CHAPTER – 9

THIN FILMS OF $Bi_{1-X}Sb_x$ SINGLE CRYSTALS

The theoretical and experimental investigations of the optical behavior of solids deal primarily with optical reflection, transmission and absorption properties and their relation to the optical constants. As a result of these studies, complex multilayer optical device systems, with remarkable reflection, antireflection, interference and polarization properties have emerged for both laboratory and industrial applications. The absorption studies have led to a variety of interesting thin film optical phenomena which have thrown considerable light on the electronic structure of solids. From reflection, transmission and absorption measurements it is possible to evaluate the optical constants such as refractive index (n), absorption index or extinction coefficient (k), absorption coefficient (α) and complex dielectric constant (ε^*) of solids. The dielectric constant also gives information about the electrical nature of the individual species constituting the solid. The study of refractive index also provides an understanding of chemical bonding and structure of the material[1-3]. In addition to the wide use of thin films in optical devices as mirror coatings or absorption filters, protective coatings to prevent oxidation or antireflection coatings, thin films have also been used to control the temperature of objects in outer space and as optical and thermal detectors. In all such applications, an accurate knowledge and deep sense of the optical properties of thin films are essential. Films are easier to use than bulk samples since surface roughness and lattice disorder are more easily avoided and large optically flat samples can be prepared. Very careful sample preparation techniques are required, however, if the films are to have reproducible optical properties.

For absorption studies, photons of selected wavelengths are directed at the samples. The optical measurement constitutes the most important means of determining the band structure of semiconductors. Optical properties of a thin film generally differ from those of the bulk. The differences are usually attributed to the microstructure of the films.

Principally there are several methods to determine the optical constants such as Abbe's method, spectroscopic methods, polarometric method and the critical angle method[4-7]. The spectroscopic method is probably the most widely used one for optical measurements. The most direct and simplest method for determining the band structure is to measure the absorption spectrum.

It is apparent that a photon with energy $h\nu > E_g$ can be absorbed in a semiconductor, where E_g is the band gap of the semiconductor. Since, the valence band contains many electrons and the conduction band has many empty states into the which the electrons may be excited, the probability of photon absorption is high. Figure-1 indicates an electron excited to the conduction band by optical absorption possibly gaining more energy than is common for conduction band electrons [almost all electrons in the conduction band are near E_c unless the sample is heavily doped].

Hence an excited electron loses energy to the lattice in scattering events until its velocity reaches the thermal equilibrium velocity of the other conduction band electrons. The electrons and holes created by this absorption process are excess carriers; since, they are out of balance with their environment, they most eventually recombine. The excess carriers exist in their respective bands. However, they are free to contribute to the conductivity of the material if not recombined.

A photon with energy less E_g is unable to excite an electron from the valence band to the conduction band. Thus, in a pure semiconductor, there is negligible absorption of photons with $h\nu < E_g$. This explains why some materials are transparent in certain wavelength ranges. Because the momentum of photon, h/λ (λ = wavelength of light) is very small compared to the crystal momentum h /a (a = lattice constant), the photon absorption process should conserve the momentum of electron. We are able to "see through" certain insulators such as an NaCl crystal, because, a large energy gap exists in this material. If the band gap is about 2 eV, only long wavelength (IR) and the red part of visible spectrum are transmitted. On the other hand, a band gap of about 3 eV allows IR and the entire visible range of spectrum to be transmitted. Band gaps of some common semiconductors relative to the optical spectrum are given in figure- 2.

Now, if a beam of photons with energy hν > E_g falls on the semiconductor, there will be some amount of absorption determined by the properties of the material. The ratio of transmitted to incident light intensity depends on the photon wavelength and thickness of the sample.

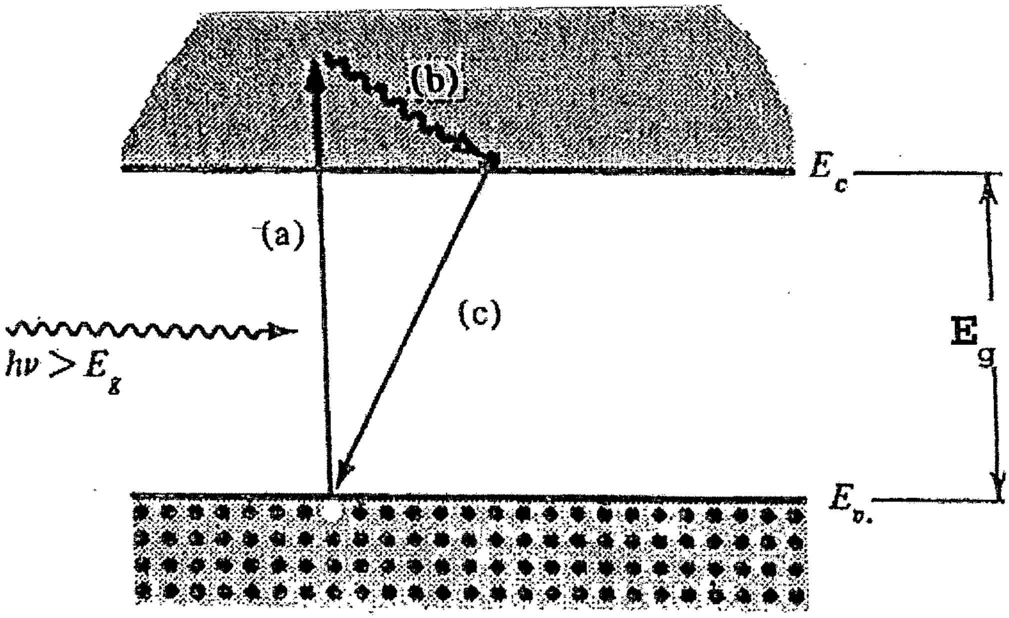

Figure - 1.

