

ELECTRICAL AND STRUCTURAL PROPERTIES OF  $\text{Bi}_x\text{Ge}_{20}\text{Se}_{80-x}$   
CHALCOGENIDE SYSTEM

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Assiut, Egypt.**Abstract:**

*Different compositions of the system  $\text{Bi}_x\text{Ge}_{20}\text{Se}_{80-x}$  with  $5 \leq x \leq 10$  at .% were produced by quenching from the melts. The D.C. electrical conductivity seemed thermally activated. The type of conduction, the value of the electrical conductivity and the activation energy were dependent on the amount of Bi in the compositions. The metal-like behaviour could be mainly shown for the most Bi rich composition especially in the low range of the ambient temperature. It could be attributed mainly to the excess of Bi with its semi-metallic behaviour.*

*Thermally induced changes in the structural properties have been investigated using x-ray diffraction, differential thermal analysis and scanning electron microscopy.*

**Introduction**

Studies done so far for melt-quenched chalcogenide glasses have indicated that impurities slightly affect the electrical properties of the glass with a few exceptions and that dominant charge carriers in those glasses are holes, which could not be changed even if the combination of constituent elements is varied(1-4). Ovshinsky et al.(5), however, have recently proposed an idea of "chemical modification", which claims that the conductivity could be changed independently of the band gap by the incorporation of a fairly large amount of proper elements. The application of their idea is confined to films prepared, for example, by the cosputtering.

In recent years, the nature of gap states of the glasses has been made clear, and it has been shown that the fermi energy is pinned by "charged dangling bonds" close to the middle of the band gap(6-8). However, n-type conduction could be hold in a melt quenched  $\text{Bi}_{10}\text{Ge}_{20}\text{Se}_{70}$  glass and the importance of the role played



**Table (1):** Variation of both  $(T_c)_M^{\circ}\text{C}$  and  $(T_m)_M^{\circ}\text{C}$  with the amount of Bi in the compositions. As-prepared and annealed at 300°C for 1 hr. specimens.

x at.%	As-prepared		Annealed	
	$(T_c)_M^{\circ}\text{C}$	$(T_m)_M^{\circ}\text{C}$	$(T_c)_M^{\circ}\text{C}$	$(T_m)_M^{\circ}\text{C}$
5	555	540	565	550
10	430	515	425	490
20	425	545	450	390
30	405	555	460	530
40	535	270	360	455

In table (1), it is remarkable that no unique impression could be concluded that either  $(T_c)_M$  or  $(T_m)_M$  is decreasing or increasing by annealing. The only confirmed conclusion is that new phases can be formed and pre-existed crystalline phases may be dissolved as a result of heating. These results are confirmative of those obtained by XRD and SEM investigation.

The x-ray diffractograms of virgin specimens shown in Fig. (3) indicated the possibility of existence of different crystalline phases in each composition, which are denoted by special marks. As shown in Fig. (4), the intensity of crystallization increases with x increases up to 20 at.%. Beyond this maximum, further enriching with Bi was associated with monotonic decrease of the intensity of crystallization.

Fig. (5) shows the x-ray diffractograms of different specimens of the composition  $\text{Bi}_5\text{Ge}_{20}\text{Se}_{75}$  after being annealed at 120, 200 and 300°C for 1 hr each. Comparing with that diffractogram shown in Fig. (3.a), it could be concluded that the most distinguished crystalline phases with the maximum relative intensities are identified to be Ge,  $\text{GeSe}_2$ ,  $\text{BiSe}_2$  and  $\text{Bi}_2\text{Se}_3$  for as-prepared and annealed for 1 hr at 120, 200 and 300°C specimens respectively. Fig. (6) shows that, the most possible intense crystallization is corresponding to the case of annealing at 200°C.

The morphology of samples after annealing at 300°C for 1 hr was examined using SEM. The corresponding photomicrographs were as shown in Fig. (7). For the composition  $\text{Bi}_5\text{Ge}_{20}\text{Se}_{75}$ , the photomicrograph (7.a) showed the possibility of occurrence of both crystallization and phase separation. The crystallites are large in size and occupying most of the structure. The photomicrograph shown in Fig. (7.b) which belongs to the composition  $\text{Bi}_{10}\text{Ge}_{20}\text{Se}_{70}$  indicated in general discontinuous structure consisting of small crystallites dispersed in amorphous matrix. The crystallites are with different forms predicting of different compounds. The photomicrograph shown in Fig. (7.c) indicated that the surface microstructure of the composition  $\text{Si}_{20}\text{Ge}_{20}\text{Se}_{60}$



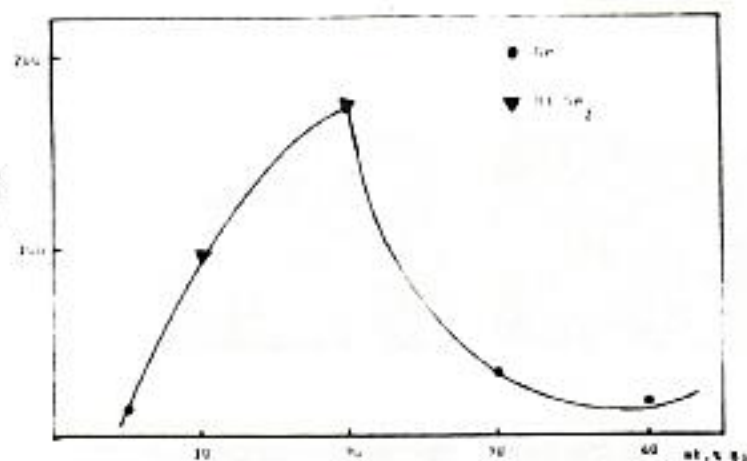


Fig.(4): Shows the effect of composition on the maximum intensity ( $I_{max}$ ) of crystalline phase.

