Pramāṇa, Vol. 16, No. 4, April 1981, pp. 309–313. © Printed in India.

Chemical ordering in As-Se glasses: X-ray Absorption edge and XPES studies*

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MS received 29 October 1980

Abstract. X-ray absorption edge and X-ray photoelectron spectroscopic studies of As-Se glasses seem to support a chemical ordering model.

Keywords. As-Se glasses; chemical shifts; X-ray photoelectron spectroscopy.

1. Introduction

Arsenic and selenium form glasses very easily over a wide range of composition (Rawson 1967). Many structural properties of these glasses have been reported in literature. The arsenic and selenium elements being next to each other in the periodic table and their bonding being primarily covalent, it is difficult to establish partial structure factor decisively and hence comment on the nature of ordering of atoms. If it involves merely random ordering, the As-Se (covalent) network may contain like atom neighbours of both types in the entire range of compositions. A chemically-ordered network of As-Se glasses should however contain homoatom linkages of only those atoms in excess of As_{40} Se_{60} composition. Several studies both in our laboratory (Mohan *et al* 1980; Rao and Mohan 1980) and elsewhere (Bette *et al* 1970; Lucovsky *et al* 1974, 1977) seem to favour a chemically-ordered network model. From purely energetic considerations also, a preponderance of heteroatom bonding is to be expected. The x-ray photoelectron spectroscopy (XPES) in the valence band region is expected to sensitively reflect the nature of bonding. Similarly the *K*-absorption chemical shifts of the individual atoms may also be expected to throw light on this problem. In this paper we report the *K*-absoprtion edge shift measurements from x-ray absorption studies of both arsenic and selenium and XPES studies in the valence band region. We have found evidence to support a chemical ordering in As-Se glasses.

2. Experimental

Glasses were prepared from arsenic and selenium of five nine purity (Koch-Light, Co., U.K.) The method of preparation has been described elsewhere (Mohan *et al* 1980).

Communication No. 94 from Solid State and Structural Chemistry Unit.

X-ray absorption spectra were recorded with a bent crystal spectrograph. x-ray tubes having copper and molybdenum targets were used as sources of radiation. The energy analysis of the spectra was carried out using a Carl-Zeiss G III photometer (Sarode *et al* 1979). The absorption edge was taken as the inflexion point on these photometric plots (Richtmyer *et al* 1934; Sandström 1957). The x-ray photoelectron spectra of these glasses were recorded from ESCA-3 Mark II spectrometer of VG Scientific Ltd., U.K. using Al-K_α radiation. The spectra of As-Se glasses were obtained from their respective powders (Sarode *et al* 1979) and were recorded upto 20 eV binding energy. The vacuum was generally of the order of 5×10^{-10} torr.

3. Results and discussion

The X-ray absorption edge shifts of As and Se (chemical shifts with respect to pure elements in metallic state) are shown as functions of composition (%As) in figures 1a and 1b. XPES in the valence band region of five different compositions and the two elements are shown in figure 2. Chemical shifts of As decrease almost linearly upto 40% As, corresponding to the composition As_{40} Se_{60} and level off beyond that composition. Chemical shifts of Se also indicate a similar trend. It is increasing towards As_{40} Se_{60} composition and almost levels off beyond that.

In a chemically ordered network we would expect the presence of Se-Se bonds beyond As_{40} Se_{60} and As-As bonds below that composition. In X-ray absorption edge measurements, a *K*-electron is excited to the lowest unoccupied levels which correspond to the antibonding states of As-As, Se-Se or As-Se. These antibonding states are such that E_σ^* (As-As) $<$ E_σ^* (Se-Se) $<$ E_σ^* (As-Se) (Kastner 1972). In solids these energy levels are spread out and overlap considerably. The spread of the

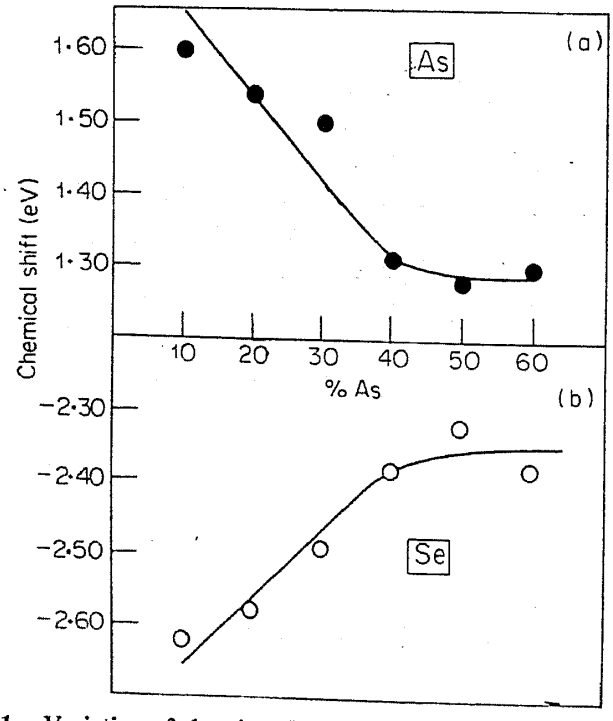

Figure 1. Variation of chemical shifts of As and Se with composition in As-Se glasses.