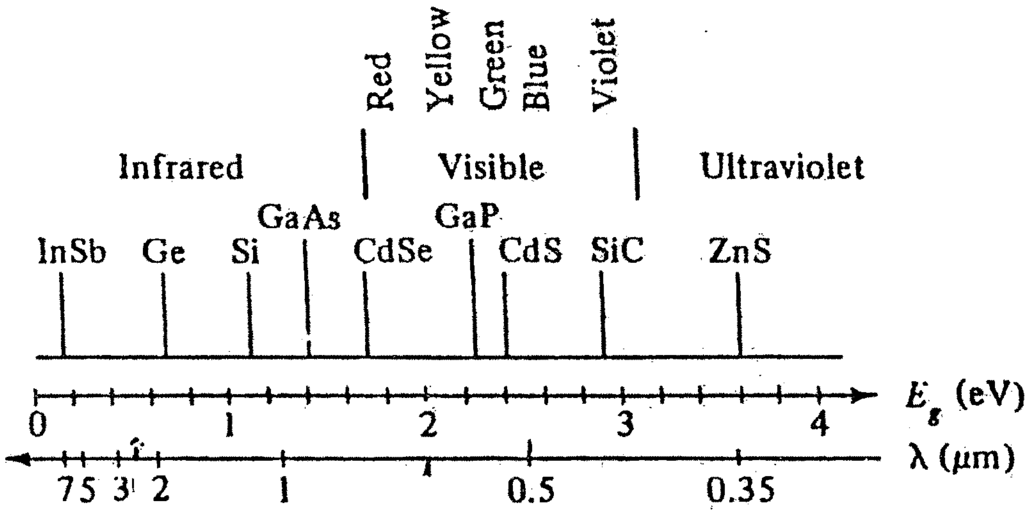
Red
Yellow
Green
Blue
Violet
Infrared
Visible
Ultraviolet
GaAs
GaP
InSb
Ge
Si
CdSe
CdS
SiC
ZnS
0
1
2
3
4
E_g (eV)
75
3
2
1
0.5
0.35
λ (µm)

Figure -2

The intensity of light transmitted through the sample of thickness 't' is

$$I = I_0 e^{-\alpha t} \quad \ldots\ldots\ \ldots\ldots\ \ldots\ldots (1)$$

where, α = absorption coefficient, I_0 = incident beam intensity and

I = transmitted intensity.

Near the absorption edge, the absorption coefficient can be expressed as

$$\alpha \sim (h\nu - E_g)^{\gamma} \ldots\ldots\ \ldots\ldots\ \ldots\ldots (2)$$

where, $h\nu$ = photon energy, E_g = optical band gap and γ = a constant which is equal to 1/2 and 3/2 for allowed direct transition and forbidden direct transition, respectively, [with k ~~(min)~~ = k (max) as in the transition (a) and (b) shown in figure 3]. It is also equal to 2 for indirect transition [transition (c) shown in figure.3] [8], where phonons must be incorporated. In addition γ equals 1/2 for allowed indirect transitions through the exciton states where an exciton is a bound electron - hole pair with energy levels in the band gap and moving through the crystal lattice as a unit.

In the absorption process, a photon of a known energy excites an electron from a lower to a higher energy state. Thus by inserting a slab of semiconductor at the output of a monochromator and studying the changes in the transmitted radiation one can determine all the possible transitions an electron can make and learn much about the distribution of states. There are different possible transitions:

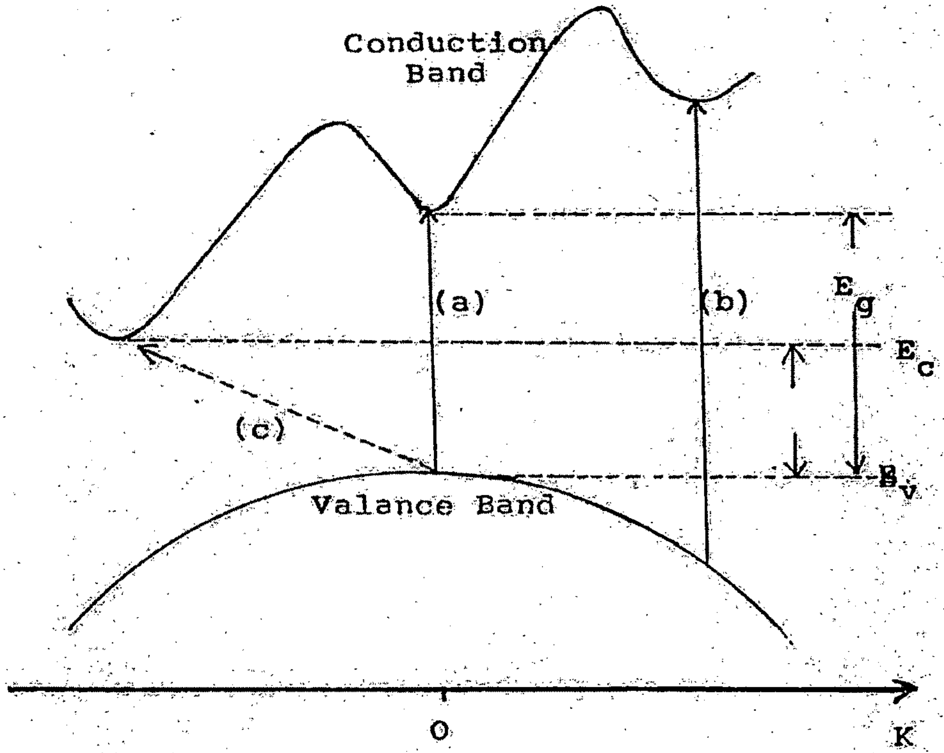

Figure -3

(1) Band to Band (2) excitonic (3) between subbands (4) between impurities and bands (5) transition of free carriers within a band and (6) the resonances due to vibrational states of the lattice and of the impurities.

