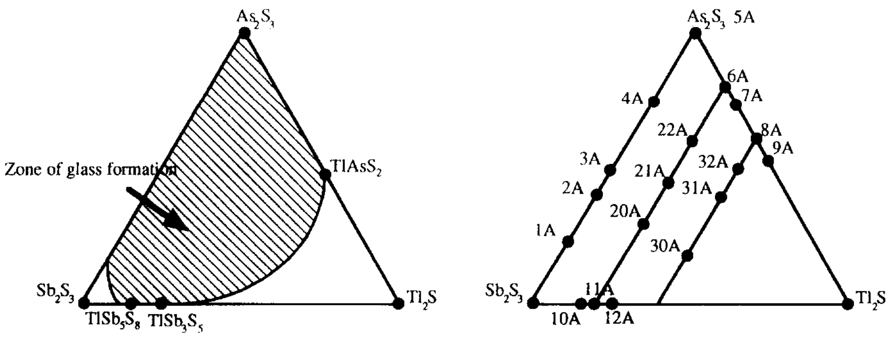

Fig. 2. Crystalline compound, numbering and positions of the glassy samples in the Sb_2S_3–As_2S_3–Tl_2S system. The region of glass formation is hatched.

Table 1
Composition of the amorphous samples

Vitreous compound	Sb_2S_3 (%)	As_2S_3 (%)	Tl_2S (%)
1A	80	20	0
2A	60	40	0
3A	50	50	0
4A	25	75	0
5A	0	100	0
6A	0	80	20
7A	0	72.8	27.2
8A	0	60	40
9A	0	50	50
10A	83.3	0	16.7
11A	80	0	20
12A	75	0	25
20A	50	30	20
21A	35	45	20
22A	20	60	20
30A	40	20	40
31A	20	40	40
32A	10	50	40

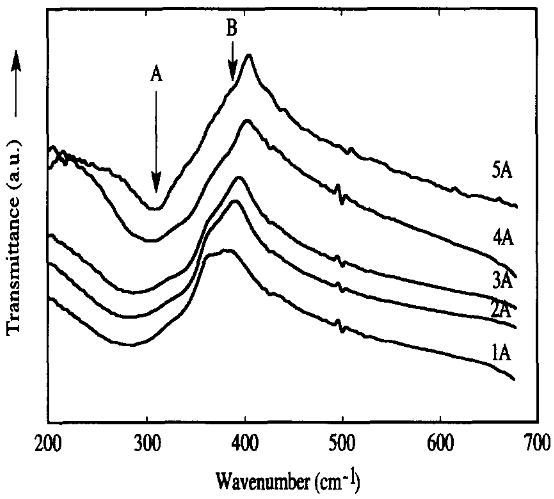

Fig. 3. Far infrared transmission spectra of the vitreous compounds of the Sb_2S_3–As_2S_3 binary system.

bonds. The preceding XAS study at the S and As K-edges [17] showed that the local environments of the arsenic and sulfur atoms in vitreous and crystalline compounds As_2S_3 are similar. The infrared transmission spectrum of the vitreous compound As_2S_3 seems to confirm this result.

As the Sb_2S_3 concentration increases, band A becomes broader and is shifted towards lower wavenumbers. The results of EXAFS at the As K-edge [17] and of XAS at the Sb L_{III}- [18] and S K-edges [19] showed that the binary system Sb_2S_3–As_2S_3 is characterized by a random substitution of arsenic by antimony. Thus, in accordance with earlier work, the widening and shift of the band A can be attributed to the existence of the antisymmetric stretching mode ν_3' of the pyramidal SbS_3E units.

