Anan'ina et al[29] also investigated spectral response of photoconductivity in single crystal In_2Te_3 at 300K and 77K in the range 0.6-2.4 μm and observed negative photoconductivity not observed by others which was attributed to a surface effect. The experiments were carried out with two different orientations with light incident perpendicular to a large surface area and also parallel to it. In the first case maximum response occurred at λ = 1.1 μ m with a weak sub-band gap peak near 1.75 μ m. In the second configuration the second peak was more prominent. This suggests that this contribution was due to defect states providing a transition near 0.7 eV.

Finkman and Tauc[30] studied the lattice vibrations of both α and β -In_2Te_3 by far infra-red and Raman scattering techniques and found the spectra to be relatively simple despite the large unit cell in these materials. Infra-red reflection spectra of disordered structures showed two strong 'Restrahlen' bands each of which is split in the ordered structure. The simplicity of the infra-red spectra suggested that the structure of the phonon spectra can be understood if the crystal structure is zincblende. The interpretation of the observed spectra was based on the existence of uninterrupted chains of tetrahedra along the direction interconnecting

the two next nearest neighbours in the (110) direction in the cubic lattice, showing that the phonons propagating along this direction dominated the spectra and that in the first approximation their frequencies could be obtained by a 6-fold folding of the Brillouin zone of the simple zincblende structure in the (110) direction.

Finkman et al[31] also observed an interesting trend in the lower TA mode of In_2Te_3. This mode approached a deep minimum at the edge of the (110) direction. By fitting the observed spectra, a comparison of the calculated force constants with those of III-V and II-VI compounds showed that the central forces between nearest neighbours (α) were affected only slightly by presence of defects, while the non-central forces (β) were changed more significantly, affecting mostly the TA branches to which the elastic constants are sensitive.

Raman scattering experiments on polycrystalline In_2Te_3 did not yield any positive results since only lines corresponding to free Te were obtained, probably due to non-stoichiometric samples. More fruitful results are expected from single crystals.

1.2.2 Gallium Telluride (Ga_2Te_3)

Ga_2Te_3 has been studied in far less detail than In_2Te_3 though it is isostructural with the latter and has

similar properties. It has been reported by Hahn[14] to have zincblende structure with lattice parameter a = 5.89 Å which changes to wurtzite structure at 670°C. The phase diagram of Ga-Te system is shown in Fig.1.2.2.

Thermal & Electrical Properties :

Woolley and Pamplin[13] found the thermal conductivity of Ga_2Te_3 to be 1.3×10^{-2} watts/cm °K very close to the value for In_2Te_3. They also determined the energy gap from electrical conductivity experiments and found it to be 1.15 eV. Harbeke and Lautz[15], on the other hand, obtained the activation energy as 1.56 eV at 0°K from an extrapolation of the conductivity vs temperature curve. They observed that near 670°C the conductivity increased to much larger values than would correspond to intrinsic conductivity. The effect was interpreted as a phase transition to the wurzite structure. The electrical conductivity of these samples determined as a function of the impurity concentration and temperature also showed intrinsic behaviour in spite of high impurity concentration. This was attributed to the chemically inert nature of unshared electron-pairs surrounding impurity atoms located at vacancies as in the case of In_2Te_3.

Gadzhiev et al[32] studied the frequency dependence of a.c. conductivity which could be described by the relation $\sigma \propto w^n$ where n = 0.8 at 300°K. This was attributed

