Chalcogenide Letters Vol. 5, No. 12, December 2008, p. 359 – 365

# ANNEALING EFFECTS ON OPTICAL PROPERTIES OF a- $Se_{75}S_{23}Ag_2$ AND $Se_{75}S_{21}Ag_4$ THIN FILMS DURING CRYSTALLIZATION

A. S. FAIDAH*
*Department of Physics, Faculty of Science, Post Box. No- 80203*
*King Abdul Aziz University, Jeddah-21589, Kingdom of Saudi Arabia*

Bulk glasses of the $Se_{75}S_{23}Ag_2$ and $Se_{75}S_{21}Ag_4$ alloys were prepared by melt quenching technique. Thin films were prepared onto glass substrates by using thermal evaporation technique under a vacuum of $10^{-6}$ Torr. Thin films with thickness 3000 $A^0$ were thermally annealed for 2 hours at a temperature below their crystallization temperatures. The crystallization temperatures were measured using non-isothermal DSC measurements. Optical band gap and optical constants of thermally annealed films of amorphous $Se_{75}S_{23}Ag_2$ and $Se_{75}S_{21}Ag_4$ alloys have been studied as a function of photon energy in the wave length range region 400-1000 nm. The effect of heat treatment on the optical properties was investigated. The absorption coefficient, optical band gap and extinction coefficient increases with increasing annealing temperatures. The results are interpreted in terms of concentration of localized states.

(Received November 11, 2008; accepted December 2, 2008)

*Keywords:* Amorphous semiconductor, Thin films, Chalcogenides, Optical constants

## 1. Introduction

Due to the intensive application in solid state devices and future prospects, chalcogenide thin films have received much attention for the last two decades due to their technological applications, namely electronics, optoelectronics, optical and memory switching devices. Chalcogenide glasses are very well known semiconductor materials owing to their high transmittance in the IR spectral region and to the variety of phenomena they show when exposed to light or other radiation. In general, these phenomena are associated with significant changes in the optical constants and absorption-edge shifts allowing the use of these materials in the fabrication of a great number of optical devices. Therefore, the accurate determination of the optical constants of these materials is important, not only in order to know the basic mechanisms underlying these phenomena, but also to exploit and develop their interesting technological applications. Optical absorption measurements are used to obtain the band structure and the energy gap of ternary chalcogenide amorphous thin films, because the analysis of the optical absorption spectra is one of the most productive tools for understanding and developing the energy band diagram of both crystalline and amorphous materials. The degree of disorder and defects present in the amorphous structure changes due to the heat treatment. Therefore the study of variation of optical band gap and optical constants as a function of annealing time is aimed to provide a deep insight about the mechanism of disorder and defect formation in the chalcogenide glasses composition. In the above context chalcogenide glasses are the candidates for opto-electronic devices, infrared optical materials used for temperature monitoring, thermal imaging etc.. These glasses have proved their potential applications for acousto-optic devices, solid state optical limiters [1], solid state switching devices, optical memory devices, X-ray imaging [2], photonics, inorganic photoreceptors, optical wave guides e.g. in welding and surgery [3]. Many studies have been made on switching phenomena in chalcogenide glasses. Besides these interesting phenomena, the effect of thermal annealing on optical properties of chalcogenide glasses has attracted more attention because of their solid state technical importance. Several investigators [4-15] have studied the optical and electrical properties for chalcogenide thin films. Thermal processes are known to be important in inducing crystallization in chalcogenide thin films. Efforts have also been made by many workers [16-22] from time to time to investigate the crystallization under thermal annealing of amorphous thin films. Although, plenty of work has been done to understand the physics of amorphous materials, yet, a great deal of experimental data is required to explore the potential applications of chalcogenide glasses. The aim of the present research work is to see the effect of heat treatment on optical properties of $Se_{75}S_{23}Ag_2$ and $Se_{75}S_{21}Ag_4$ thin films and to study the progressive change in optical band gap during crystallization. Selenium and sulfur are basic elements in many ternary systems in which the third component is added as a glass network or as impurity to modify the investigated physical properties. Here in the present system, we have added a third element Ag, which expands the glass forming area and creates compositional and configurational disorder in the system. Ag-doped chalcogenide glasses become attractive materials for fundamental research of their structural properties and preparation. They have many current and potential applications in optics, optoelectronics, chemistry, biology (optical elements, gratings, memories, microlences, waveguides, bio and chemical sensors, solid electrolytes, batteries etc) [23]

