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The influence of antimony impurity on optical and electrical properties of amorphous selenium

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Abstract. Amorphous $\text{Se}_{1-x}\text{Sb}_x$ alloys were prepared using a conventional rapid quenching technique. It is found that antimony can only be substituted up to approximately 10 at.% in selenium to produce Se-Sb glassy alloys. The photoacoustic technique is employed for the first time to determine the optical energy gaps of $\text{Se}_{1-x}\text{Sb}_x$ glasses. The optical energy gap of amorphous selenium is found to be 1.99 ± 0.02 eV. It reduces drastically on substitution of 2 at.% Sb after which its variation with x is small. The activation energies of $\text{Se}_{1-x}\text{Sb}_x$ glasses have been determined from the temperature dependence of their electrical resistivities. The activation energy as a function of x also shows a sudden decrease in the range $0.01 \leq x \leq 0.02$. Plausible explanations have been suggested based on the Street-Mott model for charged defect states in amorphous chalcogenides.

1. Introduction

Selenium (Se) and Se-based alloys and compounds in the glassy (amorphous) form, the so-called chalcogenide glasses, continue to be widely investigated not only because of their interesting and commercially exploitable physical properties but also because of the rich variety of phenomena exhibited by these glasses which have been the source of providing new physical insights and understanding of glassy semiconductors [1-3]. Se is a good glass former and, therefore, a host of Se-based chalcogenide glasses have been investigated in bulk as well as thin-film forms [4-8]. Most of the chalcogenide glasses investigated are binary systems such as Se-Te, Se-Ge and Se-As and ternary systems based on these glasses [6]. The bulk Se-Sb system does not seem to have been investigated, presumably because of difficulties in producing glasses over an extended range of Sb concentrations. There are a few reports on Se-Sb films since it is easier to produce amorphous films over the entire composition range of Sb [5, 9, 10]. However, studies on thin films usually suffer from reproducibility of results which are sensitive to various preparation conditions.

In this paper we report our work on the electrical and optical properties of Se-Sb glasses in bulk form although we could succeed in producing these glasses with Sb contents only up to 10 at.% using a conventional liquid quenching technique.

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2. Experimental details

Amorphous $\text{Se}_{1-x}\text{Sb}_x$ (a- $\text{Se}_{1-x}\text{Sb}_x$) ($0 \leq x \leq 0.10$, where x varies in steps of 0.01) bulk alloys were prepared by melting a mixture of 99.999% pure elements using evacuated sealed quartz tubes and keeping it at 900 °C for 36 h with frequent shaking to homogenize the melt. The melt was then quenched in an ice–water mixture to produce a glassy solid. Glasses obtained in this way were lustrous and uniform as observed under a microscope. The amorphous nature and homogeneity of these alloys was confirmed by taking x-ray diffractograms on different pieces of alloys taken from the same batch of a given composition, i.e. none of the x-ray diffractograms showed any peaks. Further confirmation of the glassy nature of these alloys was obtained using differential scanning calorimetry which registered both the glass and the crystallization temperatures. Our repeated efforts to produce $\text{Se}_{1-x}\text{Sb}_x$ glasses with $x > 10$ at.% using conventional ice–water quenching techniques were not successful. Thus it seems that $x = 0.1$ is the limit in the $\text{Se}_{1-x}\text{Sb}_x$ system for producing it in the bulk glassy state.

The electrical resistivity measurements of these Se–Sb alloys were performed at room temperature and above using a conventional two-probe method because of their very high resistivities. Measurements were performed only after it was ascertained that the electrical contacts were ohmic. A Keithley electrometer was used to measure the current, and the temperature was measured with an alumel–chromel thermocouple kept close to the sample.

The usual transmission and reflection methods to measure the optical properties and energy gap of semiconductors are almost impossible to employ for bulk Se-based glasses because of their very high absorption in the visible optical region. Hence, we employed a more recent method, photoacoustic (PA) spectroscopy [11–14], to measure the optical energy gap of Se–Sb glasses. This technique has been successfully employed in optical studies of amorphous Se (a-Se) and Se–Te alloys by us previously [15–18]. Detailed information on the PA technique and its applications can be found in the review articles referred to above [11–14].

PA spectra of various Se–Sb glasses were taken at room temperature on a microprocessor-controlled PAR model 6001 PA spectrometer, in the wavelength region 200–1000 nm. Each spectrum was normalized to carbon black powder taken as the reference material. Holmium oxide was used to check the calibration of the spectrometer. An estimated error in the energy gap determination is about 0.02 eV.

