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► **To cite this version:**

Do-Young Seung, Alain Levasseur, Michel Couzi. Raman spectroscopic study of Li_3AsS_3 crystal and $\text{As}_2\text{S}_3\text{-Li}_2\text{S}$ based glasses. *Physics and Chemistry of Glasses*, 1997, 38 (3), pp.116-119. hal-00334310

HAL Id: hal-00334310

<https://hal.science/hal-00334310>

Submitted on 24 Oct 2008

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Raman spectroscopic study of Li_3AsS_3 crystal and As_2S_3 - Li_2S based glasses

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Manuscript received 10 April 1996

Revision received 4 July 1996

Accepted 25 July 1996

The Raman spectrum of Li_3AsS_3 single crystal can be explained by the presence of AsS_3^{3-} pyramidal units linked together by Li^+ ions. In binary $x\text{Li}_2\text{S} \cdot (1-x)\text{As}_2\text{S}_3$ ($0.67 \leq x \leq 0.75$) glasses the molecular frame of As_2S_3 pyramids is still present even for the most modified glass ($x=0.75$) where, like in Li_3AsS_3 , AsS_3^{3-} units seem to be present. The addition of LiI as doping salt to binary Li_2S - As_2S_3 glasses does not induce any modification of Raman spectra confirming the general expectation that dissolving LiI into glass matrices does not affect their structures

Crystalline As_2S_3 is well known as a layered structure. This structure is based on distorted pyramidal AsS_3 units (As atoms at the apex and the three S atoms forming the base). These units are coupled together by bridging sulphur to form helices. Helices are connected via other bridging sulphurs to form a 2D layer structure.^(1,2)

The structure of glassy As_2S_3 has been extensively studied using techniques sensitive to local order, i.e. infrared and Raman spectroscopies, NMR and EXAFS.⁽³⁻⁹⁾

The dominant infrared and Raman modes occur at different frequencies because of retaining their inherent symmetry and are only observed in their respective domain of wavelength.^(4,10) The origin of high frequency region is evidently attributed to vibrational mode of pyramidal $\text{AsS}_{3/2}$ units and the low frequency Raman region interpretation is still argued.

In the molecular model proposed by Lucovsky *et al.*^(10,11) for glassy As_2S_3 the Raman and infrared spectra are interpreted in terms of intermolecular and intramolecular vibrations of the basic $\text{AsS}_{3/2}$ pyramid (C_{3v} symmetry). The intermolecular modes were identified with the deformation of the triatomic bent chain As-S-As

'water molecule' (C_{2v} symmetry). The intermolecular coupling is presumed to be sufficiently weak.⁽¹⁰⁻¹³⁾

Kobliska *et al.* realised calculations of vibrational states in molecular and planar random network models. According to the observation of infrared and Raman spectra, the best correlation was obtained for the first model giving more evidence of the presence of As_2S_3 pyramidal linked molecular units.⁽⁴⁾

Ionic conducting glasses, usually oxide glasses, are considered to be made up of 'covalent' network formers such as SiO_2 , B_2O_3 , P_2O_5 , GeO_2 , Sb_2O_3 , As_2O_3 , etc. which give rise to random arrangements of corner linked tetrahedra, triangles or pyramids, and of network modifiers such as Ag_2O , Li_2O or Na_2O . It is well known that the network modifiers lead to the fragmentation of the 'covalent' entities.⁽¹⁴⁾ More recently similar studies have been carried out on alkali thioborate glasses,⁽¹⁵⁻²⁰⁾ alkali phosphate glasses,⁽²¹⁻²³⁾ and alkali germanate glasses.⁽²⁴⁾ Chalcogenide based glasses with heavy metal halides (Cl, Br and I) and As_2S_3 have been widely investigated because of their excellent electrical and optical properties and good chemical stability.^(25,26) However, compared to the other covalent network formers alkali modified As_2S_3 based glasses have not been studied as extensively and the structural modification by Li_2S was only recently known partly by the work done by Shastry *et al.*^(13,27)

Recently, lithium thioarsenite (Li_3AsS_3) single crystal was obtained and its structure determined by some of the authors. The space group was found as $\text{Pna}2_1$.⁽²⁸⁾

This work is devoted to the study of the structural modification processes occurring in As_2S_3 - Li_2S based glasses. The short range order found in Li_3AsS_3 crystals is compared to the short range order expected in glasses by means of Raman spectroscopy. Additionally, the LiI doping effect on As_2S_3 - Li_2S binary glasses is analysed.

