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Chemical bond approach to optical band gap in $Se_{100-x}Sb_x$ chalcogenide glasses

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In the present work, values of the optical band gap E_g of glassy $Se_{100-x}Sb_x$ alloys are determined from experimentally observed data of transmission at different wavelengths using three different methods. The theoretical prediction of E_g values is also made using random bond network model proposed by Shimakawa. The composition dependence of E_g is discussed using chemical bond approach.

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1. Introduction

The Se-Sb alloys are the optical materials, which have found applications based on their electrical and optical properties [1-16]. Desired values of these properties can be obtained by systematic change of the composition. Hence, considerable attention has been focused on glasses of Se-Sb system [1-16]. These glasses exhibit switching effect [1, 2]. The effect of Sb alloying on the electrographic properties of a-Se and laser induced amorphous to crystalline phase transition in glassy $Se_{100-x}Sb_x$ alloys is reported by Mikla et al [3, 4]. The thermal stability and carrier drift mobilities of a-$Se_{100-x}Sb_x$ photoconductors is studied by Tonchev et al [5]. The optical properties of thin films of Se-Sb alloys has been investigated by Reddy et al, Fouad et al, Singh et al and Majeed et al [6-9]. The structure of some Se-Sb thin films is analysed by Kaito et al [10]. Optical recording characrteristics of Sb_2Se_3 thin films using CW-Ar^+ laser has been studied by Jayakumar et al [11]. Laser-induced crystallization in amorphous films of Sb_2M_3 (C = S, Se, Te), has been reported by Arun et al [12]. Study of trapping in Sb_xSe_{1-x} amorphous semiconductors has been done by Mikla et al [13]. Calorimetric studies on Se-Sb thin films have also been reported in literature [14, 15]. The dielectric study on Se-Sb alloys is reported by our group [16].

The continued scientific interest in Se-Sb binary system is due to its potential use in phase change optical recording. The optical storage based on the amorphous-crystalline phase transition utilizes the large optical reflectivity and optical absorption changes [10, 11]. A significant understanding of the optical properties of these materials required by the technology aspects of phase change optical recording technique has been produced in the past years but still the engineering and developments aspects of the field surpass the underlying basic scientific understandings.

From the above discussion, it is clear that study of the optical properties of chalcogenide glasses is very important for the determination of the electronic band structure as well as optical parameters, such as optical energy gap and refractive index. There is no pronounced feature of the optical absorption spectrum that can be directly related to an optical gap. For crystalline semiconductors, the associated optical absorption spectrum terminates abruptly at the fundamental gap, while in amorphous semiconductors a tail in the absorption spectrum encroaches into the gap region [17] and [18]. This tail in the optical absorption spectrum, arising as a consequence of the tail and gap states, makes the optical gap of an amorphous semiconductor difficult to define experimentally. The Tauc model [19] has been used as a standard model whereby the optical gap of an amorphous semiconductor may be determined. In this model, it is assumed that the disorder characteristic of amorphous semiconductors relaxes the momentum conservation rules. Assuming square root distribution of conduction band and valence band states, and assuming that the momentum matrix element is independent of $h\nu$, Tauc et al [19] assumed that an extrapolation of the essentially linear functional dependence of $(\alpha h\nu)^{1/2}$, observed in amorphous semiconductors at a sufficiently large $h\nu$, allows an empirical optical energy gap to be defined. According to Tauc et al. the optical energy gap, can be determined by

$$\alpha h\upsilon = B\left(h\upsilon - E_g\right)^m \tag{1}$$

here B^{-1} is the band edge parameter and m is an exponent that may take values 1, 2 or 3 as found for various amorphous semiconductors. In the case of amorphous chalcogenides, the transitions are known to be non-direct ones, and hence the exponent s, is found to be1l–2.

Unfortunately, there are difficulties associated with the analysis using Tauc's method. First, the spectral variation of the momentum matrix element is in question. Cody et al [20] suggest that it is the dipole matrix element instead is independent of $h\nu$. Thus, they assert, one should instead extrapolate $(\alpha/h\nu)^{1/2}$ to define the optical gap. Sokolove et al [21], while assuming that the disorder characteristic to amorphous semiconductors will modify the basic form of the optical absorption. They suggest that an extrapolation of $(\alpha h\nu)^{1/3}$ is even more appropriate [22] and [23]. However, as was pointed out by Cody et al [20] with the tail in the optical absorption spectrum it is always possible to plot any root of $\alpha(h\nu)$ as a function of $h\nu$ and obtain an appropriate linear variation with $h\nu$ over some range of energy. The energy over which this apparent linear variation is observed is also subject of some controversy.