3. Results

Typical PA spectra, i.e. PA signal versus wavelength, of various a- $\text{Se}_{1-x}\text{Sb}_x$ alloys are shown in figure 1. The PA signal shows constant behaviour at high and low wavelengths. In between, the change in the signal is interpreted as arising from electronic transitions between valence and conduction bands [13]. The wavelength at which the PA signal starts to drop (as the wavelength of the incident radiation increases) is taken as the threshold wavelength at which excitation or electrons from the valence band to the conduction band starts to diminish. This wavelength corresponds to the optical energy gap E_g or mobility gap of the sample [13, 14]. Very fine powder was used to record the spectra of each alloy. The homogeneity of each sample was checked by taking spectra on powders taken from different sections of a given composition

sample. These spectra were found to be akin to each other within the experimental accuracy, confirming the homogeneity of each sample. Varying the particle size of powders also did not affect the PA spectra of the samples. The energy gap of a-Se measured this way was found to be 1.99 eV, which is in good agreement with the value reported by us earlier by us, and by others [16–21]. The energy gap versus concentration x for the $\text{Se}_{1-x}\text{Sb}_x$ alloy system, determined by this method, is shown in figure 2. It is observed that the optical gap E_g does not change much as x changes from 0.0 to 0.01, but there is a drastic change in the gap when x changes from 0.01 to 0.02, i.e. it decreases from 1.96 to 1.48 eV. As the concentration of Sb is further increased, i.e. $x > 0.02$, E_g continues to decrease but slowly and linearly with increasing Sb concentration. Data for E_g in the antimony concentration range $0.2 < x < 0.10$ can be represented by the equation

$$E_g \text{ (eV)} = -3.25x + 1.54.$$

Measurements were repeated a few times on samples prepared at different times and the results were found to be reproducible within the experimental accuracy. It is also noted that, as the concentration of Sb increases, the transition region in the PA spectra becomes larger.

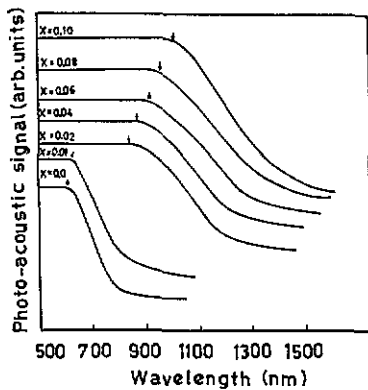


Figure 1. PA signal versus wavelength for a- $\text{Se}_{1-x}\text{Sb}_x$ alloys.

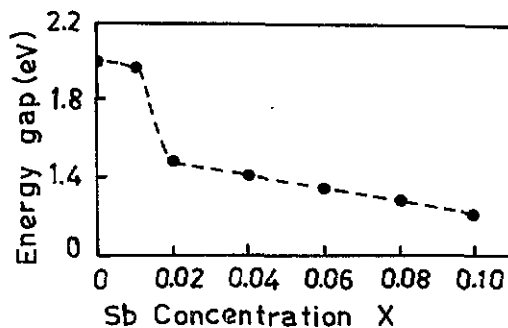


Figure 2. Energy gap E_g versus antimony concentration x for $\text{Se}_{1-x}\text{Sb}_x$ glassy alloys.

Resistivity measurements showed that all samples were highly resistive and exhibited semiconducting behaviour. The logarithmic value of resistivity of $\text{Se}_{1-x}\text{Sb}_x$ is almost the same for $x = 0$ and 0.01 but, as x changes from 0.01 to 0.02, it reduces drastically from 11.96 to 9.12. For x larger than 0.02, the resistivity decreases slowly and monotonically as shown in figure 3.

Figure 4 shows the variation in $\log \sigma$ as a function of $10^3/T$, where σ is the conductivity (inverse of resistivity) and T is the temperature, for various amorphous Se-Sb alloys. All data points for each sample lie on a straight line, indicating that the following Arrhenius relation is very well followed by these glasses:

$$\sigma = \sigma_0 \exp(-E_c/k_B T). \quad (1)$$

Here σ_0 is the conductivity pre-factor, k_B is the Boltzmann constant and E_c is the activation energy for conduction. Each sample is characterized by a single activation energy over the temperature interval used here.

