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ELECTRICAL PROPERTIES OF GeSeTl THIN FILMS DEPOSITED BY E-BEAM EVAPORATION TECHNIQUE

M. M. ABD EL-RAHEEM
Department of physics, Faculty of science, Sohag University, 825824 Sohag, Egypt

Five compositions of $Ge_{14}Se_{86-x}Tl_x$ (x=20,22,23.5,26.8 and 28%) are prepared using the melt quench technique. Thin films of thickness d = 15,30,60,90,120 and 180 nm were deposited using electron beam evaporation technique. All the films showed a non-Ohmic behavior. At higher range of ambient temperature, the activation energy ΔE_σ was studied as a function of the coordination number r, average number of constraints $N_{\cos}$ and heat of atomization H_s. Mott's parameters of the system $Ge_{14}Se_{86-x}Tl_x$ were studied at lower range of temperature. The effect of annealing temperature T_{ann} on the activation energy were taken in consideration.

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Keywords: Electrical properties, GeSeTl, Number of constraints, Activation energy, Mott parameter.

1. Introduction

The system Ge-Se-Tl considered to be one of the new generation of chalcogenide glasses. Therefore, a lot of work has been done on impurities effect on conductivity and optical properties [1-5]. The chemical bonds determine the structures and all properties of a body in any state of aggregation. The effect of the chemical ordering in determining the structure as compared to the influence of mechanical forces such as, strain associated with bond distortions, bond-stretching forces acting as mechanical constrains are present in Ge, Se and Tl, bond-bending constraints are also important in Ge, Se and Tl, this make Ge-Se-Tl a useful glass system to study. The change in transport properties of some chalcogenides is attributed to a corresponding change in thallium content [6-17]. Also, the addition of thallium to chalcogenide glasses causes a marked change in their structural properties [18-19]. The electrical conductivity found to increase with increasing thallium content [20]. Furthermore, it is reported that the activation energy decreases with increasing thallium content [21].

It is intended in this work to study the effect of the composition, the thicknesses and annealing temperature on the DC electrical properties of the films under test.

2. Experimental technique

99.999 purity Ge, Se and Tl were used with their appropriate mole percentage to prepare bulk samples of $G_{14}Se_{86-x}Tl_x$ (x = 20, 22, 23.5, 25, 26.5, and 28%) using the melt-quenching technique [5]. Thin films of the prepared compositions were deposited at room temperature by electron- beam evaporation at a pressure of 10^{-5} torr using an Edwards high-vacuum coating unit model E306A. The rate of deposition was 1-2 nm s^{-1}. Ultrasonically cleaned Corning glass was used as a substrate. The film thickness was controlled by means of an Edwards TM200 Maxtek high vacuum film thickness monitor. The microstructure analysis was carried out using x-ray diffractometer type Philips model PW1710 which revealed that the prepared films under test were in amorphous state. The electrical measurements were carried out using two-terminal configuration by applying constant voltage to the sample and measuring the current through it using Keithley 614 electrometer. The electrical contacts were made by applying silver paste over the surface of the films with separation of 2 mm [22].

3. Results and discussions

The I - V characteristics for the thin films of the composition $Ge_{14}Se_{86-x}Tl_x$ (x=20,22,23.5,26.5 and 28%) of the same thickness 90 nm measured at the same ambient room temperature are shown in figure 1.

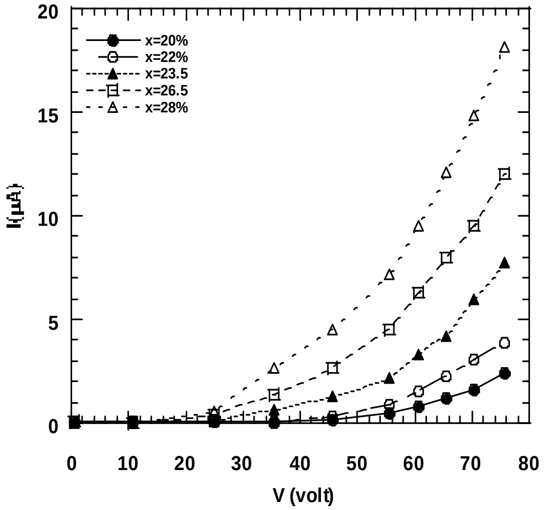

Fig. 1. I-V characterisctic curves of $Ge_{14}Se_{86-x}Tl_x$ thin films

It is clear from figure 1 that the current I increase with increasing thallium content. At low applied voltages, the current of the considered compositions approach to zero, the transition voltage V_o at which the current increase abruptly depend on the composition as shown in figure 2.

