

## Photoacoustic spectroscopic study of optical properties of solids

**R. C. Gupta**

Department of Physics, Institute of Engineering and Management, Mathura 281406, India  
Email: sspbks@yahoo.co.in

---

### ABSTRACT

---

*In photoacoustic spectroscopic (PAS) technique, acoustic piston model is considered and the optical properties of solids are studied. One has to detect the photoacoustic (PA) signal produced when a sample placed in a cell is irradiated by an intensity modulated beam of light. The PA signal is used to investigate the optical properties of solids. In this paper we report on the theoretical, experimental issues on the application of photoacoustic spectroscopy for the investigation of optical properties of  $\text{Cu}_2\text{GeSe}_3$  compound. Optical-absorption spectra has been obtained in the range of 0.76 – 0.81 eV photon-energy at temperatures between 70 and 300 K. The thermal variation of band-gap energy has been estimated from the optical-absorption spectra at different temperatures.*

**Keywords** - Photoacoustic spectroscopy, Optical properties, Band gap,  $\text{Cu}_2\text{GeSe}_3$ .

---

### I. INTRODUCTION

The photoacoustic (PA) effect is the generation of an acoustic signal when the sample under investigation, placed inside a closed cell, is irradiated by an intensity modulated beam of light. This phenomenon was detected by alexander Graham Bell in 1880 [ 1, 2]. In case of gas and liquid samples, the sample fills the entire volume of the cell and the acoustic signals are detected by a microphone and a piezoelectric transducer respectively. In the case of solid samples, the sample fills only a portion of the cell and the remaining volume of the cell is filled with a non-absorbing gas such as air, and a sensitive microphone is suitably placed inside the cell to pick up the acoustic signals. The internal energy levels of the sample are excited by the absorption of incident radiation and upon subsequent de-excitation, all or part of the absorbed photon energy is converted into heat through non-radiative de-excitation processes. In the case of solid samples, the periodic heating of the sample results in a periodic heat flow from the interior of the sample to the surrounding gas which in turn produces pressure fluctuations in the gas which can be detected as an acoustic signal by the microphone. Photoacoustic spectroscopy (PAS) is essentially a combination of optical absorption spectroscopy and calorimetry [3]. From the calorimetric viewpoint, the heat input into the sample is supplied indirectly by the incident beam of light and the rise in temperature is detected by another indirect method using an acoustic transducer instead of a thermal detector. In this paper the theoretical model and application of photoacoustic spectroscopy (PAS) will be presented.

We have taken  $\text{A}_2\text{B}^{\text{IV}}\text{C}_3^{\text{VI}}$  type ternary compound,  $\text{Cu}_2\text{GeSe}_3$  for optical properties study. This compound possesses considerable interest [4–9] as small band-gap semiconductors for electro-optic device applications in the IR region. We present the photoacoustic spectroscopic investigation of optical absorption for  $\text{Cu}_2\text{GeSe}_3$  obtained at temperatures T between 70 and 300 K. The temperature dependence of band gap  $E_g$  for  $\text{Cu}_2\text{GeSe}_3$  is determined from the photoacoustic signal spectra taken at different temperatures.

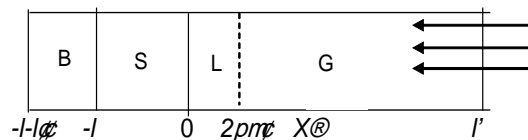
## II. EXPERIMENTAL

The quartz ampoule graphitized by acetone was filled with a charge of Cu:Ge:Se = 2:1:3 mixture in atomic ratio and then sealed off under  $10^{-6}$  Torr. Cu, Ge, and Se were 99.9999% pure. The ampoule was gradually heated from room temperature to 300 °C at the rate of 25 °C/h. The mixture was held in reserve at this temperature for one day and then heated at 8 °C/h up to 950 °C. After keeping the mixture at this temperature for one day, again it was heated to 1100 °C at the rate of 25 °C/h., melted, and then equilibrated for 2 days. Crystals were grown by cooling at 50 °C/h down to 850 °C with a stay of 24 h followed by a cooling from 850 °C to 600 °C at 10 °C/h with a stay of 24 h. The ampoule was then cooled to 500 °C at 25 °C/h and the ingot was annealed at this temperature for about one week. The furnace was then cooled to room temperature at 35 °C/h. The energy dispersive X-ray spectroscopy (EDX) performed on samples taken from the central part of the ingots revealed the composition ratio close to the ideal value 2:1:3.