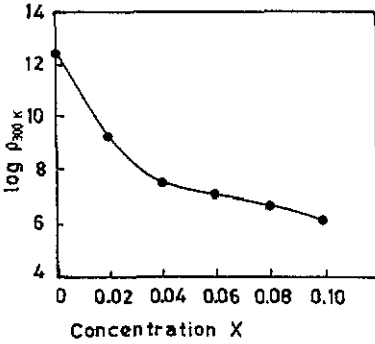


Figure 3. Variation in $\log \rho_{300\text{ K}}$ as a function of Sb concentration for $\text{Se}_{1-x}\text{Sb}_x$ glassy alloys. $\rho_{300\text{ K}}$ is in ohm centimetres.

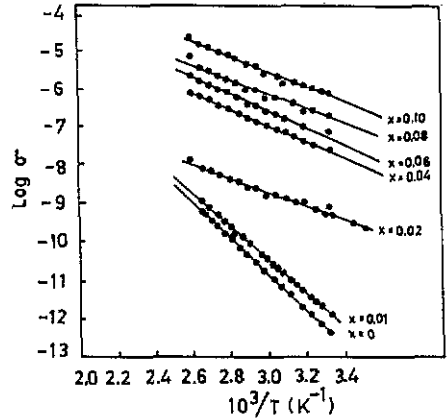


Figure 4. Variation in $\log \sigma$ as a function of temperature for $\text{Se}_{1-x}\text{Sb}_x$ glassy alloys. σ is in $(\Omega\text{ cm})^{-1}$.

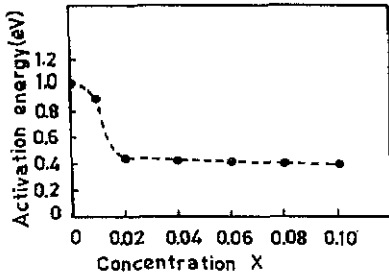


Figure 5. Activation energy as a function of Sb concentration for $\text{Se}_{1-x}\text{Sb}_x$ glassy alloys.

The activation energy E_c of each glassy alloy was calculated from the slope of the $\log \sigma$ versus $10^3/T$ plot. The variation in E_c as a function of Sb concentration x for $\text{Se}_{1-x}\text{Sb}_x$ alloys is shown in figure 5. The activation energy for amorphous Se is found to be 1.01 eV which is in good agreement with the value reported in the literature [22]. From this figure it is observed that there is a sudden change in activation energy from 0.88 eV for the $x = 0.01$ alloy to 0.44 eV for the $x = 0.02$ alloy. This observation is similar to, and consistent with, the sudden drop in the optical gap versus x at the same values of x , as shown in figure 2. The activation energies for these alloys vary linearly with Sb concentration for $x > 0.02$ and with a small slope. This variation can be represented by the relation

$$E_c(\text{eV}) = -0.60x + 0.45.$$

The extrapolation of the $\log \sigma$ versus $10^3/T$ plot to a zero value of $10^3/T$ gives the values of the conductivity pre-factor σ_0 . These are listed in table 1 together with the values of E_g and E_c .

4. Discussion

Our unsuccessful efforts to produce Se-Sb glassy alloys in bulk with an Sb concentration of more than 10 at.% by the conventional ice-water quenching technique clearly

Table 1. Values of the optical energy gap E_g , the activation energy E_c , $\log \rho_{300\text{ K}}$ and the conductivity pre-factor σ_0 .

Sample	E_g (eV)	E_c (eV)	$\log \rho_{300\text{ K}}$ ($\Omega\text{ cm}$)	σ_0 ($\Omega^{-1}\text{ cm}^{-1}$)
Se	1.99±0.02	1.01±0.02	12.40	1.48×10^3
Se _{0.99} Sb _{0.01}	1.96±0.02	0.88±0.02	11.96	1.65×10^3
Se _{0.98} Sb _{0.02}	1.48±0.02	0.44±0.02	9.12	4.5×10^{-4}
Se _{0.96} Sb _{0.04}	1.41±0.02	0.42±0.02	7.53	1.65
Se _{0.94} Sb _{0.06}	1.36±0.02	0.41±0.02	7.12	1.93
Se _{0.92} Sb _{0.08}	1.28±0.02	0.40±0.02	6.76	2.21
Se _{0.90} Sb _{0.10}	1.22±0.02	0.39±0.02	6.10	2.70

indicate that the inclusion of Sb in Se reduces its glass-forming ability tremendously. Tellurium, which has a structure similar to that of Se, can also be incorporated in Se only to a maximum of 30 at.% [15, 16]. Thus it is not surprising that Sb, which has quite a different structure, leads to a decrease in the glass-forming ability of Se. A possible reason for this is that Sb is responsible for reducing the Se_s ring concentration and acting as a *via media* to change the weak bonding between the Se linear polymeric chains to relatively strong covalent bonds. A large decrease in the resistivity of a-Se with the addition of only 2 at.% Sb to a-Se also points towards the possibility of substantial change in the coordination in the melt. Some of the reports that bulk Se_{1-x}Sb_x glasses have been produced with $x > 0.10$ and up to $x = 0.225$ with the conventional ice-water quenching do not agree with our results [8].