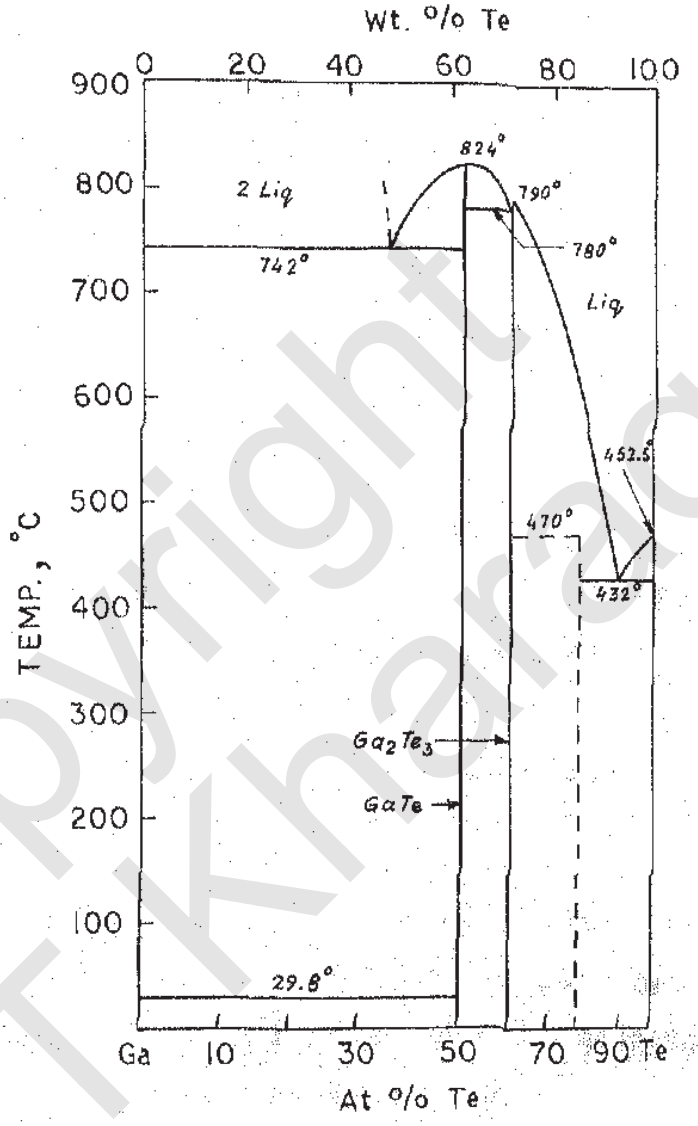

Fig. 1.2.2 Phase diagram of Ga-Te system

to a hopping conduction mechanism between states near the Fermi level which was said to originate due to the defect structure of Ga_2Te_3.

Zuze et al[23] observed the temperature dependence of electrical conductivity and thermo-emf in the solid and liquid states. Above 350°C and below the melting point for Ga_2Te_3 (780°C), intrinsic conductivity was observed, with a band-gap of 1.7 eV. At the melting point, the electrical conductivity of Ga_2Te_3 increased approximately by a factor of 10 and continued to increase in the liquid state with further increase of temperature while the band-gap became 2.3 eV. With further increase of temperature upto 950°C, the activation energy for conduction in the melt decreased and again approached 1.7 eV. It follows from the above observation that Ga_2Te_3 preserves its semiconducting properties in the liquid state.

With increasing temperature, the thermo-emf retained the same sign as electrical conduction, but rapidly decreased and changed its sign near the melting point to indicate hole conduction. Cutler[33] found the value of thermoelectric power in molten Ga_2Te_3 to be $(40\text{-}60)\times10^{-6}$ V/°K.

Optical Properties :

Gorjunova[34] studied photoconductivity of Ga_2Te_3 and deduced a band-gap of 1.08 to 1.11 eV. Harbeke and Lautz[15] examined the optical absorption of single crystal Ga_2Te_3 and obtained a band gap of 1.22 eV at room temperature. The difference between the band-gap energy determined by Harbeke and Lautz[15] from electrical conductivity and photoconductivity studies was attributed to the temperature dependence of the band-gap. The same workers in their later work[12] on optical absorption of Ga_2Te_3 found it to be an indirect band-gap semiconductor with temperature coefficient of band-gap $(-4.6 - 7.7) \times 10^{-4}$ eV/°C.

Guizzetti et al[27] whose work has been referred to earlier, calculated the fundamental interband transition energies, estimated from the Phillips - Van Vechten dielectric theory by appropriately averaging the properties of III-V and II-VI analogs, taking cation disorder into account. According to their calculation Ga_2Te_3 is also a direct band-gap semiconductor with spin-orbit splittings at the E_0 gap, the energy at the band-gap being equal to 1.4 eV. This contradicts the observation of Harbeke et al[12] who found Ga_2Te_3 to have an indirect gap.

Finkman and Tauc[30] studied the infra-red reflection spectra of In_2Te_3, Ga_2Te_3 and Ga_2Se_3. A comparison

of the spectra showed a great similarity between the spectra of different materials of the A_2B_3 group. The most striking observation about the spectra was their simplicity in spite of a rather complicated structure.

