JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 7, July 2007, p. 1994 - 1999

Theoretical calculation of physical parameters of $Ge_{10}Se_{90-x}Te_x$ glassy alloys

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In the present paper we have theoretically calculated the number of constraints, effective coordination number, optical band gap ($E_{g,th}^{opt}$), oscillator strength and dispersion energy based on Wemple-DiDomenico model, average heat of atomization and average single bond energy for *a*-$Ge_{10}Se_{90-x}Te_x$ where $x = 0, 10, 20, 30, 40, 50$. The theoretically calculated and experimentally observed optical band gap for *a*-$Ge_{10}Se_{90-x}Te_x$ thin films prepared by vacuum evaporation technique at base pressure ~10^{-5} Torr were found to be in good agreement. The results are explained on the basis of density of states model proposed by Mott and Devis.

(Received January 5, 2007; accepted June 27, 2007)

Keywords: Thin films, Optical properties, Chalcogenide glasses, Ge-Se-Te

1. Introduction

Se based chalcogenide glasses are promising materials due to their wide range of applicability in the field of infrared optical elements, optical fibres, xerography, switching and memory devices, photolithography, fabrication of inexpensive solar cells, more recently for reversible phase change optical records and are well known for their IR transmittance [1-12]. Se in its pure state has disadvantages because of its short life time and low sensitivity. To overcome this difficulty several researcher have worked with the addition of the certain additives like Ge, As, Bi, Sb etc [13-16] to make binary alloys with Se which in turn give high sensitivity, high crystallization temperature and smaller aging effect. With the addition of third element like Te, In, Sn etc [17-19] the glass forming region is found to increase and creates compositional and configurational disorder in the system.

In our present work, we have prepared thin films from *a*-$Ge_{10}Se_{90-x}Te_x$ $(x = 0, 10, 20, 30, 40, 50)$ glassy alloys and calculated theoretically the effective coordination number, number of constraints, average heat of atomization, average single bond energy, theoretical optical band gap ($E_{g,th}^{opt}$), oscillator strength and dispersion energy based on Wemple-DiDomenico model and the compositional dependence of band gap by analyzing the transmission spectrum of thin films. The optical band gaps so obtained are in good agreement with the results calculated theoretically. The band tailing parameter (B) is calculated from the slope of Tauc plot and is found to be of the order of 10^6.

2. Experimental procedure

Bulk sample of $Ge_{10}Se_{90-x}Te_x$ where $x = 0, 10, 20, 30, 40, 50$ were prepared by the well known melt quenching technique. Materials (99.999% purity) were weighed according to their atomic percentages and sealed in quartz ampoules in a vacuum ~ 10^{-5} Torr. The sealed ampoules were heated up to 1000 ^{0}C at a rate of 2-3 ^{0}C/min and rocked for 24 hours at the highest temperature to make the melt homogeneous. Thin films of bulk samples were grown on ultrasonically cleaned glass substrate by vacuum evaporation technique at ~10^{-5} torr at room temperature using molybdenum boat. The detailed experimental procedure is given elsewhere [20]. The amorphous nature of thin films and bulk samples has been confirmed by X-ray diffraction studies as no sharp peak is observed. The normal incidence transmission spectra of *a*-$Ge_{10}Se_{90-x}Te_x$ $(x=0, 10, 20, 30, 40, 50)$ thin films have been measured by a double beam UV/VIS/NIR computer controlled spectrometer [Hitachi-330] in the transmission range 400-1200 nm. The spectrophotometer was set with a slit width of 1 nm.

3. Results and discussion

The values of optical band gaps were calculated from the graph $(\alpha h\nu)^{1/2}$ vs. $h\nu$. For indirect transitions the energy gaps were determined by the extrapolated intercept on the energy axis using

$$\alpha h\nu = B(h\nu - E_g^{opt})^2 \qquad (1)$$

where B is a constant called band tailing parameter with a value ranging from 10^5 to 10^6 cm^{-1} eV$^{1/2}$. The optical band gap decreases from 1.87 to 1.03 eV with the increase of Te content from $x = 0, 10, 20, 30, 40, 50$ in *a*-$Ge_{10}Se_{90-x}Te_x$ thin films.