These lead to the appearance of band or absorption peaks in the absorption spectrum. Hence the spectral positions of bands determine the types of transitions occurring during the process. Absorption of light by an insulator takes place broadly by two processes

(a) by raising the electrons from valence band to conduction band.

(b) by exciting the lattice vibrations of the material.

The latter provides information regarding bond lengths in the lattice, the effective charge on the lattice atoms and the characteristic lattice vibration frequency. From the first process, it is possible to find the electronic band structure. Thus the optical technique is a very easy way to find the band gap as compared to the electric method using the thermal excitation which is less reliable because of the fact that the effective masses of electrons and holes also influence most of the electrical parameters. The measurement of the effective mass is not very straightforward since it is coupled with many other parameters.

The absorption is expressed in terms of a co-efficient which is defined as the relative rate of decrease in light intensity L(hν) along its propagation

$$\alpha(h\nu) = \frac{1}{L(h\nu)} \frac{d(h\nu)}{dx} \quad \dots\dots \dots\dots \dots\dots \dots\dots (3)$$

where, L(hν) is incident light intensity and α is absorption co-efficient [3,9-11].

The basic theory of direct and indirect transitions in the semiconductors is formulated by Bardeen et al [12]. The direct transitions are generally supposed to be taking place from valence band to conduction band under the selection rule,

$$K - K' + \frac{2\pi i}{\lambda} = 0 \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

where, K & K' are the wave vectors of electron before and after transitions, respectively. λ is the wave length of the photon and i is the unit vector along the direction in which the photon travels before it is absorbed. This can be simplified to K = K', since $2\pi / \lambda$ is small compared to either K or K'.

This shows that only vertical transitions are allowed. Other transitions, if taking place, will be of very small probability. Thus the steep edge in absorption is attributed to the highly possible direct transitions. The weak lingering absorption in the tail part is considered to be due to indirect transitions involving the participation of phonons in the process and this will happen when the minima of the conduction band energy surface do not coincide with the maxima of the valence band surface. A phonon is either emitted or absorbed depending on whether the energy of photon is more or less than the indirect band gap energy.

For a direct transition, the absorption coefficient relates to the photon energy as

$$(\alpha h\nu) = B\,(h\nu - E_g)^x \;\ldots\ldots\;\ldots\ldots\;\ldots\ldots (5)$$

Where, $x = 1/2$ for allowed transitions and $x = 3/2$ for forbidden transitions, E_g = direct band gap energy and B is a parameter that depends on the transition probability.

For an indirect transition,

$$(\alpha h\nu) = A\,(h\nu - E_g \pm E_p)^x \ldots\ldots\;\ldots\ldots\;\ldots\ldots (6)$$

Where, $x = 2$ for indirect allowed transition and $x = 3$ for forbidden transitions, E_g = band gap and E_p is absorbed or emitted photon energy [13-15].

In actual practice, for allowed transitions, $(\alpha h\nu)^2$ is plotted against photon energy ($h\nu$) to give straight line for direct transitions [intercept on energy axis giving band gap for direct transitions] and $(\alpha h\nu)^{1/2}$ is plotted against photon energy ($h\nu$) to give a straight line for indirect transition [intercept on energy axis giving band gap for indirect transition]. Actually, two straight lines and two intercepts are usually obtained for indirect transitions; one corresponds to $E_g + E_p$ and other corresponds to $E_g - E_p$.

The lower straight line portion disappears at low temperatures. This portion corresponds to phonon absorption and no longer occurs when the population of phonon states of required energy becomes small with decreasing temperature.

The presence of excitons [usually manifested as a series of narrow absorption lines at low energy side of the intrinsic band gap absorption] appears for measurements at low temperatures only, since for most of the materials the excitons are thermally dissociated at room temperature[16].

A wide range of studies on thin films has been made using the optical measurements by various workers. For example, F.F. Sizov[17] has studied optical properties and electronic structures of IV – VI superlattice based quantum wells and has made comparison with the corresponding properties of bulk semiconductors. S.Bauer et al[18] have studied the optical properties of thin films with thickness less than the wavelength of radiation and investigated the skin depth using energy balance for incident, reflected and transmitted as well as absorbed energies. Effect of substrate structure on the optical properties of thin films from the absorption measurements has been studied by them. The absorption measurements of the samples were made on the Michelson series FTIR spectrophotometer (BOMEM, Canada).The use of FTIR spectrometer possesses several advantages over dispersive spectrometers. Instead of spatially separating the optical frequencies, the FTIR spectrometer modulates all wavelengths simultaneously with distinct modulation frequencies for each wavelength. This can be done by means of variable interference effect created by separating the incoming beam into two parts and then introducing the path difference and finally recombining the beam. The resulting beam intensity is recorded as a function of optical path difference with IR detector and computing the Fourier transform interferogram yields the IR spectrum (figure 4).