The temperature dependence of the conductivity of glasses provides information on the type of electronic conduction which dominates. Our results in figure 4 show that the $\log \sigma$ versus $10^3/T$ data lie on a straight line, indicating that equation (1) is obeyed well and also suggesting that the Fermi level is pinned in the gap. The present data are not sufficient to say whether this pinning of Fermi level is due to a high local density of defect states in the gap, as suggested by Mott and Davies [23], or due to a charge neutrality conduction involving localized states tailing into the gap and consequently resulting in an overlap as per the CFO model [24]. Similarly the activation energy values and their concentration dependence do not distinguish whether electrical conduction is taking place in the extended states above the mobility edge or by hopping in the localized states. Mott [25] has suggested that this distinction can be made by ascertaining the magnitude of the conductivity pre-factor σ_0 . This factor in amorphous Se for conduction due to extended states is of the order of $10^4\ \Omega^{-1}\text{ cm}^{-1}$, and it becomes two to three orders smaller for conduction through localized states. The value of σ_0 for glassy Se from our measurements is of the order of 10^3 , indicating that the conduction process in a-Se is through the extended states. The addition of 1 at.% Sb to Se, i.e. $x = 0.01$, does not change σ_0 much. However, when $x = 0.02$, σ_0 reduces to $4.5 \times 10^{-4}\ \Omega^{-1}\text{ cm}^{-1}$ and then it increases as the Sb concentration is increased, as given in table 1. The value of σ_0 for $x = 0.10$ is $2.7\ \Omega^{-1}\text{ cm}^{-1}$. Thus, for $x \geq 0.02$, the conduction process in Se_{1-x}Sb_x seems to be due to hopping in the localized states. This observation helps us to understand the main result of this paper as discussed below. It should be noted that these results are quite different for Se-Sb films which show σ_0 much higher [15, 26].

The observation of a sharp drop in E_g and E_c when x changes from 0.01 to 0.02 is quite a surprising result. We try to give, in the following, two plausible physical

reasons to account for the observed steep drop in E_g and in the activation energy E_c as the concentration of Sb is raised to 2 at.% from 1 at.% in a-Se. Both are based on the Street-Mott [27] model for charged defect states in amorphous chalcogenides.

The ESR measurement revealed a weak signal for pure a-Se and hardly any change in the signal was noticed on the addition of Sb. However, it is known that dangling bonds are there in abundance in a-Se. So we deduce, following Street and Mott [27], that most of the dangling bonds are either devoid of electrons or have an extra electron, i.e. they are charged. We will denote the neutral, positively charged and negatively charged bonds by D^0 , D^+ and D^- , respectively. The twofold-coordinated chains of Se are highly flexible—a feature that favours electron-lattice coupling which, according to Anderson [28], offers a negative correlation potential for electrons to become attracted to the D^0 bonds. Exchange of an electron between two D^0 centres gives rise to a D^+-D^- pair. The D^+ centre forms a bond with the lone-pair electrons of a nearby fully bonded atom. Since the lone-pair electrons, otherwise on the top of the valence band, go into the deep bonding states, a lot of electronic energy (about 0.5 eV) is released together with strong local distortions in the structure. The polaron thus formed helps to overcome the Coulomb repulsion and makes a pair $\uparrow\downarrow$, which occupies one D^- state. Subsequently the D^+ and D^- centres, respectively, localize electrons and holes and form effectively neutral D^0 centres. These D^0 states move deeper into the band gap (away from the D^+ and D^- states) since the localized electrons and holes require, for their excitations, extra energy to overcome the polaron energy.

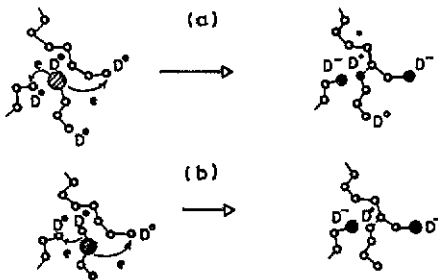


Figure 6. Formation of one D^+ and two D^- (cross-hatched circles) centres with the addition of Sb (hatched circles) in a-Se (open circles).

