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Carrier-sign reversal in Bi-doped bulk amorphous semiconductors $Ge_{20}Te_{80-x}Bi_x$

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A *p-n* transition in the electronic conduction in Bi-doped bulk amorphous semiconductors $Ge_{20}Te_{80-x}Bi_x$ at about $x=3.5$ has been observed for the first time. *n*-type conduction has been established by the measurement of thermoelectric power that becomes negative at $x\sim3.5$. Measurement of the electrical transport under high quasihydrostatic pressure ($p\leq120$ kbar) has also been studied in $x=0,2,3,4,6$ compositions. Electrical resistivity (ρ), thermal activation energy (ΔE), and ($d\log_{10}\rho/dp$) show a sudden drop in their values in the *p-n* transition region ($x=3$–4). Results are discussed in the light of Phillip's model of microclusters and constraint theory.

The chalcogenide glasses prepared by quenching from the melt are an important category of noncrystalline solids. They are generally *p*-type semiconductors with a positive Seebeck coefficient describing the thermoelectric power. This is the case not only for chalcogenide elements themselves, but also for binary, ternary, and multicomponent glass forming alloys of S, Se, and Te with metalloid elements such as Si, Ge, Sn, As, and Sb. Further, addition of impurities to them does not alter the nature of *p*-type conductivity.

In this respect chalcogenides of germanium have recently been found to have the unique property of showing a *p-n* transition when doped with large concentrations of Bi [more than 7 and 11 at.% Bi in $(GeSe_{3.5})_{100-x}Bi_x$ and $Ge_{20}S_{80-x}Bi_x$, respectively].[1,2] This remarkable behavior of Bi dopants is not understood and has been a current topic of extensive investigation.[3–13] In this context it would be interesting to investigate the Bi-doped GeTe glasses to ascertain the effect of Bi dopant on the nature of *p*-type conductivity. In our continuing program of investigation of Bi-doped germanium chalcogenide glasses we have undertaken the study of amorphous $Ge_{20}Te_{80-x}Bi_x$ for the first time and have observed the *p-n* transition in these glasses at about $x=3.5$. We report our first results in this communication. Further, electrical transport under high quasihydrostatic pressure was also studied.

For preparation of the samples $Ge_{20}Te_{80-x}Bi_x$, high-purity elements (99.999%) were used. The stoichiometric compositions of the individual elements were first mixed and then filled inside a quartz tube (thickness 0.5 mm) that has a rectangular cross section to increase the cooling rate. The ampule was evacuated (10^{-6} Torr) and purged with argon gas several times to reduce the presence of residual oxygen and finally sealed in an argon environment. The sample was heated up to 1300 K for about 36 h and was continuously agitated to achieve homogenization. The ampule was then quenched in a mixture of ice cold water and NaOH. The glassy nature of the prepared samples was confirmed by x-ray and electron diffraction studies. The electrical resistivity was measured under high pressure (up to 120 kbar) with a Bridgman anvil setup described elsewhere.[14] The specimen was embedded in a steatite pressure transmitting medium and surrounded by a heat-treated pyrophillite gasket. The resistance was measured by a four-probe method using Keithley electrometer model no. 616 and a Keithley constant current source (model no. 225). The electrical resistivity at ambient condition was measured by the van der Pauw technique.[15] The thermoelectric power was measured in a conventional setup. The sample was placed between two copper rods and two small heater wires electrically insulated but thermally well connected with the sample. The temperature gradient was measured by a differential thermocouple. The whole system was placed in a copper block and the temperature was controlled within ±0.1 K. Thermoelectromotive force (EMF) was measured with a Keithley microvoltmeter.

The results of thermoelectric measurements on $Ge_{20}Te_{80-x}Bi_x$ glasses are presented in Fig. 1. Thermo-EMF first decreases continuously from 1000 to about 450 μV/K. Thereafter, a sudden drop in its value with change in its sign to negative value at about 3.5 at.% Bi, takes place. This transition point evidently corresponds to a *p-n* transition in the electrical conductivity of the Bi-doped semiconductors. The behavior of thermo-EMF in $(GeSe_{3.5})_{100-x}Bi_x$ glasses in the *p-n* transition region, as determined by Nagels, Tichy, Triska, and Ticha,[1] is also plotted in Fig. 1 for comparison. It is interesting to observe that Ge-Se-Bi glasses exhibit a continuous linear transition from *p*-type to *n*-type conductivity in the

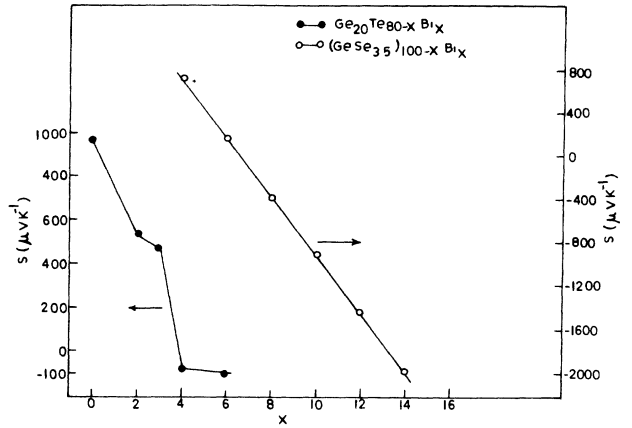

FIG. 1. Composition dependence of thermoelectric power S in $Ge_{20}Te_{80-x}Bi_x$ (solid line with solid circles) and $(GeSe_{3.5})_{100-x}Bi_x$ (solid line with open circles). The ordinate scale for $(GeSe_{3.5})_{100-x}Bi_x$ is given on the right-hand side.

