

Preparation and characterization of $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ pseudo-binary alloy semiconductors

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Abstract. A *p*-type pseudo-binary alloy semiconductor, $\text{Pb}_{0.3}\text{Sn}_{0.7}\text{Te}$, has been prepared from *p*-type specimens of PbTe and SnTe and lattice constants determined with an accuracy of 0.0001 nm. Vacuum annealing of $\text{Pb}_{0.3}\text{Sn}_{0.7}\text{Te}$ reveals two new x-ray powder diffraction lines bearing indices (444) and (800), while others become more sharp, $\text{CuK}\alpha$ -doublets get clearly resolved and the lattice constant is increased by ~ 0.0002 nm. Slight deviation from Vegard's law linearity is observed showing that the sample must be considered as ternary in nature. Thin films deposited on mica and glass substrates kept at room temperature are found to have a little higher SnTe content. The effective carrier concentration calculated from Hall measurements at room temperature is $\sim 3.4 \times 10^{20} \text{ m}^{-3}$.

Keywords. Narrow-gap semiconductors; pseudo-binary alloys; x-ray analysis.

1. Introduction

The alloy semiconductor $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ is being extensively studied nowadays, as it has small and controllable band-gap (E_g), depending on Sn-content (X), temperatures (Dimmock *et al* 1966) and hydrostatic pressure (Meingailis *et al* 1970) etc. Thus the emission wavelength of the sources (light-emitting diodes) based on this material is within the IR-region of the spectrum (6-32 μm). This makes the material potentially useful as IR-detectors and lasers (Butler *et al* 1966), specially in the cryogenic range.

The variation of the band gap of $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ with x has been explained with a band-inversion mechanism (Dimmock *et al* 1966) which has also been verified by several experiments *viz.* measurements of electrical conductivity as a function of temperature for several alloys near the crossing. (Bis and Dixon 1968).

The alloy $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ with $x > 0.5$ has not been so widely studied and so in this work we choose $x = 0.7$ because it is very close to, and on the SnTe-side of, the band-crossing point at room temperature.

2. Preparation

Both PbTe and SnTe have the same rock-salt structure and they exhibit complete solid solubility over the entire composition range. Hence a pseudo-binary assumption is justifiable for $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ for $x = 0$ to 1.

Here a polycrystalline ingot of p -Pb_{0.3}Sn_{0.7}Te is prepared from p -PbTe and p -SnTe. For p -PbTe, the bulk specimen is obtained from Bhabha Atomic Research Centre, Trombay and p -type SnTe bulk is prepared from 99.99% pure semiconductor grade tin and tellurium.

Crushed samples of p -PbTe and p -SnTe are taken in proportions appropriate to their molecular weights for $x=0.7$. The relation is $[w_1/w_2 = 1.3593(1-x/x)]$ where w_1 and w_2 are the masses of PbTe and SnTe respectively and x is the mol fraction of SnTe. Weights are taken in an electronic microbalance and then the samples are placed in a quartz tube, which is subsequently evacuated to $\sim 8 \times 10^{-3}$ Pa and sealed. The sealed ampoule is then heated to $\sim 975^\circ\text{C}$ in a furnace for 6 hr, thorough mixing of the components is ensured and finally it is quenched in cold water.

3. Experiments

The ingot thus prepared is powdered in an agate mortar, sieved through a 270 ASTM mesh and then a small amount of it is taken in a glass (corning) capillary of internal diameter $\sim 0.25 \times 10^{-3}$ m. The (capillary and the sample) assembly is then kept mounted in a Debye-Scherrer camera (i.d.=0.1145 m) for 40 hr and an x-ray powder photograph of the combination is obtained from which different lines for the sample are clearly identified. The same combination is then annealed at 500°C for 6 hr at a vacuum of $\sim 1.3 \times 10^{-2}$ Pa (Hewes *et al* 1973), after which another powder photograph of the combination is taken with the same exposure time.