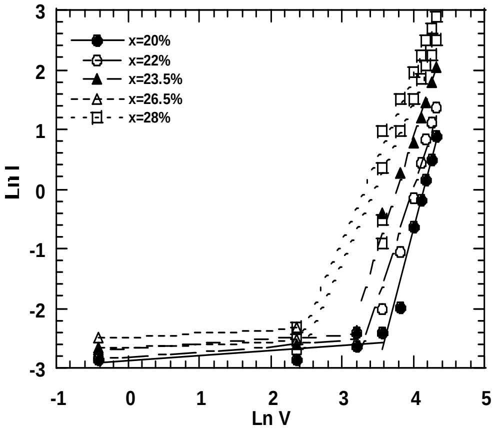

Fig. 2. Plots of Ln I-LnV of the compositions $Ge_{14}Se_{86-x}Tl_x$ thin films.

Fig. 2 shows that the transition voltage V_o decrease with increasing thallium content. Also, non of the slopes equal or approach to zero revealing non-Ohmic behavior.

The change of the current I with changing the ambient temperature is demonstrated in figure 3.

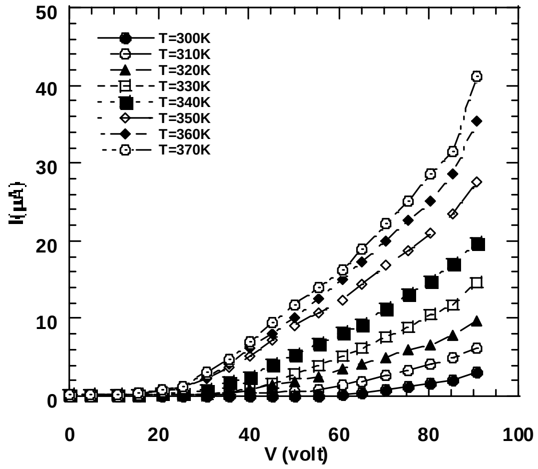

Fig. 3. I-Vvariations of the comopositions $Ge_{14}Se_{86-x}Tl_x$ thin films at different ambient temperatures.

It is clear from Fig. 3 that, for the same thicknesses (120 nm) of the composition $Ge_{14}Se_{66}Tl_{20}$ as an example to avoid repetition, as the measuring temperatures increase, the current I increase too. In plotting the relations Ln I – Ln V for the thin films of the equal thicknesses at different measuring temperatures, the transition voltage V_o found to decrease with increasing the measuring temperature. It was found also that, non of the slopes equal nor approach to unity revealing non-Ohmic behavior.

The thickness dependent of the I – V characteristics is demonstrated in figure 4, where for the same composition (x= 22%) and at fixed temperature (room temperature), the current I found to decrease with increasing the thickness of the film.

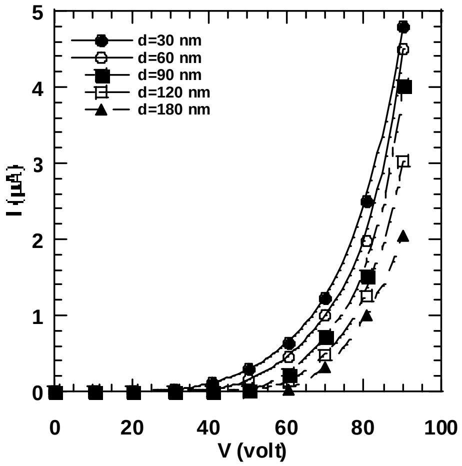

Fig. 4. I-V variations of the $Ge_{14}Se_{86-x}Tl_x$ thin films of different thickness.

The ln σ - 1/T relations for the system $Ge_{14}Se_{86-x}Tl_x$ was found straight lines at higher range of T as shown in figure 5 which follow the equation;

$$\sigma = \sigma_o e^{-\Delta E_\sigma / kT} \tag{1}$$

Where σ_o the pre-exponential factor, k is is the Boltzmann constant, T is the absolute temperature and ΔE_σ is the activation energy for conduction which is a function of the energy gap. Both values of ΔE_σ and σ_o are calculated from figure 5.