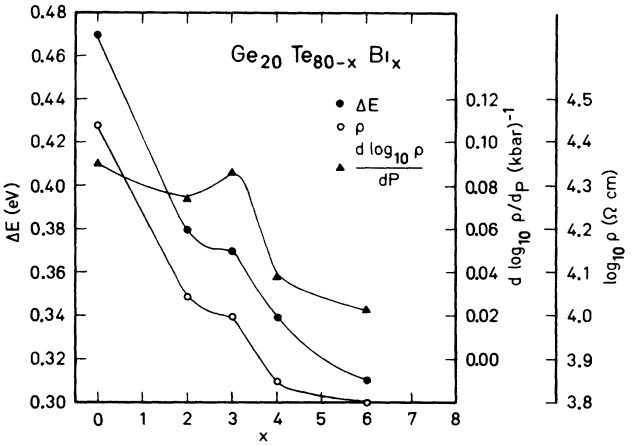

FIG. 3. Composition dependence of activation energy ΔE, resistivity ρ, and $d\log_{10}\rho/dp$ in $Ge_{20}Te_{80-x}Bi_x$. The ordinate scale for $d\log_{10}\rho/dp$ and $\log_{10}\rho$ is given on the right-hand side.

thermo-EMF versus Bi concentration plot whereas Ge-Te-Bi glasses show an abrupt transition. The results of measurement of electrical transport under high quasihydrostatic pressure on $Ge_{20}Te_{80-x}Bi_x$ are summarized in Fig. 2. In the undoped composition $Ge_{20}Te_{80}$, the resistivity decreases exponentially with the increase of pressure by three orders of magnitude up to 50 kbar. The resistivity drops suddenly by six orders of magnitude at about 50 kbar. Beyond 55 kbar the variation of resistivity with the increase of pressure is very small. With the addition of Bi to $Ge_{20}Te_{80}$ alloy the pressure of sharp transition increases. An interesting point to be noticed is that for $x > 3.5$, the transition does not remain sharp but tends to become broad or continuous. A least-squares fit to the $\log_{10}\rho$-pressure data was made in the pressure range 0–40 kbar and the slope $d\log_{10}\rho/dp$ of curves for various compositions was determined in this pressure range. These values of the slope are plotted in Fig. 3 as a function of x. A sudden drop in the slope appears in the composition range of x from 3 to 4 where the p-n transition takes place. A plot of the transition pressure as a function of Bi concentration is presented in Fig. 4. The transition pressure goes on increasing up to the p-n transition region ($x = 3$–4) and there is little increase in its value for $x > 4$.

The variation of resistivity as a function of temperature at ambient pressure follows the Arrhenius relation

$$\rho = \rho_0 \exp\left(\frac{\Delta E}{k_B T}\right), \tag{1}$$

where ρ_0 is the preexponential factor, ΔE the activation energy for electronic conduction, k_B Boltzmann's constant, and T the absolute temperature. The composition dependence of resistivity (ρ) and activation energy (ΔE) is given in Fig. 3. Both, ΔE and $\log_{10}\rho$ exhibit a sudden drop in the region where x ranges from 3 to 4.

Silicon and germanium chalcogenide glasses possess unique physical properties. In particular, anomalous variations in the physical properties of $A_x^{IV}B_{100-x}^{VI}$ glasses at a

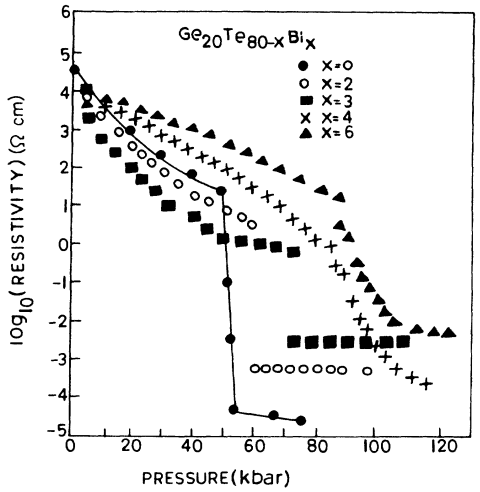

FIG. 2. Variation of resistivity ρ of $Ge_{20}Te_{80-x}Bi_x$ with pressure at room temperature: $x = 0$ (●), $x = 2$ (○), $x = 3$ (■), $x = 4$ (×), $x = 6$ (▲).