Fig.(5): X-ray diffractograms of different specimens of the composition  $Bi_5Ge_{20}Se_{75}$ , a) annealed at 120 for one hour, b) annealed at 200 for one hour and c) annealed at 300 for one hour.

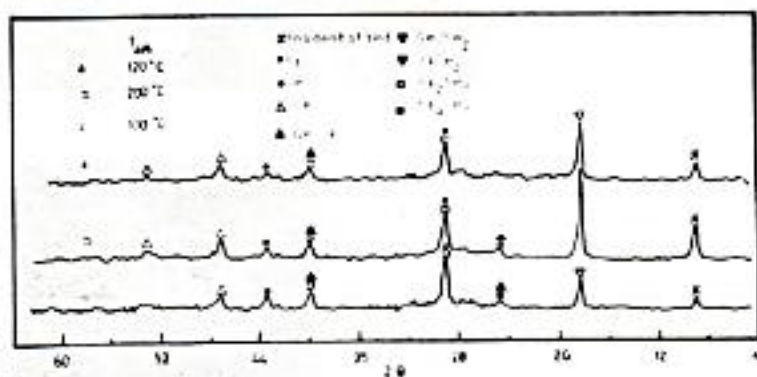
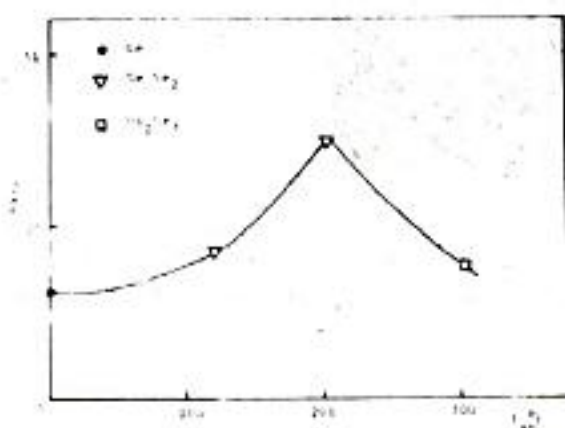


Fig.(6): Shows the relation between the maximum intensity ( $I_{max}$ ) and the temperature of annealing ( $T_{ann}$ ), a)  $x=5$  at.% & b)  $x=40$  at.% Bi.





is also discontinuous. The microcrystallites are concentrated in certain zones of the whole structure. However, the crystallites are oriented in almost the same direction and are with relatively large sizes and high intensities. Completely different structure could be shown in the photomicrograph in Fig. (7.d) which belongs to a specimen of the composition  $\text{Bi}_{30}\text{Ge}_{20}\text{Se}_{50}$ . Crystallites with different shapes and sizes are dispersed homogeneously in the amorphous matrix and occupying most of the structure. However, a particular microcrystalline phase seemed more growing and more dominant. As shown in the photomicrograph in Fig. (7.e) which belongs to the most Bi rich composition ( $x=40$  at.%), the crystallization is pronounced. The structure is homogenous and the liquid phase is minor. The boundaries of the crystallites are distinguished and clear. However, the results of XRD and SEM examinations are seeming confirming of existence of crystalline phases which are dependent on both the Bi content and annealing.

The temperature dependence of the dc electrical conductivity ( $\sigma$ ) was as shown in Fig. (8). In the considered range of the ambient temperature and for the whole compositions, the expression for  $\sigma$  was that of normal semiconductors where

$$\sigma = \sigma_0 \exp(-\Delta E_g/KT) \quad (1)$$

The activation energy ( $\Delta E_g$ ) and the pre-exponential factor  $\sigma_0$  were obtained by least squares fit to experimental data.

The composition dependence of the electrical conductivity at different ambient temperatures (data extracted from Fig. (8) was as shown in Fig. (9). The relation between  $\log \sigma$  and  $x$  seemed positive slope linear verifying the following empirical equation.

$$\sigma = c e^{mx} \quad (2)$$

The calculated values of  $\Delta E_g$  corresponding to the semiconductor regions and their dependence on composition were as shown in Fig. (10).  $\Delta E_g$  increased slightly up to  $x=10$  at.%. Then it decreased in almost monotonic manner with further enriching with Bi. The values of  $T_g$  (the temperature of transition between the two regions of conduction shown in Fig. (8) and  $\sigma_0$  and their variations with the Bi content were as recorded in table (2).

Table (2): Variation of both  $T_g$  (°C) and  $\sigma_0$  ( $\Omega^{-1}\text{cm}^{-1}$ ) with composition

x at.%	5	10	20	30	40
$T_g$ °C	122	88	90	119	127
$\sigma_0$ ( $\Omega^{-1}\text{cm}^{-1}$ )	91200	1995	1259	1270	1319





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