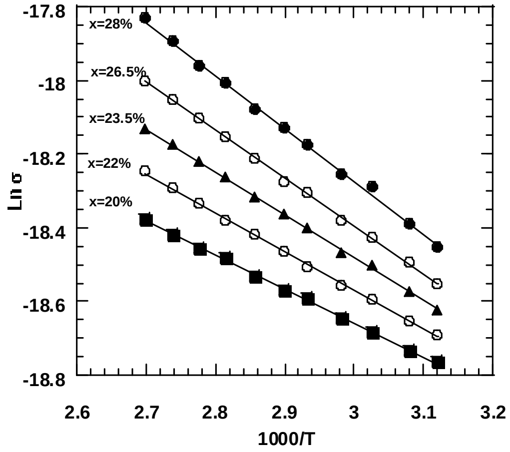

Fig. 5. Plots of Ln σ versus 1000/T for the compositions $Ge_{14}Se_{86-x}Tl_x$ thin films.

The conduction activation energy ΔE_σ calculated from figure 5 found to decrease with increasing thallium content as recorded in table 1 which may owed to the decrease in the number of defected bonds in the selenium matrix [21]. For different thicknesses, the conduction activation energy ΔE_σ derived from figure 6 found to decrease slowly with increasing the film thickness, since it change from 0.667 to 0.604 as the thickness increase from 30 to 180 nm as seen in table 1.

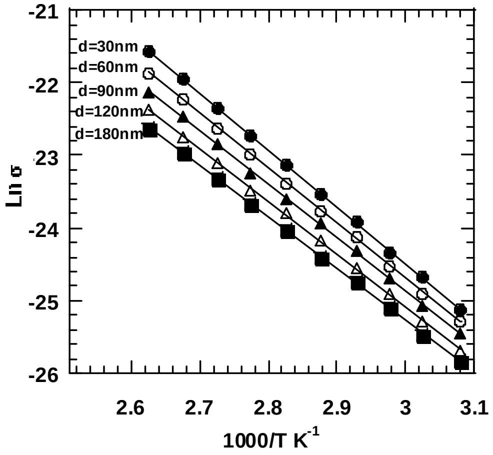

Fig. 6. Temperature dependence of the electrical conductivity for $Ge_{14}Se_{66}Tl_{20}$ thin films of different thickness.

Table1 activation energy dependence on both composition and thickness.

X%	$\Delta E_{\sigma}(eV)$	$\sigma_{o}(\Omega m)^{-1}$	d nm	$\Delta E_{\sigma}(eV)$	$\sigma_{o}(\Omega m)^{-1}$
20	0.915	499	30	0.667	824
22	0.844	219	60	0.646	692
23.5	0.781	103	90	0.625	639
26.5	0.716	48.6	120	0.619	503
28	0.646	21.2	180	0.604	389

It is obvious from table 1 that the pre-exponential factor σ_o decrease with increasing both thallium content and the thickness of the films which mean that the charge carrier mobility in the trap states decrease s with increasing thallium content.

The variation of the activation energy ΔE_{σ} with respect to the parameter which determine the deviation from stoichiometry S, coordination number r, average coordination number $\langle r_{eff} \rangle$, average number of constrain N_{con} and average heat of atomization H_s can be studied from table 2, whereas, theses parameters were calculated from the following equations [23]:

$$r = 4XGe + 2XSe + 5XT_l \qquad (2)$$

$$N_{con} = N^{\alpha} + N^{\beta} \qquad (3)$$

Where, $N^{\alpha} = \frac{r}{2}$, $N^{\beta} = 2r - 3$

$$\langle r_{eff} \rangle = \frac{2}{5}(N_{con} + 3) \qquad (4)$$

$$H_s = (\alpha H_s^{\alpha} + \beta H_s^{\beta} + \gamma H_s^{\gamma})/(\alpha + \beta + \gamma) \qquad (5)$$

$H_s^{\alpha} and H_s^{\beta}$ are the average non-polar bond energy of the two atoms.