In our recent paper [24], we have measured optical constants in thin films of glassy $Se_{100-x}Sb_x$ alloys, where we have used the Tauc's method for calculation of optical band gap. From above discussion, it is clear that the other two methods are also suggested by some workers for evaluation of optical band gap. This inspired us to use the other two methods mentioned above for the evaluation of optical band gap in glassy $Se_{100-x}Sb_x$ alloys and compare their results with our previous reported values. The theoretical approach suggested by Shimakawa [25] for determination of E_g is also used to compare the experimental results with the theoretical values of optical band gap.

2. Experimental

Glassy alloys of $Se_{100-x}Sb_x$ were prepared by quenching technique. The exact proportions of high purity (99.999%) Se and Sb elements, in accordance with their atomic percentages, were weighed using an electronic balance (LIBROR, AEG-120) with the least count of 10^{-4} gm. The material was then sealed in evacuated (~10^{-5} Torr) quartz ampoule (length ~ 5 cm and internal diameter ~ 8 mm). The ampoule containing material was heated to 800 ^{0}C and was held at that temperature for 12 hours. The temperature of the furnace was raised slowly at a rate of 3 - 4 ^{o}C / minute. During heating, the ampoule was constantly rocked, by rotating a ceramic rod to which the ampoule was tucked away in the furnace. This was done to obtain homogeneous glassy alloy. After rocking for about 12 hours, the obtained melt was rapidly quenched in ice-cooled water. The quenched sample was then taken out by breaking the quartz ampoule. The glassy nature of the alloy was ascertained by X-ray diffraction. The glassy nature of alloys was checked by x-ray diffraction technique. For this, x-ray diffraction (XRD) patterns of all the five samples were taken at room temperature by using a x-ray diffractometer (Philips, PW 1140/09). The copper target was used as a source of x-rays with λ =1.54 Å (Cu $K_{\alpha 1}$) XRD pattern of glassy $Se_{90}Sb_{10}$ is shown in Fig. 1. Absence of any sharp peak in XRD pattern in Fig. 1 confirms the glassy nature of $Se_{90}Sb_{10}$ alloy. Similar XRD patterns were obtained for the other glassy alloys.

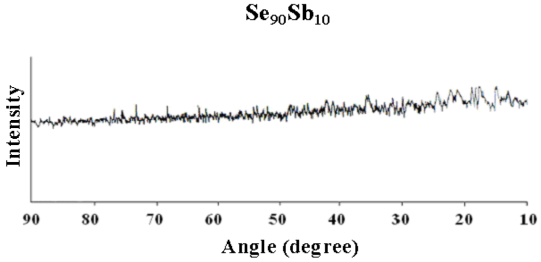

Fig. 1. XRD pattern of glassy $Se_{90}Sb_{10}$ alloy

Thin films of glassy alloys of a $Se_{100-x}Sb_x$ were prepared by vacuum evaporation technique, in which the substrate was kept at room temperature at a base pressure of 10^{-6} Torr using a molybdenum boat. The composition of each thin film was checked by Electron Probe Micro Analyzer (EPMA). No significant shift was observed in the chemical composition of the materials in thin film form. The thickness of the films was measured by optical methods using a thickness monitor and was 500 ± 10 nm. Thickness was kept almost constant to avoid thickness effects on the optical parameters. The films were kept inside the deposition chamber for 24 hours to achieve the metastable equilibrium. A Double UV/VIS/NIR Computer Controlled Spectrometer (Hitachi-330) is used for measuring optical transmission of $Se_{100-x}Sb_x$ thin films. The optical transmission was measured as a function of wavelength.

3. Results and discussion

3.1 Determination of absorption coefficient α

The absorption coefficient α is determined from the fringe patterns in the transmittance spectrum using the method proposed by Swanepoel [26]. In the transmittance region where the absorption coefficient ($\alpha = 0$), the refractive index n is given by

$$n = \left[N + (N^2 - s^2)^{1/2} \right]^{1/2} \qquad (2)$$

Here

$$N = \left(\frac{2s}{T_m} \right) - \frac{(s^2 + 1)}{2}$$

T_m is the envelope function of the transmittance minima and s is the refractive index of the substrate.