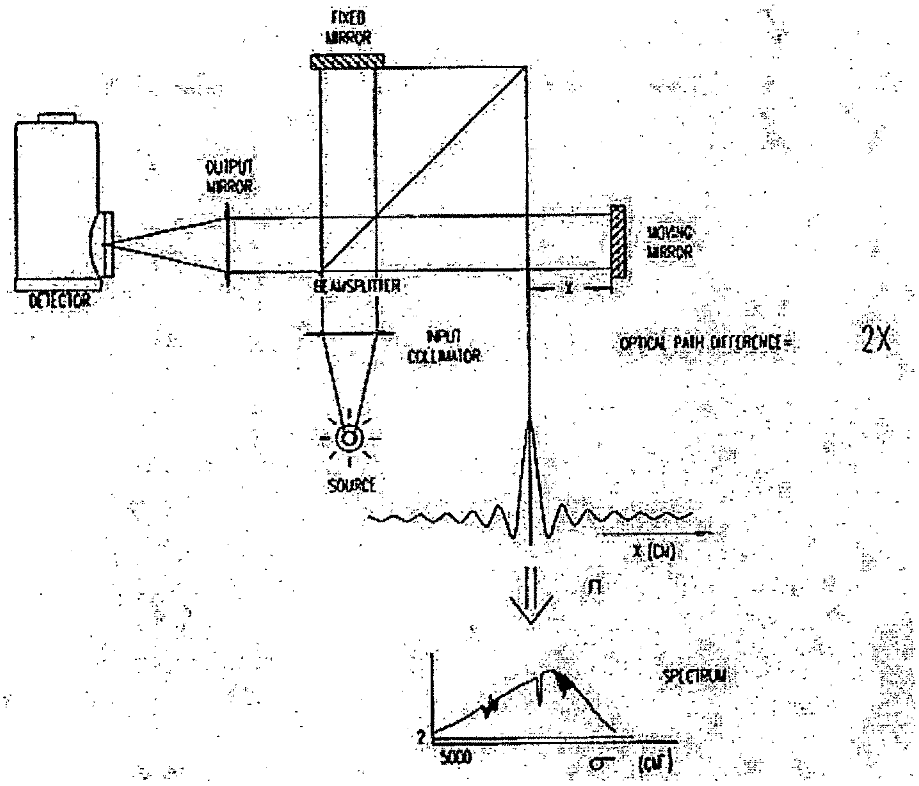
FIXED MIRROR
OUTPUT MIRROR
DETECTOR
BEAMSPLITTER
MOVING MIRROR
X
INPUT COLLIMATOR
OPTICAL PATH DIFFERENCE = 2X
SOURCE
X (CM)
SPECTRUM
2
5000
σ (CM⁻¹)

Figure -4

In the present case, the KBr pressed disk technique was used because of its simplicity and its ability to produce good spectra from very small samples. Further using KBr as a matrix has following advantages:

(1) High transmission of radiation

(2) Chemical stability

(3) High purity

(4) Low sintering pressure.

The crystalline powder sample (30 mg) and spectroscopic grade KBr (dry) powder matrix (300 mg) was ground to a very small particle size and was mixed thoroughly. Then it was transferred to a die of about 1 cm diameter and evacuated at 10^{-2} torr for at least 5 min.. Then a pressure of about 1.2 ton was applied for 7 min and then vacuum was released. This gives the mixture formed into a pellet. The pelletted samples were used to obtain the absorption data which were used to obtain the optical band gap.

The optical absorption was measured in the wave number range 510 cm^{-1} to 4000 cm^{-1} and the absorption spectrum was recorded. By analyzing the spectrum, absorption coefficient was calculated as a function of the photon energy. Since in the case of pelletted samples, the thickness of the material is undetermined, an arbitrary thickness was assumed. Of course this would not give absolute absorption coefficient. However, the relative variations only are significant for the purpose of evaluating the band gap. Similarly for the thin film studies, the film was deposited on (100) KBr crystal as a substrate and then absorption data was taken.

Optical Band Gap of the $Bi_{1-x}Sb_x$ Crystals :

The plots of $(\alpha h\nu)^2$ versus $h\nu$, where $h\nu$ is the photon energy were obtained for samples as described above. The plots are shown in figures 5(a), (b) and (c) for $Bi_{1-x}Sb_x$, for different x . The extrapolation of the straight line on the higher energy side to $(\alpha h\nu)^2 = 0$ gives the band gap values that are listed in Table 1. As observed, the addition of Sb as impurity in Bi is found to convert the material into a semiconductor with an average bandgap of about 0.045 eV, in the x – range studied. The conversion has also been reported by other workers through Mossobauer / conductivity studies [19].

