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Electrical conductivity of $Cu_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$ glasses

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Results of the dc electrical conductivity (σ) measurements (from 90 to 420 K) on 15 compositions of the $Cu_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$ glasses (x from 0 to 30) are presented. Similar to that observed [1] in the composition dependencies of the mean atomic volume (V) and the glass transition temperature (T_g) of these glasses, it is possible to delineate three regions in the composition dependence of the σ of these glasses. (i) For addition of Cu up to 1 at %, the σ register a decrease compared to that of the parent $As_{0.4}Se_{0.3}Te_{0.3}$ glass. (ii) For Cu $>$ 1 at %, the conduction activation energy (ΔE) and the pre-exponential factor (C) decrease, with a concomitant increase in σ (at 250 K) by about six orders of magnitude. (iii) Both ΔE and C show saturation for Cu $>$ 23 at %. The σ-composition data are examined using the model developed earlier [1] to understand, the V (and T_g)-composition dependencies of these glasses. © *1999 Kluwer Academic Publishers*

1. Introduction

As part of a programme on the synthesis and study of the role of metallic additives to chalcogenide glasses, the effect of addition of Cu to the $As_{0.4}Se_{0.3}Te_{0.3}$ glass was investigated. In an earlier communication [1], the mean atomic volume (V) and the glass transition temperature (T_g) of $Cu_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$ glasses (with Cu from 0.2 to 30 at %) were discussed.

It was found that [1], the V showed a small decrease (about 0.53%) and T_g was essentially invariant up to addition of 1 at % of Cu to the parent $As_{0.4}Se_{0.3}Te_{0.3}$ glass. These results were accounted with clusters of Cu atoms occupying interlayer positions in the layered network of the parent glass, without drastically affecting its basic structure.

For Cu $>$ 1 at %, a decrease in V and an increase in T_g were seen. For Cu $>$ 1 at %, the Cu atoms form bonds with As, Se and Te. A structural model was proposed [1] to account for the V-composition and T_g-composition data. Accordingly, with progressive increase in the Cu content in these glasses, structural units of $CuAsSe_2$ and of CuAsTe begin to form in lieu of some of the original As_2Se_3 and As_2Te_3 structural units of the parent $As_{0.4}Se_{0.3}Te_{0.3}$ glass. For Cu $\geq$ 23.08 at %, after the formation of $CuAsSe_2$ structural units, there is no Se available for the formation of As_2Se_3 structural units. Due to this, changes in slope are seen in the V-composition and T_g-composition data at $x = 23.08$. In this communication, the results of measurements of σ for these glasses are reported and discussed.

2. Experimental

High purity (99.999%) As and Cu (from Johnson Matthey, UK), Te and Se (from Atomergic Chemmetals, USA) were used to synthesise the glasses using two-stage melt quenching method [2]. Appropriate quantities (2 to 3 g total per batch) of these elements were weighed into 10 mm diameter fused silica ampoules, which were sealed under a pressure of 10^{-5} Torr. The ampoules were first heated gradually to 1000 °C in a rotary furnace (for homogenisation). After a couple of hours, the temperature of the ampoule was reduced to 800 °C and held under constant rotation at this temperature for about 8 or 10 hours. The temperature was then reduced to ~500 °C and the ampoule containing the viscous melt was dropped into an ice cooled copper boat and the ampoule immediately cooled by a lateral flow of ice cooled water. This procedure was found to yield bright, shiny and pore-free glasses. The investigated compositions have glassy state which was confirmed by using X-ray diffractograms of the bulk samples.

As in our earlier measurements [3–5], the samples for σ measurements were flat (about 0.8 to 1 mm thick and cross sectional area $\sim$0.25 cm^2), with the opposite surfaces rendered parallel. Silver paste was applied on the surfaces of the sample to ensure proper electrical contacts with the spring loaded Cu electrodes. A chromel-alumel thermocouple in contact with the sample was used to register the temperature. The σ was measured from 90 K to the respective T_g's (T_g's ranging from ~400 K to ~470 K) on annealed samples. The annealing was performed for about 15 min at the respective T_g and then the sample was furnace cooled to room temperature. Low temperature (90 to 300 K) runs were performed in a cryostat using liquid nitrogen under reduced pressure as the refrigerant. To prevent condensation of moisture on the sample, the sample chamber was evacuated during the low temperature runs. An appropriate tubular furnace was used for the high temperature (300 to 400 K) measurements. The resistance of the samples, ranging from $\sim 10^{13}\ \Omega$ to $\sim 50\ \Omega$ (depending on the composition and the temperature range investigated) were measured using a Keithley model 610C Electrometer at high impedance ranges and a Keithley model 2000 digital multimeter at low impedance ranges.