energy levels may be assumed (to a first approximation) to be proportional to the concentration of such bonds. The resulting σ^* bonds are shown schematically in figure 3. The excited K-electrons are expected to occupy these antibonding levels. The

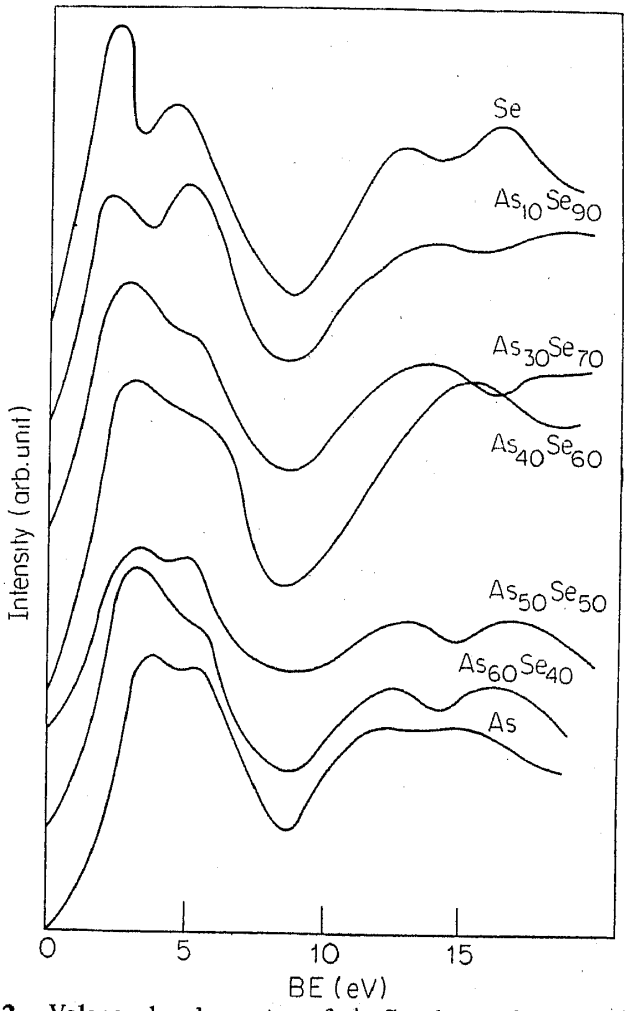

Figure 2. Valence band spectra of As-Se glasses from XPES.

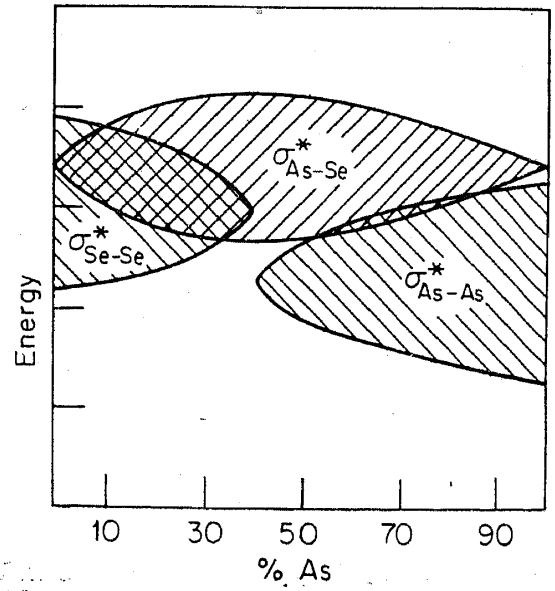

Figure 3. Schematic energy band diagram of the antibonding levels in As-Se glasses.

excited *K*-electron is more likely to go into its own antibonding state, rather than into the lowest available antibonding levels. This would imply that a *K*-electron from Se in Se-rich composition region goes into E_{σ}* (Se-Se) level, whereas a *K*-electron of As gets excited to E_{σ}* (As-Se) level. It is thus obvious from figure 3 that the chemical shifts observed should show an increasing trend for Se (decreasing negative value) while it should be decreasing in the case of As chemical shifts. On the As-rich side, Se *K*-electrons should be going into As-Se antibonding level with increasing preference. In the regions close to $As_{40}Se_{60}$ *K*-electrons of both As and Se gets excited to E_{σ}* (As-Se) level. Experimentally the observed change of slope at $As_{40}Se_{60}$ composition strongly supports this scheme of *K*-electrons excitation and hence the chemically ordered network model.