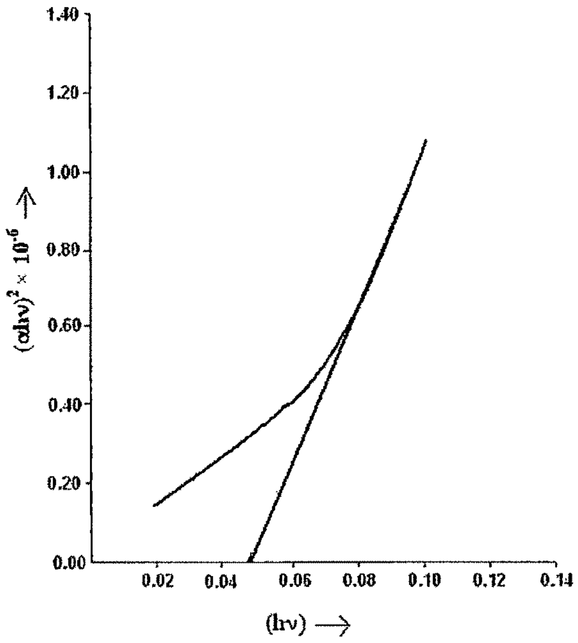

Figure- 5(a) **$Bi_{0.90}Sb_{0.10}$**

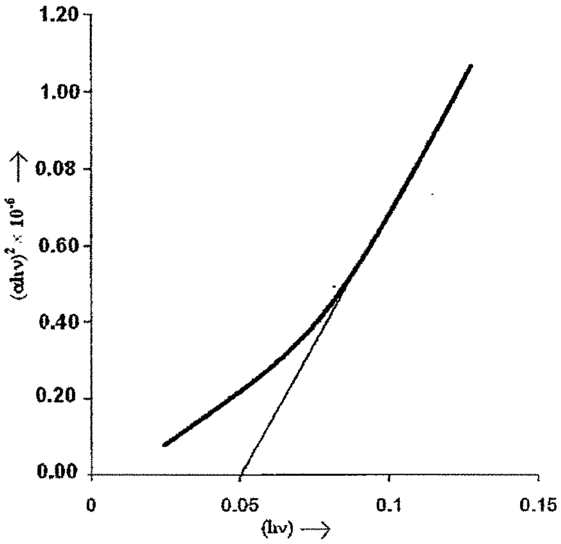

Figure- 5(b) **$Bi_{0.85}Sb_{0.15}$**

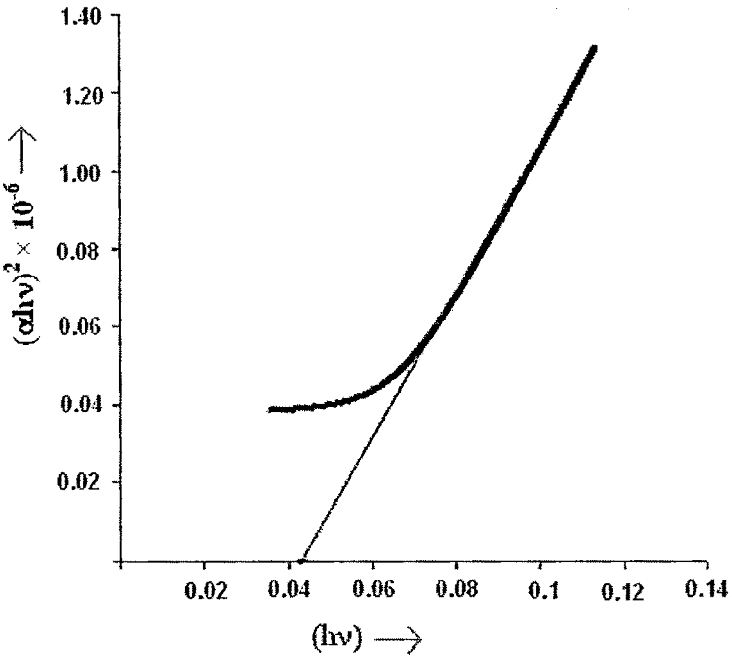

Fig. 5(c) **$Bi_{0.80}Sb_{0.20}$**

Table – 1

Material	Optical band gap in eV
$Bi_{0.90}Sb_{0.10}$	0.044
$Bi_{0.85}Sb_{0.15}$	0.050
$Bi_{0.80}Sb_{0.20}$	0.042

Optical band gap of $Bi_{1-x}Sb_x$ thin films:

To carry out the absorption measurements on the thin films, the films were deposited on KBr crystal substrates and were placed in the sample compartment of the IR spectrophotometer. The absorbance was measured in the wave number range 510 cm^{-1} to 6000 cm^{-1}. The data was used to obtained the band gap. The band gap was found to depend on the film thickness and also on the content of Sb.

The plots of $(\alpha h\nu)^2$ versus $h\nu$ obtained for films $Bi_{1-x}Sb_x$ (x=0.1,.15,.20) of different thicknesses prepared by thermal evaporation of the compounds are given in figures 6 (a), 6(b) and 6(c) . The plots are observed to be straight lines in the region of high absorption. Hence by extrapolating the linear portion to $h\nu = 0$ (zero abscissa), the band gap was evaluated [10,20,21], shown in table -2.

The optical band gap 'Eg' plotted versus inverse square of film thicknesses (t) is shown in figures 7 (a) , 7(b) and 7(c), respectively, for $Bi_{1-x}Sb_x$(x=0.10,0.15,0.20) films. Such thickness dependence of band gap has been explained in terms of quantum size effect and dislocation density. In semiconductors, the quantum size appears when their film thickness is comparable with or less than the mean free path or effective de Broglie wavelength of carriers. Because of the small thickness of the films, the transverse component of quasi momentum of carriers is quantized and it assumes discrete values along the thickness dimension. The energy spectrum represents a system of the discrete levels with the separation between them given by the uncertainty principle. Due to this quantization, the bottom of the conduction band and the top of the valence band are separated by an additional amount of E_z [21]. In the thin film specimens, provided smearing of energy levels by temperature and diffuse scattering of the carriers at the film surfaces are not significant, this shift will increase the band gap and affect the optical behavior of semiconducting films.