## 2. Experimental techniques

The melt quenching technique was adopted to prepare bulk $Se_{75}S_{23}Ag_2$ and $Se_{75}S_{21}Ag_4$ chalcogenide glasses. Appropriate amounts of high pure elements (99.999 % purity) were weighed into quartz ampoules. The contents of the ampoules were sealed in vacuum of $10^{-5}$ Torr. The sealed ampoules were then placed in a furnace where the temperature was increased up to 1273K at a heating rate of 4 K/min. The ampoules were frequently rocked for 14 hours at 1273K to ensure the homogenization of the melt. The quenching was done in ice-cold water. The crystallization temperatures of bulk samples of $Se_{75}S_{23}Ag_2$ and $Se_{75}S_{21}Ag_4$ were measured by using non-isothermal DSC measurements at constant heating rate of 15 K/min, shown in Fig. 1, which verify the presence of glassy nature of the materials. The chalcogenide thin films with thickness 3000Å used in the present study were deposited by a thermal evaporation technique onto glass substrates at room temperature on a base pressure of $10^{-6}$ Torr using an Edward Coating Unit E-306. To avoid the fractionation of the alloy during evaporation and, thereby, to ensure the correct average composition of the films formed, a high deposition rate was used to prepare the studied films. Thin film of glassy alloys of $Se_{75}S_{23}Ag_2$ and $Se_{75}S_{21}Ag_4$ were annealed at 348, 358 K and 368 K, which are in between the glass transition and crystallization temperature of the samples for two hours in a vacuum furnace under a vacuum of $10^{-3}$ Torr. The optical absorbance and transmittance data were obtained using a JASCO,V-500, UV/VIS/NIR computerized spectrophotometer. The optical absorption was measured as a function of wave length and incidence photon energy. The measurements were carried out in the wavelength range from 400 to 1000 nm.

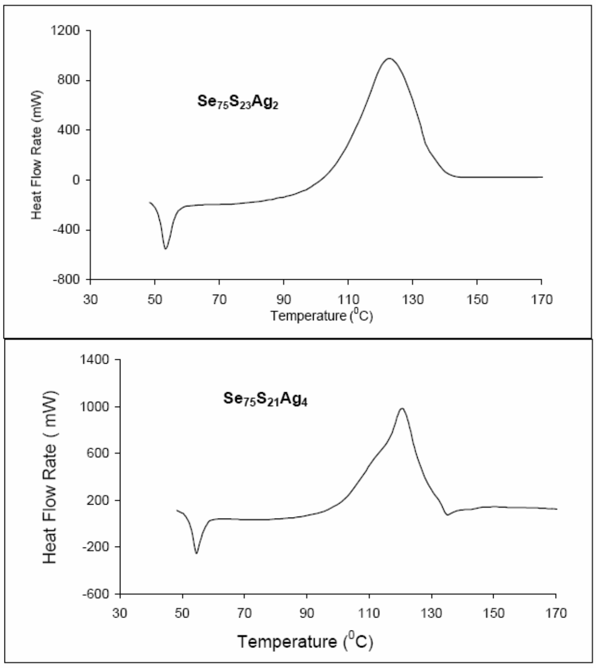

*Fig. 1. DSC plots for $Se_{75}S_{23}Ag_2$ and $Se_{75}S_{21}Ag_4$ glasses at heating rate of 15 K/min.*

## 3. Results

In the case of amorphous chalcogenides semiconductors, the optical absorption coefficient changes rapidly with photon energies giving rise to an absorption edge. The effect of thermal annealing on the optical properties of the sample has been investigated by heating the as prepared films of $Se_{75}S_{23}Ag_2$ and $Se_{75}S_{21}Ag_4$ for 2 hours at various temperatures according to the DSC trace of the sample.

The absorption coefficient ($\alpha$) has been calculated by using the following equations [24-27],

$$\alpha = OD/\ t \qquad (1)$$

where OD is the optical density measured at a given layer thickness (t).

The variation of absorption coefficient ($\alpha$) as a function of incident photon energy ($h\nu$) for as-prepared and annealed films of a-$Se_{75}S_{21}Ag_4$ with different annealing temperatures is shown in Fig. 2. The value of $\alpha$ increases linearly with an increase in photon energy. Similar patterns have also been observed for $Se_{75}S_{23}Ag_2$ which are not shown here.