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Experiments

Commercially available As_2S_3 , Li_2S and LiI were used for the preparation of all glasses and crystal; as these materials are sensitive to moisture, all the preparation process was done under dry argon atmosphere in a glove box.

Preparation of single crystal

A $\text{Li}_2\text{S}:\text{As}_2\text{S}_3=3:1$ mole ratio mixture was introduced into a carbon crucible, itself placed in a silica tube sealed under vacuum. The tube was then heated to 650°C and held at this temperature for 20 h allowing complete chemical reaction. The assembly was cooled slowly to room temperature at a rate of $0.6^\circ\text{C}/\text{h}$ and annealed at 240°C for 7 days. The ampoule was opened inside a glove box, whereupon green coloured crystals inside a block of polycrystalline material was recovered. Chemical analysis showed that the single crystals had the Li_3AsS_3 composition.

Preparation of $\text{Li}_2\text{S}-\text{As}_2\text{S}_3$ and $\text{LiI}-\text{Li}_2\text{S}-\text{As}_2\text{S}_3$ based glasses

The binary $x\text{Li}_2\text{S} \cdot (1-x)\text{As}_2\text{S}_3$ ($0.67 \leq x \leq 0.75$) glass forming range was already reported by Shastry *et al.*⁽²⁷⁾ The ternary $(1-y)[x\text{Li}_2\text{S} \cdot (1-x)\text{As}_2\text{S}_3] \cdot y\text{LiI}$ glasses were formed in the range $0 \leq y \leq 0.5$, $0.70 \leq x \leq 0.75$. The glasses were prepared from the weighted powder which was well ground and then introduced in a vitreous carbon crucible, itself introduced into a silica tube. The ampoule was sealed under vacuum and then heated at 650°C for 18 h. The reacted ampoule was quenched into cold water. The obtained materials were generally partially opaque indicating either partial crystallisation or demixing. They were ground again and heated in an amorphous carbon crucible using a high frequency furnace fitted glove box. The charge was melted and then quenched between two stainless steel blocks. Following these conditions, reddish brown transparent glasses were obtained. The obtained samples were checked by powder x-ray diffraction (XRD).

Raman spectroscopy measurements

The crystals of Li_3AsS_3 were introduced in a glass capillary of 0.5 mm in diameter because of their hygroscopic nature; the spectra were obtained using a Dilor OMARS 89 micro Raman spectrometer equipped with a liquid nitrogen cooled CCD for detection. A backscattering geometry was used with the sample placed under the microscope. The excitation laser wavelength was 514.5 nm with an incident power of a few mW at sample; spectral resolution was 3 cm^{-1} .

Raman spectra of glasses were recorded in right angle geometry using a Dilor Z24 triple monochromator instrument. The excitation source was a Spectra Physics model 2000 Kr ion laser with an emission line at 647.1 nm. The power source was 200 mW and detection was achieved using a Hamamatsu model R94302 cooled photomultiplier coupled with a photon counter; spectral resolution was 1.8 cm^{-1} . To avoid moisture contamination sealed quartz containers were used. No beam damage was observed at the surface of the sample.