3. Results

Figs 1 to 4 and Table I summarise the σ data of the $Cu_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$ glasses. The σ-T data of the

TABLE I Data on $\log\sigma$ (at 250 K), ΔE and $\log C$ for the $Cu_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$ glasses

	Composition x	$\log\sigma$ (Ω^{-1} cm^{-1}) (at 250 K)	ΔE (eV)	log C (Ω^{-1} cm^{-1})
Random scatter	—	±0.1	±0.02	±0.05
	0	−9.02	0.59	2.86
	0.2	−9.45	0.58	2.24
	0.4	−9.60	0.57	1.89
	0.6	−9.35	0.58	2.34
	1.0	−9.20	0.59	2.70
	2.0	−8.80	0.56	2.54
	3.5	−8.00	0.50	2.10
	5.0	−7.60	0.47	1.84
	10	−6.40	0.39	1.46
	15	−5.12	0.30	0.94
	20	−4.38	0.26	0.86
	23.08	−3.95	0.23	0.72
	25	−3.40	0.22	0.80
	26.5	−3.34	0.24	0.80
	30	−2.9	0.22	1.3

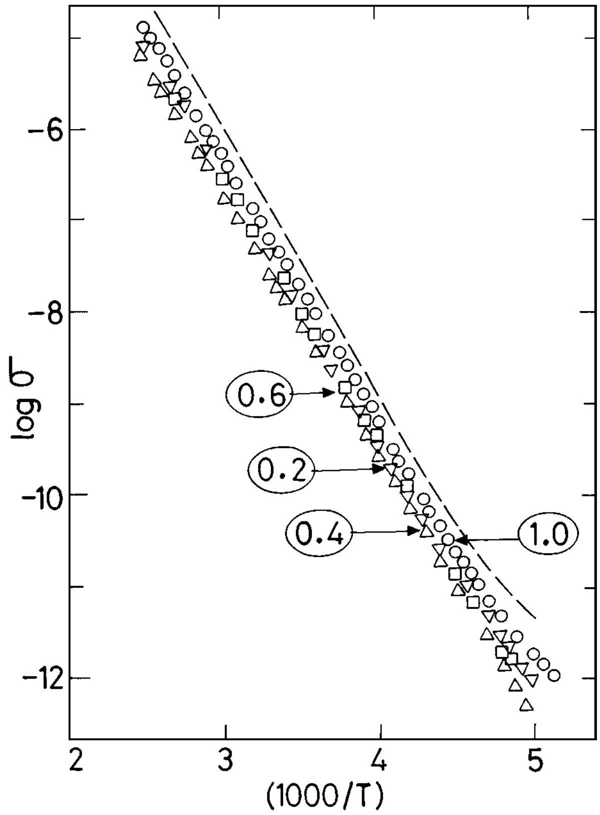

Figure 1 log σ vs. $1/T$ data for the $Cu_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$ glasses with x of 0.2 (∇ data points), 0.4 (Δ data points), 0.6 (□ data points) and 1 (O data points). The broken curve is the data for the parent $As_{0.4}Se_{0.3}Te_{0.3}$ glass.

