AN X- RAY PHOTOELECTRON SPECTROSCOPIC EXAMINATION OF GLASSES FROM THE Se-S ALLOY SYSTEM

By

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ABSTRACT

Mixtures of sulphur and selenium have been prepared in the form of bulk glasses over the composition range Se, 10, to 50 at % S. X-ray diffraction measurements on these alloys give structure factors which have first sharp diffraction peaks (FSDP) indicating medium as well as short range order. To investigate possible local order, x-ray photoelectron spectroscopic (XPS) measurements have been obtained on these glasses. The emphasis of the measurements has concentrated on two features, (a) the valence band, which depends on the over-all density of states and (b) the plasmon energies from the $L_3M_{4,5}M_{4,5}$ selenium Auger peaks which may be looked upon as being determined by the local electron density about the selenium atoms. It is found that the s-type peaks of the valence band split into two components between 15 and 40 at % S while the p-type peaks remain similar to pure selenium. The plasmon energies from the Auger peaks change markedly with composition. As sulphur is added to selenium the plasmon energy decreases, compared with the pure element, but starts to increase at 20 at % S so that at a composition of 40 at % S the plasmon energy is the same as that of elemental selenium. A simple model is proposed to explain these results.

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INTRODUCTION

Collective excitement of plasma in the form of quantised plasmon oscillations has been discussed by many authors[1-5]. The energy associated with these oscillations may be calculated from simple electron theory[6,7] as :

$$\hbar\omega_p=\hbar(ne^2/\epsilon_0 m)^{1/2} \qquad (1)$$

where ω_p is the plasmon frequency, n is the electron density of the plasma under consideration, and the other symbols have their usual meaning. Plasmon energies have been measured either directly through electron energy-loss spectra (EELS) or from energy loss associated with photoelectron or Auger peaks in electron spectroscopy. The feature of plasmon excitations is that they occur whether the solid is crystalline or disordered and hence can be used to enhance the available information about both states of matter.

The excitation of plasmons in photoelectron spectroscopy is often described in two ways : (1) an intrinsic process due to the collective response of valence electrons to the creation of a core hole as a consequence of photoelectron emission; (2) an extrinsic process due to the collective excitation of valence electrons as photoelectrons are transmitted to the material vacuum interface and is manifested most clearly in the free electron metals, for example Al or Mg[8]. The relative intensity and existence of the two types of plasmons in photoemission has not been clearly resolved[9,10], but the intrinsic process is believed to contribute a minor part of the total intensity[8], who state that intrinsic processes contribute 25% of the total plasmon loss intensity from Al metal and 22% of the total loss intensity from Mg metal.

In the x-ray (Al Kα) photoelectron spectroscopy of the chalcogenide glasses the most intense features are provided by the LMM series Auger lines. The kinetic energies of the lines of

selenium are well known through the work of[11]. A vital property of selenium Auger transitions is that the kinetic energies of the Auger electrons are sufficiently large (about 1300 eV), for which the mean free path in the material will be several atomic layers from the surface[12], so only those selenium atoms with about 30 Å of the material - vacuum interface will contribute to the Auger line, and assuming only extrinsic plasmons are excited, will sample the local electron density. Thus, the measured plasmon energies from electron spectroscopy becomes a local probe of the selenium electron density in the various glass compositions[13]. Since the number of Auger electrons is large, the number of plasmon excitations will also be large. Furthermore, since plasmon dispersion occurs over small angles with respect to the forward direction[3], the majority of the plasmon exciting electrons will be collected into a cone accepted by the entrance slit of the energy analyser of the photoelectron spectrometer on which the measurements are performed.

In the present work we use the measured plasmon energies, x-ray structure factors, macroscopic densities and glass transition temperatures to assist in the understanding of the structure of selenium sulphur bulk glasses for which scarce data have been published[14]. It is well known that the comelting of comparable glass structures like selenium and sulphur results in a copolymer system. An equilibrium copolymerization theory has been developed for the liquid structure in which copolymer molecules are in dynamic equilibria with S_8 and Se_8 monomer molecules and in which the relative monomer-polymer concentrations depend not only on temperature but also on the relative S and Se concentrations[15]. Experimentally the copolymerization is demonstrated by the temperature dependence of the viscosity of the various copolymer compositions and by the measurement of the variation of T_g with compositions on quenched glasses consisting of the polymer and monomer[16]. The effect of adding S to Se is to increase the monomer concentration as predicted by copolymerization theory. Berkes[17] developed a simple analytical model to

calculate the compositional dependence of T_g for the binary selenide systems.