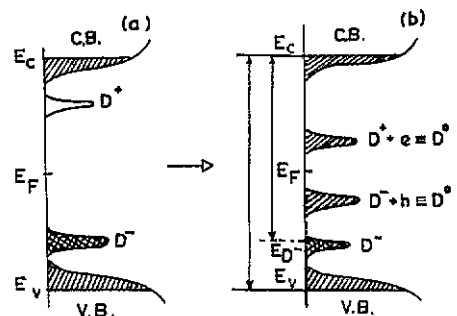


Figure 7. Schematic representation of the change in the energy band structure of a-Se with the addition of Sb: C.B., conduction band; V.B., valence band. $D^+ + e \equiv D^0$ and $D^- + h \equiv D^0$ are single-electron neutral states. D^- represents $2e$ states. Valence electrons cannot be excited into these states.

Sb is threefold coordinated; so the substitution of an Sb creates two D^- and one D^+ centre as shown in figure 6. After the D^- and D^+ centres have localized holes and electrons and have become converted into D^0 states, about half of the D^- states would still remain unchanged because, for them to localize holes, the electrons in them will have to be excited to quite far-off states in the conduction band. The corresponding energy level diagram is shown in figure 7.

We have shown in an earlier paper on a-Se [18] that the E_g measured by PA spectroscopy is the mobility gap, i.e. $E_c - E_v$ in figure 7. After Sb is introduced and a sufficiently high density of D^- states is created, as shown in figure 7(b), electrons from these D^- states can be excited to the conduction band by the optical radiation and the measured E_g may be $E_c - E_{D^-}$ rather than $E_c - E_v$. Thus a drop in E_g of magnitude $E_D - E_v$ is expected from the value $E_c - E_v$ at a concentration of Sb that generates a 'good' number of D^- states in the space. With the present data it is not possible to estimate the critical concentration of Sb that will give rise to such a drop in E_g . If the above understanding is correct, then we can deduce from our data that, as the concentration of Sb rises from 1 to 2 at.%, a sufficiently large number of D^- states remain in the system that do not convert into D^0 states. Once the excitation from the D^- band sets in, it is understandable that E_g should reduce gradually (after the initial drop) with the concentration of Sb increasing beyond 2 at.% as our data show (figure 7); this is because, with increasing Sb, the D^- band will become increasingly broader, and the density of D^- localized states will steadily increase, facilitating a hopping conduction along the localized states as the above discussion about σ_0 also indicates.

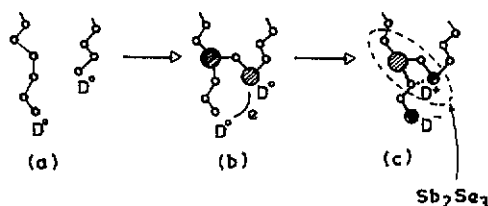


Figure 8. Suggested bonding of atoms of Sb (hatched circles) in a-Se (open circles), leading to Sb_2Se_3 structure as explained in the text.

We suggest another plausible explanation for the observed drop in E_g which is based on the possibility of local formation of the Sb_2Se_3 configuration. The Sb_2Se_3 compound has been studied thoroughly [9] and it is known that the band gap of a- Sb_2Se_3 is about 1.6 eV. In figure 8 we propose that, if two Sb atoms suitably replace two Se atoms substitutionally on two nearby Se chains and the threefold-coordination requirement of Sb makes it convenient for an a-Se atom to become bonded to both these Sb atoms and thereby to join the two chains, then a further lone-pair bond can be formed between one of these Sb atoms and its nearest Se atom on the other chain as shown in figure 8(c). This results in a local formation of an a- Sb_2Se_3 molecular structure [29]. If there are a few such structures scattered throughout the whole system, then we expect a tendency for E_g to drop to a value close to the value of the band gap for the a- Sb_2Se_3 system which is about 1.6 eV. We find a drop in E_g from 1.96 eV to about 1.48 eV as Sb goes from 1 at.% to 2 at.%. Again, it is difficult to estimate the typical concentration of Sb at which the probability of local formation of Sb_2Se_3 structures is sufficiently high. If it is known that Sb-Se-Sb bonding of the type shown in figure 8(b) is particularly favoured in Se-Sb systems for energetic reasons, then our results suggest that Sb_2Se_3 structures apparently begin to form as the Sb concentration exceeds 1 at.% or so. Further experimental work to explore the local structure of these alloys is needed to confirm this explanation.