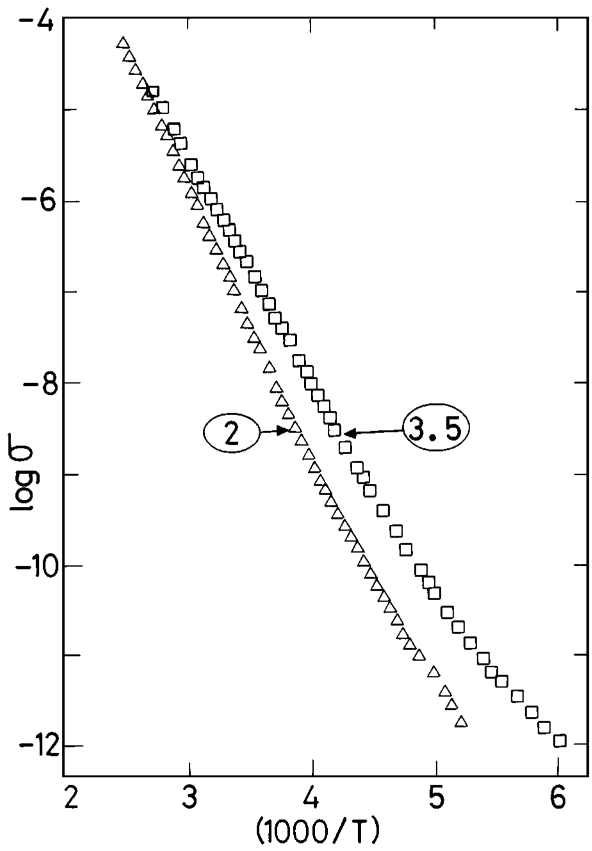

Figure 2 log σ vs. $1/T$ data for the $Cu_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$ glasses with $x = 2$ and 3.5.

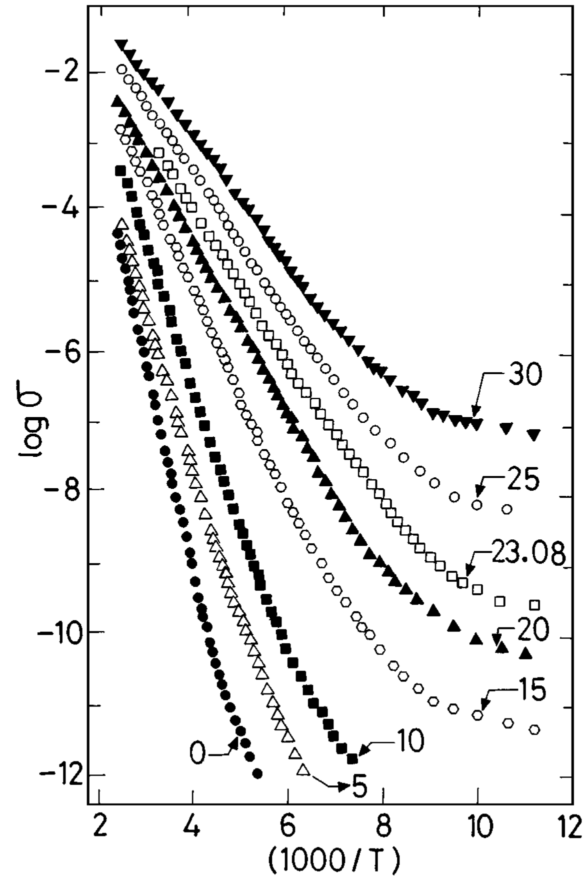

Figure 3 log σ vs. $1/T$ data for the $Cu_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$ glasses with $x > 1$. The data for x of 2 and 3.5 which lie between the data of compositions with $x = 0$ and 5 are given separately in Fig. 2 for purposes of clarity.

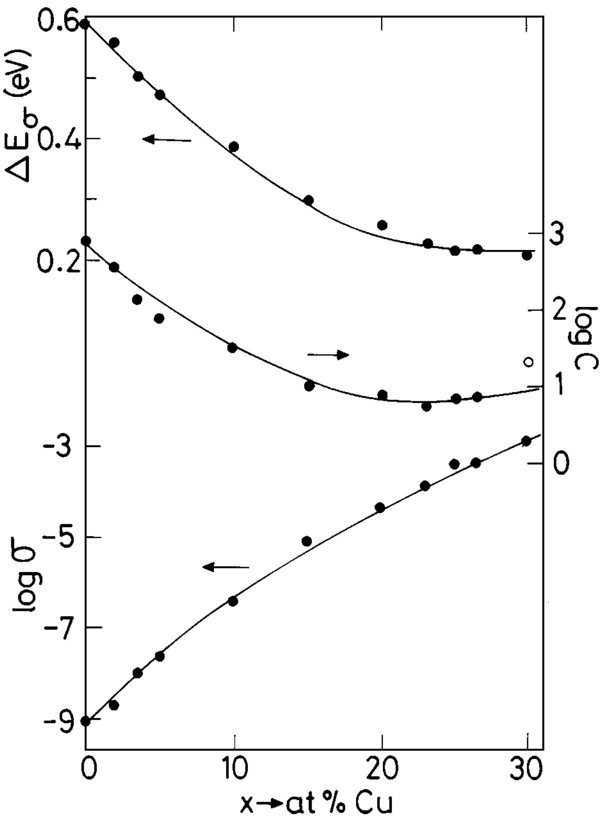

Figure 4 Variation of ΔE, log C and log σ (at 250 K) with at % of Cu for the $Cu_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$ glasses.