EXPERIMENTAL

The glasses were prepared by the conventional melt quenching method using high purity elements (99.999%). The method consisted of sealing, under a high vacuum, the weighted amounts of selenium and sulphur in a carefully outgassed, argon flushed, rectangular section silica ampoules. The ampoules were then placed in a rocking furnace in which they were heated to above the melting point of selenium and were agitated to ensure thorough mixing of the melt. After homogenizing for 6 hours, the ampoules were quenched to room temperature in a large volume water bath. The silica ampoules were cut open prior to the examination of sample surfaces by XPS. The measurements were carried out on ES300 electron spectrometer using AlKα rays as the exciting radiation. Seven compositions were examined and all surfaces were found to be richer in selenium than the bulk material. Zero binding energy was located at the point of inflection on the rising part of the electron density curve (EDC). The number of Auger electrons involved in plasmon excitation cannot be calculated easily and a large inelastic background makes any intensity estimate difficult; however, from a large Auger peak, the plasmon energy can be determined with an estimated accuracy of ± 0.3 eV.

The flat surfaces of the quenched glasses adjacent to the walls of the silica tubes were examined using a θ-θ x-ray diffractometer and all the samples were found to be glassy. The structures factors over the composition range 10 to 50 at % S are shown in Figure 1.

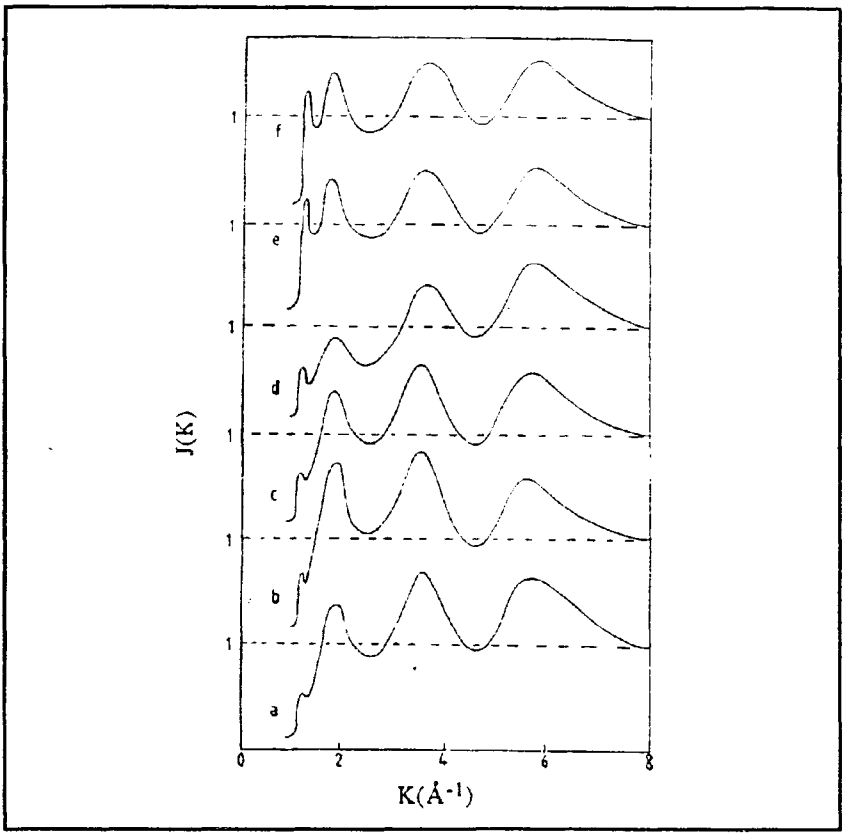

Fig. 1: The structure factors for Se_{1-x} S_x alloys, (a)x= 10 at %, (b)x= 15 at %, (c) x= 20 at %, (d)x= 25 at %, (e) x=40 at %, and (f)x= 50 at %.

