

Effect of Te doping on thermal diffusivity of Bi₂Se₃ crystals: A study using open cell photoacoustic technique

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An open cell configuration has been employed for the photoacoustic measurement of the thermal diffusivity of undoped Bi₂Se₃ crystals and Bi₂Se₃ crystals doped with various concentrations of Te. The amplitude of the photoacoustic signal obtained under heat transmission configuration as a function of chopping frequency is used to evaluate the numerical value of thermal diffusivity, α . Doped samples show a substantial reduction in the value of α compared to undoped samples. The variations in the thermal diffusivity of the doped samples are explained in terms of the phonon assisted heat transfer mechanism. It is seen that α is very sensitive to structural variations arising from doping. The experimentally observed results are correlated with X-ray diffraction studies.

1 Introduction

In recent years, thermal wave physics has become an active area of research, particularly in characterizing and analysing the material parameters [1–3]. The non-intrusive and non-destructive laser induced photoacoustic (PA) and photothermal methods are widely used to investigate the thermal, transport and optical properties of semiconductors, ceramics, liquid crystals etc. [4–6]. Photothermal techniques are based on the detection, by one means or other, of periodic thermal waves generated due to non-radiative de-excitations in the sample following a chopped or pulsed optical excitation. The experimentally measured PA response depends on both the amount of light absorbed and the nature of heat diffusion through the sample. The PA technique, using the heat transmission configuration or the so-called open photoacoustic cell (OPC) technique is found to be more useful than the one employing the reflection detection configuration to evaluate the structural and transport properties of the sample, especially in the low chopping frequency range [7]. An added advantage of the OPC technique is that it allows in situ as well as in vivo measurement of material properties [8]. The attenuation of thermal waves is determined by the thermal diffusivity of the specimen, which can be accurately measured using this technique.

This paper is concerned with the evaluation of the thermal diffusivity of intrinsic Bi₂Se₃ crystals and Bi₂Se₃ crystals doped with varying concentrations of Te, using the OPC technique. Thermal diffusivity is an important thermophysical parameter which determines the temperature distribution in systems where heat flow occurs, while the reciprocal of the thermal diffusivity is a measure of the time required to heat a conducting material to a specific temperature level. This parameter is closely dependent on the micro-

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structural variation and composition as well as on the processing conditions of the sample. Thus the evaluation of thermal diffusivity and the study of its variation with the concentration of various dopants incorporated into the sample form an indirect way of identifying the structural variations in the sample that may occur when the material is doped [10]. In crystals, heat is essentially transported by phonons and the value of the thermal diffusivity depends directly on the phonon mean free path, which is governed by the various phonon scattering processes occurring in the specimen. These scattering processes in the sample are affected by the nature of the dopants and their concentration. Therefore, the evaluation of this thermophysical property and its variation with doping concentration can throw much light on the phonon relaxations in the crystal and, as a consequence, the effect of scattering processes on thermal transport [10]. Since Bi_2Se_3 is an important material in the thermoelectric industry, evaluation of its thermal diffusivity and its variation with the doping concentration of Te have great practical applications. As the figure of merit of these devices is inversely proportional to the thermal diffusivity or thermal conductivity, an accurate measurement of the thermal diffusivity of these crystals has great physical and practical significance. In the present investigation we have attempted to correlate the variation of thermal diffusivity in the material with the lattice spacing obtained by X-ray diffraction. A study of the variation of thermal diffusivity with doping, along with its dependence on lattice spacing, is extremely important in the context of device modelling.

2 Experimental details

Single crystals of Bi_2Se_3 and its Te doped samples were prepared from 5N pure Bi, Se and Te. The synthesis of the compounds was carried out in tapered quartz ampoules evacuated to a pressure of 10^{-5} Torr. The sealed ampoules containing the charge were kept in a muffle furnace having a flat temperature profile at 600°C for 24 h. The ampoule was rotated and rocked periodically to ensure complete mixing and reaction. The identification of the compound was made using a Rigaku X-ray diffractometer with monochromatic nickel filtered $\text{CuK}\alpha$ radiation as the X-ray source. The powder diffractogram revealed that pure Bi_2Se_3 , as well as Bi_2Se_3 with varying concentrations of Te (1%, 4%, 6% and 8%), had been formed. The crystals were grown using the vertical normal freezing method. It is possible to obtain single crystals of good quality by this method. The ampoule containing the melt was heat treated at 720°C for 24 h and then moved at the rate of 4 mm/h through a temperature gradient of about $10^\circ\text{C}/\text{cm}$. Single crystals of 50 mm length and 8 mm in diameter were obtained by this method. The samples used in the PA measurement have dimensions of the order of $7 \times 7 \text{ mm}^2$ and have an average thickness of the order of $250 \mu\text{m}$. The crystals are cleaved in the (111) plane.