Table 2 ΔE_{σ}, r, S, $\langle r_{eff} \rangle$, N_{con}, H_s for the system $Ge_{14}Se_{86-x}Tl_x$.

x %	S	r	$\langle r_{eff} \rangle$	N^{α}	N^{β}	N_{con}	H_s	$H_s / \langle r_{eff} \rangle$	ΔE_{σ}
20	0.532	2.880	2.880	1.440	2.76	4.200	53.87	18.71	0.915
22	0.598	2.940	2.940	1.470	2.88	4320	53.74	18.28	0.844
23.5	0.649	2.985	2.985	1.493	2.97	4.463	53.64	17.97	0.781
26.5	0.757	3.074	3.073	1.533	3.15	4.63	53.44	17.39	0.716
28	0.814	3.120	3.13	1.560	3.24	4.800	53.35	17.04	0.646

It is seen from table 2 that, non of the compositions is a stoichiometric chalcogenide because non of the values of S equals unity. The coordination number r and the average coordination number $\langle r_{eff} \rangle$ increase with increasing thallium content, that is due to the larger coordination number of thallium with respect to that of selenium. The average number of constrain N_{con} also increases with more enriching with thallium due to the larger value of the coordination number of thallium with respect to that of selenium. The average heat of atomization H_s decrease with increasing thallium ratio which may owe to the larger value of the heat of atomization of selenium (49.4 k cal / gm .atom) with respect to that of thallium (43 k cal / gm .atom).Therefore, an increase in Tl leads to an increase in N_{con} and r, on the other hand ΔE_{σ} ,

σ_o and H_s decrease. Accordingly [24], the intercept σ_o is related to the density of localized states, as σ_o decreases the density of localized states increases. Replacing Tl instead of Se sites, leads to increasing the coordination number and corresponding modification in the chemical bond should directly affect the electrical properties of the $Ge_{14}Se_{86-x}Tl_x$ system. Besides, the observed changes in ΔE_σ result from the local changes in the chemical bonding, therefore, the decrease in ΔE_σ , σ_o should be associated with a decrease in H_s and $H_s/\langle r_{eff}\rangle$ where H_s represents the relative bond strength and $H_s/\langle r_{eff}\rangle$ is the average single bond energy in the composition. Furthermore, It is suggested [24] that, the electrical conduction takes place in the extended states in the range of σ_o from 10^3 to 10^4 $\Omega^{-1}m^{-1}$, and lower values of σ_o indicate greater participation of localizes states in the conduction process. The continuous decrease of ΔE_σ , σ_o, H_s and $H_s/\langle r_{eff}\rangle$ with increasing Tl content can be attributed to the presence of non-bridging selenium, which influenced the electron density around the bridging selenium that makes up the vitreous network [28].

At low temperature range , conduction take place through variable range hopping in localized states near the Fermi level. The plot of $Ln[\sigma(T)T^{1/2}] vs T^{-1/4}$ found to be straight lines as shown in figure 7 which is in accordance with Mott's variable range hopping process .

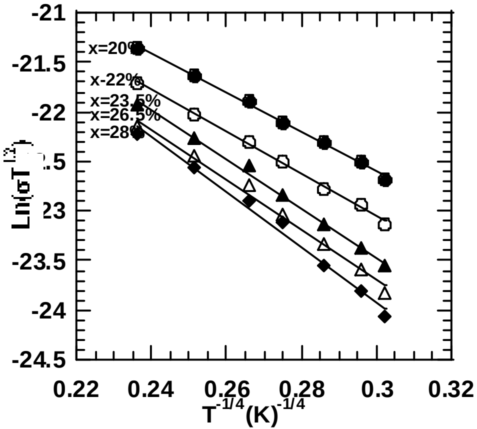

Fig. 7. Plots of $Ln(\sigma T^{1/2})$ *versus* $T^{1/4}$ *of the compositions* $Ge_{14}Se_{86-x}Tl_x$ *thin films.*

Since, Mott assumes that, at very low temperatures, long hops from one site to the other become more likely than the sum of all other auxiliary hops so that the one-electron theory is applicable:

$$\sigma(T) = \sigma_o T^{-1/2} e^{-AT^{-1/4}} \tag{6}$$

Where

$$A^4 = \frac{\lambda\alpha^3}{Kg} \tag{7}$$

and $\lambda \approx 16$ is a dimensionless parameter, α^{-1} the spatial extension of the wave function associated with the localized states and g is the density of localized state at the Fermi level. Also, the pre-exponential factor σ_o is given by:

$$\sigma_o = 3e^2 \nu_{ph} (\frac{g}{8\pi\alpha K})^{1/2} \tag{8}$$

Since, $\nu_{ph} \approx 10^{12} - 10^{13} Hz$ is the characteristic phonon frequency in most amorphous materials. The average hopping distance R and the hopping energy W are given by:

$$R = (\frac{9}{8\pi\alpha KTg})^{1/4} \tag{9}$$

$$W = \frac{3}{4\pi R^3 g} \tag{10}$$

The calculated Mott's parameters are recorded in table 2.