1.2.3 Applications

The large stoichiometric vacancy concentration results in the A_2B_3-type lattice being loosely packed in comparison with other crystals of similar structure. Experiments done by Dmitriev et al[35], for example, showed that rapid quenching of In_2Te_3 after annealing does not result in a change in electrical conductivity, charge carrier mobility and concentration.

Koshkin et al[36] pointed out that the presence of these vacancies lead to a special type of defect in these crystals different from conventional Frenkel and Schottky defects. This third type of point defect appears as vacancy-interstitial (v-i) pair located in an instability zone, which exists near a vacancy in such a crystal. The distinguishing feature of such an "instability zone" is that an interstitial atom (i) may recombine without activation energy with its own vacancy. The activation energy of diffusion is then equal to the energy of formation of a vacancy and this therefore does not occur in the expression for the diffusion coefficient. Koshkin et al[36] estimated that in these cases the activation energy

of self-diffusion and of diffusion of any impurity should be a constant value. This was verified by Ekkerman et al[37] who observed identical activation energies for diffusion of In, Te and Cd in In_2Te_3, as was expected by Koshkin et al[36]. The coefficients of self-diffusion of In and Te were the same ($D = 4.3 \times 10^{-3} e^{-1.0}$ eV/KT cm^2/sec) and identical with the activation energy for Cd-diffusion ($D = 2.6 \times 10^{-1} e^{-1.0}$ eV/KT cm^2/sec).

The most direct and useful application of such "instability zones" is in the fact that defects caused by radiation are healed in these crystals without any activation energy. The principal type of radiation-induced or thermally-induced defect is an unstable pair which is expected to annihilate in crystals with large instability zones. This leads to anomalously high radiation stability. On the microscopic level, the instability of radiation defects in these structures could be attributed to a vanishingly small energy barrier which must be overcome by an atom ejected from its lattice position in order to recombine with a vacancy. Gal'chinetskii et al[5] estimated that extremely heavy In, Ga and Te atoms remain very close to the new vacancy formed when the atoms were ejected in a collision with an incident particle i.e. within a distance of the order of a few Å. Estimates also showed that channeling and focussing of atomic collisions, which could result in a large separation between the vacancy and the interstitial atom were significantly suppressed in

crystals having a high stoichiometric vacancy concentration.

Koshkin et al[6] demonstrated experimentally that irradiation of doses of 10^{16} γ -quanta/cm^2 (E = 1.1 Mev), 10^{19} elec/cm^2 (E = 100 Mev), 10^{16} fast fission neutrons/cm^2 carried out at near room temperature did not result in a change of electrical and optical parameters of In_2Te_3 and Ga_2Te_3. The carrier mobility, concentration and microhardness of the specimens also remained unaltered.

The experimental results in Table 1.2.3 show that room temperature physical properties of In_2Te_3 and Ga_2Te_3 were not affected by specimen quenching. Further, irradiation by large doses of high energy particles did not result in stable radiation defect formation whereas the physical parameters of Ge, ZnTe and CdTe crystals changed very appreciably. The materials could thus serve as a basis for fast electron detectors, γ -radiation detectors and for high sensitivity energy-release sensors.

Table 1.2.3

Substance		Ge	CdTe	ZnTe	In_2Te_3	Ga_2Te_3
Melting point in ^oK		1209	1314	1514	940	1067
Quenching temp.in ^oK		1058	1143	1323	829	1053
Resistivity ρ in Ω cm	before quenching	76.5	6×10^3	3.9×10^8	1.8×10^6	1.71×10^7
	after quenching	0.8	6.2×10^2	1.1×10^3	1.8×10^6	1.79×10^7
	after annealing	28.6	4.1×10^3			
Carrior Conc.n cm^{-3}	before quenching		2×10^{13}		1.1×10^{11}	
	after quenching		2.3×10^{14}		1.3×10^{11}	
Mobility μ $cm^2V^{-1}sec^{-1}$	before quenching		33		32	
	after quenching		27		28	
TEP S v/degree	before quenching	+45	+375	+860	-1030	+540
	after quenching	+355	+ 40	+150	-1200	+100
	after annealing	+100	+300	+300		
Sp.elec. res. ρ in Ω cm	before irradiation	27	5×10^2	3×10^2	1.6×10^6	1.1×10^6
			5×10^2	1.2×10^3	1.1×10^6	
	after irradiation	4×10^{-2}*	5×10^8*	4×10^4*	1.7×10^6*	1.0×10^7*
			1.1×10^7+	2.8×10^9+	1.7×10^6+	