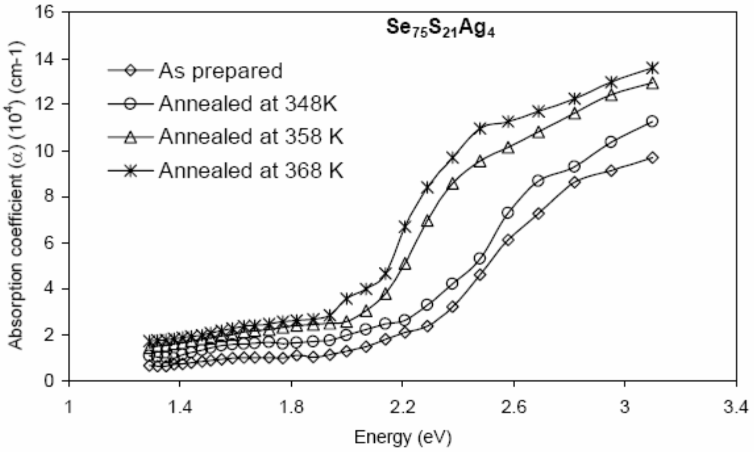

*Fig. 2. Absorption Coefficient ($\alpha$) against photon energy in $Se_{75}S_{21}Ag_4$: as-prepared and annealed films for two hour.*

The variation of $(\alpha h\nu)^{1/2}$ with photon energy ($h\nu$) for as-prepared and annealed films of $Se_{75}S_{23}Ag_2$ are shown in Fig. 3. The value of indirect optical band gap ($E_g$) has been calculated by taking the intercept on the X-axis. The calculated values of $E_g$ for the glassy samples of $Se_{75}S_{23}Ag_2$ and $Se_{75}S_{21}Ag_4$ (as-prepared and annealed films) are given in Table 1. It is clear from this table that the values of optical band gap increases with increasing annealing temperature, i.e., during crystallization process.

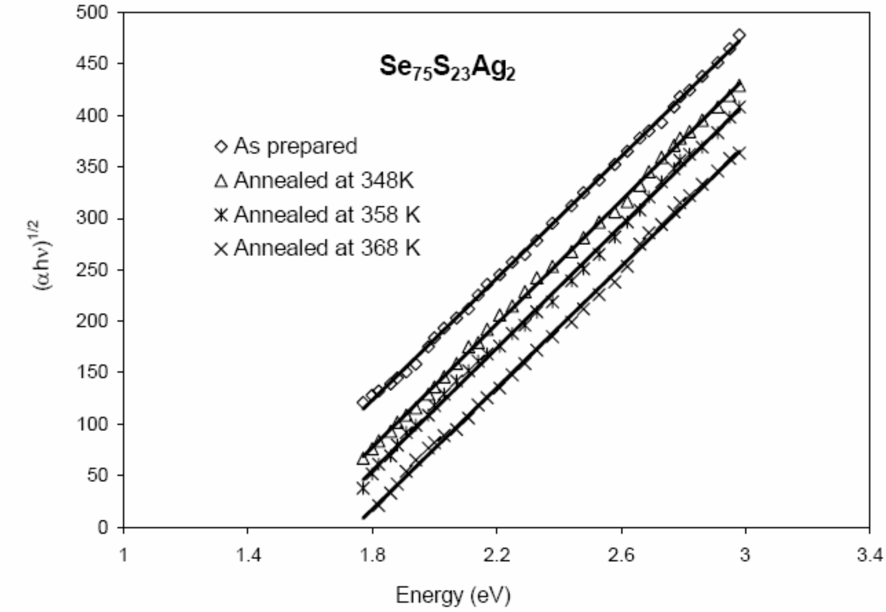

*Fig. 3.* $(\alpha h\nu)^{1/2}$ *against photon energy* ($h\nu$) *in* $Se_{75}S_{23}Ag_2$*: as-prepared and annealed films for two hour.*

*Table 1 Absorption coefficient and optical band gap in* $Se_{75}S_{23}Ag_2$ *and* $Se_{75}S_{21}Ag_4$ *films at different annealing temperatures.*

| Sample | Absorption coefficient α ($cm^{-1}$) ($10^4$) at 560 nm | | | | Optical Band Gap($E_g$) (eV) | | | |
|---|---|---|---|---|---|---|---|---|
| | *As-prepared* | *Annealed at 348K* | *Annealed at 358K* | *Annealed at 368K* | *As-prepared* | *Annealed at 348K* | *Annealed at 358K* | *Annealed at 368K* |
| **$Se_{75}S_{23}Ag_2$** | 1.57 | 1.76 | 1.89 | 2.21 | 1.38 | 1.53 | 1.61 | 1.74 |
| **$Se_{75}S_{21}Ag_4$** | 2.08 | 2.62 | 5.09 | 6.69 | 1.51 | 1.67 | 1.71 | 1.82 |

The variation of transmittance (T %) for the present system of $Se_{75}S_{21}Ag_4$ for as-prepared and annealed films are shown is Fig. 4. This figure shows that transmittance (T %) increases with wavelength and with increasing annealing temperature. Similar trends have also been observed for $Se_{75}S_{23}Ag_2$, which are not shown here.