By the same procedure, x-ray powder photographs are also taken for PbTe and SnTe. In all cases, $\text{CuK}\alpha$ -radiation (from a NORELCO unit using Ni-foil as β -filter) is used.

Then, with glass and mica as substrates (kept at room temperature), thin films of Pb_{0.3}Sn_{0.7}Te are deposited by thermal evaporation, using a heating current of 70 amps and a vacuum of 6.6×10^{-3} Pa, the rate of deposition being ~ 20 -30 nm/min. The substrates are kept at room temperature and so the films are expected to be polycrystalline. Diffractometer analysis with these films shows that only few peaks appear and they do so at a slightly higher angle (θ) than the corresponding powder diffraction lines. This reveals (using Vegard's law) that the films have a slightly increased SnTe-content as compared to the bulk sample.

4. Measurements

For annealed Pb_{0.3}Sn_{0.7}Te, interplanar spacings (d) of different crystallographic planes and lattice parameter (a) of the crystal are calculated from measurements on its powder photograph. Using the Taylor-Sinclair function $\frac{1}{2}\cos^2\theta(1/\sin\theta + 1/\theta)$ (obtained from tables), the most accurate value of a is determined by the extrapolation method (figure 1) with an accuracy of ~ 0.0001 nm. Similar measurements are performed with the powder photographs for only unannealed Pb_{0.3}Sn_{0.7}Te, PbTe and SnTe. In all cases, lines with $\theta \geq 29^\circ$ only are considered for graphical extrapolation.

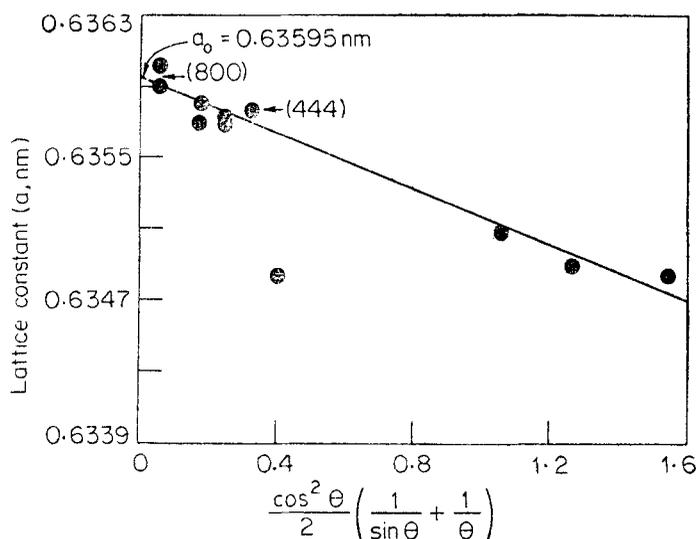


Figure 1. Lattice constant (a) determination of annealed $\text{Pb}_{0.3}\text{Sn}_{0.7}\text{Te}$ by graphical extrapolation

Room temperature measurements are carried out for electrical conductivity (σ), thermoelectric power (α) and Hall effect with thin films on glass and mica substrates for a thickness of 200 nm. Film thickness is measured with one film on glass by the Tolansky method (Holland 1966), which uses an optical interference microscope to measure the "Fizeau fringes". The accuracy attained is ~ 5 nm. For the above measurements, pressure contacts with film surfaces are used along with graphite paint. A magnetic field of 0.8 Tesla is used for Hall measurements and readings are taken with direct and reversed fields and their average taken. Different voltages are measured with a dc microvoltmeter.

5. Results

The extrapolated values of a for PbTe and SnTe are 0.6462 nm and 0.6327 nm respectively which agree very well with their standard values. For $\text{Pb}_{0.3}\text{Sn}_{0.7}\text{Te}$, the value of a is obtained as 0.6357 nm for the unannealed sample and 0.6359 nm (figure 1) for the annealed one *i.e.* an increase of 0.0002 nm in the value of the lattice constant of the sample is observed due to vacuum annealing. Moreover, it is found that two new lines appear in the powder pattern near 57° and 76° bearing indices (444) and (800) respectively when the sample is annealed. Also, in the powder pattern of the annealed sample, the lines are far more sharp and K_α -doublets are clearly resolved.