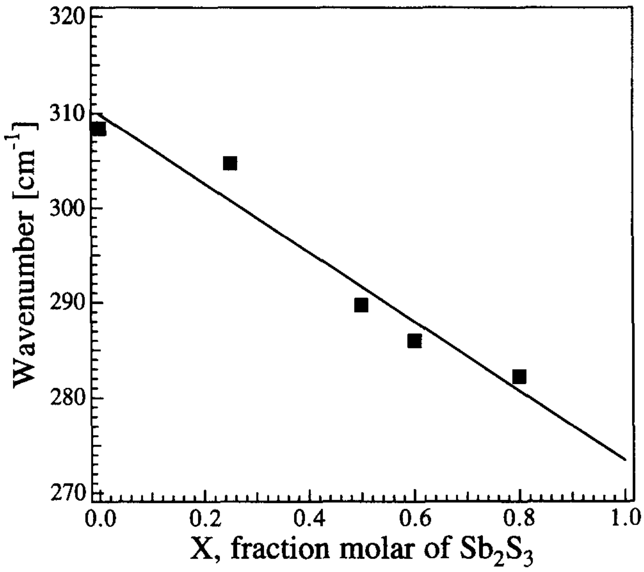

Fig. 4. Wavenumbers of band A with Sb_2S_3 concentration in the Sb_2S_3–As_2S_3 binary system.

The change in frequency of band A with Sb_2S_3 concentration is almost linear (Fig. 4). By extrapolation we can thus determine the frequency of the antisymmetric stretching mode ν_3' of the pyramidal SbS_3E units. The value obtained, around 275 cm^{-1}, corresponds to the values reported by Kato et al. [8] and Sun et al. [14].

4.2. Binary system As_2S_3–Tl_2S

The far infrared transmission spectra of the vitreous compounds of the binary system As_2S_3–Tl_2S are shown in Fig. 5.

As the Tl_2S concentration increases, the principal band (labeled A) is displaced towards lower wavenumbers (Fig. 6) and the band (labeled B) at about 390

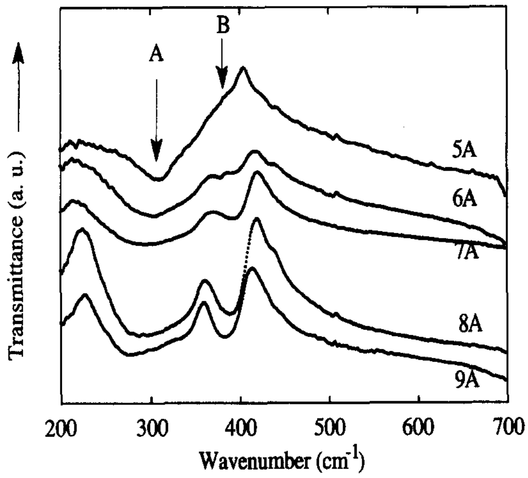

Fig. 5. Far infrared transmission spectra of the vitreous compounds of the As_2S_3–Tl_2S binary system.

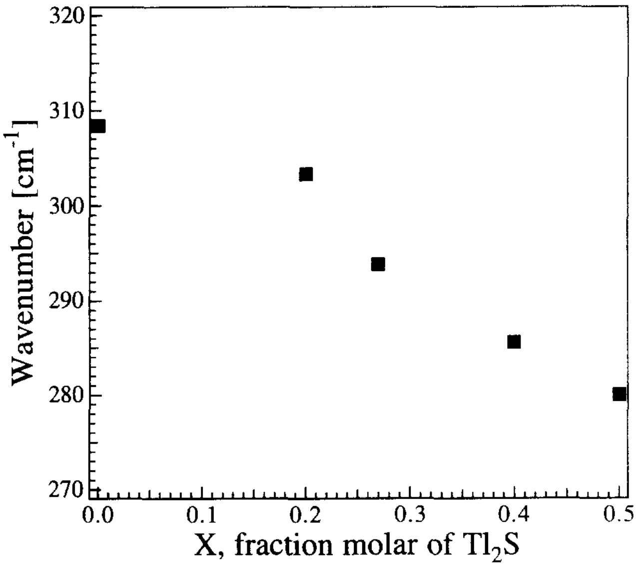

Fig. 6. Wavenumbers of band A with Tl_2S concentration in the As_2S_3–Tl_2S binary system.