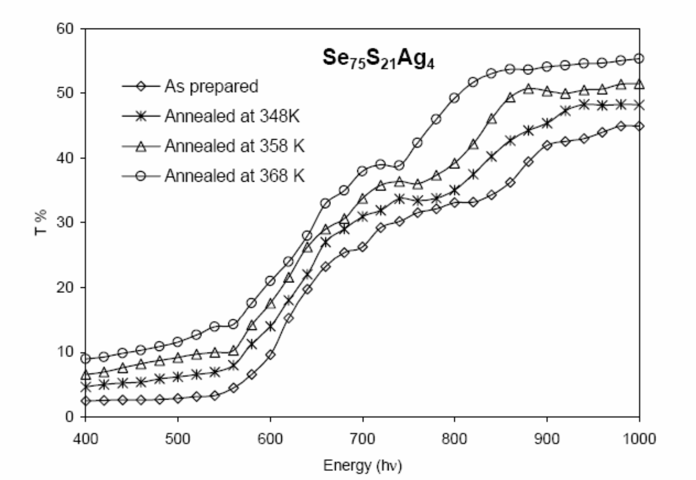

*Fig. 4. Variation of Transmittance (T %) with wavelength in* $Se_{75}S_{21}Ag_4$*: as-prepared and annealed films for two hours.*

The values of extinction coefficient (k) have been calculated using the following relation [25-28]:

$$k = (\alpha\lambda) / (4\pi) \tag{2}$$

The values of k for $Se_{75}S_{23}Ag_2$ and $Se_{75}S_{21}Ag_4$ (as-prepared and annealed films) are shown in table 2 and the variation of k with photon energy for $Se_{75}S_{21}Ag_4$ films (as-prepared and annealed films) are shown is figure 5. It increases with increasing photon energy and also annealing temperature. Mott and Davis [29] have mentioned a similar trend for thin films of various other amorphous semiconductors.

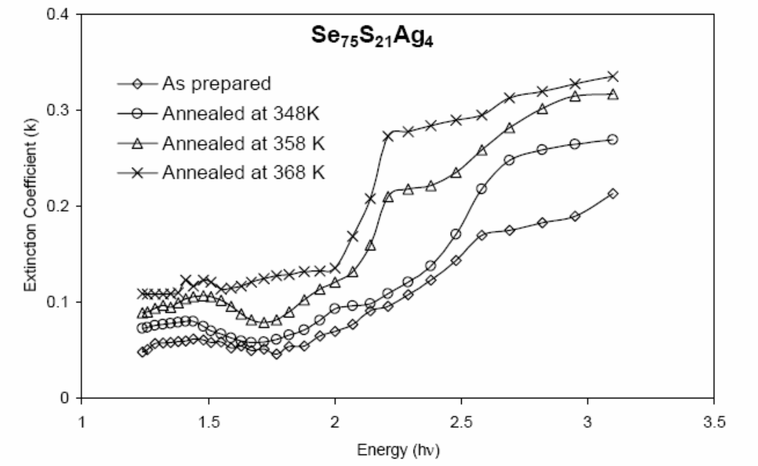

*Fig. 5. Variation of extinction coefficient (k) with incident photon energy (hν) in $Se_{75}S_{21}Ag_4$: as prepared films and annealed films for two hours.*

