Infrared absorption spectra of As-Se glasses

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Abstract. IR absorption spectra of As–Se glasses have been studied over a wide range of compositions. Various two-phonon, multiphonon (combination tones) and impurity absorptions have been identified. Compositional variation of relative band intensities has been explained in terms of the chemically ordered network model.

Keywords. Infrared spectra; As–Se glasses.

1. Introduction

Infrared spectroscopy of chalcogenide glasses has attracted wide attention because of their special IR transmitting properties. In particular, As_2Se_3 glass has been studied in detail by many workers (Edmond and Redfearn 1963; Hilton *et al* 1966; Taylor *et al* 1970; Lucovsky 1972; Moynihan *et al* 1975). Recently Moynihan *et al* (1975) have reported the IR spectra of glassy As_2Se_3 doped with As_2O_3 in the region 250 to 4000 cm⁻¹. Spectra of amorphous As (Lucovsky and Knight 1974; Greaves *et al* 1979), Se (Hilton *et al* 1966; Savage and Nielsen 1964; Lucovsky *et al* 1967; Siemsen and Riccius 1969) and As–Se (Hilton *et al* 1966; Moynihan *et al* 1975) have also been reported in the literature and absorption frequencies of amorphous As, Se, As–Se and As_2Se_3 below 500 cm⁻¹ are summarised in table 1. Molecular vibration calculations have been performed by Lucovsky (1972) and Lucovsky and Martin (1972) who find that the spectrum of As_2Se_3 conforms to that of vibrating $AsSe_3$ units. In the 200 to 1200 cm⁻¹ region As_2Se_3 exhibits several peaks due to multiphonon absorption (Moynihan *et al* 1975). Some of the rather intense absorption bands appear to be due to the presence of As_2O_3 and SeO_2 impurities. As_2O_3 having a very high extinction coefficient (Hilton *et al* 1966; Moynihan *et al* 1975; Jerger and Sherwood 1964) gives rise to bands even at low concentrations of ∼ 100 ppm (below the saturation solubility of As_2O_3 in As_2Se_3).

Various properties of binary As–Se glasses have been investigated in this laboratory (Mohan *et al* 1980; Rao and Mohan 1980) and the properties support a

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Table 1. Literature data on absorption frequencies below 500 cm^{-1} for amorphous As, Se, As–Se and As$_2$Se$_3$.

System	Absorption frequencies cm^{-1}	Designation v_i	Reference
As	130	v_1	Lucovsky and Knight 1974;
	230	v_2	Greaves *et al* 1979
Se	256	v_3	Hilton *et al* 1966; Savage and Nielsen 1964;
	487	v_4	Lucovsky *et al* 1967; Siemsen and Riccius 1969
As–Se	196	v_5	
	217	v_6	
	227	v_7	Hilton *et al* 1966
	250	v_8	
	270	v_9	
As$_2$Se$_3$	100	v_{10}	
	230	v_{11}	Hilton *et al* 1966; Moynihan *et al* 1975
	480	v_{12}	

chemically-ordered network model (Betts *et al* 1970; Lucovsky *et al* 1974, 1977). We therefore considered it interesting to examine the IR spectra of these glasses. In this paper we report IR absorption spectra of As–Se glasses in the region 250–1100 cm^{-1} and discuss the spectra in the light of the chemically ordered network model.

2. Experimental

As–Se glasses were prepared as described earlier (Mohan *et al* 1980) from the elements (As and Se) of 5N purity (Koch-Light Company, U.K.). Thin sections of these glasses were prepared by grinding and polishing (using rouge powder) to less than 1 mm thickness (most of them were 0·5 to 0·8 mm thick). They were repeatedly washed with distilled water and dried. Spectra of these glasses, which were prepared under almost identical conditions, were obtained from a Perkin Elmer Model 580 IR spectrometer. No special efforts were made to prevent oxygen contamination at the preparative stage except evacuation of the quartz tube previously flushed with nitrogen or argon, before sealing.