*Irradiation by stationary flux of the fast neutron (energy $\approx$ 1 MeV)
Dose $\phi_n = 1.8 \times 10^{17}$ neutrons/cm^2

+Irradiation by fast neutrons impulse source (energy $\approx$ 1 MeV)
Dose $\phi_n = 1.2 \times 10^{16}$ neutrons/cm^2

Switching phenomena have also been observed in thin films of In_2Te_3 which may lead to possible applications. Amorphous films prepared by flash evaporation with a deposition rate of 2 - 2.5 nm/s on unheated molybdenum or glass-carbon substrates exhibited both threshold and memory switching effects in the same sample. Balevicius et al[7] examined I-V characteristics of 2-5 μm thick films. The switching time was less than 2 nanosec and delay time about 20-50 μ sec if the applied voltage was just above threshold voltage V_t. The delay time decreased with the increase of applied voltage. A typical dependence of $\tau_d = f(V)$ taken at different temperatures was shown to be nonlinear.

An increase in the number or duration of the pulses led to memory effects and in this situation a short pulse of either polarity could return the device from the on to the off-state. Current in the off-state was one-hundreth of that in the on-state for the memory switch. Balevicius et al[38] in their later work observed that if pulses of only one polarity are used, the device could endure only a few cycles of switching, and that changing the polarity increased the stability. For applied voltage $V > V_t$ oscillations occurred, the highest frequency achieved being several MHz.

Zabrodskii et al[39] considered impact ionization to be the probable reason for threshold switching, since any pulse which was less than 10 ns in duration was too short

for a thermal process to develop. Kolomiets et al[40] on the other hand, explained the above process as tunneling breakdown due to presence of high internal field which may occur at considerably lower external fields in disordered semiconductors compared with Zener breakdown in crystals.

Salaev et al[8] reported memory switching effect in Ga_2Te_3 single crystals. The switching effect in Ga_2Te_3 crystals was investigated by Aliev et al[41] in a wide temperature range (77-300 ^{o}K) in static and pulsed electric fields to determine the mechanism of this process and its temporal characteristics. It was found that cooling increased the threshold switching voltage and lowered the threshold current. The critical switching time was $\tau_s = 4$ ns and delay time $\tau_d = 4\,\mu s$. It was pointed out that switching effect was initiated by an electronic mechanism, involving carrier injection from the metal contacts in Ga_2Te_3 and electric field ionization of local levels, whereas the switching effect itself was thermal.

A different type of phenomenon was observed by Matsuhita et al[42] in which a high current density filament formed on the surface of quenched In_2Te_3 was found to emit red luminescence. The filament temperature was established

to be 600-650°C, close to the melting point of In_2Te_3. On cooling it was found that the colour of the perimeter of the filament had changed but that of the centre remained unchanged. It seems probable that the red luminescence occurred not due to an electronic but due to a thermal process which resulted in the formation of a new compound of In-Te with much lower resistivity and activation energy and having a different colour.

1.3 Scope of the Thesis

The above introductory survey of the above two compounds In_2Te_3 and Ga_2Te_3 shows some interesting at the same time some contradictory results which require clarification.

It is evident that for a proper understanding of the fundamental characteristics of a semiconducting material, the following basic characteristics should be known :

(1) The nature of chemical bonding ;

(2) The magnitude and nature of the band-gap E_g (between the valence and the conduction band) ;

(3) The type and nature of charge carriers and their concentration at any given temperature;

(4) The effect of the scattering on the mobility of the charge carriers ;

(5) The role of defects in determining carrier trapping, recombination and scattering.

These different parameters can be determined by studying properties to which the charge carriers contribute and may be categorized as :

(1) Static properties such as dielectric constant, optical, magnetic, thermal properties and specific heat.

(2) Transport properties which include electrical, galvanomagnetic, thermoelectric and thermal properties such as the electrical conductivity, magnetoresistance, Hall effect, Seebeck and Peltier effects, thermal conductivity.

The transport properties have been found to be the most direct tools in determining the carrier parameters. However, some static measurements are needed for acquiring insight into the nature of bonding and band-structure in a solid.