parent $As_{0.4}Se_{0.3}Te_{0.3}$ glass (broken line data, Fig. 1) obtained presently agree with the earlier reported data [4, 6–8]. The log σ vs. $(1/T)$ data of the $As_{0.4}Se_{0.3}Te_{0.3}$ glass is linear above 250 K and can be represented as $\sigma = C\exp(-\Delta E/kT)$, where ΔE is the activation energy for electrical conductivity and C is the preexponential factor. The absence of any time dependent effects in the dc conductivity data indicated that the conduction was essentially electronic in nature.

The σ of the glasses with x from 0.2 to 1 are lower than that of the parent glass by about 0.4 log units (Fig. 1). Their ΔE values are almost the same as that of the $As_{0.4}Se_{0.3}Te_{0.3}$ glass. A reduction in σ for the parent glass by about 0.6 log units is observed at $x = 0.2$. On further increase of Cu up to 1 at %, no substantial change occurs in the σ-T data.

For $x > 1$, σ of these glasses are higher than that of the parent glass (Figs 2 and 3). There is a decrease in the ΔE and an increase in the σ values with increasing Cu content. With increasing Cu content, the temperature over which the linearity of the log σ vs. $(1/T)$ data is valid, extends to lower temperatures (Fig. 3). Due to hopping conductivity, the σ of the various compositions level off at lower temperatures.

Decreases in ΔE from ~0.6 eV to ~0.23 eV and in log C from 2.85 to ~0.8 and an increase in log σ (at 250 K) by about five orders of magnitude are observed as x varies from 0 to ~23 (Fig. 4). The ΔE and log C values level off at x ~23. Thus, similar to that observed in the V-composition and T_g-composition data [1], three regions can be delineated in the σ-composition data of these glasses; (i) the region up to 1 at % of Cu, with their σ being lower than that of the $As_{0.4}Se_{0.3}Te_{0.3}$ glass (ii) the region from 1 to ~23 at % of Cu, with decreases in ΔE and C and an increase in σ with increasing x and (iii) The region for Cu > 23 at %, with levelling off in the ΔE and C values.

4. Discussion

4.1. Compositions with Cu < 1 at %

The σ-T data of $Cu_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$ glasses for x up to 1 are only marginally affected compared to the $As_{0.4}Se_{0.3}Te_{0.3}$ glass (Fig. 1), indicating that the electronic structure of the parent glass is not drastically affected as Cu does not form bonds with the other elements of the parent glass [1]. The observed small decrease in σ is due to the increase in the scattering of the carriers by the clusters of Cu atoms. A similar small reduction in σ is observed on addition of Cu, Ag or T1 from 0.2 to 1 at % to $As_{0.4}Se_{0.6}$ glass [9]. This is attributed to an increase in the carrier scattering either by the introduced impurities or by the lattice imperfections caused by them. In the $Ag_x(As_{0.4}Te_{0.6})_{100-x}$ glasses also, the small decrease in σ observed for addition of Ag of up to 1 at % is attributed to the dispersed Ag atoms acting as neutral scattering centres [3].

4.2. Compositions with Cu > 1 at %

Though the σ-T data of Fig. 3 are reminiscent of the 'chemical modification' observed in chalcogenide glasses [10–16], the following differences are seen on a closer examination of the data. Large changes in σ are brought about in chalcogenide films [10–16] by the introduction of transition metals (such as Ni, Mn, W, Mo) by the co-sputtering method in which the reaction between the host and the modifier takes place on a cold substrate and not in the corresponding melt. In the present study, large changes in σ are observed in bulk samples by introducing Cu in the melt itself. In the case of $Ge_{32}Te_{32}Se_{32}As_4$ films modified with Ni [11–13], the modification effect starts only around room temperature or higher, while, in the present case the modification effect starts from ~150 K (Fig. 3). Also, the changes in σ observed presently result from changes in the overall gap of the glasses, rather than due to neutralisation of charge carriers which cause shift of the Fermi level.