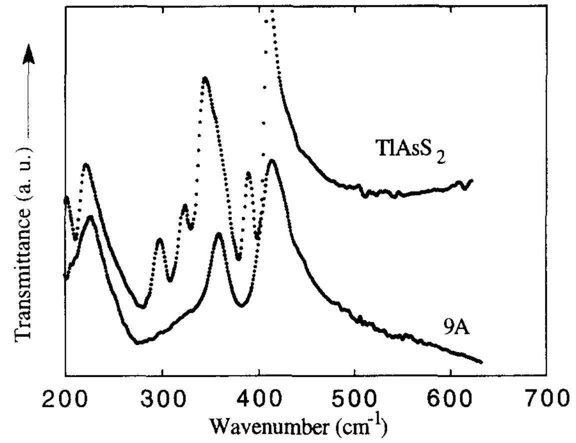

Fig. 7. Comparison of infrared transmission spectra of the crystalline and vitreous compounds $TlAsS_2$.

cm^{-1} increases in intensity. The spectrum of the vitreous compound 6A (80 mol.% As_2S_3 + 20 mol.% Tl_2S) is characterized by an additional narrow band at 378 cm^{-1}. EXAFS at the arsenic K-edge [17] has revealed modifications in the As_2S_3 host matrix caused by the introduction of Tl_2S. In fact, thallium sulfide breaks the As–S–As bridges and leads to terminal As–S bonds. The terminal As–S bonds are shorter than the bridging As–S–As bonds. The symmetry of the pyramidal AsS_3E unit formed by the As–S bonds of various lengths (bridging and terminal) alters from C_{3v} to C_s symmetry, and degeneracy of the antisymmetric modes of the pyramidal AsS_3E unit (ν_3 (E) and ν_4 (E)) results. Finally, the six vibrational modes become active in the infrared. The presence of these additional modes explains the widening of band A seen in vitreous compounds when thallium sulfide is introduced into the As_2S_3 host matrix.

In addition, we compared the infrared transmission spectrum (Fig. 7) of the crystalline compound $TlAsS_2$ with that of the vitreous compound 9A ($TlAsS_2$). The spectrum of the crystalline compound $TlAsS_2$ includes a large number of peaks (280, 310, 330, 380, and 400 cm^{-1}). It appears that bands A and B are derived from the sum of the 280, 310 and 330 cm^{-1} peaks and of the 380 and 400 cm^{-1} peaks respectively. Our earlier work using X-ray absorption [17] showed that the local environment of the arsenic atoms in the vitreous compound 9A ($TlAsS_2$) is very similar to that of its crystalline homologue $TlAsS_2$. The infrared transmission spectra of the crystalline compound $TlAsS_2$ and of the vitreous compound 9A ($TlAsS_2$) seem to confirm the earlier result.

It is very difficult to attribute each of these peaks without carrying out a study on a single crystal. In the compound As_2S_3 [23], arsenic is found in two different sites of the pyramidal AsS_3E units. The three As–S bonds are bridging and the symmetry of the sites is thus C_{3v}. In the compound $TlAsS_2$ [24], arsenic occupies two different sites of the pyramidal AsS_3E-type. Each site has two bridging bonds and one terminal bond and the symmetry of the sites is therefore C_s. The infrared transmission spectra of the crystalline compounds As_2S_3 and $TlAsS_2$ have respectively three (309, 354 and 383 cm^{-1} [21]) and five vibrational modes in the spectral range 200–700 cm^{-1}. The two vibrational modes of the compound As_2S_3 with the lowest frequencies can be attributed to molecular stretching modes for the frequencies, and the last mode to interactions between the pyramidal AsS_3E units [22]. In crystalline compounds, the change from C_{3v} to C_s symmetry in the pyramidal AsS_3E units is accompanied by an increase in the number of active vibrational modes in the infrared. For vitreous compounds within the same spectral range we can state that the vibrational modes of the pyramidal AsS_3E units having a C_{3v} symmetry are principally: the stretching mode ν_1 with a frequency close to 340 cm^{-1}; the stretching mode ν_3 with a frequency centered on 310 cm^{-1}; and the mode ν_c (with a frequency close to 390 cm^{-1}) linked to interactions with pyramidal AsS_3E units [22].

Only the stretching mode ν_3 is active in the infrared. The other two modes are active in the infrared as a result of intermolecular coupling. They can be observed in the infrared transmission spectrum of the crystalline compound As_2S_3 [8].