## 4. Discussion

The variation of optical absorption near the fundamental absorption edge has allowed us to determine the optical energy gap. The electronic transition between the valance and conduction bands starts at the absorption edge corresponding to the minimum energy difference between the lowest energy of the conduction band and the highest energy of the valance band in crystalline materials. In the case when the extremes lie at the same point of K space, the transitions are called direct. Otherwise the transitions are possible only when photons are involved [30]. However in non-crystalline materials a transition takes place, which gives a shift of the absorption edge [31-32]. The identification of optical absorption and the other related optical processes occurring at energies below the energy gap ($E_g$), in the presence of intrinsic, disorder-induced localized states is least understood. The first test for this classification is the simple requirement that the optical process be unique to the amorphous state. In chalcogenide glasses, a typical absorption edge can be broadly ascribed to one of the three-processes: firstly residual below-gap absorption, secondly Urbach tails and thirdly interband absorption. Chalcogenide glasses have been found to exhibit highly reproducible optical edges which are relatively insensitive for preparation conditions and only the observable absorption [30] with a gap under equilibrium conditions account for the first process. In the second process the absorption edge depends exponentially on the photon energy according to the Urbach relation [33]. In amorphous materials, α increases exponentially with the photon energy near the energy gap. This type of behavior has also been observed in many other chalcogenides [28]. The calculated values of the absorption coefficient (α) for $Se_{75}S_{23}Ag_2$ and $Se_{75}S_{21}Ag_4$ films is in the range ~ $10^4$ $cm^{-1}$, which is consistent with the result of other workers [34]. The present system obeys the role of indirect transition and the relation between the optical gap, optical absorption coefficient α and the energy of the incident photon is given by [34-38],

$$\alpha = B(h\nu - E_g)^2 / h\nu \quad (3)$$

Where B is a constant determined by the extent of tail states, hν is the incident energy and $E_g$ is the optical band gap. The values of absorption coefficient listed in table 2 indicate that the absorption is due to indirect transition. It is evident from table-1 that the value of optical band gap ($E_g$) increases with increasing both annealing temperature and on increasing silver concentrations. The increase in the optical band gap with increasing annealing temperature may be due to an increase in grain size, reduction in the disorder and decrease in density of defect states (which results in the reduction of tailing of bands) [31-34].

*Table 2. Extinction coefficient (k) in $Se_{75}S_{23}Ag_2$ and $Se_{75}S_{21}Ag_4$ films at different annealing temperatures at 560 nm:*

| Sample | *extinction coefficient (k)* | | | |
|---|---|---|---|---|
| | *As-prepared* | *Annealed at 348K* | *Annealed at 358K* | *Annealed at 368K* |
| **$Se_{75}S_{23}Ag_2$** | 0.056 | 0.062 | 0.069 | 0.077 |
| **$Se_{75}S_{21}Ag_4$** | 0.096 | 0.109 | 0.212 | 0.273 |

The increase in the optical band gap with increasing annealing temperature could also be discussed on the basis of density of state model proposed by Mott and Davis [29]. Chalcogenide thin films always contain a high concentration of unsaturated bonds or defects. These defects are responsible for the presence of localized states in the amorphous band gap. During thermal annealing at temperature below the crystallization temperature, the unsaturated defects are gradually annealed out producing a large number of saturated bonds. The reduction in the number of unsaturated defects decreases the density of localized states in the band structure consequently increasing the optical band gap.

## 5. Conclusion

Different parameters related to optical properties were calculated for the films of $Se_{75}S_{23}Ag_2$ and $Se_{75}S_{21}Ag_4$ films (as prepared and thermally annealed). Optical band gap in indirect in nature. The crystallization of chalcogenide films is accompanied by a change in the optical band gap. The effect of thermal annealing is interpreted on the basis of amorphous-crystalline transformation. The optical band gap increases on increasing annealing temperature and on increasing silver concentration. This change in the optical band gap may be due to the increase in the grain size and the reduction in the disordered of the system. The absorption coefficient and extinction coefficient increases with increasing photon energy and increasing annealing temperature.

## Acknowledgement

Thanks are due to Deanship of Scientific Research, King Abdul Aziz University, Jeddah, Saudia Arabia (Ref. No- 428/186), for providing financial assistance in the form of research project. Thanks are also due to Prof. A. A. Al-Ghamdi and Dr. Shamshad Ahmad Khan for their useful discussion and valuable suggestions.

## References

[1] J. Troles, F. Smektala, G. Boudebs, A. Monteil, B. Bureau, J. Lucas, Opt. Mater. **25,** 231 (2004).

[2] J. Rowlands, S. Kasap, Phys. Today **50**, 24 (1997).

[3] J. Nishi, S. Morimoto, I. Inagawa, R. Iizuka, T. Yamashita,T. Yamagishi, J. Non-Cryst. Solids **140**, 99 (1992).

[4] N. El-Kabany, Physica B **403**, 2949 (2008).

[5] K.A. Aly, A.M. Abousehly, M.A. Osman, A.A. Othman , Physica B **403**, 1848 (2008).

