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Study of impurity induced modifications in amorphous N-type $(GeSe_{3\cdot5})_{100-x}Bi_x$ using high pressure technique

K L BHATIA*†, G PARTHASARATHY and E S R GOPAL††

†Department of Physics, Maharshi Dayanand University, Rohtak 124001, India

Instrumentation and Services Unit, Indian Institute of Science, Bangalore 560012, India

††Also at Department of Physics

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Abstract. The technique of high pressure is utilized to study the carrier transport behaviour in doped and undoped bulk amorphous $(GeSe_{3\cdot5})_{100-x}Bi_x$ ($x = 0, 2, 4, 10$) down to liquid nitrogen temperature to observe impurity induced modifications in amorphous semiconductors. It is observed that pressure induced effects in lightly doped (2 at % Bi) and heavily doped ($x = 4, 10$) semiconductors are markedly different. Results are discussed in view of the incorporation behaviour of the bismuth impurity.

Keywords. Amorphous semiconductors; pressure induced effects; chalcogenide glasses; doping of chalcogenide glasses.

1. Introduction

The scientific community has recently shown tremendous interest in amorphous semiconducting materials due to their possible wide applications in science and technology. Both the major categories of amorphous semiconductors: (i) those tetrahedrally bonded (e.g. Si, Ge etc) and (ii) the chalcogenides (e.g. As_2S_3, Ge_xS_{1-x}, Ge_xSe_{1-x} etc) have been extensively investigated. Their development and characterization with controlled doping is of utmost importance for their technological applications. Many problems of controlled doping (*n*-type and *p*-type) of the first category of semiconductors have been studied and understood. But the problem of controlled doping (*n* and *p*-type) of amorphous chalcogenides remains unsolved and is in its initial stages (Brodsky 1979). It has only been recently discovered that some bulk Germanium chalcogenides can be doped *n*-type (which are otherwise always *p*-type), by incorporation of certain heavy metal atoms in large concentration (Nagels *et al* 1981). This is a surprising result of great significance.

We have initiated an extensive study of the problem of controlled doping of amorphous chalcogenide semiconductors (Bhatia 1983; Bhatia *et al* 1983, 1984). In this continuing programme, we have utilized the high pressure technique to study the carrier transport behaviour in doped and undoped bulk amorphous $(GeSe_{3.5})_{100-x}Bi_x$ down to liquid nitrogen temperature for the first time to learn more about the modifications induced in the network by the dopant metallic atoms in such large concentrations.

* To whom all correspondence should be addressed.

2. Experiment

The doped semiconducting materials $(GeSe_{3\cdot5})_{100-x}Bi_x$ ($x = 0, 2, 4, 10$) are prepared by the conventional melt quenching technique using high purity elements (99·999 %). Non-crystalline nature of the synthesised material is confirmed by x-ray diffraction. Thermal analysis is carried using Stanton Red Croft Model DTA-673·4 thermal analyser. Samples are always sealed in an evacuated quartz ampule for DTA work to avoid reaction with atmospheric gases. Experiments are performed using a calibrated Bridgman anvil system consisting of a tungsten carbide anvil (Bandyopadhyay *et al* 1980). Pyrophillite gaskets are used with steatite as a pressure transmitting medium. The cell is pressurised in a hydraulic press upto about 100 k bar. The system geometry produces approximately hydrostatic pressure at the sample. Measurements of resistivity are made using a four probe method with a Kiethly digital electrometer and a constant current source. Low temperature experiments are carried out using a sample bath type cryostat (Bandyopadhyay *et al* 1980). Three runs are taken for each type of sample and results are found reproducible within experimental error.

3. Results and discussion

Figure 1 exhibits the log resistivity as a function of applied pressure in four Bi doped samples ($x = 0, 2, 4, 10$) at room temperature. The resistivity of $x = 0$ sample shows a slight increase with pressure upto about 10 k bar and then saturates followed by a

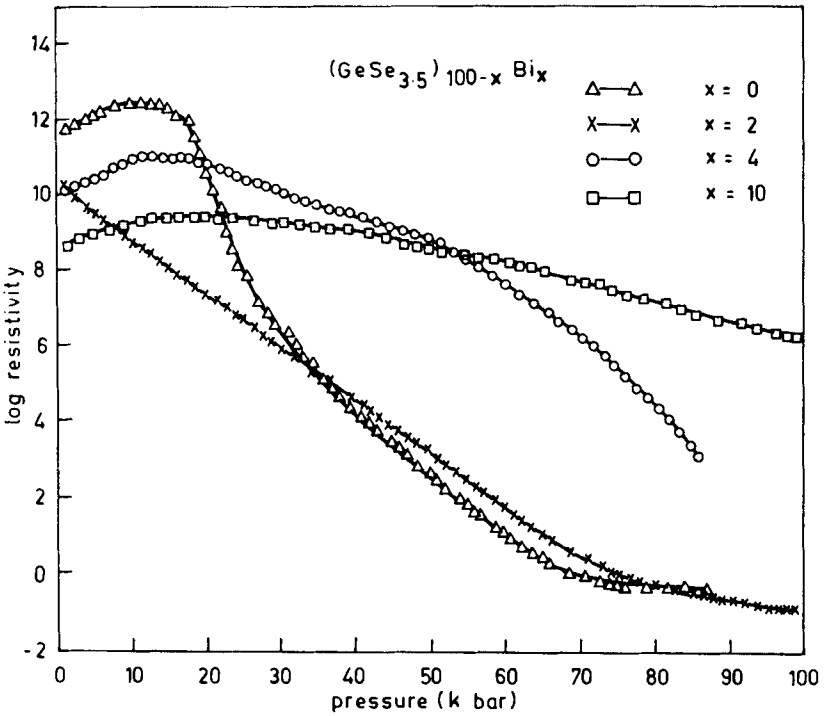

Figure 1. Variation of resistivity of $(GeSe_{3\cdot5})_{100-x}Bi_x$ with pressure at room temperature.

