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ANISOTROPY MEASUREMENTS IN $GeSePb_x$ (x = 0.02, 0.04, 0.06) CRYSTALS

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ABSTRACT

Lead doped germanium monoselenide ($GeSePb_x$(x=0.02, 0.04, 0.06)) crystalswere grown by direct vapour transport technique.Electrical transport properties like resistivity measurements (parallel and perpendicular direction to the c-axis) were performed on these crystals. Transition metal chalcogenides have different characters of bonds in directions parallel and perpendicular to c-axis. These differentnatures of interactions introduce structural as well as electrical anisotropy in these crystalline compounds.Anisotropy measurements in electrical properties like electrical resistivity were performed from room temperature to 723 K at ambient condition of pressure. Preliminary electrical measurements suggest semiconducting nature of $GeSePb_x$ (x=0.02, 0.04, 0.06) crystals.

Keywords: Extrinsic conductivity, donor exhaustion, anisotropy.

INTRODUCTION

In the past few years,tremendous attention has been paid to layered metal chalcogenides of IV-VI group, constituting an important class of materials for photovoltaic applications [1-3]. These compound semiconductors exhibit good solar cell efficiency due to multiple exciton generation [4-6]. Among these compounds, there is a growing interest in the semiconductors like GeSe, GeS, SnSe and SnS [7-13], which show a promise as low cost components of photovoltaic cells.These materials possess orthorhombic crystals structure (D_{2h}^{16} P_{nma}) whose structure may be considered as distorted NaCl structure. This type of structure is of particular interest due to the arrangement of the cations and anions with in the structure lattice. The layers of cations are separated by Van der Wall's forces, which provide a chemically inert surface free from dangling bonds and surface density of state. Consequently, there is no Fermi level pinning at the semiconductor surface. This fact leads to a considerably high chemical and environmental stability [14].Its lattice parameters are a=3.82Å, b=4.14 Å and c=10.862 Å. The unit cell of the GeSe contains eight atoms organized into two adjacent double layers that are perpendicular to the major axis (c-axis). In each double layer, a single Ge atom attached with its three nearest Se atoms by covalent bonds and form zigzag chain along the direction of minor (a or b-axis) axis of the crystal. As the bonds between adjacent double layers are van der Waals type, this material cleaves easily along a-b [001] planes.The electrical resistivity changes with temperature in quite irregular manner because of various mechanisms, including phonon scattering, mutual scattering of electrons and so forth are involved in the electrical transport in different temperature range.Further, the crystalline anisotropy in these compounds leads to anisotropy in their electrical properties.Thus, the GeSe has an intermediate behavior between two- and three- dimensional materials.The temperature dependence of the electrical conductivity is inclined to many influencing factors.The objective of this study is to evaluate electrical resistivity (perpendicular and parallel to thec-axis) of GeSePbx (x=0.02, 0.04, 0.06) crystals.)

EXPERIMENTAL

The crystals of $GeSePb_x$ (x=0.02, 0.04, 0.06) were grown by direct vapour transport technique. The optimum growth conditions have been reported in Table 1.

Table 1: Growth conditions for $GeSePb_x$ (x = 0.02, 0.04, 0.06) crystals.

Compositions	Temperature (K)		Growth Period (hours)	Crystal Dimensions (mm × mm)
	Source zone	Growth zone		
$GeSePb_{0.02}$	873	823	80	15 ×8
$GeSePb_{0.04}$	873	823	80	12 × 8
$GeSePb_{0.06}$	873	823	80	16 × 8

The temperature dependent resistivity measurements parallel and perpendicular to c-axis were carried out in the temperature range 303-723 K for all the samples using two probe set up. The experimental set up consist of two parts: one is vertical single zone furnace with D.C. power supply and a steel sample holder with four measuring probes. The temperature is measured by Alumel-Chromel (K- type) thermocouple, which is placed in sample holder.Then, the sample holder along with sample and thermocouple was placed in high temperature furnace. The resistance of the rectangular sample was measured in interval of 5 K using Keithly 2400 multi-meter. Several readings were taken over different regions of specimen and consistent results were obtained in each case. The anisotropy ratio was calculated using the values of resistivity parallel and perpendicular to c-axis.

RESULT AND DISCUSSION

The resistivity variations in $GeSePb_x$ (x=0.02, 0.04, 0.06) with temperature (both parallel and perpendicular to c-axis) were studied from 303-723 K. The result plotted as logρ vs. 1000/T for parallel and perpendicular to c-axis are shown in Fig.1 and Fig.2. It is

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seen from Fig.1 and Fig.2, that there is continuous decrease in resistivity with temperature up to 723 K, which is a characteristic of semiconducting materials. Also, the values of resistivity are higher in parallel direction (across plane) than in the perpendicular direction (in-plane), which attribute to the high conduction of charge carriers in perpendicular direction. This suggests that, grown crystals have intermediate conduction between three dimensions and two dimensions, which is the most prominent characteristic of transition metal chalcogenides and it is due to their layered crystal structure.The theoretical model suggested by Arrhenius has been applied to the obtained resistivity curves for $GeSePb_x$ (x=0.02, 0.04, 0.06) crystals. This modelis corresponding to emission of thermal carrier across grain boundary where the conductivity is anticipated to be linear with temperature [15]. The resistivity curves for grown samples are divided into two or three region over entire temperature range investigated. For these regions the activation energy was calculated and mentioned in Table 2. The thermal activation energy was calculated from the slope of the curve by using the relation:

$$\sigma = \sigma_0 \exp\left(\frac{E_a}{k_B T}\right) \qquad (1)$$

where, E_a is activation energy, k_B is Boltzmann constant and T is absolute temperature.