3.1 Comparison of theoretically calculated and experimentally found optical band gap and band tailing parameter

It is found that the variation of energy gap with composition in amorphous alloys can be described by assuming random network using relation [21]

$$E_g(AB)(Y) = YE_g(A) + (1-Y)E_g(B) \qquad (2)$$

where Y is the volume fraction of element A, $E_g(A)$ and $E_g(B)$ are the optical gaps for A and B elements, respectively. The conversion from atomic composition (at%) or molecular composition (mol %) to volume fraction Y is made using atomic or molecular mass and density of both Te and Se. Fig. (1) shows the variation of theoretically calculated and experimentally observed band gap for *a-*$Ge_{10}Se_{90-x}Te_x$ tin films. In conclusion the optical gap $E^{opt}_{g,th}$ for *a-*$Ge_{10}Se_{90-x}Te_x$ determined by volume fraction and the optical gap $E^{opt}_{g,\exp}$ calculated using the experimental data decreases with the increase of Te content lead to the conjecture that a modified virtual crystal approach for mixed crystals is acceptable for an amorphous system. The band tailing parameter *(B)* calculated from the slope of Tauc's extrapolated plots i.e. $(\alpha h\nu)^{1/2}$ vs. $h\nu$ is given in Table (1). It is found that the band tailing parameter is of the order of 10^6 as reported in the literature [22].

Table 1. Values of number of constraints arising from bond stretching (N^{α}), number of constraints arising from bond bending (N^{β}), average number of constraints (N_c), effective coordination number $<m_{eff}>$ and band tailing parameter (B) for a-$Ge_{10}Se_{90-x}Te_x$ *(x=0, 10, 20, 30, 40, 50).*

x	N^{α}	N^{β}	N_c	$<m_{eff}>$	B ($cm^{-1}eV^{-1}$)
0	1.10	1.4	2.50	2.2	1.44×10^6
10	1.15	1.6	2.75	2.3	1.17×10^6
20	1.20	1.8	3.00	2.4	2.27×10^6
30	1.25	2.0	3.25	2.5	1.46×10^6
40	1.30	2.2	3.50	2.6	0.92×10^6
50	1.35	2.4	3.75	2.7	0.57×10^6

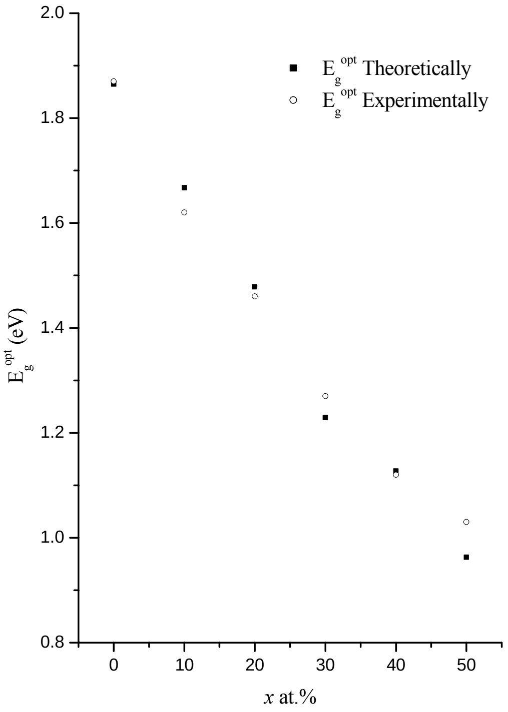

Fig. 1. Theoretical and experimental optical band gap for a-$Ge_{10}Se_{90-x}Te_x$ *where x=0, 10, 20, 30, 40, 50) thin films.*

The experimentally obtained optical band gap and the theoretically calculated values for *a-*$Ge_{10}Se_{90-x}Te_x$ both were found to decrease with increasing Te content and are in good agreement. Since optical absorption depends on short range order in the amorphous state and defects associated with it, the decrease in optical gap with the increase of Te content may be explained on the basis of the "density of states" model in amorphous solids proposed by Davis and Mott. According to this model, the width of the localized states near the mobility edges depends on the degree of disorder and defects present in the amorphous state [23].