RESULTS

The measured plasmon energy losses for the $L_3M_{4,5}$ $M_{4,5}$ Auger lines for elemental selenium and $Se_{90}S_{10}$ are shown in Figure 2. The averaged values of plasmon energy losses and the values

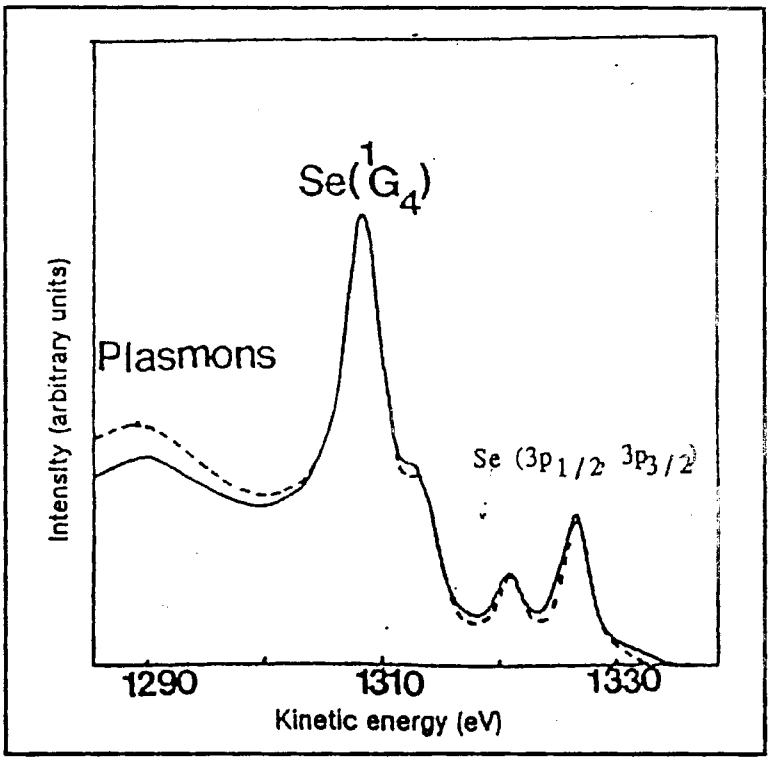

Fig.2 : The measured plasmon energy loss for the $L_3M_{4,5}M_{4,5}$ Auger lines for Se (broken curve) and $Se_{90}S_{10}$ alloy (full curve).

calculated from equation (1), using the measured macroscopic densities of the alloys, are shown in Table 1. The measured glass transition temperatures T_g and macroscopic densities are also

shown in Table 1. The change in plasmon energy with change in

Table 1 : Plasmon energies in eV (measured and calculated), measured relative densities and measured glass transition temperatures for Se-S glasses.

Composition	$\hbar\omega_p$ Exp. (± 0.3)	$\hbar\omega_p$ Calc.	Density gm cm^{-3} (± 1%)	T_g(k) (± 0.2%)
Se	19.3	16.5	4.31	317
$Se_{90}S_{10}$	18.3	16.7	4.15	314
$Se_{85}S_{15}$	18.2	16.9	4.10	309
$Se_{80}S_{20}$	18.8	17.0	4.02	308
$Se_{75}S_{25}$	18.8	17.1	3.92	306
$Se_{70}S_{30}$	18.8	17.3	3.87	303
$Se_{60}S_{40}$	19.3	17.2	3.56	293
$Se_{50}S_{50}$	19.3	16.9	3.19	288
Se*	19.3			
Se+	19.3			

[21]* N.J. Shevchick, M. Cardona, and Tejeda, J., Phys. Rev B 8, 2833 (1973).
[22]+ A.E. Meixner, and C.H.Chen, Phys.Rev. B 27, 7489 (1983).

selenuim content for the alloys is shown in Figure 3. The corrected valence band spectra for two compositions, $Se_{75}S_{25}$ and