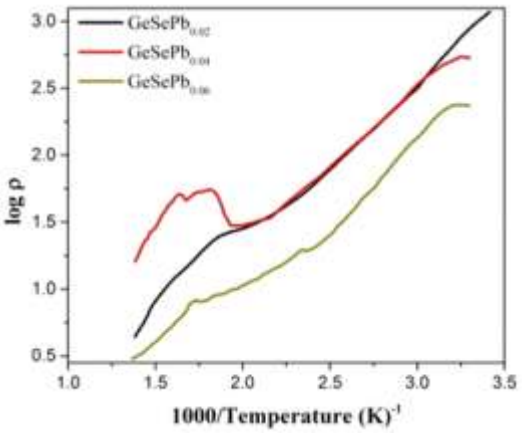

Fig: 1. log ρ vs. 1000/T for perpendicular to c-axis.

Initially, electrical resistivity falls rapidly with temperature and the reason is that the charge carriers are liberated from the impurity levels to the conduction band.The carrier concentration in this temperature range is number of ionized donor liberated from impurity levels. The activation energies for grown crystals are tabulated in Table 2. The calculated activation energies in parallel to c-axis are 0.37 eV for $GeSePb_{0.02}$ in 403-533 K, 0.20 eV for $GeSePb_{0.04}$ in 428-558 K and 0.26 eVfor $GeSePb_{0.06}$ in 463-573 K temperature range. In above mentioned temperature ranges for different compositions, the activation energies are lowest among all other. All the donor electrons will be energized at mentioned temperature ranges, with the result that donor exhaustion occurs.Further intensifications in temperature result in somewhat higher values of activation energies, which is owing to the saturation of charge carriers in the conduction band. However, the low values of activation energy in entire temperature range suggest that the measured resistivity is result of the extrinsic process in all these crystals. This can be ascribing to the high carrier concentration which gives rise to impurity energy levels very close to the conduction band [16].

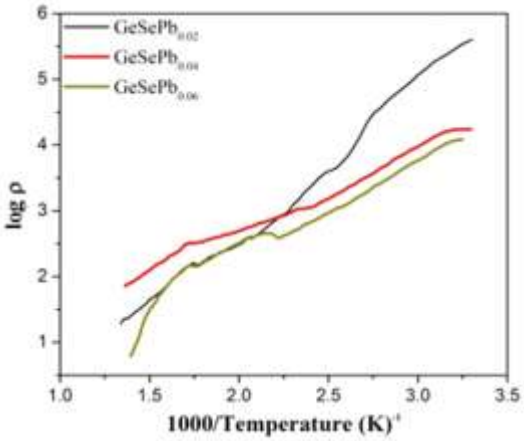

Fig: 2. log ρ vs. 1000/T for parallel to c-axis.

Fig. 3 clearly indicates that electrical conduction in $GeSePb_x$(x=0.02, 0.04, 0.06) crystals is highly anisotropic. The anisotropy (Y) was calculated as the ratio of resistivity in parallel direction to c-axis to that in perpendicular direction to c-axis. This high anisotropy is arising due to different strength of the interactions in parallel and perpendicular direction to the c-axis. As shown in Fig. 3, the anisotropy decreases with increase in temperature.

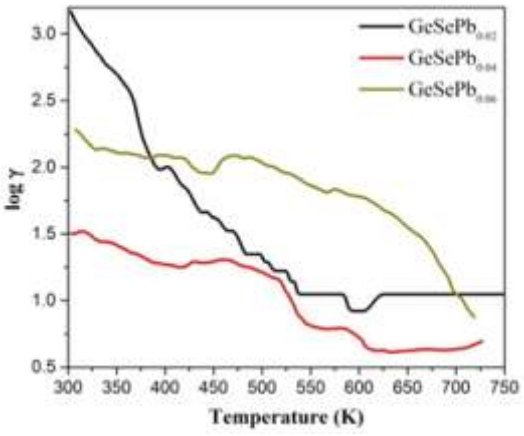

Fig: 3. Variation of anisotropy with temperature.

Table: 2. Activation energy calculated from log ρ vs. 1000/T.

Compositions	Perpendicular to c-axis		Parallel to c-axis	
	Temperature Range (K)	Activation Energy (eV)	Temperature Range (K)	Activation Energy (eV)
$GeSePb_{0.02}$	293-453	0.25	303-368	0.42
	533-743	0.31	403-533	0.37
	-	-	583-748	0.46
$GeSePb_{0.04}$	313-488	0.18	323-403	0.31
	503-663	0.30	428-558	0.20
	-	-	598-713	0.36
$GeSePb_{0.06}$	303-538	0.21	308-448	0.31
	593-703	0.24	463-573	0.26
	-	-	573-653	0.54

CONCLUSION

The anisotropy in electrical transport properties in $GeSePb_x$ (x=0.02, 0.04, 0.06) crystals have been studied with high temperature resistivity measurements. This work has shown that $GeSePb_x$ (x=0.02, 0.04, 0.06) crystals have a semiconducting nature. Analysis of the electrical resistivity allows us to deduce important parameters such as activation energy and anisotropy. Anisotropy in electrical conductivity decreases as the temperature increases.

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