The PA measurements were performed using an open photoacoustic cell. A geometrical view of the open photoacoustic cell is given in Fig. 1. The minimal volume OPC configuration gives a large signal-to-noise ratio compared to the conventional photoacoustic cell. The sample is fixed to the top of the air chamber of the OPC using vacuum grease and is irradiated on the surface facing the ambient. Continuous wave laser radiation at 488 nm from an Argon ion laser is used as the source of optical excitation. The laser beam, which has a $1/e^2$ radius of 0.6 mm, is used without further focussing so as to avoid lateral

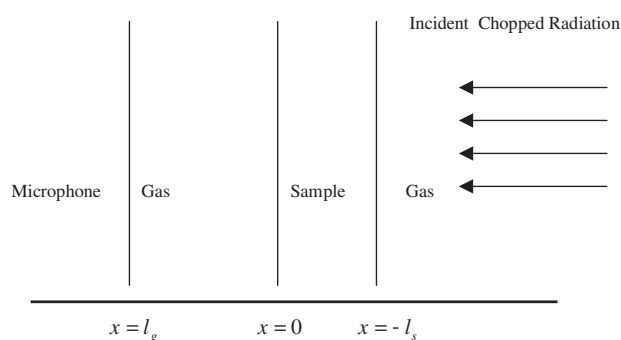


Fig. 1 PA cell geometry for the heat transmission configuration.

diffusion. Laser radiation with a power level at 50 ± 0.25 mW is intensity modulated using a mechanical chopper (Stanford Research Systems SR 540) before it is made to fall on the specimen. The pressure fluctuations created in the acoustic chamber are detected by a sensitive microphone (Knowles BT 1754). The output of the microphone, which has a built in preamplifier, is fed to a dual channel digital lock-in amplifier (Stanford Research Systems SR 830).

3 Theoretical background

According to the one-dimensional model of Rosencwaig and Gersho, the pressure fluctuations detected by the microphone depend on the acoustic pressure disturbance at the sample-gas interface. The generation of the surface disturbance, in turn depends on the periodic temperature at the sample-gas interface. For an optically opaque sample of absorption coefficient β , all the incident light is absorbed at the front surface. Here the two faces of the crystal are sprayed with a very thin layer of black coating so as to produce good light absorbing surfaces. This also provides the same heat transmission coefficient for each surface [10]. Thus, under irradiation with a laser radiation with intensity I_0 , the heat density produced at any point x due to the light absorbed at this point can be given by the expression

$$\frac{1}{2} \beta I_0 e^{\beta x} (1 + \cos \omega t). \quad (1)$$

The periodic pressure fluctuation in the open photoacoustic cell chamber under heat transmission configuration is given by

$$Q_{th} = \frac{\gamma P_0 I_0 (\alpha_g \alpha_s)^{1/2}}{2\pi T_0 l_g k_s f} \frac{e^{j(\omega t - (\pi/2))}}{\sinh(l_s \sigma_s)}, \quad (2)$$

where γ is the ratio of the specific heat capacities of air, $P_0(T_0)$ is the ambient pressure (temperature), f is the modulation frequency, l_i, k_i and α_i are the thickness, thermal conductivity and the thermal diffusivity of the medium i , where g and s denote gas and sample, respectively. Also $\sigma_i = (1+i) a_i$ where $a_i = (\pi f / \alpha_i)^{1/2}$ is the thermal diffusion coefficient of the medium i . In arriving at the above expression it is assumed that the heat flux into air in contact with the irradiated surface of the sample is negligible.

Thus for a thermally thin sample (i.e. $l_s \sigma_s \ll 1$) Eq. (2) reduces to

$$Q_{th} \cong \frac{\gamma P_0 I_0 \alpha_g^{1/2} \alpha_s}{(2\pi)^{3/2} T_0 l_g l_s k_s} \frac{e^{j(\omega t - 3\pi/4)}}{f^{3/2}}. \quad (3)$$

The amplitude of the PA signal varies as $f^{-3/2}$.

At higher chopping frequencies, the sample becomes thermally thick (i.e. $l_s \sigma_s \gg 1$)

$$Q_{th} = \frac{\gamma P_0 I_0 (\alpha_g \alpha_s)^{1/2}}{\pi T_0 l_g k_s} \frac{e^{-l_s (\pi f / \alpha_s)}}{f} e^{j(\omega t - (\pi/2) - l_s \sigma_s)}. \quad (4)$$

Then for a thermally thick sample, the amplitude of the photoacoustic signal [9] varies as

$$(A/f) \exp(-c \sqrt{f}), \quad (5)$$

where the coefficient, c , is given as $c = (l^2 \pi / \alpha)^2$.