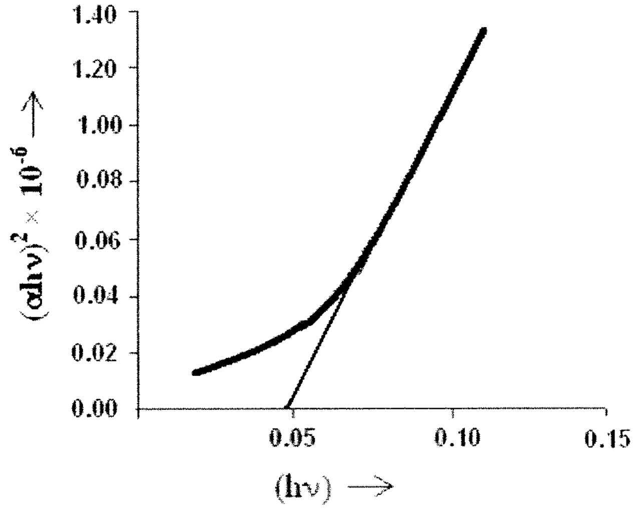

Figure- 6 (a) $Bi_{0.90}Sb_{0.10}$

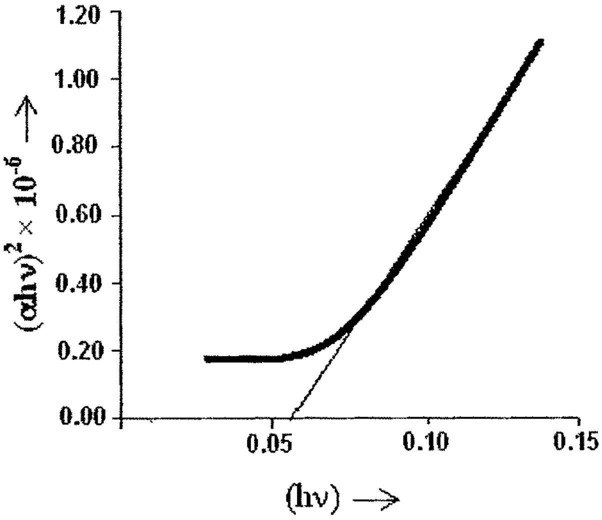

Figure- 6 (b) $Bi_{0.85}Sb_{0.15}$

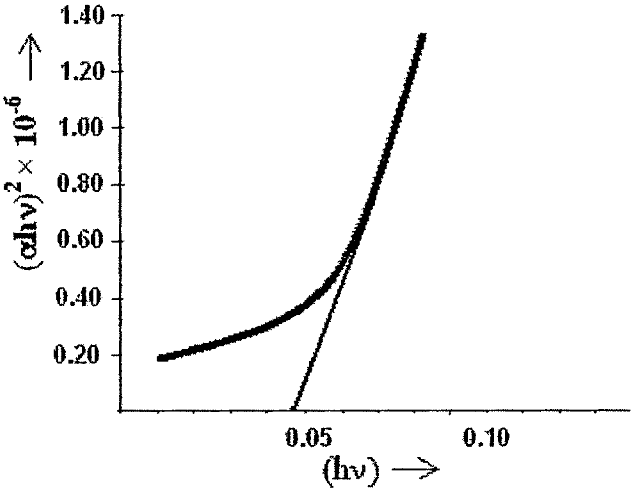

Figure- 6(c) $Bi_{0.80}Sb_{0.20}$

Table -2

Material	Optical band gap in eV
$Bi_{0.90}Sb_{0.10}$	0.048
$Bi_{0.85}Sb_{0.15}$	0.053
$Bi_{0.80}Sb_{0.20}$	0.047

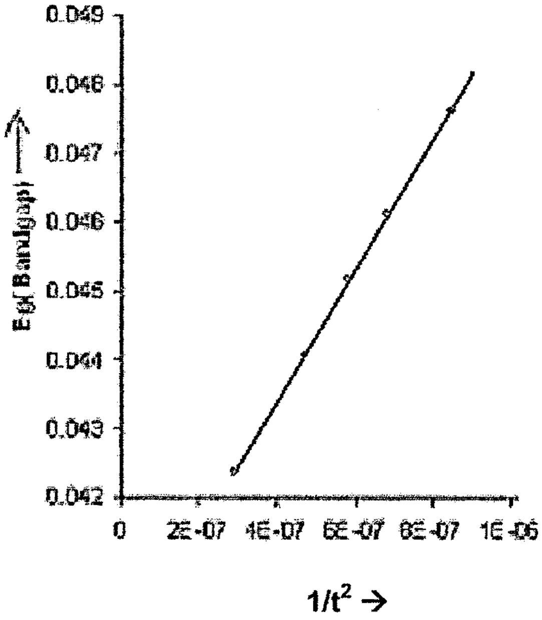

Figure- 7(a) $Bi_{0.90}Sb_{0.10}$

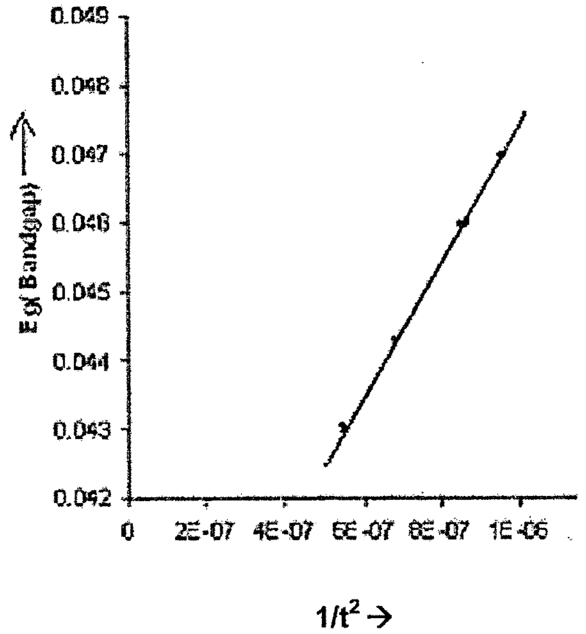

Figure- 7(b) $Bi_{0.85}Sb_{0.15}$

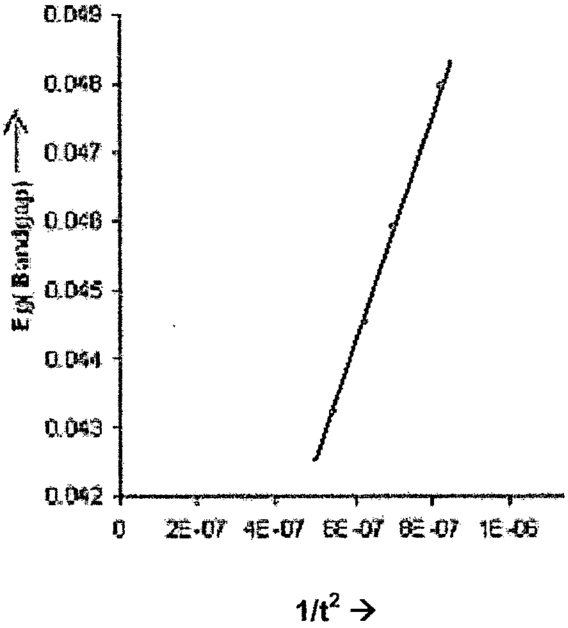

Figure-7(c) $Bi_{0.80}Sb_{0.20}$

The absorption is reduced in thinner films as compared with the bulk. E_z is given by [21] :

$$E_z = \frac{\hbar^2\pi^2}{2\,m^*}\,\frac{1}{t^2}$$

Here m* is the effective mass of the charge carrier, t is the thickness of the film and E_z is the kinetic energy contribution due to motion normal to the film plane.