Powder diffraction lines bearing only the all-even indices appear in all the cases, which reveal that $\text{Pb}_{0.3}\text{Sn}_{0.7}\text{Te}$ has the same rock-salt structure as PbTe and SnTe.

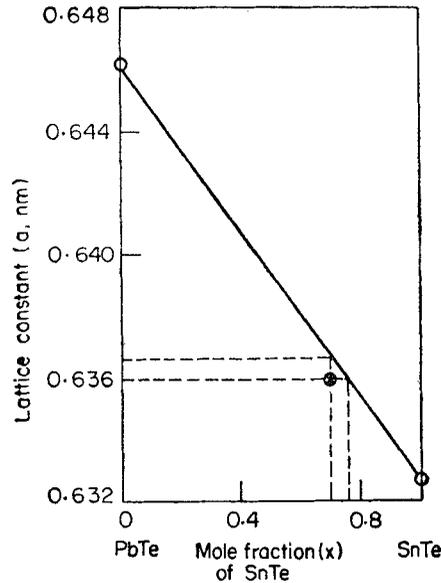


Figure 2. Vegard's law variation of lattice constant (a) of $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ with x .

A test of Vegard's law is made using the determined a values of PbTe and SnTe as end-points (figure 2). The linear relation according to Vegard's law can be expressed as

$$a_0(\text{PbSnTe}) = a(\text{PbTe}) - 0.135x. \quad (1)$$

A slight variation ($\sim 0.13\%$) from Vegard's law is noted which can be viewed as a failure of this alloy to behave exactly as a binary one *i.e.* it must be considered as slightly ternary in nature (Bis and Dixon 1969).

PbTe is a direct energy-gap semiconductor whose valence and conduction band-edges have L_6^+ and L_6^- symmetry respectively while SnTe has an inverted band structure. The energy gaps (E_g) at 300 K for PbTe and SnTe are respectively 0.32 eV and 0.18 eV. Also, it is now established that for $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$, E_g varies almost linearly with x (Dimmock *et al* 1966; Tauber and Cadoff 1967). On this basis, for our sample $E_g \approx 0.04$ eV at 300 K. Its corresponding emission wavelength is $\sim 30 \mu\text{m}$. Obviously, its conduction and valence band-edges will have L_6^+ and L_6^- symmetry respectively like SnTe.

From Hall voltage (V_H) measurements with the films, we find $R_H \sim 1.6 \times 10^{-8} \text{ m}^3/\text{c}$, and the effective carrier concentration ($p \approx 1/eR_H$) comes to be about $3.4 \times 10^{26} \text{ m}^{-3}$. Both the bulk and the film are found to be *p*-type *i.e.* there is an excess of Te-atoms (or Pb/Sn vacancies or possibly non-metal interstitials) in them. The value of σ at 300 K is found to be $540 \text{ mho}\cdot\text{m}^{-1}$ and Hall mobility ($\mu_H = R_H\sigma$) is found to be $8.42 \times 10^{-6} \text{ m}^2/\text{V}\cdot\text{sec}$.

The thermoelectric power (α) at 300 K for the thin films of $\text{Pb}_{0.3}\text{Sn}_{0.7}\text{Te}$ is found to be $\sim 150 \mu\text{V}/^\circ\text{K}$.

6. Conclusion

With such high hole concentrations as in this case, the carriers would be 'degenerate'. This may possibly explain the observed deviation from Vegard's law; Bis and Dixon (1969) have indeed pointed out that for carrier concentrations exceeding $1 \times 10^{26} \text{m}^{-3}$, relatively large shifts occur in Vegard-type relations. This deviation is also consistent with the observations of Short (1968) and of Wagner and Woolley (1967) that marked deviations from stoichiometry occur as in PbSnTe as the SnTe content increases.

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