The vibrational modes of the pyramidal AsS_3E units with a C_s symmetry are mainly: the stretching mode ν_1 with a frequency close to 330 cm^{-1}; the stretching modes ν_{3a} and ν_{3b} resulting from the degeneracy of the mode ν_3 with frequencies close to 280 and 310 cm^{-1}

respectively; and the stretching modes ν_{ca} and ν_{cb} (with frequencies close to 380 and 400 cm^{-1} respectively) resulting from the degeneracy of the mode ν_c.

All these vibrational modes are active in the infrared.

The bands A and B of the vitreous compound 9A ($TlAsS_2$) can be attributed to the sum of modes ν_1, ν_{3a} and ν_{3b} and of modes ν_{ca} and ν_{cb} respectively. The creation of terminal As–S bonds, implying a change in the symmetry of pyramidal AsS_3E units from C_{3v} to C_s, leads: for band A to a widening (three vibrational modes) and a reduction in the value of the frequency; and for band B to an increase in intensity and a widening resulting from the two vibrational modes.

The presence of the two modes explains the appearance of band C observed in the spectrum of the vitreous compound 80 mol.% As_2S_3 + 20 mol.% Tl_2S.

As the concentration of Tl_2S increases, the shift of band A towards lower wavenumbers (Fig. 6) and the increase in intensity of band B reveals an increase in the number of pyramidal AsS_3E units of C_s symmetry and, consequently, in the number of terminal As–S bonds.

4.3. Binary system Sb_2S_3–Tl_2S

The range of glass formation of this system Sb_2S_3–Tl_2S is doubtless too small to derive general trends for far infrared transmission spectra of the amorphous samples with sample composition.

In the small domain of glass formation, there are two crystalline compounds $TlSb_5S_8$ (83.3 mol.% Sb_2S_3 + 16.7 mol.% Tl_2S) and $TlSb_3S_5$ (75 mol.% Sb_2S_3 + 25 mol.% Tl_2S). In the compound $TlSb_5S_8$ [25,26], antimony occupies ten crystallographically different sites, six of the pyramidal SbS_3E-type, three of the triangular-based bipyramidal-type SbS_4E, and one of the square-based pyramid SbS_5E. The compound $TlSb_3S_5$ [26,27] is characterized by three different antimony sites. Two of them are of the SbS_3E-type and the third is of the SbS_4E-type. These two thallium compounds are remarkable as far as the ionic behavior of the thallium atoms is concerned. In the compound Sb_2S_3 [28], antimony is found on two crystallographically different sites. One is of the pyramidal SbS_3E-type and the other is of the SbS_5E-type.

The infrared transmission spectra of the crystalline compounds Sb_2S_3, $TlSb_5S_8$ and $TlSb_3S_5$ are compared with those of the vitreous compounds 10A ($TlSb_5S_8$) and 12A ($TlSb_3S_5$) in Fig. 8. The infrared transmission spectra of vitreous compounds 10A ($TlSb_5S_8$) and 12A ($TlSb_3S_5$) show a large band centered at 280 and 275 cm^{-1} respectively. Those of the crystalline compounds consist of many peaks which are very difficult to attribute. In these compounds, antimony occupies sites of different coordination type. In addition, in contrast to the observations for vitreous 9A ($TlAsS_2$), the spectra of vitreous 10A ($TlSb_5S_8$) and 12A ($TlSb_3S_5$) do not correspond to those of the crystalline compounds except where the peak is broad. The local environment of antimony atoms in vitreous compounds thus differs from that in the crystalline samples. This result is in agreement with earlier research, which demonstrated that in vitreous compounds of binary Sb_2S_3–Tl_2S the coordination patterns of antimony are principally of the pyramidal SbS_3E-type. By way of contrast, in the crystalline compounds Sb_2S_3, $TlSb_5S_8$ and $TlSb_3S_5$, a non-negligible fraction of SbS_4E and SbS_5E sites is found.