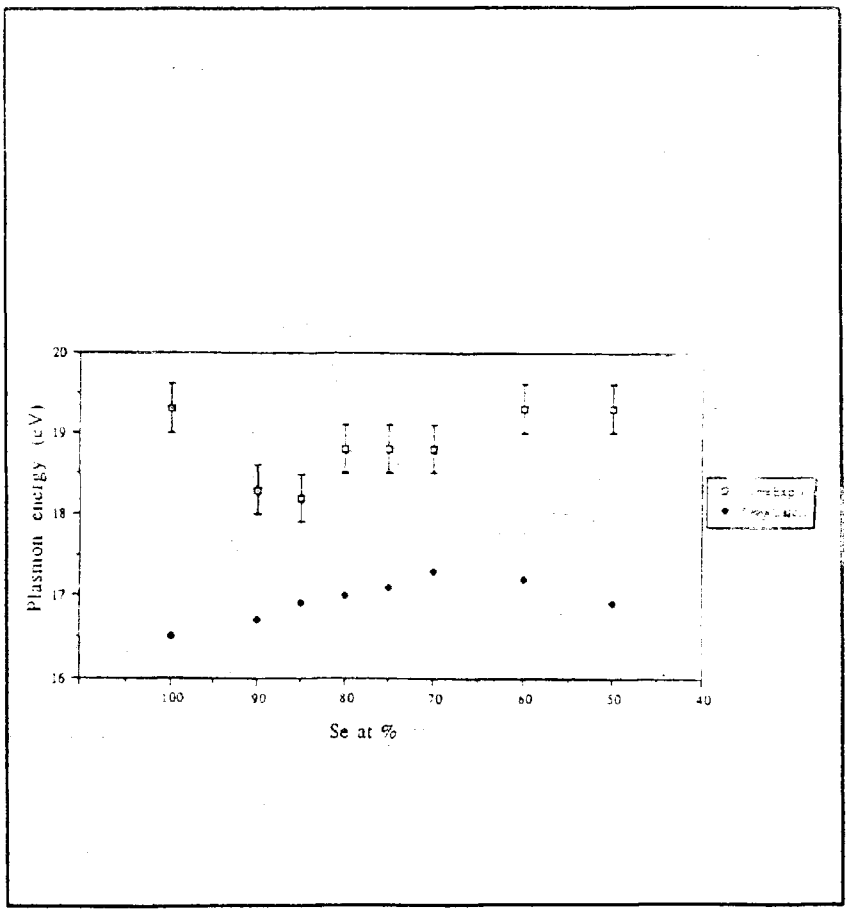

Fig.3: The change in plasmon energy (measured and calculated) with selenium content in the alloys.

$Se_{50}S_{50}$ are shown in Figure 4. The binding energies in eV of the

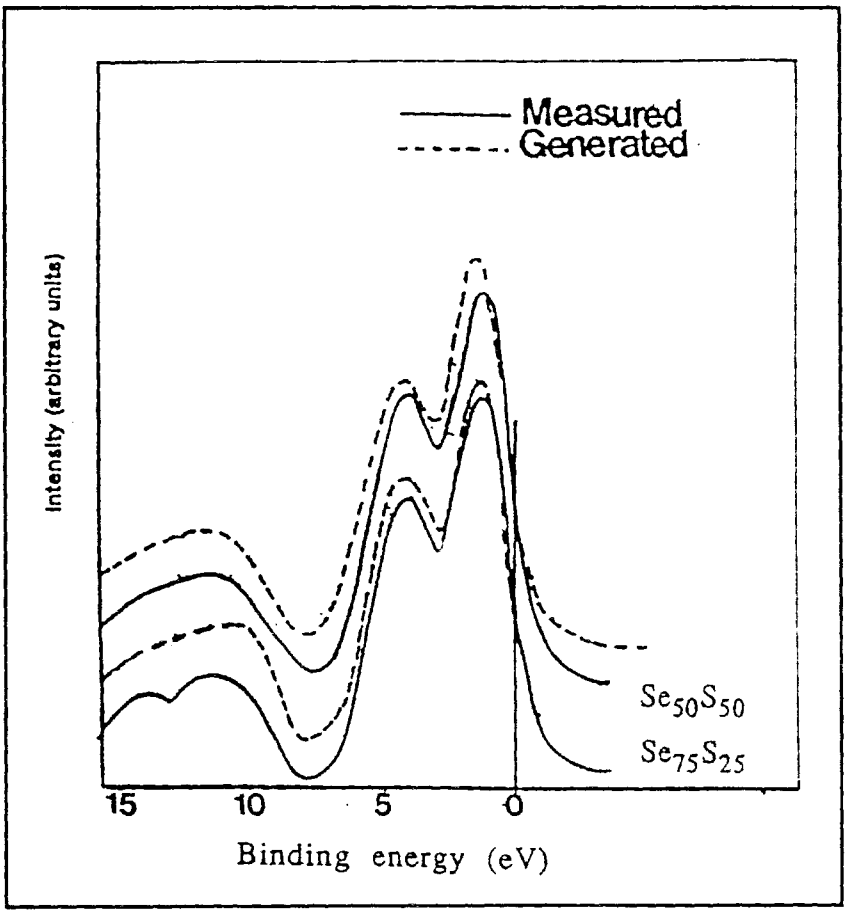

Fig.4: The corrected valence band spectra (measured and generated) for $Se_{75}S_{25}$ and $Se_{50}S_{50}$ alloys.

peaks of the valence bands referenced to the Fermi level are given in Table 2. The variation of glass transition temperatures and the

Table 2 : Binding energies in eV of the peaks of the valence bands referenced to the Fermi level for Se-S glasses.