Thus, plotting the natural logarithm of the amplitude of the PA signal under heat transmission configuration against the square root of the frequency, we can evaluate the thermal diffusivity of the specimen under investigation [10].

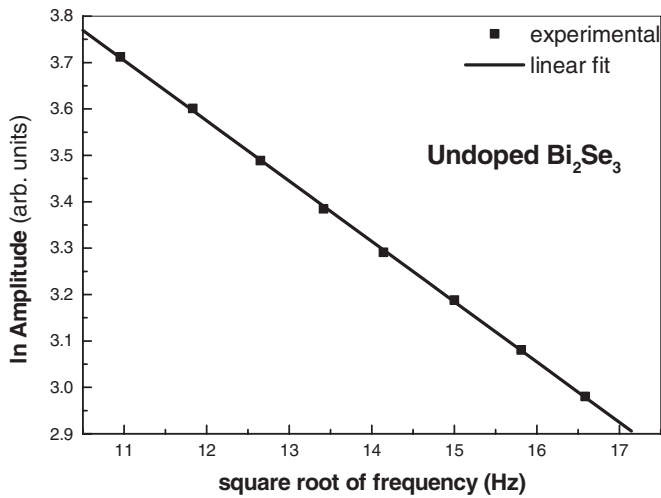


Fig. 2 PA signal amplitude as a function of the square root of modulation frequency for an undoped Bi_2Se_3 crystal.

4 Results and discussion

The present experimental set up was calibrated by the evaluation of the thermal diffusivity of Al and Si. The values were found to be 0.979 ± 0.003 and 0.88 ± 0.003 , which agrees well with reported values of Al and Si [11, 12]. The amplitude of the PA signal as a function of the chopping frequency obtained under the heat transmission configuration for the undoped Bi_2Se_3 crystal is shown in Fig. 2. From Fig. 2, the thermal diffusivity of undoped Bi_2Se_3 is evaluated as $(0.312 \pm 0.002) \text{ cm}^2 \text{ s}^{-1}$. It is seen from the analysis that the amplitude plots for the Te doped Bi_2Se_3 crystals also show similar behaviour (not shown here). The thermal diffusivities for all the samples at room temperature are given in Fig. 3. Results show that the thermal diffusivities of the doped samples are less than that of the undoped sample and vary in a non-linear manner with Te concentration. The thermal diffusivity values obtained here are given in Table 1.

The reduction in the thermal diffusivity of the doped samples compared to undoped samples can be understood in terms of the phonon assisted heat transfer mechanism in crystals. Phonons in the lattice suffer various additional scattering processes on the introduction of dopant. Introduction of dopants into a lattice generates extra scattering centres for phonons. This results in the reduction of the phonon mean

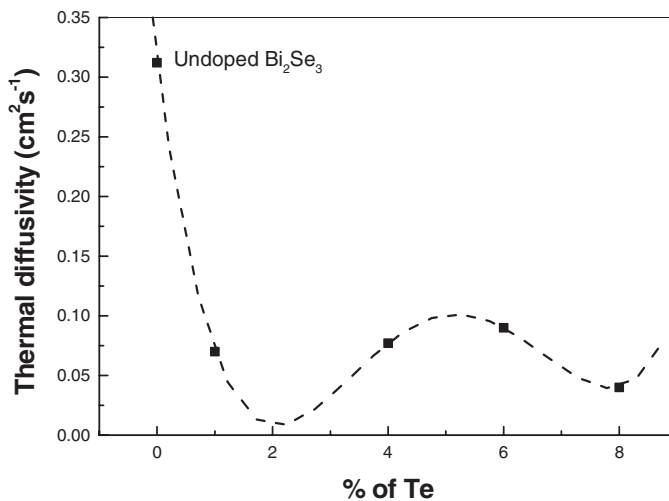


Fig. 3 Effective thermal diffusivity data obtained under OPC technique for the Te doped Bi_2Se_3 crystals as a function of Te at% concentration. The full curve represents the fit to the data.

Table 1 Variation of lattice spacing and thermal diffusivity of Bi₂Se₃ crystals with Te concentration.

% of tellurium	lattice spacing (Å)	thermal diffusivity (cm ² s ⁻¹)
0	4.134	0.312 ± 0.002
1	4.139	0.070 ± 0.001
4	4.148	0.077 ± 0.002
6	4.166	0.090 ± 0.003
8	4.139	0.041 ± 0.004

free path. It is known that the lattice thermal conductivity (diffusivity) is directly proportional to the phonon mean free path. Thus the introduction of dopants reduces the phonon mean free path and gives a reduced value for thermal diffusivity in doped specimens.