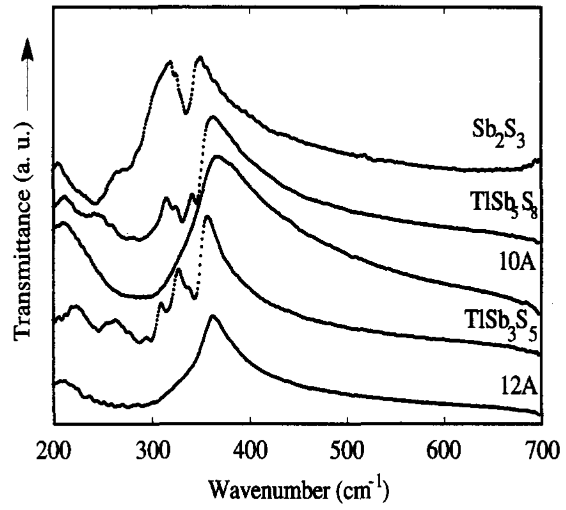

Fig. 8. Comparison of infrared transmission spectra of the crystalline compounds Sb_2S_3, $TlSb_3S_5$, and $TlSb_5S_8$ with those of the vitreous compounds $TlSb_3S_5$ and $TlSb_5S_8$.

4.4. Ternary system Sb_2S_3–As_2S_3–Tl_2S

Two series of samples were examined, one with a constant concentration of 20% Tl_2S and another with 40% Tl_2S. The far infrared transmission spectra of the former are shown in Fig. 9, the spectra of the latter in Fig. 10.

The infrared transmission spectra of the vitreous compounds with constant concentration of 20% and 40% of Tl_2S show a broad band (labeled A) and a second, narrower band (labeled B), the latter being found at about 380 cm^{-1} with the exception of the vitreous compound 11A (80 mol.% Sb_2S_3 + 20 mol.% Tl_2S). In addition, the spectra of the vitreous compound 6A (80 mol.% As_2S_3 + 20 mol.% Tl_2S) has a band C centered at 400 cm^{-1}. The bands B and C can be attributed to the vibrational modes ν_c, ν_{ca} and ν_{cb}. When the concentration of Sb_2S_3 is increased, the intensity of bands B and C decreases for both constant concentrations of Tl_2S. This reveals a change in

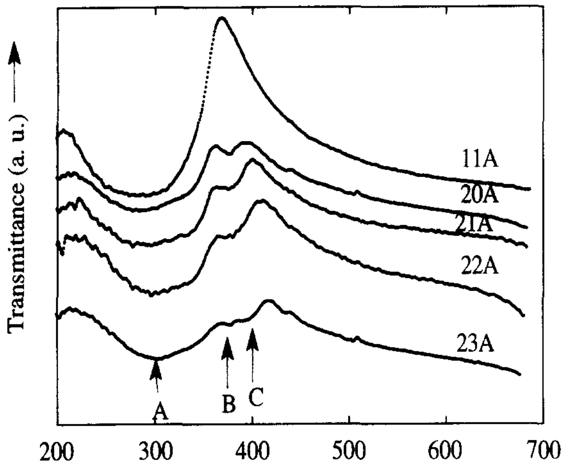

Fig. 9. Far infrared transmission spectra of the vitreous compounds of the Sb_2S_3–As_2S_3–Tl_2S ternary system for a constant concentration of 20% Tl_2S.

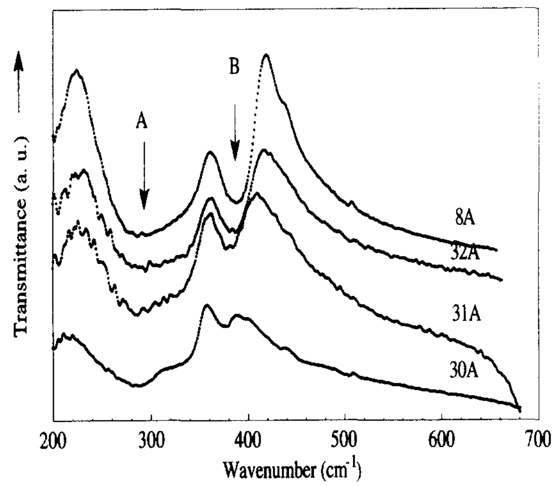

Fig. 10. Far infrared transmission spectra of the vitreous compounds of the Sb_2S_3–As_2S_3–Tl_2S ternary system for a constant concentration of 40% Tl_2S.

symmetry of the AsS_3E units from C_s to C_{3v}, which is due to the reduction of the number of terminal As–S bonds. The decrease in intensity is more pronounced for samples containing 40% Tl_2S. This can be explained by the fact that there is a higher number of terminal As–S bonds in the vitreous compound 8A (60 mol.% As_2S_3 + 40 mol.% Tl_2S) than in the vitreous compound 6A (80 mol.% As_2S_3 + 20 mol.% Tl_2S).