The plots of Eg versus $1/t^2$ for $Bi_{0.90}Sb_{0.10}$, $Bi_{0.85}Sb_{0.15}$, $Bi_{0.80}Sb_{0.20}$ given in figures 7 (a), 7(b), and 7(c) are linear and in agreement with the above relation and imply the quantum size effect operative in the present case. The estimates of de Broglie wavelength, by taking the Fermi energy to be half of the average band gap, turns out to be about 101 nm,103 nm and 102 nm of thin films of $Bi_{0.90}Sb_{0.10}$, $Bi_{0.85}Sb_{0.15}$, $Bi_{0.80}Sb_{0.20}$, respectively.

It is also known that a fairly large number of dislocations are created during the formation of the thin films and their density increases as the thickness increases up to a particular thickness beyond which the density is practically constant. However, the dependence of dislocation density on thickness has not been quantified and in any case the dependence is complex. There are considerable lattice disturbances due to dislocations, viz., the local stress fields around a dislocation, disrupted or dangling bond with its specific charge and the space charge domain that forms immediately in semiconductors. The compression and dilation in strain patterns brought about by edge dislocations have an effect in changing the forbidden gap of the semiconductor. This is because of resulting local compression increment in the deformation potential relation. Another influence is due to dangling bond resulting in an energy level within the forbidden gap.

With the increase in film thickness, the effect of the initial granular structure on the optical properties decreases but is not eliminated completely. Therefore, thickness dependence is still observed although the general behavior of the optical parameter, i.e. band gap , follows that of the bulk, at least qualitatively. For a very thick crystal, (i.e., ideally infinite thickness) the electron energy is a multi valued continuous function of the quasimomentum. The variation of band gap with the crystallite size has been explained by the modified form of Steller's formula [22]. According to him the increased barrier height is given by

$$E = E_0 + C\,(X - fD)^2 \;\ldots\ldots\;\ldots\ldots\;\ldots\ldots\; (7)$$

where, C = term depending on density of charge carriers,

and dielectric constant of the material,

E_0 = original barrier height,

X = barrier width,

D = grain dimension,

f = factor depending on the charge accumulation and carrier

concentration.

From literature, it is known that the grain size is approximately proportional to the thickness. Hence grain size increases due to the increase in thickness of the film[11]. So, if we replace D, the grain size in the above equation, by the film thickness t, E should be proportional to $(X - f\,t)^2$.

In the present observations we find that the band gap varies inversely as the square of the film thickness. Hence it can be concluded that the observed band gap variation with thickness cannot be attributed to the above effect. Thus in these $Bi_{1-x}Sb_x$ films the quantum size effect is dominant, rather than the effect produced by the dislocation density variation.[8].

Band gap variation with composition:

The band gap of different compositions are seen to depend on the x value as illustrated by the plots of E_g versus x in figures 8(a) and 8(b) for crystals and thin films, respectively. It is seen that the magnitude of variation of E_g among the three compositions is about the same, viz., 0.0055 eV both in the cases of crystals and thin films. This can only be taken to imply that the Sb content does affect the band gap, though may not be systematically.

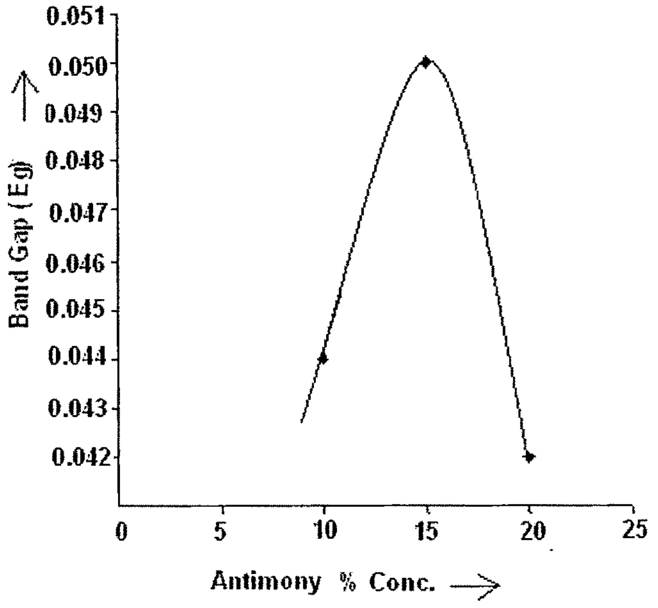

Figure- 8(a) $Bi_{1-x}Sb_x$ (x= 0.1,0.15,0.20) crystals

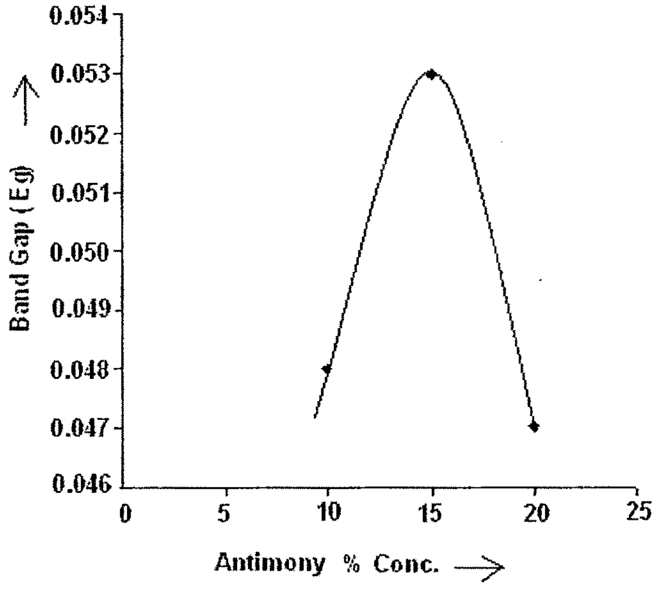

Figure- 8(b) $Bi_{1-x}Sb_x$ (x= 0.1,0.15,0.20) thin films maximum temperature inside the furnace core is kept about 100 ^{0}C above the melting point of the material. The temperature is measured and controlled (within ± 5 ^{0}C) with a proportional temperature controller. The temperature is sensed with a Choromel-Alumel thermocouple. The rotation cum rocking of the quartz tube gives stirring effect to the molten charge. For thorough mixing and reaction of the charge, this treatment is continued for 2 to 3 days. The molten charge is then slowly cooled to room temperature.