The spectra of six different As–Se compositions are given together in figure 1. Since the thicknesses of the samples were not identical the peak absorbances cannot be compared. Intensities of the shoulders in the spectra were determined approximately by decomposing the actual absorption peaks into required number of Gaussian peaks adopting a simple trial and error technique (but not by computer fitting). The actual values of intensities reported may therefore have large uncertainties but would suffice to examine trends in the related series of glasses. In order to check how the intensities vary with composition, the relative variations
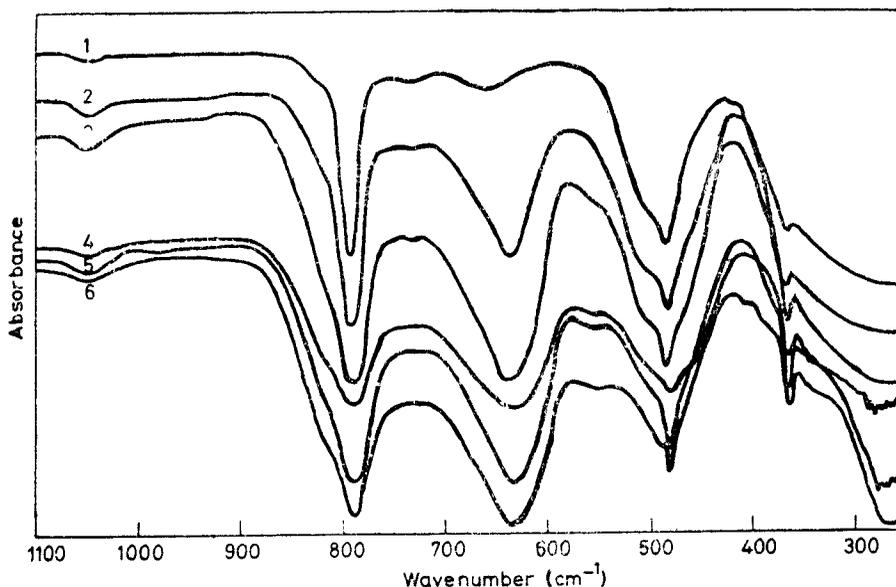
Figure 1. IR absorption spectra of As–Se glasses. The numbers correspond to the following compositions : (1) $As_{10}Se_{90}$, (2) $As_{20}Se_{80}$, (3) $As_{30}Se_{70}$, (4) $As_{40}Se_{60}$, (5) $As_{50}Se_{50}$, and (6) $As_{60}Se_{40}$.

of intensities of various absorption peaks have been determined with respect to the fundamental absorption peak at $365 \, cm^{-1}$. We have assumed that the $365 \, cm^{-1}$ band is due to a fundamental although doubts have been expressed in the literature (Moynihan *et al* 1975) with regard to this assignment.

3. Results and discussion

Infrared bands of As–Se glasses are listed in table 2. The relative intensities of bands with respect to $365 \, cm^{-1}$ band are plotted against the composition in figure 2. The 475, 485 and $495 \, cm^{-1}$ bands which show continuous variation of intensity with the percentage As arise from a two-phonon absorption processes as suggested by the earlier workers (Moynihan *et al* 1975). Since As and Se have almost the same masses, it should be expected that two close lying absorption frequencies due to As–As and Se–Se vibrations are present in the spectra. In Se-rich glasses the absorption band in this region may be due to the contributions of $487 \, cm^{-1}$ absorption of Se (Hilton *et al* 1966 ; Savage and Nielsen 1964; Lucovsky *et al* 1967; Siemsen and Riccius 1969). In the As-rich compositions it is possible that the intensity of the absorption is due to a two-phonon process involving the $230 \, cm^{-1}$ absorption band as seen in amorphous As (Lucovsky and Knight 1974; Greaves *et al* 1979). It may be noted that IR absorption of pure As and Se are of dynamical origin, since the static lattices do not permit any dipole moment changes (Greaves *et al* 1979).

The 635, 790 and $1050 \, cm^{-1}$ absorption bands have been attributed by the previous workers (Moynihan *et al* 1975) to the presence of two different oxide

Table 2. IR absorption frequencies in As–Se glasses

Composition	Frequencies (cm^{-1})									
$As_{10}Se_{90}$	1050 b and w	820 sh	790 s	635 b and w	555 sh	495 s.sh	485 s	475 s.sh	375 sh	365 s
$As_{20}Se_{80}$	1050 b and w	815 sh	790 s	635 b and s	555 sh	495 s.sh	483 s	475 s.sh	375 sh	365 s
$As_{30}Se_{70}$	1050 b and w	815 sh	790 s	635 b and s	555 sh	495 s.sh	480 s	475 s.sh	380 sh	365 s
$As_{40}Se_{60}$	1050 b and w	815 sh	790 s	635 b and s	555 sh	495 s.sh	480 s	475 s.sh	380 sh	365 s
$As_{50}Se_{50}$	1050 b and w	815 sh	790 s	635 b and s	555 sh	495 s.sh	480 s	475 s.sh	380 sh	365 s
$As_{60}Se_{40}$	1050 b and w	815 sh	790 s	635 b and s	555 sh	495 s.sh	480 s	475 s.sh	380 sh	365 s
Tentative assignment using from table 1 and ref. (Moynihan et al 1975)	impurity band of oxide form-I (Moynihan et al 1975)	$\nu_1 + 3\nu_2$	impurity band of oxide form-I (Moynihan et al 1975)	impurity band of oxide form-II (Moynihan et al 1975)	$2\nu_1 + \nu_9$	intrinsic two-phonon processes	intrinsic two-phonon processes (Moynihan et al 1975)	intrinsic two-phonon processes	$\nu_3 + \nu_{10}$	fundamental As-Se-As stretch (Moynihan et al 1975)

