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Raman spectroscopic study of the ternary system Sb_2S_3-As_2S_3-Tl_2S

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Abstract

Raman spectroscopy has been used to study the local structure in glassy compositions of the ternary system As_2S_3-Sb_2S_3-Tl_2S. The evolution of the positions and shapes of the bands observed is attributed to modifications in the environment of arsenic and antimony corresponding to structural changes as the composition is varied. © 1997 Elsevier Science S.A.

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1. Introduction

A number of recent studies have been denoted to glasses formed from arsenic, antimony and thallium sulfides [1–8]. These have demonstrated that, as a function of the stochiometry, the properties [1,2] and structure [3–8] of the glass can be modified.

Our particular interest in this ternary system springs form its broad glassy domain [1], which is shown in Fig. 1. Such glasses have high thermal stability, are transparent over a wide range in infrared [2], and present an absorption edge which can be tuned between the near infrared to ca. 2.5 eV [3] by varying the composition. The use of a range of complementary techniques is necessary if a structural model of an amorphous solid is to be proposed. We present here results obtained on As_2S_3-Sb_2S_3-Tl_2S glasses using Raman spectroscopy, and propose a correlation between our conclusions and those of previous works [5–8].

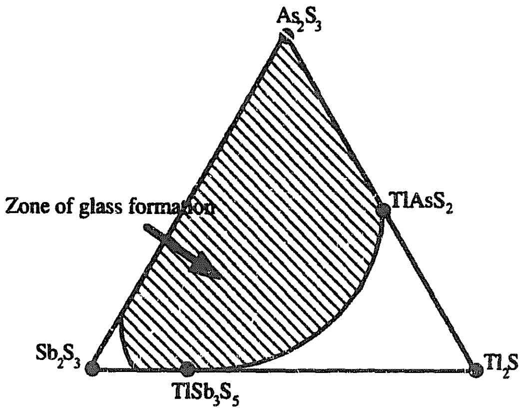

Fig. 1. The region of glass formation.

2. Experimental section

2.1. Glass preparation

Binary antimony, arsenic and thallium sulfides were first prepared by direct reaction from the elements in sealed, evacuated (10^{-5} torr) silica tubes. Mixtures of the binary sulfides were then heated to 1173 K in sealed, evacuated silica tubes and stirred for 1 h. The tubes were quenched in a water–ice–salt bath. The glasses were then stabilised by heating at 50 °C below the glass transition temperature for 48 h, in order to eliminate the strain produced by quenching. The compositions of the samples studied are given in Table 1.

2.2. Characterisation

The glassy nature of the samples can be shown by X-ray diffraction. Diffractograms are characterised by several diffusion rings and present no Bragg diffraction lines. Scanning electron microscopy was used to verify the homogeneity of the samples.

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Table 1
Composition of amorphous samples.

Vitreous compound	Sb_2S_3 %	As_2S_3 %	Tl_2S %
1	80	20	0
2	60	40	0
3	50	50	0
4	0	100	0
5	0	95	5
6	0	90	10
7	0	80	20
8	0	70	30
9	0	60	40
10	0	50	50
11	83.3	0	16.7
12	80	0	20
13	75	0	25
20	50	30	20
21	35	45	20
22	20	60	20
30	40	20	40
31	20	40	40
32	10	50	40

2.3. Raman spectroscopy

Raman spectra were recorded at room temperature in the range 200–4000 cm^{-1} using a Bomem FT spectrometer DA8. Spectra of samples 1, 2, 3 and 4 were obtained using a Dilor triple monochromator spectrometer. These instruments are equipped with YAG (1064 nm) and argon (488 nm) lasers respectively.

3. Results and discussion

3.1. As_2S_3-Sb_2S_3

Raman spectra of glasses in the As_2S_3-Sb_2S_3 system are shown in Figure 2. That of glassy As_2S_3 (Figs. 2–4) presents a single broad and intense line, denoted A. When the concentration of Sb_2S_3 increases, the line shape of A is seen to broaden further, and its maximum is displaced to lower wavenumbers. As a first approximation, these spectra can be interpreted in terms of a molecular model [9], in which the Raman lines are assigned according to the constituent base units. In the case of glassy arsenic and antimony sulfides, the base unit generally used is pyramidal XY_3 (X=As or Sb; Y=S), having C_{3v} symmetry. Using this model, band A can be assigned to the symmetric stretching modes of the AsS_3 pyramid, which is in good agreement with previous studies [5–8]. Lucovsky et al. [10] have interpreted the four modes of pyramidal AsS_3 by reference to the $AsCl_3$ molecule.