In order to explain the non-monotonic decrease in the thermal diffusivity of Bi₂Se₃ with the increase in concentration of Te, we studied the crystal structure using X-ray diffraction. The values obtained for the lattice spacing for doped and undoped samples are given in Table 1. It is seen that the lattice spacing varies from 4.134 Å for an undoped sample to 4.166 Å (for 6% of Te) and then it decreases to 4.139 Å (for 8% of Te). Such a rapid variation in lattice spacing with the doping concentration has been reported for II–VI doped semiconductors such as CdTe [13]. This variation in lattice spacing has been attributed to native defects in the crystals. When Bi₂Se₃ is doped with substitutional Te atoms, the lattice may distort because Se is replaced with Te of relatively larger atomic dimensions. It is seen from Table 1 that with an initial increase in doping concentration (up to 6%), the lattice spacing also increases, which in turn increases the phonon mean free path. An increase in phonon mean free path gives an increased value for thermal diffusivity with increase in concentration of Te. However, once the Se vacancies are completely compensated by the Te atoms, they go interstitially into the host lattice and as a consequence the lattice spacing may decrease. Thus a reduced value for lattice spacing explains a further reduced value for thermal diffusivity of Bi₂Se₃ when doped with 8% of Te. This non-linear variation in thermal diffusivity may attain a saturation value with further increase in doping concentration.

5 Conclusions

In conclusion, we have measured the thermal diffusivity of pure Bi₂Se₃ crystals and Bi₂Se₃ crystals doped with varying concentrations of Te atoms. From the analysis it can be seen that the doped samples show a considerably reduced value for thermal diffusivity compared to undoped samples. The thermal diffusivity of the doped sample can be correlated with structural variations arising due to doping. The experimentally obtained results are explained in terms of lattice spacing obtained using X-ray measurement. This is an example where PA measurements can be correlated with the structural variations in the sample. The reduction in thermal diffusivity of doped samples suggests that with the proper concentration of Te atoms we can vary the intrinsic thermal diffusivity of the Bi₂Se₃ crystal, which has wide applications in the fabrication of thermoelectric devices.

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References

- [1] A. Mandelis, Photoacoustic and Thermal Wave Phenomena in Semiconductors (North-Holland, New York, 1987).
- [2] A. Rosencwaig, Photoacoustic and Photoacoustic Spectroscopy (Wiley, New York, 1983).

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- [3] Yu. Gurevich, G. Gonzalez de la Cruz, G. N. Logvinov, and M. N. K. Kasyabkluck, *Semiconductors*, **32**, 1179 (1998).
 - [4] I. Reich, P. Diaz, T. Prutskij, J. Mendoza, H. Vargas, and E. Marin, *J. Appl. Phys.* **86**, 6222 (1999).
 - [5] S. Sankara Raman, V. P. N. Nampoori, C. P. G. Vallabhan, G. Ambadas, and S. Sugunan, *Appl. Phys. Lett.* **67**, 2939 (1995).
 - [6] N. A. George, C. P. G. Vallabhan, V. P. N. Nampoori, A. K. George, and P. Radhakrishnan, *J. Phys., Condens. Matter* **13**, 365 (2001).
 - [7] D. M. Todorovic and P. M. Nikolic, *Opt. Eng.* **36**, 432 (1997).
 - [8] M. V. Marguenzini, N. Cella, A. M. Mansanares, H. Vargas, and L. C. M. Miranda, *Meas. Sci. Technol.* **2**, 396 (1991).
 - [9] M. E. Rodriguz, O. Zelaya Angel, J. J. Perez Bueno, J. Jimenez-Sandoval, and L. Tirado, *J. Cryst. Growth* **213**, 259 (2000).
 - [10] R. Castro-Rodriguez, M. Zapata-Torres, V. Rejon Moo, P. Bartolo-Perez, and J. L. Pena, *J. Phys. D, Appl. Phys.* **32**, 1194 (1999).
 - [11] S. Sankara Raman, V. P. N. Nampoori, C. P. G. Vallabhan, G. Ambadas, and S. Sugunan, *Appl. Phys. Lett.* **67**, 2939 (1995).
 - [12] A. Calderon, R. A. Munoz Hernandez, S. A. Tomas, A. Cruz Orea, and F. Sanchez Sincencio, *J. Appl. Phys.* **84**, 6327 (1998).
 - [13] J. Ptruzeo, J. Gaines, P. Van der Sluis, D. Olego, and C. Ponzoni, *Appl. Phys. Lett.* **62**, 1496 (1993).