s. = strong;   w = weak;   sh = shoulder;   b = broad.
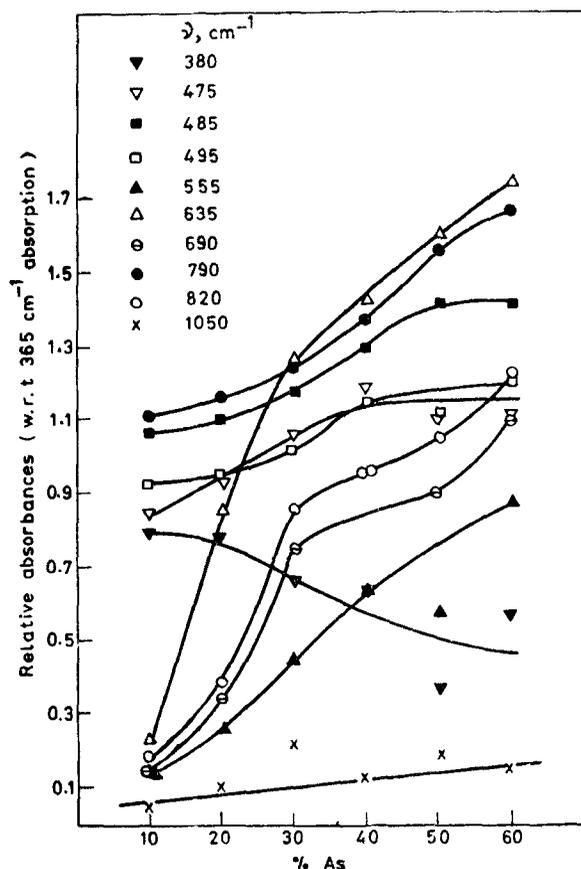
Figure 2. Composition variation of relative absorbances (relative to 365 cm^{-1} absorption peak).

(impurity) structures. The 635 and 790 cm^{-1} absorption peaks increase in intensity with increase in As content which is quite reasonable. But the steep decrease in intensity of oxide II structure below 30% of As is interesting. It is either due to the pronounced decrease in the solubility of oxide II in Se-rich glasses or due to a consequence of the greater solubility of oxide II structure in As-rich glasses. The 1050 cm^{-1} absorption is relatively weak and it has been assigned to the oxide I form of As_2O_3 impurity (Moynihan *et al* 1975). Its intensity does not seem to vary sufficiently with composition. The origin of these oxides in As–Se glasses is not clear; one possibility is a reaction involving silica reaction tubes (Moynihan *et al* 1975).

The band at 820 cm^{-1} also shows an increase in intensity with As concentration. This band could arise from multiphonon absorption such as $(v_1 + 3v_2)$. The intensity of the 380 cm^{-1} band seems to increase with Se concentration in these glasses; its origin is not clear. One possible assignment of this would be $(v_3 + v_{10})$ since such combinations are likely to occur in a chemically ordered network. The 555 cm^{-1} band seems to increase continuously with As content which could be due to $(2v_1 + v_9)$.

The infrared region investigated by us covers only regions of multiphonon absorptions in As–Se glasses. The multiphonon absorption reported here can be roughly assigned employing literature data from table 1. The relative intensities of some of the absorption bands such as the ones at 815 cm^{-1}, 555 cm^{-1} and the 380 cm^{-1} vary gradually with the concentration of As or Se. We feel that the likely assignments of these bands are the combinations indicated in table 2. The chemically ordered network possibly permits such combination tones on a network of atoms in which there are quasi-independent vibrating units such as As–As and As–Se in a manner similar to that in glassy As–Se$_3$ (Lucovsky 1972).

Acknowledgements

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