In the present thesis, we wish to carry out a study of electrical conductivity, Hall effect (in the case of thin films), thermoelectric power, dielectric properties, optical absorption, photoconductivity and Schottky barriers. The different aspects covered under the thesis can broadly be classified under six major headings.

Essential theories for the investigations are given in the respective chapters.

After the introduction to the materials in Chapter 1, the various experimental methods and techniques adopted for the present investigation are described in Chapter 2. The theory required for the understanding of transport properties and the nature of defects in semiconductors is also discussed here.

Chapter 3 deals with the study of thin films of In_2Te_3 and Ga_2Te_3 prepared by electron and thermal evaporation. Different substrates were used to study the variation of thin film properties with type of substrates and substrate temperatures ($300-450^{o}K$). Carrier concentration, mobility and activation energy of the thin films were measured. The results obtained on the variation of film properties with substrate temperature were explained with the help of theory of re-evaporation proposed by Vincett, Barlow and Roberts[43] which predicts an optimum substrate temperature $\frac{T_o}{T_b} = 0.3$.

The study of single crystal properties are covered in Chapter 4. Single crystals were grown by Bridgman method. The single crystalline nature of the material was verified using Laue back-reflection technique. The

impurity content was analyzed by spectrographic and stoichiometry by electron microprobe analyses. Microhardness of both types of crystals were measured and were found to be strongly dependent on annealing. The absolute value was dependent on the covalency and hence was higher for Ga_2Te_3 than for In_2Te_3.

The variation of conductivity and thermoelectric power with temperature were also studied. From the former the intrinsic activation energy for In_2Te_3 was found to be 0.55 eV while for Ga_2Te_3 the impurity activation energy was found to be 0.44 eV. Thermoelectric power measurements showed that at 300°K the Fermi levels were located 0.60 ev below the conduction band for In_2Te_3 and 0.42 ev below the conduction band for Ga_2Te_3. The scattering mechanism determining the Seebeck coefficient could not be attributed to conventional lattice or impurity scattering. Pronounced effects of annealing were found which were related to the introduction of increasing disorder and carrier concentration. The radiation hardness of In_2Te_3 as reported in the literature has also been verified using Co^{60} (1.3 Mev) gamma radiation.

The spectral response of photoconductivity in In_2Te_3 in the wavelength range 0.6-1.4 μm was investigated and was found to show a maximum at 1.10 ev. The

majority carrier life-time was established from photoconductivity studies and was found to be 5.0×10^{-4} sec for holes in In_2Te_3 and 2.0×10^{-4} sec for electrons in Ga_2Te_3. The influence of annealing temperature on photoconductivity was studied and was correlated with the lattice ordering through x-ray diffraction studies. The band gaps and the dependence of band-gap on annealing temperature were found from optical absorption experiments. The direct nature of the band gaps (E_g = 1.01 eV for In_2Te_3 and E_g = 1.08 eV for Ga_2Te_3) was thus demonstrated.

The chapter 5 reportes dielectric measurements of the samples. The static dielectric constants were measured by usual two terminal measurement of capacitance and were found to be 12.3 and 10.95 respectively for In_2Te_3 and Ga_2Te_3. The plasmon frequency was experimentally found out with the help of ESCA and was used to determine high frequency dielectric constant. Theoretical calculations based on Phillips' theory[44] of dielectric model were carried out to determine high frequency dielectric constant and was compared with the value determined from plasmon energy measurement. The Phillips ionicities of In_2Te_3 and Ga_2Te_3 were thus found to be 0.503 and 0.475 and the predicted high frequency dielectric constants were 9.65 and 8.00 and compared with experimentally determined values of 10.54 and 10.58 respectively.

Although widely studied, the properties of metal-semiconductor have not yet been satisfactorily explained. These theories are briefly reviewed before the results of Schottky barrier studies on p-In_2Te_3 are presented in Chapter 5. The barrier heights were measured for Al, Ag, Au and Bi elements. The J-V characteristics have been represented graphically and the ideality factor determined. The results are found to be in accordance with the surface state theory for a solid that is more covalent than ionic.

In the final chapter, results of different investigations are used to construct an overall picture of the nature of bonding, band-structures, transport and defect properties in In_2Te_3 and Ga_2Te_3. Further work that may be carried out to elucidate these properties are also indicated in the conclusion.