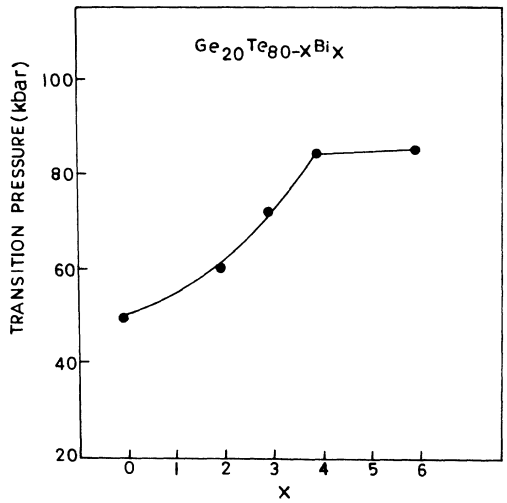

FIG. 4. Composition dependence of the transition pressure for the amorphous semiconductor to metal-like solid transition in $Ge_{20}Te_{80-x}Bi_x$.

composition $x=20$ is a feature which concerns the present study.[16] Several anomalous features appear at $x=20$ in the Ge_xTe_{x-80} glass system.[17,18] The thermal crystallization of Ge_xTe_{100-x} glasses shows a marked change in behavior at 20 at.% Ge. The Ge_xTe_{100-x} glasses with $x \leq 20$ undergo a double glass transition and double stage crystallization. On the other hand, glasses with $x > 20$ show only a single glass transition and single stage crystallization.[18] High-pressure studies on Ge_xTe_{100-x} glasses indicate that glasses in the system undergo pressure-induced glassy semiconductor to crystalline-metal transition.[19] The variations of the transition pressure, the activation energy for electrical conduction, etc., with composition, show anomalies at $x=20$.[20] The present study reveals a *p-n* transition at 3.5 at.% Bi doping of $Ge_{20}Te_{80}$ alloy. According to the Phillips constraint theory[16] the $x=20$ glass system is an ideal glass in which the number of operative constraints equals the number of degrees of freedom. Glasses with $x < 20$ are under cross linked and the glasses with $x > 20$ are over constrained. Phillips[21] has recently applied his constraint theory to formulate a model to explain the presence of *p-n* transition in $Bi_xGe_{20}M_{80-x}$ (M=S, Se) glasses. We try to understand the behavior of Bi dopants in $Ge_{20}Te_{80}$ glass using Phillips constraint theory. $Ge_{20}Te_{80-x}Bi_x$ can also be taken as phase separated glasses, with glassy Bi_2Te_3 clusters embedded in the background matrix of $GeTe_2$ and Te chains or layers. The binary alloy composition $Ge_{20}Te_{80}$ is just at the stiffness threshold. As Bi concentration is increased in the binary alloy $Ge_{20}Te_{80}$, the Bi_2Te_3 clusters, having tetradymite structure find themselves in a matrix of increasing mechanical rigidity. At $x < 3.5$ the mechanical misfit between Bi_2Te_3 and $GeTe_2$ clusters is relieved by distortion of Te chains or layers. For $x > 3.5$ the rigidity of combined elastic medium Te and $GeTe_2$ increases steadily. These arguments are reflected in the pressure-induced effects where the sharp transition shifts towards higher pressures as Bi content is increased in the alloy indicating the increasing rigidity of the system. As in Ge-Bi-S and Ge-Bi-Se glasses,[21] the *n*-type defects can also be associated with the tetradymite structure of a-Bi_2Te_3 clusters. At lower Bi concentration ($x < 3.5$) the Te, *n*-type dangling bond defects mostly undergo reconstruction. However, for $x > 3.5$ due to larger stiffness of the background matrix these defects remain unreconstructed thus leading to *n*-type electronic conduction. It is interesting to observe that the Bi concentration for *p-n* transition decreases from 11 at.% in Ge-S, 7 at.% in Ge-Se to 3.5 at.% in Ge-Te glasses. This trend is in accordance with the atomic size effect in S, Se, and Te atoms. (The atomic radius of S, Se, and Te atoms are 1.04, 1.14, and 1.32, respectively.) It is pointed out that the variation of activation energy (ΔE) and the conductivity (ρ) with composition in $A_x^{IV}B_{100-x}^{VI}$ glasses exhibit a maxima or peak around $x=20$ composition.[18] The Bi-doped glasses: $(GeSe_{3.5})_{100-x}Bi_x$, $(GeSe_{3.5})_{88}Sb_{12-x}Bi_x$, and $Ge_{20}Bi_xS_{80-x}$ do not show any peaking effect around the Bi concentration where a *p-n* transition takes place.[1,22] One observes a steep fall in ΔE and ρ as a function of Bi concentration (x) in the region of *p-n* transition in these glasses as in the present system $Ge_{20}Te_{80-x}Bi_x$. Further experiments to reveal the microscopic structure and the nature of electronic transport in this new variety of doped glasses are actively progressing.

In summary, we have observed *p-n* type transition in the electronic transport in $Ge_{20}Te_{80-x}Bi_x$ glasses at $x=3.5$ for the first time. Thermoelectric power measurement and pressure-induced effects in these glasses unambiguously establish the carrier sign reversal. An attempt has been made to understand the *p-n* transition using arguments of Phillips constraint theory.

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