3.2 Number of constraints and the effective coordination number for the system

The glassy networks are influenced by mechanical constraints (N_c) associated with the atomic bonding and an average effective coordination number $< m_{\text{eff}} >$ which is also related to N_c. In a covalently bonded glassy network two types of constraints, bond stretching N^{α} and bond-bending N^{β} need to be counted [24]. For atomic species with coordination number *(m)*, the number of constraints per atom arising from bond bending $N_b = 2m - 3$ and from bond stretching $N_a = m/2$. Knowing the average number of constraints $N_c = N_a + N_b$ and the average coordination number m for different composition of *a-*$Ge_{10}Se_{90-x}Te_x$ *(x = 0, 10, 20, 30, 40, 50)* glassy system, the effective average coordination number $< m_{\mathrm{eff}} >$ can be calculated [25] using the formula

$$< m_{\mathrm{eff}} > = (2/5)(N_c + 3) \qquad (3)$$

The values of N^{α}, N^{β}, N_c along with $< m_{\mathrm{eff}} >$ for the *a-*$Ge_{10}Se_{90-x}Te_x$ *(x = 0, 10, 20, 30, 40, 50)* glassy system are given in Table (1). In our system the average number of constraints per atom N_c exceeds the number of degrees of freedom $N_d = 3$ for the compositions x = 20, 30, 40, 50, the heteropolar bonded Te concentration is found to be less than one. Thus the non-monotonic behaviour of various properties observed in these glasses is explained in terms of interplay between "mechanical" and "chemical" forces which affect the structure of the glass as a function of $< m_{\mathrm{eff}} >$. According to Thorpe [26] in the range of the glass-forming compositions, the system should contain rigid and floppy regions. In the *a-*$Ge_{10}Se_{90-x}Te_x$ *(x = 0, 10, 20, 30, 40, 50)* compositions the average coordination number varies from 2.2 to 2.7. The transition from floppy mode to rigid mode takes place for the composition $Ge_{10}Se_{70}Te_{20}$. This means m = 2.4 corresponds to the mechanical percolation threshold. According to Zachariasen [27], atoms combine more with atoms of different kinds than with the same kind. This condition is equivalent to assuming the maximum amount of chemical ordering possible. This means that bonds between like atoms will only occur if there is an excess of a certain type of atom, so that it is not possible to satisfy its valence requirements by bonding it to atoms of different kinds alone, so bonds are formed in the sequence of decreasing bond energy until all available valences of the atoms are saturated.

The possible bond distribution at various compositions using chemically ordered network (CON) model [28]. The model assumes that atoms combine more favourably with atoms of different kinds than with the same and bonds are formed in the sequence of bond energies [28]. As Te replaces Se the number of Te-Se bonds increase at the expense of Se-Se. The bond energies E_{AB} for heteronuclear bonds have been calculated by using the relation [29]

$$E_{AB} = (E_{AA} + E_{BB})/2 + 23(\chi_A - \chi_B)^2 \qquad (4)$$

where E_{AA} and E_{BB} are the energies of the homonuclear bonds and χ_A and χ_B are the electronegativies of the atoms involved. The bonds formed in *a-*$Ge_{10}Se_{90-x}Te_x$ system and their energies are given in Table (2) and electronegativity for Ge = 2.01, Se = 2.55 and Te = 2.1. The assumption mentioned above can be applied in its simplest form to memory materials, where there is no ambiguity about the formal order in which the bonds are formed [30].

3.3 Dispersion energy and oscillator strength from WDD model

According to the single-effective oscillator model proposed by Wemple and DiDomenico [31,32] the optical data could be described to an excellent approximation by the following relation

$$n^2 - 1 = \frac{E_d E_0}{E_0^2 - (h\nu)^2} \qquad (5)$$

where $h\nu$ is the photon energy, n is refractive index, E_0 is the energy of the effective dispersion oscillator also called average energy gap, E_d is the oscillator strength or the dispersion energy. The latter quantity measures the average strength of the interband optical transitions. Plotting $(n^2-1)^{-1}$ against $(h\nu)^2$ allows us to determine the oscillator parameters by fitting a straight line to the points. The value of E_0 and E_d can be directly determined from the slope $(E_0 E_d)^{-1}$ and the intercept on the vertical axis (E_d / E_0). The values so obtained for the dispersion parameters E_0 and E_d are given in Table (2). As it was found by Tanaka [33] the first approximate value of the optical band gap E_g^{opt} is also derived from the Wemple-DiDomenico dispersion relationship, according to the expression $E_0 \approx 2E_g^{opt}$. The values so obtained from this equation are in good agreement with the values obtained from the Tauc's extrapolation [34] using the value of the absorption coefficient from the transmission measurements. The results are similar to that of the other Se rich alloys reported in literature [35,36].