In the region of weak and medium absorption, where (α ≠ 0), the transmittance decreases mainly due to the effect of n and the refractive index n is given by

$$n = [N + (N^2 - s^2)^{1/2}]^{1/2} \qquad (3)$$

Here

$$N = \left\{ \frac{2s(T_M - T_m)}{T_M\ T_m} \right\} + \frac{(s^2 + 1)}{2}$$

and T_M is the envelope function of the transmittance maxima.

In the region of strong absorption, the transmittance decreases drastically due almost exclusively to the influence of α and n which can be estimated by extrapolating the values in the other regions. Because the thickness of our film is uniform, interference give rise to the spectrum as shown in Fig. 2. The fringes can be used to calculate the refractive index n of the film using Eqs. (2) and (3) as indicated previously.

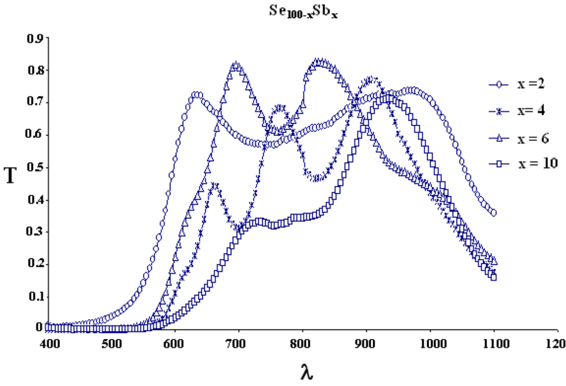

Fig. 2. Variation of transmittance (T) with wavelength (λ) in $Se_{100-x}Sb_x$ thin films.

The absorption coefficient α can be calculated from the relation

$$\alpha = \left(\frac{1}{d}\right) \ln\left(\frac{1}{\chi}\right) \qquad (4)$$

Here χ is the absorbance and d is the film thickness.

If n_1 and n_2 are the refractive indices at two adjacent maxima or minima at λ_1 and λ_2 then the thickness is given by

$$d = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)} \qquad (5)$$

In the region of weak and medium absorption, using the transmission minima T_m, χ is given by

$$\chi = \frac{\left[E_m - \{E_m^2 - (n^2 - 1)^3 (n^2 - s^4)\}^{0.5}\right]}{\left[(n - 1)^3 (n - s^2)\right]} \qquad (6)$$

here

$$E_m = \left[(8n^2 s/T_m) - (n^2 - 1)(n^2 - s^2)\right] \qquad (7)$$

The spectral distributions of both n and k for $Se_{100-x}Sb_x$ films are shown in Figs. 3 and 4 respectively. Fig. 5 depicts the variation of the absorption coefficient α with incident photon energy for the as-deposited thin film samples of the prepared alloys.

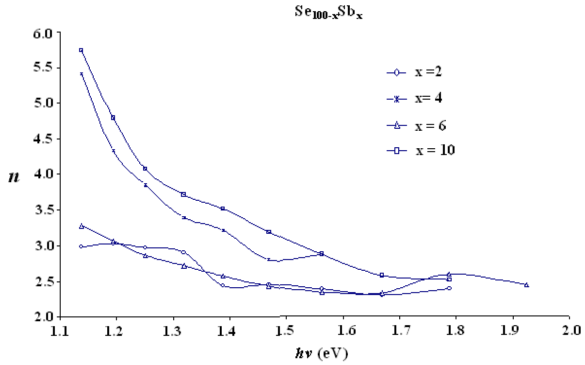

Fig. 3. Variation of refractive index (n) with photon energy (hν) in $Se_{100-x}Sb_x$ thin films.

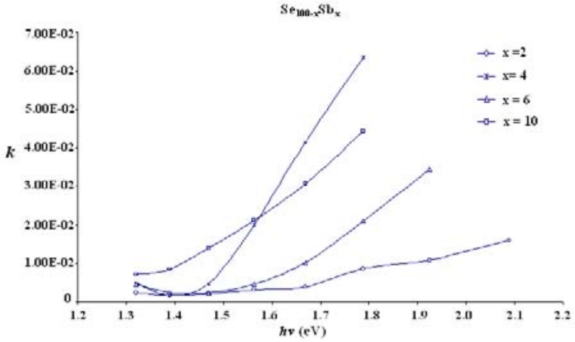

Fig. 4. Variation of extinction coefficient (k) with photon energy (hν) in $Se_{100-x}Sb_x$ thin films.