The broadening of band A and its shift to lower wavenumbers as the concentration of Sb_2S_3 increases can be explained by existence of the symmetric stretching mode of the pyramidal SbS_3 units. Several different positions are given in the literature for the latter. Using Raman spectroscopy on compounds similar to those studied here, Kato et al. [11] reported this mode at 297 cm^{-1}. Barnier et al. [12] assigned a shoulder at 330 cm^{-1} in the infrared spectrum of amorphous Sb_2S_3 to symmetrical vibrations of the SbS_3 pyramid, by reference to the

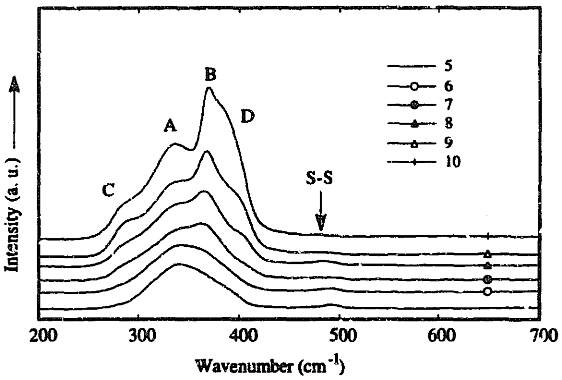


Fig. 3. Raman spectra of the vitreous compounds of the As_2S_3-Tl_2S binary system.

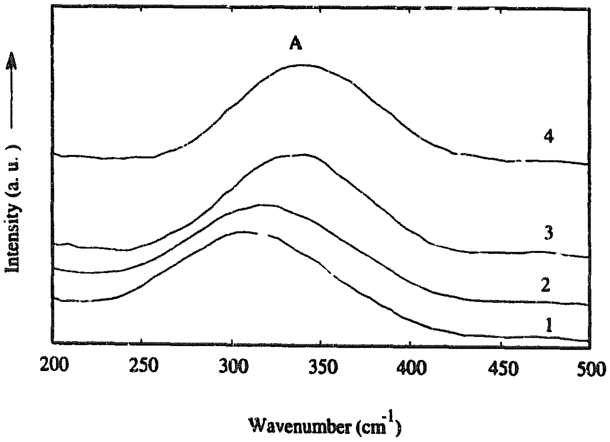


Fig. 2. Raman spectra of the vitreous compounds of the Sb_2S_3-As_2S_3 binary system.

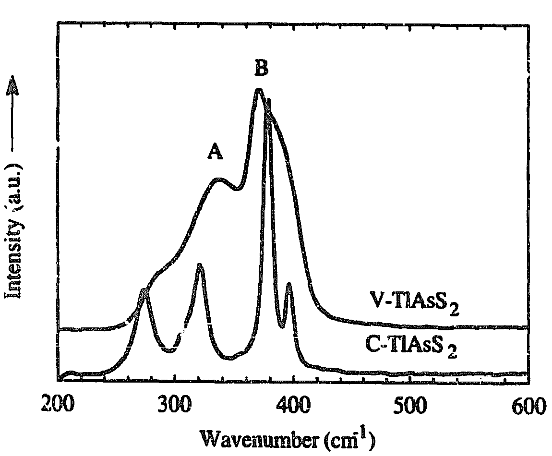


Fig. 4. Comparison of Raman spectra of the crystalline and vitreous compounds $TlAsS_2$.

$SbCl_3$ molecule. Koudelka et al. [13] assign this mode to a line at 302 cm^{-1} in the Raman spectra of Ge-Sb-S glasses.

Analysis of these spectra indicate that there are two type of mode assigned to pyramidal (C_{3v}) AsS_3 and SbS_3. Previous studies [8] of this binary system have shown the substitution of arsenic by antimony.

3.2. As_2S_3-Tl_2S

The Raman spectra of representative samples $Tl_{2x}As_{2-2x}S_{3-2x}$ for $0<x<0.5$ are shown in Fig. 3. On increase of the Tl_2S content, a line (B) appears at 367 cm^{-1}. At the same time, intensity of the line A decrease. In addition, two shoulders at 270 and 390–400 cm^{-1} appear, denoted C and D.