Composition	p-type Non-bonding (±0.2)	Bonding	s-type (± 0.3)	ΔE_p
Se	1.4	4.1	12.1	2.7
$Se_{90}S_{10}$	1.4	4.0	11.8	2.6
$Se_{85}S_{15}$	1.3	4.0	10.1,13.6	2.7
$Se_{80}S_{20}$	1.3	4.1	11.3,14.6	
$Se_{75}S_{25}$	1.3	4.0	10.5,14.2	2.7
$Se_{70}S_{30}$	1.4	4.1	10.0,14.0	2.7
$Se_{60}S_{40}$	1.4	4.2	10.00	2.8
$Se_{50}S_{50}$	1.4	4.2	11.6	2.8

macroscopic densities with the selenium content in the alloys are shown in Figures 5 and 6 respectively.

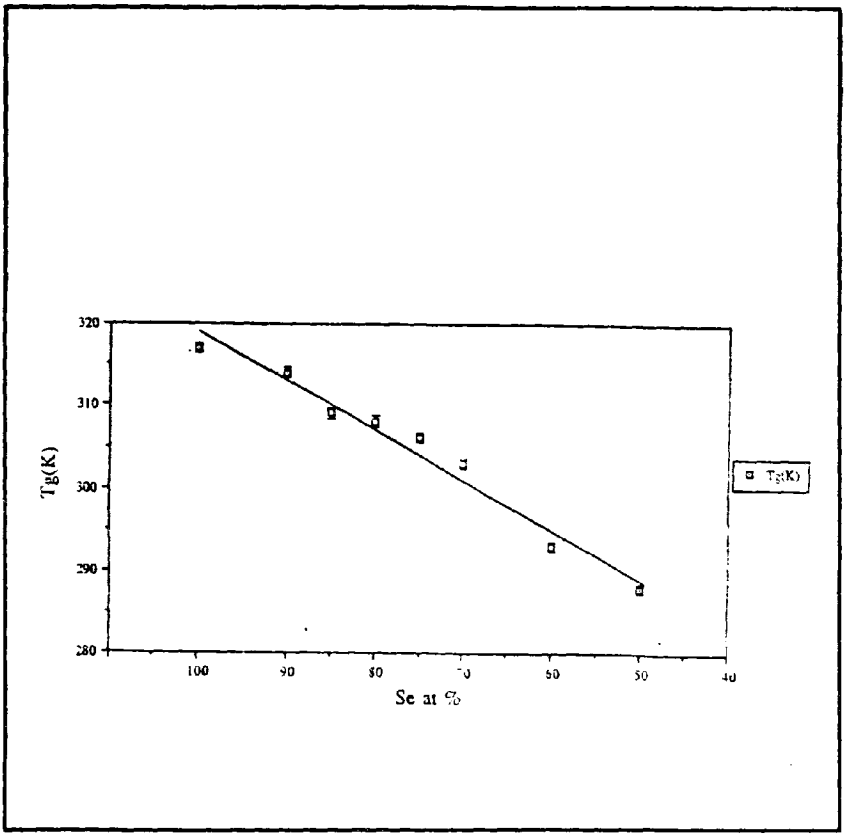

Fig.5: The variation of glass transition temperatures with selenium content in the alloys.