Table 2. Values of dispersion energy (E_d), oscillator strength (E_0) and bond energy of different bonds in a-$Ge_{10}Se_{90-x}Te_x$ *(x=0, 10, 20, 30, 40, 50).*

x	E_d (eV)	E_0 (eV)	Bond	Bond Energy (eV/bond)
0	10.20	3.29	Ge-Ge	1.63
10	11.37	3.99	Se-Se	1.91
20	4.87	1.86	Te-Te	1.43
30	5.42	2.08	Ge-Se	2.12
40	8.37	2.10	Ge-Te	1.62
50	19.95	3.00	Se-Te	1.76

On the other hand, an important achievement of the WDD model is that it relates the dispersion energy E_d to other physical parameters of the material through the following empirical relationship.

$$E_d = \beta N_e Z_a N_c \tag{6}$$

where N_e is the effective no. of valence electrons per anion, N_c is the effective coordination no. of the cations nearest neighbour to the anion, Z_a is the formal chemical valency of the anion, β is a two valued constant with either an ionic or a constant value ($\beta_i = 0.26 \pm 0.03$ eV and $\beta_c = 0.37 \pm 0.04$ eV) [37]. It is observed that the variation in the transition strength E_d results primarily from changes in the average nearest neighbour coordination number. It is proposed that the layer-layer and chain-chain bonding increases the effective coordination number. The primary optical effect is a reduction in the oscillator strength of the lone-pair to conduction band transitions causing a corresponding decrease in E_d. It is observed here that the increase in Te content increases the coordination number and decreases the energy gap E_g^{opt}. According to the WDD model the refractive index becomes dependent on the dispersion energy E_d as $h\nu \to 0$. In this case E_d is mainly affected by the nearest neighbors, i.e. by the short range order and remains unaffected by medium range order. At wavelengths in near infrared region the short range order is dominant and therefore no feature related to the medium range order is developed in the compositional dependence of '*n*' [38]. Shifting to shorter wavelengths the medium range order in the glasses becomes a decisive factor, which can affect the shape of refractive index '*n'* and the dependence of extinction coefficient on <*m_{eff}*>.

3.4 The average heat of atomization

In chalcogenide glasses containing a high concentration of group VI element the lone-pair form the top of the valence band and the antibonding band forms the bottom conduction band [39]. The optical gap corresponds closely to the energy difference between the top of the valence band and the bottom of the conduction band. Metal atoms can form a dative bond with group VI atoms (lone pair with empty orbital) without any cost of energy, due to the presence of high-energy lone pair on the latter. Dative bonds have corresponding (empty) antibonding levels which could give localized acceptors states in the gap [40].

It is interesting to relate the optical band gap with the chemical bond energy. For this purpose we calculate the heat of atomization. According to Pauling [41], the heat of atomization $H_S(A-B)$ at standard temperature and pressure of a binary semiconductor formed from atoms A and B is the sum of heat of formation ΔH and the average heats of atomization H_S^A and H_S^B that corresponds to the average non-polar bond energy of the two atoms

$$H_S(A-B) = \Delta H + \frac{1}{2}\left(H_S^A + H_S^B\right) \tag{7}$$

The first term in above equation is proportional to the square of the difference between the electronegativities χ_A and χ_B of the two atoms:

$$\Delta H \quad \alpha \quad (\chi_A - \chi_B)^2 \tag{8}$$

In order to extend this idea to ternary and higher order semiconductor compounds, the average heat of atomization $\overline{H}_S$ (in kcal per gram-atom) is defined for a compound $A_\alpha B_\beta C_\gamma$ as a direct measure of the cohesive energy and thus of average bond strength, as

$$\overline{H}_S = \frac{\alpha H_S^A + \beta H_S^B + \gamma H_S^C}{\alpha + \beta + \gamma} \tag{9}$$