A large change in σ observed due to introduction of Cu in $As_{0.4}Se_{0.6}$ glass [16, 17] is attributed to the increased content of three component $CuAsSe_2$ structural units. This unit is more conducting than the rest of the material and enters as a whole unit into the structure of the glass without substantially disturbing the continuity of its network. For $Cu_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$ glasses also, with increase in the Cu content, three component $CuAsSe_2$ and CuAsTe structural units are formed without substantially disturbing the continuity of the basic As_2Se_3-As_2Te_3 network [1]. The reason for the large change in σ observed in the present studies is therefore due to the higher conductivity of the $CuAsSe_2$ and the CuAsTe structural units, compared to the original glass.

In the $Cu_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$ glasses, with progressive increase in the Cu content, $CuAsSe_2$ and

CuAsTe structural units are formed in place of the original As_2Se_3 and As_2Te_3 structural units of the parent glass; for $x \geq 23.08$, all the Se available is used up in the formation of $CuAsSe_2$ structural units thereby precluding the formation of As_2Se_3 structural units [1]. For $x \geq 23.08$, structural units of $CuAsSe_2$, CuAsTe, CuTe and As_2Te_3 are formed [1]. Due to this, changes in slope in the V-composition data were seen at the composition with $x \sim 23$. The levelling off of ΔE and log C values from $x \sim 23$ (Fig. 4) observed presently is due to this change in the type of structural units that occurs for $x \geq 23.08$.

As chalcogenide glasses normally have p-type conductivity, the observed reduction in ΔE (Fig. 4) with increasing Cu content indicates that the difference between the Fermi level and the top of the valence band is reduced. This may be due to (i) a reduction in the mobility gap of the material which results due to alloying of Cu with the parent glass or (ii) the formation of electron hopping sites in the gap or (iii) a shift of Fermi level towards the valence band due to the filling up of the gap states by the carriers supplied by the charged additives [14]. For identification of the cause for this reduction in ΔE, data on optical gap and thermoelectric power on the $Cu_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$ glasses are necessary; but these data are not yet available for these glasses. However, according to the results available for $Cu_x(As_{0.4}Se_{0.6})_{100-x}$ and $Ag_x(As_{0.4}S_{0.6})_{100-x}$ glasses [19–23], the following observations are pertinent for the $Cu_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$ glasses.

In vitreous $As_{0.4}Se_{0.6}$, there is a decrease in the band gap (mobility gap) of the material due to the introduction of Cu [23]. The displacement of the Fermi level is small and the observed decrease of ΔE is due to the alloying effect of Cu with As and Se [19–21]. The decrease of the mobility gap manifests the appearance of the Cu-Se bonding states at the top of the valence band [21]. In the $Ag_x(As_{0.4}S_{0.6})_{100-x}$ glasses, with increasing Ag content, the structure changes markedly to tetrahedral structure and the coordination number increases from 2.4 for $As_{0.4}S_{0.6}$ to about 4.2 for the 25 at % Ag alloy [22] and there is a decrease in the pre-exponential factor C. Results on $Ag_{0.67}S_{0.33}$-$As_{0.4}S_{0.6}$, $Ag_x(As_{0.4}Se_{0.6})_{100-x}$ and $Tl_x(As_{0.4}Se_{0.6})_{100-x}$ glasses also indicate [23–25] that the decrease of ΔE with increasing Ag and Tl content is related to a corresponding decrease in the optical gap. It is also interesting in this context to note that Cu does not generate deep defects, but rather forms bonds with chalcogens in $Cu_x(As_{0.4}S_{0.6})_{100-x}$ and $Cu_x(As_{0.4}Se_{0.6})_{100-x}$ glasses, for Cu greater than 1 and 5 at % respectively [26, 27]. As a consequence, the shift of the Fermi level due to charge neutralisation is precluded in these glasses. Therefore any change in the conduction activation energy is traceable to the corresponding changes in the overall gap of these glasses.

For the $Cu_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$ glasses under consideration here, an increase in the average coordination number [1] and a decrease in the pre-exponential factor C by about two orders of magnitude occur as x changes from 0 to 30. It can therefore be conjectured that the reduction in ΔE observed presently is therefore due to a reduction in the mobility gap (brought about by structural changes on introduction of Cu).