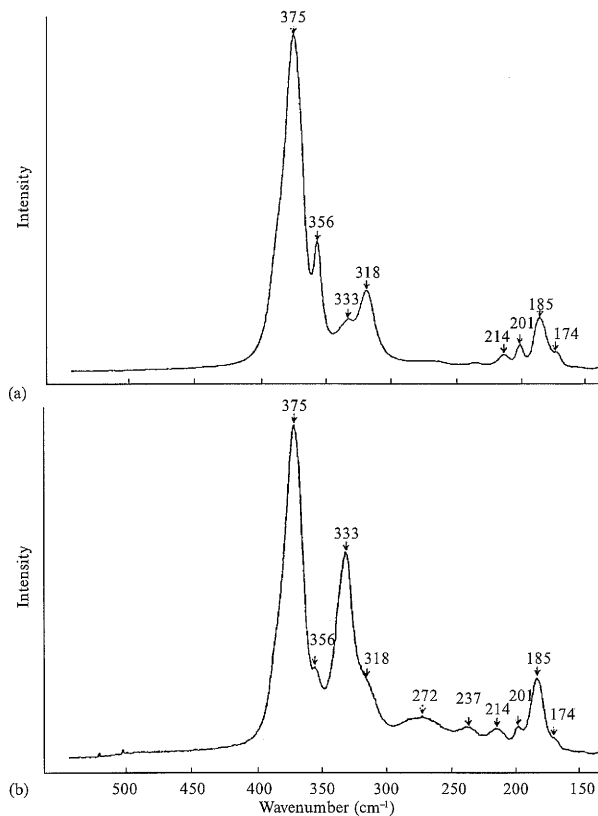


Figure 1. Micro-Raman (backscattering) spectra of an unoriented Li_3AsS_3 single crystal. The direction of polarisation of incident light is parallel to Z (a) and perpendicular to Z (b). The Z direction, chosen arbitrarily along the capillary axis, does not correspond to any crystallographic axes

Results and discussion

Li_3AsS_3

Li_3AsS_3 has 28 atoms per unit cell,⁽²⁸⁾ thus leading to 84 vibrational (81 optical and 3 acoustic) modes. All atoms are in general position in the orthorhombic Pna_2 space group ($Z=4$), so that the enumeration of the optical modes at the Brillouin zone centre gives

$$\Gamma_{\text{opt}} = 20A_1 + 21A_2 + 20B_1 + 20B_2$$

All these modes are expected to be Raman active. The obtained spectra are shown in Figure 1(a) and 1(b) for different polarisations. The assignment of the peaks in terms of symmetry species is not possible because of the unknown direction of the crystallographic axes with respect to the laboratory axes. Furthermore, the number of observed peaks is far less than expected probably because of the existence of line overlaps into unresolved bands and/or of modes giving rise to very low Raman intensity. Thus, only qualitative assignment can be made. In fact in the Li_3AsS_3 structure there are four crystallographically equivalent AsS_3^{3-} pyramids and the Li^+ ions are connected to the AsS_3^{3-} entities via $\text{S}-\text{Li}-\text{S}$ bonds.⁽²⁸⁾ Therefore, there is no direct bonding between pyramids so that the treatment has been carried out as for isolated units; the enumeration of the internal modes of AsS_3^{3-} is given in Table 1 so that

$$\Gamma_{\text{int}} = 6A_1 + 6A_2 + 6B_1 + 6B_2$$

Two main groups of peaks have been observed. The

Table 1. Irreducible representations of the internal modes of AsS_3^{3-} pyramids

Modes	Isolated AsS_3^{3-} C_{3v}	Site C_i	Unit cell $\text{Pna}2_1-C_{2v}$
ν_1	A_1	A	$A_1+A_2+B_1+B_2$
ν_2	A_1	A	$A_1+A_2+B_1+B_2$
ν_3	E	2A	$2A_1+2A_2+2B_1+2B_2$
ν_4	E	2A	$2A_1+2A_2+2B_1+2B_2$