5. Conclusions

Bulk $\text{Se}_{1-x}\text{Sb}_x$ glassy alloys with up to $x = 0.10$ (10 at.% Sb) were produced by conventional ice-water quenching technique. The substitution of more than 10 at.% Sb in Se resulted in crystalline samples as determined by x-ray diffractograms. The PA technique has been employed to determine the optical energy gaps of these alloys for the first time. The optical energy gap reduces drastically as the content of Sb in $\text{a-Se}_{1-x}\text{Sb}_x$ is increased from $x = 0.01$ to 0.02. Similar changes are observed in the variation in resistivity and activation energy as a function of Sb concentration x . For values of x greater than 0.02 the variations in optical energy gap, resistivity and activation energy are small but linear with x . An effort has been made to explain these observations on the basis of the Street-Mott model for charged defect states in amorphous chalcogenide glasses.

Acknowledgments

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References

- [1] Ovshinsky S R 1968 *Phys. Rev. Lett.* **21** 1450
- [2] Taback M, Ing S W and Scharee M E 1973 *IEEE. Trans. Electron Devices* **ED-10** 91
- [3] Gerlach E and Groose P 1979 *The Physics of Selenium and Tellurium* (Berlin: Springer)
- [4] Das G C, Bever M B and Uhlmann D R 1972 *J. Non-Cryst. Solids* **7** 251
- [5] Wood, C, Muller R and Gilbert L R 1973 *J. Non-Cryst. Solids* **12** 295
- [6] Mott N F and Davis E A 1979 *Electronic Process in Non-Crystalline Materials* (Oxford: Clarendon)
- [7] Gopal E S R, Parthasarthy G and Rao K J 1984 *Phil. Mag.* **B 50** 335
- [8] Khafagy A H, El Zaidia M M, Ammar A A and Abo-Ghazala M 1990 *Indian J. Phys.* **A 64** 263
- [9] Wood C, Hurych Z and Shaffer J C 1972 *J. Non-Cryst. Solids* **8-10** 209
- [10] Nigam P S and Pawar R R 1990 *Bull. Mater. Sci. (India)* **13** 343
- [11] Rosenzweig A 1975 *Phys. Today* **28** 23
- [12] Pao Y H 1977 *Optoacoustic Spectroscopy and Detection* (New York: Academic)
- [13] Somoano R B 1978 *Angew. Chem. Int. Edn Engl.* **17** 238
- [14] Sunandana C S 1988 *Phys. Status Solidi a* **105** 101
- [15] Bhatnagar A K and Subrahmanyam S V 1982 *Solid State Commun.* **42** 281
- [16] Venugopal Reddy K, Raman S V and Bhatnagar A K 1983 *Proc. Solid State Physics Symp. (Barc, India)* **C 26** 395
- [17] Venugopal Reddy K and Bhatnagar A K 1985 *J. Non-Cryst. Solids* **76** 409
- [18] Bhatnagar A K, Venugopal Reddy K and Srivastava V 1985 *J. Phys. D: Appl. Phys.* **18** L149
- [19] Dawar A L, Joshi J C and Narain C 1981 *Thin Solid Films* **76** 113
- [20] Lanyon H P D 1985 *Phys. Rev.* **130** 134
- [21] Venugopal Reddy K and Bhatnagar A K 1987 *Key. Eng. Mater.* **15** 813
- [22] Lakatos A I and Abkowitz M 1971 *Phys. Rev.* **B 3** 1791
- [23] Mott N F and Davis E A 1970 *Phil. Mag.* **22** 903
- [24] Cohen M H, Fritzsche H and Ovshinsky S R 1969 *Phys. Rev. Lett.* **22** 1065
- [25] Mott N F 1970 *Phil. Mag.* **22** 7
- [26] Mehra R M, Hemant Kumar, Surinder Koul and Mathur P C 1984 *Phys. Status Solidi a* **83** 341
- [27] Street R A and Mott N F 1975 *Phys. Rev. Lett.* **35** 1293
- [28] Anderson P W 1975 *Phys. Rev. Lett.* **35** 1293
- [29] Abrikosov N Kh, Bankina V F, Poretskaya V V, Shelimova L E and Skudnova E V 1969 *Semiconducting II-VI, IV-VI and V-VI Compounds* (New York: Plenum)