The XPES spectra of all the glasses are very similar (Liang 1975; Bishop and Shevchik 1975). The low energy bands (~2 eV and ~5 eV) correspond to *p* lone pairs and perhaps *p* bonding electron. We however believe that the second peak contains contributions of the sp^3 lone pair from As (Sarode *et al* 1979). The third broad band which displays two peaks in several glasses has been assigned to bonding and antibonding *s* levels. A distinctive minimum at ~8 eV is seen in all the compositions. The XPES of $As_{40}Se_{60}$ has been explained earlier by Shevchik *et al* (1973a, b) as a weighted composite of PES of As and Se. In a chemically-ordered network we

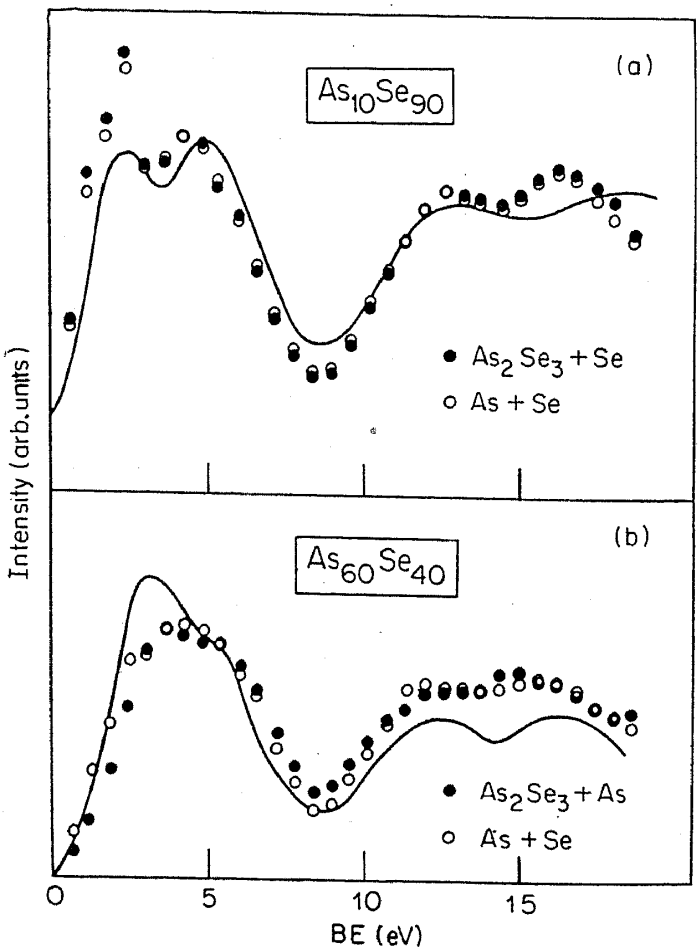

Figure 4. XPES of (a) $As_{10}Se_{90}$ and (b) $As_{60}Se_{40}$ glasses. The points correspond to calculated spectra.

would expect PES of As-Se glasses to be better represented as a weighted composite of the PES of As_{40} Se_{60} and the excess element. In figure 4, such composite spectra of As-rich As_{60} Se_{40} and Se-rich As_{10} Se_{90} are presented. For the purpose of comparison composite spectra obtained from PES of elements As and Se are also given. It is difficult to say unambiguously from figure 4 which of the composite spectra is superior. In view of other evidence reported from this laboratory (Mohan *et al* 1980; Rao and Mohan 1980) we would like to consider this as additional evidence for the presence of a chemically-ordered network structure in As-Se glasses.

The probabilities of As-As, Se-Se and As-Se bond formation may be inferred from a Boltzmann ratio. Since the bond energies are 46, 49 and 52 k cal/mol for As-As, Se-Se and As-Se respectively (Hurst and Davis 1974), the maximum probability of As-As and Se-Se bonds found in stoichiometric As_{40} Se_{60} is not more than 0·0009 and 0·03 respectively. This also strengthens a chemically-ordered network model.

Acknowledgement

We thank Professor C N R Rao, Solid State and Structural Chemistry Unit, Indian Institute of Science, for his kind encouragement. One of us (RM) is thankful to the Department of Science and Technology, Government of India, for financial support.

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