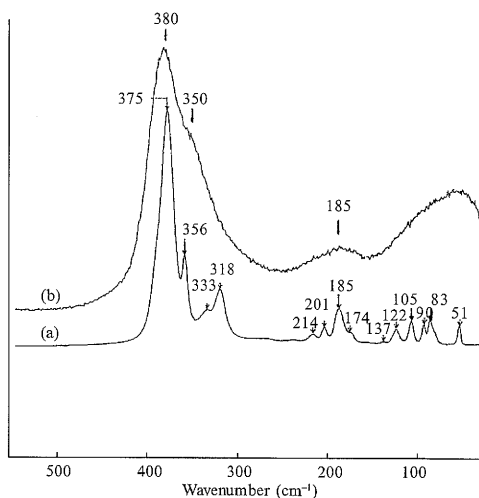
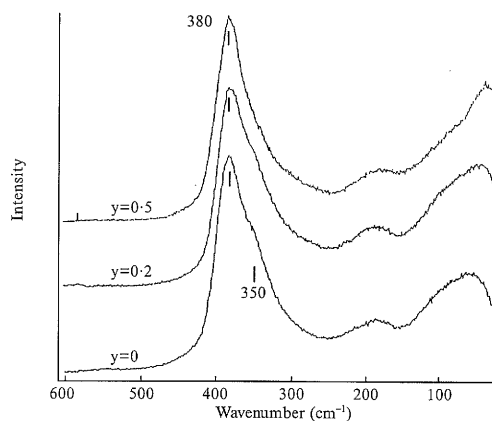
ν_1 and ν_2 are the symmetric stretching and bending modes respectively, and ν_3 and ν_4 are the degenerate stretching and bending modes respectively

first one, appearing between 318 and 375 cm^{-1} , can be assigned to As-S stretching modes ν_1 and ν_3 in AsS_3^{3-} pyramidal units. The second group, appearing between 174 and 214 cm^{-1} , is expected to arise mainly from S-As-S bending modes ν_2 and ν_4 . These assignments are supported by comparisons with previous work done on As_2S_3 ^(2,5) and Ag_3AsS_3 crystals.⁽²⁹⁾ The assignment of broad peaks observed at 237 and 272 cm^{-1} (Figure 1(b)) is not straightforward. They could be tentatively assigned to Li translatory vibrations versus sulphur atoms (stretching like Li-S modes).

$x\text{Li}_2\text{S} \cdot (1-x)\text{As}_2\text{S}_3$ glasses

Figure 2 illustrates the Raman spectra of the $x=0.75$ glass and the Li_3AsS_3 crystal. They are noted to be similar in the sense that the broad features, which characterise the glassy state, nicely resemble an unresolved envelope of the discrete peaks observed in the crystal of the same chemical composition. This comparison leads to the conclusion that the AsS_3^{3-} pyramidal units exist in both Li_3AsS_3 crystal and in the corresponding glass ($x=0.75$), which is in accordance with the assignment previously made by Shastry *et al.*⁽¹³⁾

The Raman spectra obtained for $x=0.70$ and 0.75 glasses are shown in Figure 3. The structural entities in $\text{Li}_2\text{S}-\text{As}_2\text{S}_3$ based glasses were expected to be changed depending on the amount of Li_2S .⁽¹³⁾ At $x=0.67$ and 0.70 the presence of pyramidal units in which As atoms are bonded to bridging and nonbridging sulphur atoms is expected. The most modified glass ($x=0.75$) shows its main peak at 380 cm^{-1} with a shoulder at 350 cm^{-1} . These peaks were assigned by Shastry *et al.*⁽¹³⁾ af-

**Figure 2.** Raman spectra obtained for (a) $c\text{-Li}_3\text{AsS}_3$ and (b) $0.75\text{Li}_2\text{S} \cdot 0.25\text{As}_2\text{S}_3$ glass**Figure 3.** Raman spectra of (a) $(1-y)(0.75\text{Li}_2\text{S} \cdot 0.25\text{As}_2\text{S}_3) \cdot y\text{LiI}$ and (b) $(1-y)(0.70\text{Li}_2\text{S} \cdot 0.30\text{As}_2\text{S}_3) \cdot y\text{LiI}$ system glasses

ter comparison with the polarised Raman spectrum, as the ν_1 and ν_3 stretching modes of As-S⁻ in AsS_3^{3-} pyramids and the broad feature centred around 185 cm^{-1} to the bending modes of the entities.