Table 3 Mott's parameters of the system $Ge_{14}Se_{86-x}Tl_x$.

Composition	$A(K^{1/4})$	$\sigma_o(\Omega^{-1}cm^{-1}K^{1/2})$	$\alpha(cm^{-1})$	$g(eV^{-1}cm^{-1})$	$R(cm)$	$W(eV)$
X=20%	19.77	16.666	$4.64x10^7$	$1.21x10^{20}$	2.65x10-7	0.106
X=22%	21.454	16.622	$5.45x10^7$	$1.42x10^{20}$	$2.45x10^{-7}$	0.114
X=23.5%	24.983	15.979	$7.10x10^7$	$1.70x10^{20}$	$2.19x10^{-7}$	0.134
X=26.5%	25.535	16.039	$7.47x10^7$	$1.80x10^{20}$	$2.13x10^{-7}$	0.137
X=28%	27.823	15.573	$8.58x10^8$	$1.96x10^{20}$	$2.02x10^{-7}$	0.148

As it is seen in table 3 that, $W \rangle KT$ and $\alpha R \rangle\rangle 1$ satisfy the necessary conditions for Mott's variable range hopping process, on the other side, g are unreasonably high which is observed for other materials [25-27] , this is may be owed to uncertainties involved in estimating σ_o in equation (8). This is because Mott's derivation of the variable range hopping relations implies a large number of simplifying assumption of which the most important are the energy independence of the density of localized states at the Fermi level, neglect of the correlation effect in tunneling processes and neglect of electron-phonon interaction. On the other hand, it is apparent from table 3 that the hopping distance R decrease with more enriching of thallium, whereas, the hopping energy W decrease with increasing thallium content. Further, the pre-exponential factor σ_o decreases very slightly with increasing thallium ratio ensuring that the charge carrier mobility and density of states increase.

In studying the effect of annealing temperature on the conduction activation energy, the variation of $\mathrm{Ln}\,\sigma$ vs 1/T has been drawn at different annealing temperatures (300, 328, 358, 390, 420, 450, 482, 510, 540, 570,and 598K) for thallium content 28%, and found to be straight lines verifying equation (1). From the slopes of the straight lines, the activation energies ΔE_σ have been calculated and drawn vs annealing temperature as shown in figure 8. It is obvious that ΔE_σ increase with increasing the annealing temperature which may be owed to the unsaturated defects are gradually annealed out producing a large number of saturated bond leading to a decrease in the density of localized states and consequently the energy gap increase.

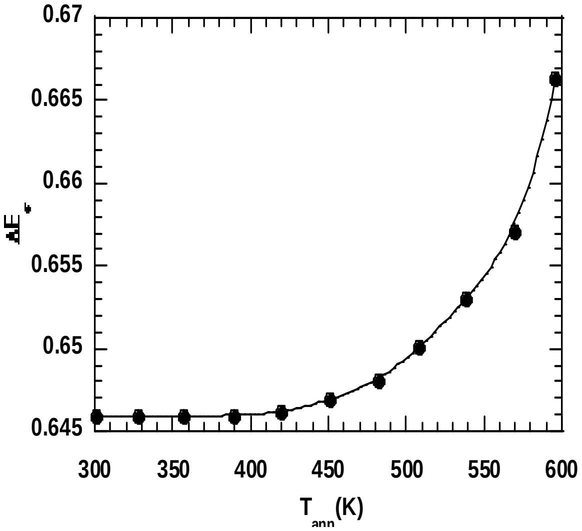

Fig. 5. Plots of ΔE_σ *versus* T_{ann} *for the system* $Ge_{14}Se_{86-x}Tl_x$ *at thallium content = 28%.*