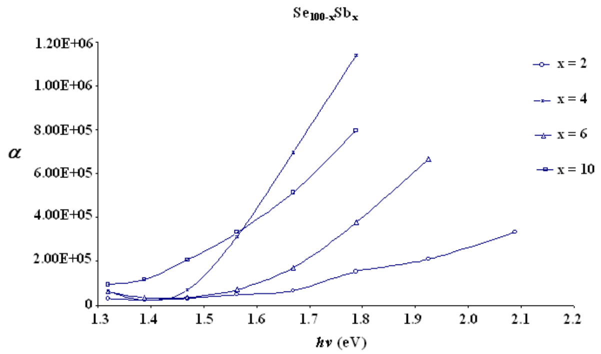

Fig. 5. The variation of the absorption coefficient α with photon energy hν for different alloys.

3.2. Experimental determination of optical band gap (E_g)

Values of the optical energy gap (E_g) of the glassy $Se_{100-x}Sb_x$ system were obtained according to the three models explained in the introduction section. In the three cases, values of the optical energy gap, were obtained from plots of $(\alpha h\nu)^{1/2}$, $(\alpha/h\nu)^{1/2}$ and $(\alpha h\nu)^{1/3}$ vs $h\nu$, respectively by extrapolating the linear portions of the curves shown in Figs. 6-8 respectively. Results are given in Table 1. The obtained results show that $(E_g)_1 > (E_g)_2 > (E_g)_3$ which is in good agreement with the results of Sweenor et al [27].

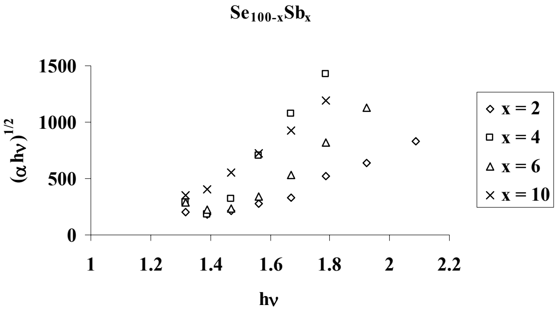

Fig. 6. Plot of $(\alpha h\nu)^{1/2}$ vs hν for different alloys.

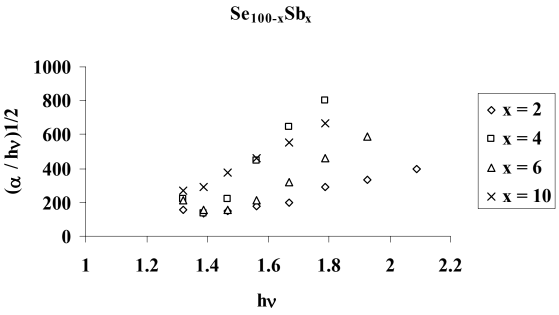

Fig. 7. Plot of (α/hν) vs hν for different alloys.

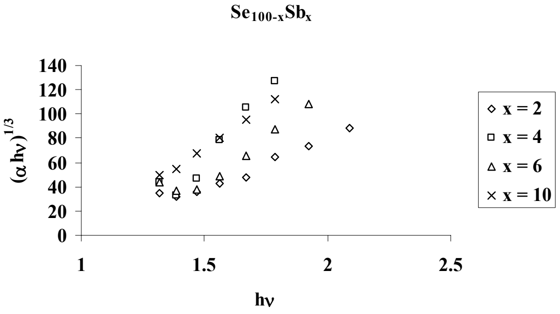

Fig. 8. Plot of $(\alpha h\nu)^{1/3}$ vs hν for different alloys.

Table 1 Experimental values of optical energy gap of glassy $Se_{100-x}Sb_x$ alloys determined from plots of $(\alpha h\nu)^{1/2}$, $(\alpha / h\nu)^{1/2}$ and $(\alpha h\nu)^{1/3}$ against hν

x	$(E_g)_1$ (eV)	$(E_g)_2$ (eV)	$(E_g)_3$ (eV)
	$(\alpha h\nu)^{1/2}$ vs $h\nu$ plots	$(\alpha / h\nu)^{1/2}$ vs $h\nu$ plots	$(\alpha h\nu)^{1/3}$ vs $h\nu$ plots
2	1.48	1.40	1.38
4	1.42	1.34	1.29
6	1.39	1.28	1.15
10	1.28	1.12	1.02

3.3 Theoretical determination of optical band gap (E_g)

It was found that the variation of optical energy gap with composition in amorphous alloys can be described by assuming random band network and using the Shimakawa relation [25]:

$$(E_g)_{AB} = Y(E_g)_A + (1-Y)(E_g)_B \qquad (8)$$

here Y and (1 – Y) are the volume fractions, $(E_g)_A$ and $(E_g)_B$ are the optical gaps for elements A and B respectively. The conversion from atom composition (at %) or molecular composition (mol %) to volume fraction is made using atomic or molecular mass and density of both Se and Sb.