5. Conclusions

The variation of σ with temperature and composition have been reported for fifteen $Cu_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$ glasses, with x ranging from 0 to 30. For Cu up to 1 at % the σ of these glasses register a decrease compared to that of the parent glass. The reduction in σ up to $x = 1$ is due to the Cu atoms acting as neutral scattering centres. For Cu > 1 at %, there is a decrease in the conduction activation energy and an increase in σ (about six orders of magnitude at 250 K) with increasing Cu content. The results suggest that the reduction of ΔE, is due to a reduction in the mobility gap, brought about by structural changes which result in the formation of $CuAsSe_2$ and CuAsTe tetrahedral complexes in the glasses.

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References

1. S. MAHADEVAN and A. GIRIDHAR, *J. Non-Cryst. Solids* **221** (1997) 281.
2. *Idem.*, *ibid.* **197** (1996) 219.
3. A. GIRIDHAR and S. MAHADEVAN, *ibid.* **197** (1996) 228.
4. S. MAHADEVAN, A. GIRIDHAR and K. J. RAO, *J. Phys.* **C10** (1977) 4499.
5. S. MAHADEVAN and A. GIRIDHAR, *J. Mater. Sci.* **29** (1994) 3837.
6. H. L. UPHOFF and J. HEALY, *J. Appl. Phys.* **32** (1961) 950.
7. M. N. ROILOS, *J. Non-Cryst. Solids* **6** (1971) 5.
8. D. L. KINSER, L. K. WILSON, H. R. SANDERS and D. J. HILL, *ibid.* **8–10** (1972) 823.
9. B. T. KOLOMIETS, YU. V. RUKHLYADEV and V. P. SHILO, *ibid.* **5** (1971) 389, 402.
10. S. R. OVSHINSKY, in "Proceedings of the 7th International Conference on Amorphous and Liquid Semiconductors, Edinburgh, 1977," edited by W. Spear (CICL, University of Edinburgh, 1977) p. 519.
11. R. FLASCK, M. IZU, K. SAPRU, T. ANDERSON, S. R. OVSHINSKY and H. FRITZSCHE, in "Proceedings of the 7th International Conference on Amorphous and Liquid Semiconductors, Edinburgh 1977," edited by W. Spear (CICL, University of Edinburgh, 1977) p. 37.
12. T. GOMI, Y. HIROSE, T. KUROSU, T. SHIRAISHI, M. IIDA, Y.GEKKA and A. KUNIOKA, *J. Non-Cryst. Solids* **41** (1980) 37.
13. M. KUMEDA and T. SHIMIZU, *Solid State Commun.* **31** (1979) 967.
14. T. AHIMUZU, I. WATANABE and S. SHIOMI, *ibid.* **38** (1981) 483.
15. S. R. OVSHINSKY, in "Physics of Amorphous Materials," edited by D. Adler, B. B. Schwarts and M. C. Steele (Institute for amorphous studies series, Plenum Press, New York) p. 105.
16. E. A. DAVIS and E. MYTILINEOU, *Solar Energy Materials* **8** (1982) 341.
17. A. DANILOV and M. EL. MOSLI, *Soviet Physics Solid State* **5** (1963) 1472.
18. Z. U. BORISOVA, "Glassy Semiconductors" (Plenum, New York, 1981).
19. M. I. FRASER and A. E. OWEN, *J. Non-Cryst. Solids* **59/60** (1983) 1031.

20. K. S. LIANG, A. BIENENSTOCK and C. W. BATES, *Phys. Rev.* **B10** (1974) 1428.
21. C. JIJIAN and L. ZHENHUA, *J. Non-Cryst. Solids* **112** (1989) 328.
22. M. F. KOTKATA, M. M. RADWAN, F. M. METAWE and C. S. MOHAMED, *ibid.* **77/78** (1985) 1229.
23. W. HENRION, in "Amorphous Semiconductors 1976, Proceedings of the International Conference Balatanfured, Hungary 1976," edited by Kosa Somogyi (Akademiai Kiado Budapest, 1977) p. 255.
24. M. OHTO, M. ITOH and K. TANAKA, *J. Appl. Phys.* **77** (1995) 1034.
25. M. KITAO, M. SENDA, Y. TAKANO and S. YAMADA, *J. Non-Cryst. Solids* **127** (1991) 36.
26. J. Z. LIU and P. C. TAYLOR, *Phys. Rev. Lett.* **59** (1987) 1938.
27. G. PFISTER, K. S. LIANG, M. MORGAN, P. C. TAYLOR, E. J. FRIEBELE and S. G. BISHOP, *ibid.* **41** (1978) 1318.

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