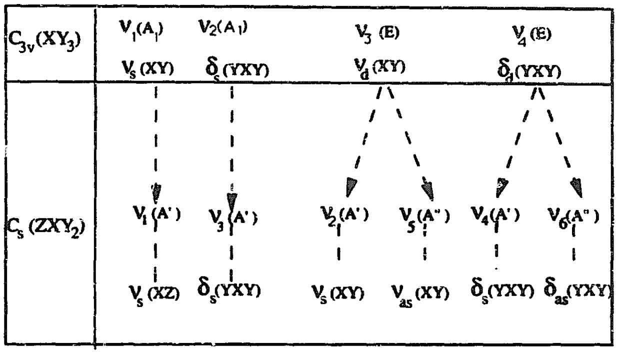
A weak line at ca. 490 cm^{-1} is seen in the spectra of samples rich in AsS_3, and is assigned to the symmetrical stretching vibration of As-S-S-As structural units [13]. Similar effects have been observed in the spectra of other chalcogenide glasses [14,15], and are reported to be related to the synthesis conditions used.

Fig. 4 shows the Raman spectrum of polycrystalline and glassy $TlAsS_2$. The number of lines, and their maxima, are identical, suggesting that the local structure is analogous. This result agrees with those obtained using X-ray absorption spectroscopy, which demonstrated that arsenic maintained the same environment in the two phases. The spectrum of polycrystalline $TlAsS_2$ has lines at 275, 325, 375 and 395 cm^{-1} but, in the absence of a single crystal, their precise assignment is difficult.

Crystalline As_2S_3 [16] is characterised by two pyramidal arsenic sites (C_{3v} symmetry). Its Raman spectrum [17] has lines at 311, 352 and 382 cm^{-1}, the first two of which are assigned to stretching vibrations of the AsS_3 pyramid, and the last to a coupling mode between two AsS_3 units. The absence of band A in the spectra of $TlAsS_2$ phases might be interpreted as indicating the absence of AsS_3 units in these materials.

It is known from X-ray diffraction that arsenic atoms occupy two different sites of C_s symmetry in $TlAsS_2$ [18]. In the crystal, the reduction in symmetry of pyramidal units AsS_3 from C_{3v} to C_s leads to degeneracy of the asymmetric modes E, which can be related to the appearance of additional lines in the spectrum of $TlAsS_2$. Table 2 shows the relationship between these symmetries.

Table 2
Relationship between the C_{3v} and C_s symmetries.



The intense line B, observed at 370 cm^{-1}, can be assigned to the vibration ν'_2 of type A′ in symmetry C_s using the molecular model of AsS_3.

The line at 325 cm^{-1}, also reported by Liu Jun et al. [19] in the Raman spectra of Ag-As-S glasses, is assigned to the presence of short chains $(AsS_{3/2})_n$, and results from the ν'_1 vibration of type A′ of AsS_3 units in C_s symmetry.

Shoulders C and D have been related to the infrared active mode [8]. The shoulder C is assigned to a coupling mode between two AsS_3 units. The weak band D appears in a region intermediate between bending and stretching modes of the AsS_3 pyramid and is provisionally assigned to the ν'_5 vibration (A″) in AsS_3 units in C_s symmetry.

In the following, lines A and B will be used as a probe for the presence of AsS_3 motifs of symmetry either C_{3v} or C_s respectively. Their simultaneous presence in the spectra of other compounds shows the coexistence of entities with these symmetries. The inversion of intensity of these bands at high concentrations of Tl_2S is explained by the progressive transformation from an entity of symmetry C_{3v} to one of symmetry C_s.

In glasses of the As_2S_3-Tl_2S system, the initial glassy matrix is dominated by a pyramidal AsS_3 arrangement of symmetry C_{3v}. The introduction of Tl-S bonds reduces the length of adjacent As-S covalent bonds, and is accompanied by a lowering of the local symmetry. EXAFS data at the arsenic K-edge [5] and XANES measurement at the sulphur K-edge [6], obtained on compounds of identical composition as these, confirm this hypothesis.