The variation of the energy gap with composition in thin films of glassy $Se_{100-x}Sb_x$ system can be fitted to a quadratic relation [25]:

$$E_g(x) = x(E_g)_A + (1-x)(E_g)_B - \gamma\, x(1-x) \qquad (9)$$

here x is the atomic fraction and γ is the bowing parameter, which is 0.02 in case of glassy $Se_{100-x}Sb_x$ system [25]. Using Eq. (9), the values of E_g are calculated for the present samples. The values are given in Table 2. From Tables 1 and 2, it is clear that the experimental values of E_g obtained from model of Tauc et al are in good agreement with theoretical values of E_g as compared to other two models.

Table 2. Theoretical values of optical energy gap and average heat of atomization for glassy $Se_{100-x}Sb_x$ alloys

x	E_g (eV)	H_{AB} (kJ/g atom)
2	1.87	49.65
4	1.80	49.90
6	1.73	50.15
10	1.59	50.66

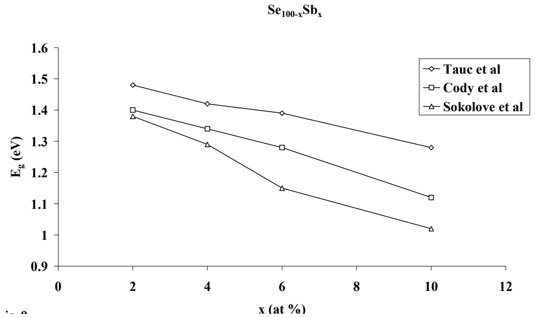

Fig. 9. Composition dependence of E_g in glassy $Se_{100-x}Sb_x$ system.

The composition dependence of E_g is shown in Fig. 9. From this figure, it is clear that E_g decreases with the increase in Sb concentration. This can be explained using chemical bond approach. According to Pauling, heteronuclear bond enthalpies can be related to homonuclear bond enthalpies [28] by the relation:

$$(H_s)_{AB} = [(H_{AA} + H_{BB}) / 2] + [96.14\,(\chi_A - \chi_B)^2]; \qquad (10)$$

where H_{AA} and H_{BB} are the homonuclear bond enthalpies, $(H_s)_{AB}$ is a heteronuclear bond enthalpy (in kJ/g atom) and χ_A and χ_B are the respective electronegativities of atoms A and B. In few materials for which it is known, the amount of heat of formation shown by second term on R.H.S. of Eq. (10) is about 10 % of the heat of atomization shown by first term on R.H.S. of Eq. (10) and is therefore be neglected. Hence, $(H_s)_{AB}$ is given quite well by:

$$(H_s)_{AB} = [(H_{AA} + H_{BB}) / 2] \qquad (11)$$

The values of $(H_s)_{AB}$ calculated using Eq. (11) for present glassy alloys are given in Table 2.

Several workers have found a correlation between the average heat of atomization $(H_s)_{AB}$ and the optical band gap in the form of an empirical relation [29-32]:

$$E_g = a\left[\left(H_{AB}\right) - b\right] \qquad (12)$$

here *a* and *b* are characteristic constants. It is suggested by the above equation that the average heats of atomization are a measure of the cohesive energy and represent the relative bond strength, that in turn are correlated with the properties like energy gap. The plot of E_g vs $(H_s)_{AB}$ is shown in Fig. 10. From this figure, it is clear that E_g vs H_{AB} plot is a straight line, which confirms the validity of above empirical relation shown by Eq. (12).

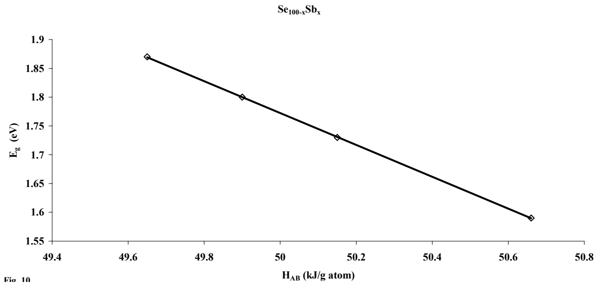

Fig. 10. Plot of E_g vs H_{AB} for different alloys.