[6] Svetlin Parvanov, Venceslav Vassilev, Katerina Tomova , Materials Letters **62**, 2021 (2008).

[7] V. Pamukchieva, A. Szekeres, Optical Materials **30**, 1088 (2008).

[8] Haitao Guo, Haizheng Tao, Yueqiu Gong, Xiujian Zhao, Journal of Non-Crystalline Solids **354**, 1159 (2008).

[9] N. El-Kabnay, E.R. Shaaban, N. Afify, A.M. Abou-sehly, Physica B **403**, 31 (2008).

[10] K.S. Bindra, Nikhil Suri, M.S. Kamboj, R. Thangaraj, Thin Solid Films **516**, 179 (2007).

[11] Anup Thakur, G. Singh, G.S.S. Saini, N. Goyal, S.K. Tripathi, Optical Materials **30**, 565 (2007).

[12] Nadeem Musahwar, M.A. Majeed Khan, M. Husain, M. Zulfequar . Physica B: Condensed Matter **396**, 81(2007).

[13] Vineet Sharma, Anup Thakur, Jeewan Sharma, Vivek Kumar, Sanjeev Gautam, S.K. Tripathi, J. Non-Cryst. Solids **353**, 1474 (2007).

[14] Didier Fasquelle, Jean-Claude Carru, Catherine Renard, J. Non-Cryst. Solids **353**, 1120 (2007).

[15] M. Dongol, M.M. El-Nahass, M. Abou-zied, A. El-Denglawey, Physica B **371**, 218 (2006).

[16] T. Okabe, S. Endu , S. Saito, J. Non-Cryst. Solids **117-118**, 222 (1990).

[17] J. M. del Pozo , M. P. Herrero, L. Diaz , J. Non-Cryst. Solids **185**, 183 (1995).

[18] T. Rajagopalen , G. B. Reddy, Thin Solid Films **353**, 254 (1999).

[19] J. M. del Pozo, L. Diaz, J. Non-Cryst. Solids **243**, 45 (1999).

[20] M Dongol, M. Abou Zied, G. A. Gamal , A. EI-Denglawey, Physica B **353**, 169 (2004).

[21] A. El-Korashy, A. Bakry, M. A. Abdel-Rahim, M. Abd El-Sattar, Physica B **391**, 266 (2007).

[22] A. S. Soltan, Abu EL-Oyoun, A. A. Abu-Sehly, A. Y. Abdel Latief, Materials Chemistry and Physics **82**, 101 (2003).

[23] Miloslav Frumar, Tomas Wagner, Current Op. Solid State and Mat. Sci. **7**, 117 (2003).

[24] K. Oe, Y. Toyoshiman, H. Nagai, J. Non-Cryst. Solids **20**, 405 (1976).

[25] S. Caudhari, S. K. Biswas, A. Chaudhary, J. Non-Cryst. Solids **23**, 4470 (1998).

[26] E. K. Shokr, M. M. Wakkad, J. of Non-Crys. Solids **23**, 1197 (1992).

[27] J. Tauc, Amorphous and Liquid Semiconductors, ed J Tauc (New York: Plenum Press) page.159 (1979).

[28] A. K. Agnihotri, A. Kumar, A. N. Nigam, Phil. Mag. B **57**, 319(1988).

[29] N. F. Mott and E. A. Davis, Electronic Processes in Non- Crystalline Materials (Oxford: Clarendon) page 428 (1979).

[30] F. Urbach, Phys. Rev. **92,** 1324 (1953).

[31] M. Ilyas, M. Zulfequar, M. Husain, J. Modern Optics **47**, 663 (2000).

[32] K. Oe, Y. Toyoshiman, J. Non-Cryst. Solids **58**, 304 (1973).

[33] T.T. Nang, M. Okuda, T. Matsushita, S. Yokota, A. Suzuki, Jap. J. App. Phys. **14**, 849 (1976).

[34] A. Kumar, M. Husain, S. Swarup, A. N. Nigam, Physica B, **162,** 177 (1990).

[35] T.T. Nang, M. Okuda, T. Matsushita, S. Yokota, A. Suzuki, Jap. J. App. Phys. **14**, 849 (1976).

[36] S. Hasegawa, S. Yazalci, T. Shimiza, Solid State Commun. **26**, 407 (1978).

[37] J. C. Phillips, J. of Non-Crys. Solids **43**, 371 (1981).

[38] A. V. Pazin, Z. U. Borisovab, M. A. Garbuzova, Izu. Akad. Nauk SSR **6**, 884 (1970).