$y\text{LiI} \cdot (1-y)[x\text{Li}_2\text{S} \cdot (1-x)\text{As}_2\text{S}_3]$ glasses

Figure 3(a) shows the Raman spectra for $x=0.75$ ($y=0, 0.2$ and 0.5) and Figure 3(b) for $x=0.70$ ($y=0, 0.3$ and 0.5). Obviously these spectra do not exhibit any modification upon introduction of LiI doping salt even for concentrations as high as ($y=0.5$) whereas, in the same time, the Li^+ ionic conductivity increases significantly with increasing concentrations of LiI:⁽³⁰⁾ for instance

$$\sigma = 0.14 \times 10^{-4} \text{ S cm}^{-1} \text{ for } x=0.75, y=0$$

and

$$\sigma = 1.26 \times 10^{-4} \text{ S cm}^{-1} \text{ for } x=0.75, y=0.5$$

At this stage, it is worth noting that glasses belonging to the As_2S_3 iodine system have already been studied by means of x-ray scattering techniques,⁽³¹⁾ the authors have proposed a twisted chain model consisting of AsS_3I units interconnected by double and/or single sulphur bridges. In contrast when AsI_3 is added in vitreous As_2S_3 , the AsI_3 molecules are preserved; they are 'dissolved' in the As_2S_3 glassy network which is kept essentially unchanged even in high AsI_3 composition range.^(32,33) Furthermore as could be seen in the case of addition of LiI doping salt to $\text{Li}_2\text{S}-\text{B}_2\text{S}_3$ glasses, LiI does not induce any change in the structure of the host matrix.⁽¹⁸⁾ Similar behaviour has been observed in other sulphide based glasses such as $\text{LiI}-\text{Li}_2\text{S}-\text{P}_2\text{S}_5$.^(21,22)

As shown now in Figures 3(a) and (b) there is no indication of new Raman peaks, appearing upon addition of LiI, at ~ 480 and $\sim 210\text{ cm}^{-1}$ which could be associated with the presence of double sulphur bridges (-S-S-) and of As-I bonds, respectively.^(32,33) Thus, we conclude that the addition of LiI does not affect the structure of the $\text{As}_2\text{S}_3 \cdot \text{Li}_2\text{S}$ host glass and the general expectation of dissolving LiI into glass matrices as an ionic species is again confirmed. However, for high LiI contents (i.e. $0.3 \leq y \leq 0.5$), on the basis of what was observed in $\text{LiI}-\text{Li}_2\text{S}-\text{B}_2\text{S}_3$ glasses⁽³⁴⁾ it can be assumed that small LiI aggregates which are not detectable by x-ray diffraction can exist in the vitreous domain. This

assumption is not at variance with the observed Raman spectra since, for symmetry reasons, the spectrum of crystalline LiI is featureless. Moreover, the presence of small size LiI aggregates may explain some specific behaviours observed in the ionic conduction properties of these glasses as a function of the LiI contents.⁽³⁰⁾

Conclusion

The Raman spectrum of crystalline Li_3AsS_3 has been observed for the first time and compared with that of the glass with the same chemical composition. Qualitative assignments of the main peaks one to $\text{As}_2\text{S}_3^{3-}$ isolated pyramids have been made. So the structural modification process upon introduction of Li_2S to As_2S_3 glass is confirmed, i.e the molecular frame of AsS_3 pyramids is conserved; it follows that in the most modified glass with composition $0.25\text{As}_2\text{S}_3 \cdot 0.75\text{Li}_2\text{S}$, all terminating sulphur atoms are nonbridging thus leading to the formation of isolated $\text{As}_2\text{S}_3^{3-}$ pyramids.

In LiI - Li_2S - As_2S_3 ternary glasses there is no evidence of a structural change occurring in the Li_2S - As_2S_3 host matrix upon doping with LiI salt.

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