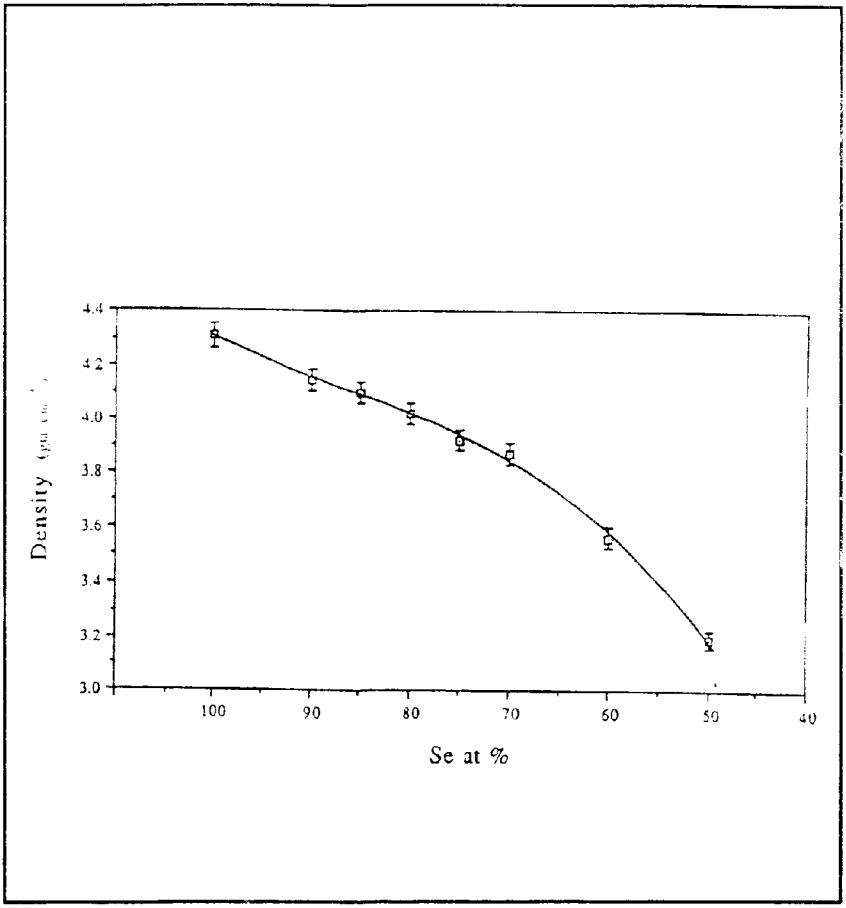

Fig.6: The variation of macroscopic densities with selenium content in the alloys.

DISCUSSION OF RESULTS

The generally accepted structural model of amorphous selenium is believed to be based on chains[18,19]. Our measured structure factors of the glassy Se-S alloys show a FSDP at k~ 1.2 $Å^{-1}$. This FSDP, whose intensity increases with the amount of S in the alloy is considered to be a signature of the medium range ordering (MRO) occurring in these glassy alloys and it is the first time that it has been identified in this system. As a starting point for a model we suggest that the addition of S to Se introduces eight-membered mixed rings. These rings are associated with the MRO in this system. This view of eight-membered mixed ring formation has support from published Raman spectra[20]. It is expected that the MRO connected with these structural units (rings) will effect the electronic structure of amorphous-Se network. This change of the electronic structure is exhibited in both the change of our measured plasmon energies and valence bands. As mentioned in the introduction, the measured plasmon energies from electron spectroscopy becomes a local probe of the selenium electron density in the various glass compositions. Since accurate electron density measurements were not available for the inclusion in equation (1), an exact comparison between simple theory and experiment was not possible and the measured values can be looked upon as a guide to the correct order of magnitude. It should be noted that all the experimental values of the plasmon energies are larger than those obtained from the use of equation (1). In general, the change in plasmon energy with selenium content imply that the local electron density is changing. Furthermore, the change in the local electron density of selenium is reflected in the valence band spectra where the s-type peak splits into two peaks at 15 at % of S and merge into a single peak at 40 and 50 at % S. In order to have some criterion of comparison for the experimental valence bands of the alloys it was decided to compare them with a superposition of the traces of Se and S weighted by the respective atomic fractions. A close agreement between the generated valence bands and the experiment was obtained especially over the p-type peak region.

As mentioned previously, the addition of S to Se will increase the ring concentration which is predicted by copolymerization theory and thereby the system is becoming more "plasticised" which produces a less rigid structure with the corresponding decrease in both the glass transition temperatures and the macroscopic densities as observed.

CONCLUSION

The model that we propose for the addition of sulphur to selenium is the formation of eight-membered mixed rings which are associated with the MRO observed for these bulk glasses. The addition of sulphur to selenium also introduces changes in the electronic structure of the amorphous selenium network which is exhibited in both the changes in the measured plasmon energies and valence bands.

The measured glass transition temperatures and macroscopic densities give a clear indication that a less rigid structure is formed when sulphur is added to selenium.

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