continuous decrease upto about 70 k bar. At still higher pressure there is little further fall in the resistivity value. Addition of Bi dopant significantly alters the picture. Two distinct regions of Bi concentration are exhibited; (1) $x = 2$, and (ii) $x \geqslant 4$. Addition of 2 at % Bi in $GeSe_{3.5}$, completely wipes out the low pressure (< 20 k bar) structure in the resistivity, but higher concentrations of Bi($x \geqslant 4$) does not appreciably affect the shallow small maxima at 10 k bar pressure. The continuous transition in $GeSe_{3.5}$ is drastically influenced by Bi. Instead of a distinct continuous transition, a much broader variation in the resistivity-pressure plot is observed in the doped samples. There is a fall in the resistivity of $GeSe_{3.5}$ by a factor of 10^{12} upto a pressure of about 90 k bar, whereas in $x = 10$ sample, the fall in resistivity is only by a factor of 10^3. It is quite interesting to note that addition of 2 at % Bi does not influence the continuous transition observed in $GeSe_{3.5}$. Study of temperature dependence of resistivity at different pressures has also been made and corresponding values of the activation energy ΔE has been determined using the relation.

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

Figure 2 compares the variation of ΔE with pressure in different samples. Again $x = 2$ sample shows quite different behaviour of ΔE with pressure as compared to $x = 4$, 10 samples. In the $x = 2$ sample, a linear decrease in ΔE is observed which extrapolates to zero value at about 97 k bar. This composition shows semiconductor behaviour upto about 80 k bar.

These compositional dependent features in the transport properties of Bi doped glasses, are discussed in the light of impurity induced structural changes in the host network of $GeSe_{3.5}$. The incorporation of 2·5 at % Bi into $Ge_{20}Se_{80}$ glass results in the reduction of the optical energy gap Eg^{opt} by as much as 0·65 eV (Tohge *et al* 1980). Further addition of Bi, however, causes very small change in Eg^{opt}. The corresponding

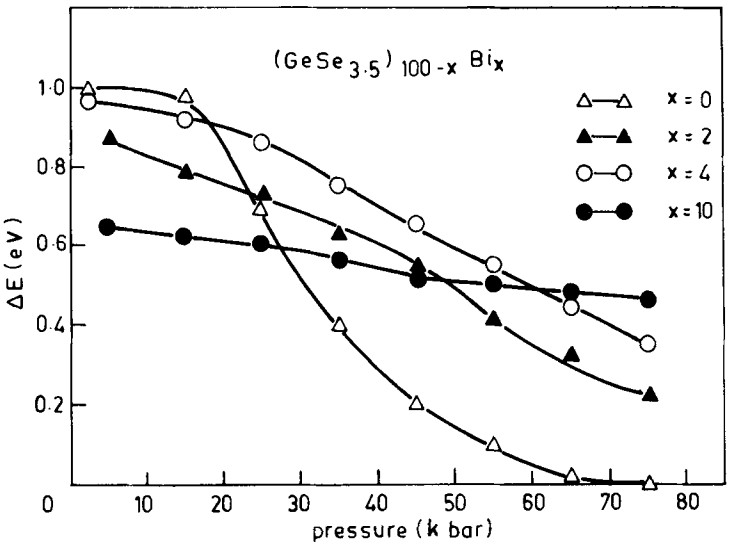

Figure 2. Pressure dependence of activation energy ΔE of $(GeSe_{3.5})_{100-x}Bi_x$.

change in ΔE is quite different. We believe that it is the incorporation behaviour of Bi into the host lattice which is responsible for the observed features. We think that the entry of Bi can be classified into two categories depending upon its concentration; (a) with Bi concentration of about 2 at.% the Bi atoms possibly enter into the host network in such a way that Bi-Se bonds are formed, which leads to the creation of charged defect states D^+, D^- (Bhatia *et al* 1984); (b) with Bi concentration greater than 2 at % the entry of Bi starts producing network modification by making clusters involving all the three atoms: Ge, Se, Bi. This modification is reflected in pressure effects in the samples with large Bi concentration as shown in figure 1. DTA of the doped samples supports the presence of units containing all the three atoms which decompose and crystallize on heating (Bhatia *et al* 1984). Some information on the existence of such clusters is provided by the Phillips medium range order (Phillips 1981) in Ge_xSe_{1-x} glass. According to it, chalcogenide glass can be described by small chemically ordered clusters embedded in a continuous network. In Se rich alloys, $(Se)_n$ chains and $Ge(Se_{1/2})_4$ corner sharing tetrahedra are the likely units in the system. At lower concentrations Bi may enter the $(Se)_n$ chains, and at higher Bi concentrations, dopant atoms can enter the tetrahedral units.

The pressure induced features of the electrical conductivity presented in figure 1 reveal the distinction between samples with low and high Bi concentrations. Further experiments with doped amorphous chalcogenide semiconductors are in progress.

In summary, we have observed the pressure induced effects in Bi doped amorphous chalcogenide semiconductors $(GeSe_{3.5})_{100-x}Bi_x$ by measuring the electrical resistivity of compositions, $x = 0, 2, 4$ and 10, down to liquid nitrogen temperature. The incorporation behaviour of the added Bi impurity is exhibited by the experimental results.

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