At 20% Tl_2S, band A is shifted (Fig. 11) towards lower wavenumbers when the concentration of Sb_2S_3 is raised. This is a result of an increase in the number of SbS_xE ($x = 3$, 4 or 5) units and a reduction of the fraction of pyramidal AsS_3E units. At constant 40% Tl_2S concentration, band A stays almost fixed at the same frequency. This may also be explained by the increase in number of SbS_xE ($x = 4$ or 5) units, which leads to a shift towards lower wavenumbers and compensates the shift to higher wavenumbers caused by the change in symmetry of the pyramidal AsS_3E units from C_s to C_{3v}. For the two Tl_2S constant concentration lines, the reduction of the number of terminal As–S bonds with increasing Sb_2S_3 concentration can be rationalized in terms of the presence of SbS_xE coordination types with $x = 4$ or 5. In contrast to the binary system Sb_2S_3–As_2S_3, a substitution model of arsenic by antimony is rejected, supporting earlier research using X-ray absorption on this ternary system Sb_2S_3–As_2S_3–Tl_2S.

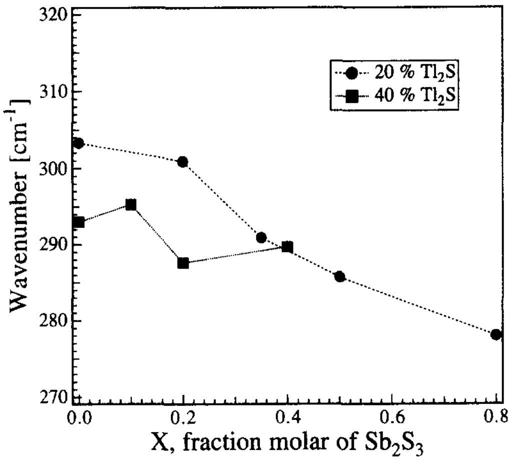

Fig. 11. Wavenumbers of band A with Sb_2S_3 concentration in the Sb_2S_3–As_2S_3–Tl_2S ternary system for constant concentration lines of 20% and 40% Tl_2S.

5. Conclusion

The infrared transmission spectra of vitreous compounds of the binary system As_2S_3–Sb_2S_3 reveal a large band A attributed to the stretching modes (ν_3 and ν_3') of the pyramidal AsS_3E- and SbS_3E-types, in agreement with the model of random substitution of arsenic by antimony drawn up in previous papers.

In the binary system As_2S_3–Tl_2S, an increase in the intensity of band B and a shift of band A towards lower wavenumbers reveal an increase in the number of terminal As–S bonds with an increase in Tl_2S concentration.

In the small domain of glass formation of the binary system Sb_2S_3–Tl_2S, the comparison of the spectra of vitreous and crystalline compounds demonstrates that the local environment of the vitreous compounds differs from that of the crystalline phases.

The results obtained as a whole on the three binary systems enabled us to interpret the features of vitreous compound spectra of the ternary system. In the 20% and 40% Tl_2S constant concentration lines, as the Sb_2S_3 concentration increases, the reduction in intensity of bands B and C demonstrates a reduction in the number of terminal As–S bonds, implying the presence of SbS_xE-types with $x = 4$ and 5. The substitution model of arsenic by antimony is therefore not valid in the ternary system, and particularly for constant 20% and 40% Tl_2S concentration.

The results show that a thorough investigation of the far infrared transmission spectra can furnish valuable information on local structure (coordination patterns and type of bonds). This information is of particular interest when amorphous samples are studied.

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