Obviously the $\overline{H}_S$ values do not contain the heat of formation (ΔH) as part of cohesive energy, however $\overline{H}_S$ is useful parameter for correlating the physical properties of semiconducting compounds. In case of chalcogenide glasses the heat of formation contributes very little towards the average heat of atomization because the electronegativities of the constituent elements *i.e.* Ge, Se, Te are very similar and in most of the cases of chalcogenide glasses the heat of formation is unknown. In few materials for which heat of formation is known it accounts only 10% of the heat of atomization and is therefore neglected. Hence for binary chalcogenide glasses $H_S(A-B)$ is given by

$$H_S(A-B) = \frac{1}{2}\left(H_S^A + H_S^B\right) \tag{10}$$

whereas for ternary and higher order compounds, $\overline{H}_S$ is given by the equation (9) is applicable. The heat of atomization for Ge, Se, Te elements [42] and average heat of atomization $\overline{H}_S$ (kcal/g-atom) and average single bond energy $(\overline{H}_S/m)$ are given in Table (3), where *m* is the average coordination number. The average coordination number *(m)* was calculated using the standard method [43–47]. For the composition $Ge_aSe_bTe_c$ is given by,

$$m = \frac{aN_{Ge} + bN_{Se} + cN_{Te}}{a+b+c} \tag{11}$$

where $N_{Ge} = 4$, $N_{Se} = 2$ and $N_{Te} = 3$, a, b and c are the ratios of Ge, Se and Te, respectively. From the Table 3 it is found that the heat of atomization decreases with the increase of Te content *i.e.* the average single bond energy decreases. This decrease in the average single bond energy with the increase of Te content may causes the decrease of optical band gap.

Table 3. Values of average coordination no. (m), average heat of atomization ($\overline{H}_S$) *(kcal/g-atom), average single bond energy* ($\overline{H}_S/m$) *and Heat of atomization for Ge, Se, Te elements in a-*$Ge_{10}Se_{90-x}Te_x$ *(x=0, 10, 20, 30, 40, 50).*

x	m	$\overline{H}_s$ (kcal/g-atom)	$(\overline{H}_s/m)$ (kcal/g-atom)	Element	Heat of atomization (kcal/g-atom)
0	2.2	53.46	24.30	Ge	90
10	2.3	53.12	23.09	Se	49.4
20	2.4	52.78	21.99	Te	46
30	2.5	52.44	20.98		
40	2.6	52.10	20.04		
50	2.7	51.76	19.17		

4. Conclusions

The following conclusions can be drawn from the present analysis:

- Both experimentally and theoretically calculated optical band gap are found to be in good agreement with each other and decreases with the increase of Te content. Band tailing parameter is found to be of the order of 10^6.
- There is no regular trend in E_d and E_0 in the floppy mode but at the composition $Ge_{10}Se_{70}Te_{20}$ the mechanical percolation threshold takes place (m = 2.4) and after that in the rigid mode there is an increase of E_d and E_0.
- The coordination number increases with the increase of Te concentration, which gives an indication that the value of optical gap will strongly depend on the heat of atomization as with the increase of Te content the heat of atomization decreases leading to the decrease of the average single bond energy and this reflects the cause of decrease in optical band gap.

Acknowledgement

One of us (PS) expresses his gratitude to Jaypee University of Information Technology for providing teaching assistantship.

References

[1] J. H. Dessaur, H. E. Clarke, Xerography and Related Processes. Local, London, (1965).

[2] S. R. Ovshinsky, Phys. Rev. Lett. **21**, 1450 (1968).

[3] E. Marquez, P. Villars, R. G. Jimenez, J. Mater. Res. **3**, 314 (1988).

[4] A. R. Hilton, D. Hayes, M. Rechtin, J.Non-Cryst. Solids **17**, 319 (1975).

[5] D. E. Carlson, C. R. Wronski, Appl. Phys. Lett. **28**, 671 (1976).

[6] N. F. Mott, Adv. Phys. **16**, 49 (1967).

[7] N. F. Mott, Philosophical Magazine, **34**, 285 (1976).

[8] A. Vasko, in: Proceedings of 11th International Congress on Glass **5,** Prague, 533 (1977).

[9] J. S. Sanghara, I. D. Agarwal, J.Non-Cryst. Solids **256 & 257,** 6 (1999).

[10] K. Schwartz, "The Physics of Optical Recording", Berlin, Springer-Verlag (1993).

[11] A. Bradley, "Optical Storage for Computers Technology and Applications", Ellis Horwood Limited, New York, (1989).

[12] J. Bardangna, S, A, Keneman, "Holographic recording Media", edited by H. M. Smith, Berlin, Springer-Verlag 229 (1977).