3.3. Sb_2S_3-Tl_2S

The glassy region in this binary system is limited to compositions rich in Sb_2S_3 [1]. Corresponding Raman spectra are shown in Fig. 5, where a broad line, denoted E, is seen, centred at 317 cm^{-1}, and bearing a shoulder (F) at

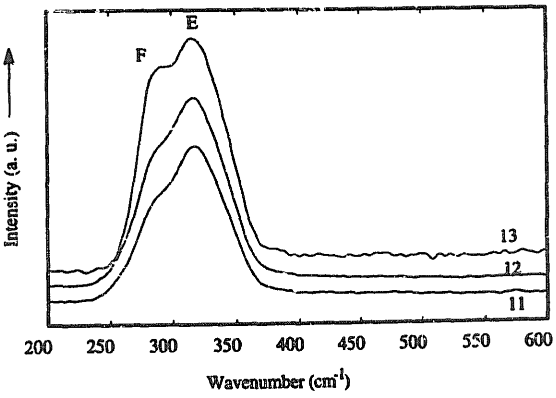


Fig. 5. Raman spectra of the vitreous compounds of the Sb_2S_3-Tl_2S binary system.

285 cm^{-1}. The similarity of all spectra suggests that the local structure in all compositions is comparable.

The spectra of polycrystalline and glassy $TlSb_3S_5$ are compared in Fig. 6, where the assignment of lines at 270, 293, 308 and 330 cm^{-1} remains tentative. $TlSb_3S_5$ is characterised by three different sites for antimony, two SbS_3 units and one SbS_4 unit [20]. Comparison of the spectra of Fig. 6 shows that band E seen in the spectrum of the glass is split into two components at 308 and 330 cm^{-1} in that of the crystalline compound. These two lines are observed also in the Raman spectrum of Ag_3SbS_3 and have been assigned [21] to the symmetric modes of the SbS_3 pyramid. The shoulder F and the broadening of line E towards lower wavenumbers can be explained by the presence of two other modes in the crystalline compound. The intensity of E suggests that the glassy matrix of these compounds is dominated by a structural arrangement of the SbS_3 type. EXAFS studies at the L_{III} edge of antimony [7] has indicated that the coordination shell corresponds largely to an SbS_3 pyramid, in good agreement with the results presented here.

3.4. As_2S_3-Sb_2S_3-Tl_2S

Two series of samples, having fixed Tl_2S contents of 20% (series I) and 40% (series II) were examined. Their Raman spectra are shown in Fig. 7 Fig. 8. The position of the intense line B is characteristic of the ν_2' mode ([illegible]$_2'$) of the AsS_3 entities; having C_s symmetry. Its intensity decreases as the Sb_2S_3 content increases, suggesting that the number of units of C_s symmetry is concomitantly reduced.

A second line, denoted G, is observed between 350 and 317 cm^{-1}. Generally associated with AsS_3 and SbS_3 units of C_{3v} symmetry are observed in this region (345 and 317 cm^{-1} respectively). Line G probably results from an overlap of lines given by both species. The shift of band G from 345 cm^{-1} for composition 7 to 317 cm^{-1} for composition 12 is explained by an inversion in the number of SbS_x (x=3, 4, 5) and AsS_3 units. Fig. 9 shows that the position of G moves non-linearly to lower frequencies as the SbS_3 content increases, and that two regions can be distinguished. For compositions with less than 30% Sb_2S_3,

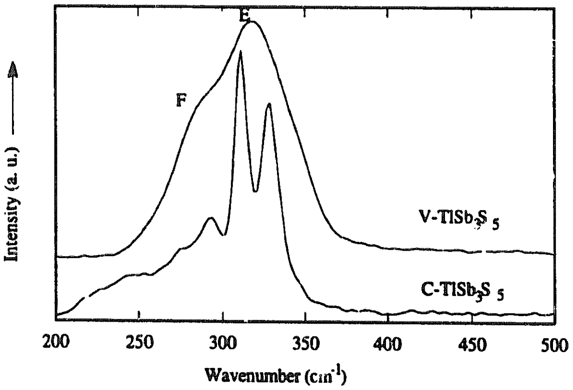


Fig. 6. Comparison of Raman spectra of the crystalline and vitreous compounds $TlSb_3S_5$.