4. Conclusions

The influence of Sb on the optical band gap in glassy $Se_{100-x}Sb_x$ system is studied. The optical band gap E_g of thin films of glassy $Se_{100-x}Sb_x$ alloys is determined experimentally using different models. The results show that optical band gap follows the decreasing trend with increase in Sb content for both experimental and theoretical approach. The results are explained in terms of average heat of atomization related to chemical bonds involved in the present glassy system.

References

[1] C. Wood, R Muller, L R Gilbert, J. Non-Cryst. Sol. **12,** 295(1973).
[2] D. Brasen, J. Non-Cryst. Sol. **15,** 395 (1974).
[3] V. I. Mikla, Yu Nagy, V V Mikla, A V Mateleshko, Mater. Sci. Engin. B **64,** 1 (1999).
[4] V. I. Mikla, I. P. Mikhalko, V. V. Mikla, Mater. Sci. Engin. B **83,** 74 (2001).
[5] D. Tonchev, B. Fogal, G. Belev, R. E. Johanson, S. O. Kasap, J. Non-Cryst. Sol. **299-302,** 998 (2002).
[6] K. V. Reddy, A. K. Bhatnagar, V. Srivsatava J. Phys.: Condens. Matter **4,** 5273 (1992).
[7] S. S. Fouad, A. H. Ammar, M. Abo-Ghazala Physica B **229,** 249 (1997).
[8] M. Singh, D. R. Goyal, A. S. Maan J. Phys. Chem. Sol. **60,** 877 (1999).
[9] M. A. Majeed Khan, M. Zulfequar, S Kumar, M Husain J. Modern Opt. **50,** 251 (2003).

[10] C. Kaito, T. Fujita, T. Kimura, K. Hanamoto, N. Suzuki, S. Kimura, Y. Saito Thin Solid Films **312,** 93 (1998).
[11] S. Jayakumar, C. Balasubramanian, Sa K. Narayandas, D. Mangalaraj, C. P. Girija Vallabhan Thin Solid Films **266,** 62 (1995).
[12] P. Arun, A. G. Vedeshwar, N C Mehra J. Phys. D: Appl. Phys. **32,** 183 (1999).
[13] V. I. Mikla, I. P. Mikhalko, Yu Yu Nagy J. Phys.: Condens. Matter. **6,** 8269 (1994).
[14] D. Dimitov, M. A. Ollacarizqueta, C. N. Afanso, N. Starbov Thin Solid Films **280,** 278 (1996).
[15] D. Dimitov, D. Tzocheva, D. Kovacheva Thin Solid Films **323,** 79 (1998).
[16] N. Choudhary, A. Kumar Turk. J. Phys. **29,** 119 (2005).
[17] G. D. Cody, T Tiedje, B Abeles, B Brooks, Y. Goldstein Phys. Rev. Lett. **47,** 1480 (1981).
[18] S. John, C. H. Grein Rev. Solid State Sci. **4,** 1 (1990).
[19] J Tauc, R Grigorovici, A Vancu Phys. Status Solidi **15,** 627 (1966).
[20] G. D. Cody, B. G. Brooks, B. Abeles Solar Energy Mater. **8,** 231 (1982).
[21] A. P. Sokolov, A P Shebanin, O A Golikova, M M Mezdrogina J. Phys. Condens. Matter **3,** 9887 (1991).
[22] V. Vorlicek, M. Zavetova, S. K. Pavlov, L. Pajasova J. Non-Cryst. Solids **45,** 289 (1981).
[23] E. A. Davis, N. F. Mott Philos. Mag. **22,** 903 (1970).
[24] V. Pandey, S. K. Tripathi, A. Kumar J. Ovonic Research **2,** 67 (2006).
[25] K. Shimakawa J. Non-Cryst. Sol. **43,** 229 (1981).
[26] R. Swanepoel J. Phys. E. **16,** 1214 (1983).
[27] D. E. Sweenor, S. K. Oleary, B. E. Foutz Solid State Commun. **110,** 281 (1999).
[28] L. Pauling The Nature of the Chemical Bond 3rd Ed., Cornell Univ., New York, (1960) Chap. 3.
[29] C. Benoit, P. Aigrainand, M. Balkanski Selected Relative Constants to Semiconductors Pergamon Press, New York, (1961).
[30] D. Arsova J. Phys. Chem. Sol. **57,** 1279 (1996).
[31] S. S. Foud Vacuum **52,** 505 (1999).
[32] A. George, D. Sushamma, P. Preedep J. Optoelectron. Adv. Mater. **3,** 33 (2006).

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