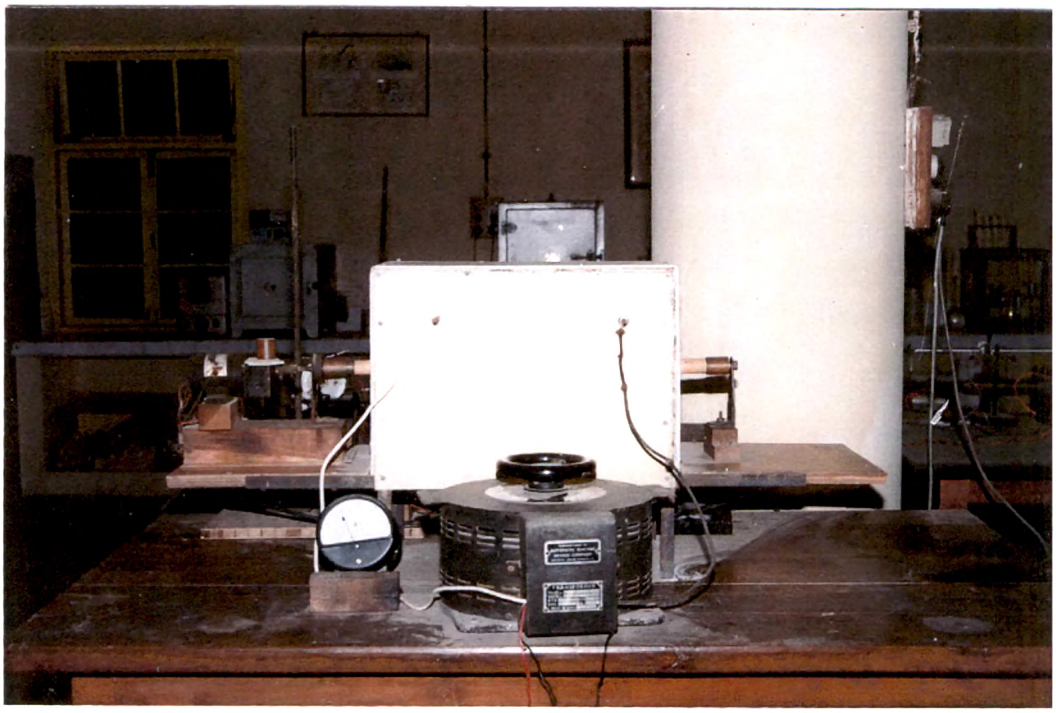

Figure -1

Fig caption?

CONCLUSIONS :

(1) The optical band gap values of $Bi_{1-x}Sb_x$ (x= 0.10,0.15,0.20) are found to be 44 meV, 50 meV and 42meV and 48 meV, 53 meV and 47meV, in the case of crystals and thin films, respectively.

(2) The optical band gap of the thin films has been found to vary as inverse square of film thickness implying quantum size effect operative for thickness up to about 100 to 150 nm.

REFERENCE:

1. Field Gradients in pure Te and Se doped InBi Systems, DAE Van Vechatan, J.A. Phys. Rev. 182 (1969), 801
2. Wemple, S.H. and Didomenico, M. phys. Rev. 133 (1971), 1338
3. Streetman B.G. Solid State Electronic Devices, Prentic Hall of Indian Pvt., New Delhi (1982)
4. Heavens O.S., Optical properties of Thin Solid Films, Butterworths, London (1955)
5. Heavens O.S., Rept. Progr. Physics, 23 (1960) 1
6. Bering P.H., Physics of Thin films, Academic Press NY (1964) 69
7. Bernnett H.E. and Bennettin J.M., Physics of Thin Films, Academic Press NY 4 (1967)1
8. Sze S.M., Physics of Semiconductor Devices, Wiley Eastern Ltd., New Delhi (1979)
9. Bhatt V.P. Gireesan K., Desai C.F., Cryst. Res. Technol., 25 (1990) 209
10. Dang Tran Quan, Thin Solid Films, 149 (1987) 197
11. Bhatt V.P. Gireesan K., Desai C.F., Cryst. Res. Technol., 24 (1989) 187
12. Barden J., Hall H., and Bhatt F.J., Proc. Of The Conf. On Photoconductivity, NY (1956) 146
13. Tovar Barradas R., Rincon C., Genzalez j. and Sancher Pertez G., J. Phys. Chem. Solids 45 (1984) 1185
14. Eva C., Freeman and Willam Paul, Phys. Rev., (B) 20 (1979) 716
15. Mendolia J. and Lemone D., Phys. State Solid. (a) 97 (1986) 601
16. Bube R.H., photoconductivity of Solids, John Wiley and Sons Inc., NY

(London) (1960)

17. Sizov F.F., Acta Phys. Pol. (A) (Poland) 79 1 (1991) 83 – 96

18. Bauer S., Am. J. Phys. (USA) 60 3 (1992) 257

19. Pal Gayatri, Sebastian K.C., Chavda N.D., Desai C.F., Chintalapudi S.N., Somayajulu D.R.S. Electric – Solid State Symposium, Vol. – 40C (1997), 240

20. Stasenko A.K., Sov. Phys. Solid State, 10 (1968) 186

21. Damodardas V. and Karunakaran D., J. Appl. Phys., 54 (1983) 5252

22. Steller.J.C: Physics Rev. 103 (1956) 1931.