[13] A. Kumar, M. Husian, S. Swarup, A. N. Nigam, A. Kumar, X-ray Spectrom, **19**, 243 (1990).

[14] R. Mathur, A. Kumar, Rev. Phys. Appl., **21,** 579 (1986).

[15] F. Mahdjuri, J. Phys. C, **8**, 2248 (1975).

[16] M. Kitao, K. Yoshi, S. Yamada, Phys. Status Solidi A, **173,** 375 (1999).

[17] Z. H. Khan, M. Zulfeqaur, A. Kumar, M. Husain, Can. J. Phys. **80**, 19 (2002).

[18] Vineet Sharma, Journal of Ovonic Research, **2**(3), 35 (2006).

[19] D. J. Sarrach, J. P. DeNeufville, W. L. Haworth, J. of Non-Cryst. Solids, **22**, 245 (1976).

[20] P. Sharma, V. Sharma, S. C. Katyal, Chalcogenide Letters **3**, 73 (2006).

[21] A. M. Andriesh, M. S. Iovu, Moldavian Journal of the Physical Sciences, **2**, 3, (2003).

[22] K. Morigaki, "Physics of Amorphous Semiconductors" World Scientific Publisher (1999).

[23] A. M. Farid, Egypt. J. Sol., **25,** 1, (2002).

[24] S. A. Fayek, A. F. Maged, M. R. Balboul Vacuum **53**, 447 (1999).

[25] M. Fadel Vacuum, **48**(1), 73 (1997).

[26] M. F. Thorpe, J. Non-Cryst. Solids **57**, 350 (1983).

[27] W. H. Zachariasen, J. Am. Chem. Soc. **57**, 3841 (1931).

[28] S. R. Elliot, Physics of Amorphous Solids, Longman Inc, New York, 134 (1984).

[29] D. J. Sarrach, J. P. DeNeufville, W. L. Haworth, J. of

Non-Cryst. Solids, **22**, 245 (1976).
[30] S. S. Fouad, S. A. Fayek, M. H. Ali, Vacuum **49**, 25 (1998).
[31] S. H. Wemple, M. DiDomenico, J. Phys. Rev. B **3**, 1338 (1971).
[32] S. H. Wemple, Phys. Rev. B. **7**, 3767 (1973).
[33] K. Tanaka, Thin Solid Films, **66**, 271 (1980).
[34] J. Tauc, A. Menth, J. Non-Cryst. Solids **8**, 569 (1972).
[35] E. Marquez, T. Wagner, J. M. Gonzalez-Leal, A.M. Bernal-Oliva, R. Prieto-Alcon, R. Jimenez-Garay, P. J. S. Ewen, J. Non-Cryst. Solids **274**, 62 (2000).
[36] J. M. Gonzalez-Leal, A. Ledesma, A. M. Bernal-Oliva, R. Prieto-Alcon, E. Marquez, J. A. Angel, J. Carabe, Materials Letters **39**, 232 (1999).
[37] J. M. Gonzalez-Leal, R. Prieto – Alcon, J. A. Angel, E. Marquez, J. Non-Cryst. Solids **315**, 134 (2003).
[38] V. Pamukchieva, A. Szekeres, E. Savova, E. Vlaikova, J. Non-Cryst. Solids **242**, 110 (1998).
[39] M. Kastner, Phys. Rev. Lett. **28**, 355 (1972).
[40] S. R. Ovshinsky, Selected papers, “Disordered Materials Science and Technology”, D. Adler (Ed.) Amorphous Institute Press, USA, p.83 (1982).
[41] L. Pauling, “The Nature of Chemical Bond”, Cornell University Press, New York, (1963).
[42] M. Yamaguchi, Philosophical Magazine B, **41(6)**, 651 (1985).
[43] A. Srinivasan, K. Ramesh, M. Mahusoodanan, Philos. Mag. Lett. **65**, 249 (1992).
[44] J. C. Philips, J. Non-Cryst. Solids **34**, 153 (1979).
[45] J. C. Philips, J. Non-Cryst. Solids **43**, 37 (1981).
[46] M. F. Thorpe, J. Non-Cryst. Solids **57**, 355 (1983).
[47] S. Mahadevan, A. Giridahar, J. Non-Cryst. Solids **152**, 42 (1993).

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