4. Conclusion

It is concluded that: (1) All the films showed non-Ohmic behavior and the transition voltage becomes smaller with increasing thallium content, the thickness of the films and annealing temperature. (2) Both the activation energy ΔE_σ and the pre-exponential factor σ_o decrease with increasing thallium content. (3)The activation energy ΔE_σ found to decrease with decreasing the heat of atomization H_s. (4) Increasing the numbers of constraints N_{con} lead to decrease the value of ΔE_σ. (5) Both the density of the localized states, hopping energy found to increase with increasing thallium concentration. (6) The hopping distance R decreases with increasing thallium content. (7) The activation energy increases with increasing the annealing temperature.

References

[1] K. Arai, T. Kuwahay, H. Namika, S. Saito Japan J. Appl. Phys. **1**, 1080 (1972)
[2] B. T. Kolomiets 1976 Electronic Phenomena in Non-Crystalline Semi-Conductors (Leningrad:Nauka).
[3] Borisovo Zu 1980 Conf. on Amorphous Semiconductor (Kishinev, 1980) vol.80.
[4] M. M. Abd El-Raheem , J. Phys.: Condensed Matter **19**, 216209 (2007).
[5] Abd El-Raheem M M, Wakkad M M, Megahed N M, Ahmed A M, Shokr E K and Dongol M J. Mater. Sci. **31**, 5759 (1996).
[6] Kolomiets B T, Rukhiyadev Y V and Shilo V P J. Non-Cryst. Solids **5,** 402 (1971).
[7] Lazel D, Tarkal V, S R B I, Dokupil S and Rosicka U Phys. Status Solidi a **12**, K39 (1972).
[8] Strunk R J. Non-Cryst. Solids **12**, 168 (1973).

[9] Kotkata M F, El-Fouly M H, Fayek S A nd El-Hakim S A Semicond. Sci. Technol. **1**, 313 (1986).
[10] Danaev A A, Borisova Z U, Mikhailov M D and Bratov A V, Phys. Chem. Glasses **6**, 174 (1980).
[11] Apikhtin N N, Mikhailov M D and Panus V R Phys. Chem. Glasses **5**, 726 (1979).

[12] Zope M, Muragi BD and Zope J K J. Non-Cryst. Solids **103**, 195 (1988).
[13] Parthasrathy G, Naik G M, Asokan S. J Mater Sci Lett, **6**, 181(1987).
[14] Kotkata M F, El-Shair H T, Afifi M A, Abdel-Aziz M M. J Phys D. **27**, 623 (1994).
[15] Kotkata M F, Afifi M A, Labib H H, Hegab NA, Abdel-Aziz M M, J Thin Solid Films, **240**, 143 (1994).
[16] Petkov P, Vodenicharov C, Kanasirski C, Phys Status Solidi A **168**, 447 (1998).
[17] Petkov P, Kanasirski C, Vodenicharov C, J Solid State Commin, **90**, 317 (1994).
[18] Feichtner J D, Gottlieb M and Conroy JJ IEEE J. Quantum Electron. **11**, 660 (1976).
[19] Gottlieb M and Ronald G W Opt. Eng. **19**, 901 (1981).
[20] Ahmed A M, Megahid N M and Ibrahim M M Indian J. Pure Appl. Phys. **41**, 863 (2003).
[21] Afifi M A, Abdel-Aziz M M, Labib H H, Fadel M and El-Metwally E G, Vacuum **61**, 45 (2001).
[22] Ali H M, Abd El-Raheem, Megahed N M and Mohamed H A, Journal of Physics and Chemistry of Solids **67,** 1823 (2006).
[23] Fadel M, Fouad S S and El-Metwally E G, Chalcogenide Letters **5**, 79 (2008).
[24] Mott N F and Davis E A, Electronic processes in Non-Crystalline Materials, 2nd ed Clarndon press, Oxford 1971, p. 328.
[25] Brodsky M H, Gambino R J, J. Non-Crys. Solids, **8-10**, 739 (1972).
[26] Paul D K and Mitra S S, Phys. Rev. Lett. **31** 1000 (1973).
[27] Lemoine D and Mendolia J, Phys. Lett. A. **22**, 418 (1981).
[28] Sanghera J S, Heo J and Mackenzie J D, J. Non-Cryst. Solids **10**, 8 (1984).