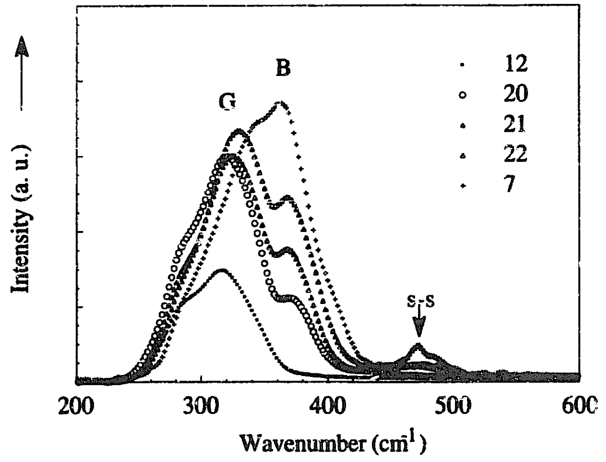


Fig. 7. Raman spectra of the vitreous compounds of the Sb_2S_3-As_2S_3-Tl_2S ternary system for a constant concentration of 20%.

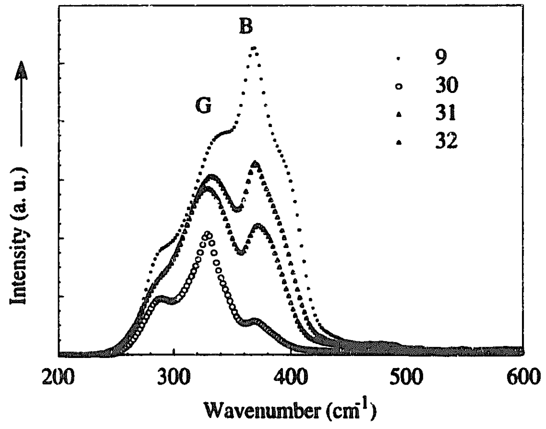


Fig. 8. Raman spectra of the vitreous compounds of the Sb_2S_3-As_2S_3-Tl_2S ternary system for a constant concentration of 40%.

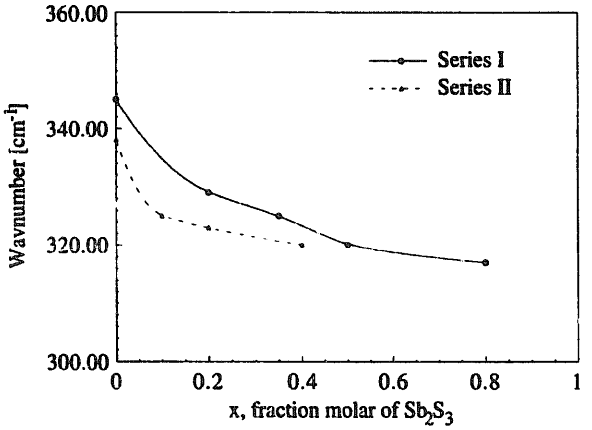


Fig. 9. Wavenumbers of line G with Sb_2S_3 concentration in the Sb_2S_3-As_2S_3-Tl_2S ternary system for constant concentration lines of 20% and 40% Tl_2S.

the shift in the position of G is strongly correlated to the Sb_2S_3 content; water correlation is found above this composition, where a less shifted frequency is observed as the Sb_2S_3 content increases.

4. Conclusion

Raman spectra of glasses in the binary system As_2S_3-Sb_2S_3 have been interpreted on the basis of a model making use of pyramidal AsS_3 and SbS_3 units, of C_{3v} symmetry. In As_2S_3-Tl_2S, the appearance of additional lines (B, C, D) is attributed to the presence of AsS_3 motifs of C_s symmetry, and the inversion of the intensity of lines A and B to transformation of the symmetry of these units. The dominant nature of band G in Raman spectra of glasses in the Sb_2S_3-Tl_2S binary system indicates that the glassy matrix is characterised by the presence of pyramidal SbS_3 units.

The results obtained on the three binary systems have enabled. interpretation of the spectra given by the ternary system, and the evolution of the spectra as a function of Sb_2S_3 concentration at two different contents (20 and 40%) of Tl_2S have been described. The reduction in intensity of line B is interpreted as indicating a reduction in the number of AsS_3 units of symmetry C_s, and the shift of line G by a modification in the coordination at antimony.

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