The single beam photoacoustic spectroscopy (PAS) was used for optical absorption measurement. PAS consists of a PA cell containing a sensitive microphone, a 1000W Xe lamp with power supply (Muller, type SVX 1000, Germany), monochromator (Oriel 77250), and a mechanical chopper (SR540) as discussed elsewhere [10]. The PA signal produced is detected by a sensitive microphone (Bruel and Kjaer 4147) and processed by using a preamplifier and lock-in amplifier (SR530) with a chopping frequency of 110 Hz. The PA spectrum obtained from highly absorbing carbon black powder was used to normalize the spectrum of the samples.

## III. THEORETICAL MODEL

According to Rosencwagt and Gersho (R-G theory) [11,12], the signal in a gas microphone PA cell, depends on the coustic pressure disturbance at the sample-gas interface and on the transport of this pressure disturbance through the gas to microphone. The pressure fluctuation at the sample-gas interface caused by the periodic heat flow is modeled as acoustic piston which is governed by thermal diffusion equations. By solving the thermal diffusion equations the periodic variation in temperature at the sample-gas interface can be obtained. A one-dimensional analysis of the production of a photoacoustic signal in a simple cylindrical cell is shown in Fig. 1. The cell has a diameter D and length L. It is assumed that the length L is small compared to the wavelength of the acoustic signal and the microphone (not shown in the figure) detects the average pressure in the cell. The solid sample is considered to be in the form of a disc having diameter D and length l. The sample is mounted so that its back surface is against a poor thermal conductor of thickness l".



→ : Incident light; B: Backing Material; S: Sample; L: Boundary layer of gas; G: Gas column

Figure1. Cross sectional view of a simple cylindrical PA cell.

The thermal diffusion equations are

$$\frac{\partial^2 q}{\partial x^2} = \frac{1}{a} \frac{\partial q}{\partial t} \quad \text{for } -l \leq x \leq l \quad (1)$$

$$\frac{\partial^2 q}{\partial x^2} = \frac{1}{a} \frac{\partial q}{\partial t} - A e^{bx} (1 + e^{i\omega t}) \quad (2)$$

where  $A = \frac{bI_0 h}{2K}$ ; for  $-l \leq x \leq 0$

$$\frac{\partial^2 q}{\partial x^2} = \frac{1}{a} \frac{\partial q}{\partial t} \quad \text{for, } 0 \leq x \leq l \quad (3)$$

Where  $q$  is the temperature and  $h$  is the efficiency with which the absorbed light is converted into heat through non-radiative relaxation process.  $a = K/\rho C$  is the thermal diffusivity with  $K$ ,  $\rho$  and  $C$  being thermal conductivity, density, and specific heat respectively. Double prime on the parameter denotes the backing material properties; single prime denotes gas medium and unprimed denotes the solid sample.  $a = (\omega/2\alpha)^{1/2}$  is the thermal diffusion coefficient ( $\text{cm}^{-1}$ ) and  $m = 1/a$  is the thermal diffusion length ( $\text{cm}$ ).  $\omega$  denotes the modulation frequency of the incident light beam with absorption coefficient  $b$ . For the solution of  $q(x,t)$ , the appropriate boundary conditions are obtained from the requirement of temperature and heat flux continuity at the boundaries  $x = 0$  and  $x = -l$ , and from the constraint that the temperature at the cell walls  $x = l$  and  $x = -l$  is at ambient.

The general solution for  $q(x,t)$  in the cell neglecting transients can be written as,

$$q(x,t) = \begin{cases} \frac{1}{l} (x+l) W_0 + W e^{s(x+l)} e^{i\omega t}, & \text{when } -l \leq x \leq -l \\ b_1 + b_2 x + b_3 e^{bx} + (U e^{sx} + V e^{-sx} - E e^{bx}) e^{i\omega t}, & \text{when } -l \leq x \leq 0 \\ q_0 e^{-s\alpha} e^{i\omega t}, & \text{when } 0 \leq x \leq l \end{cases} \quad (4)$$

where  $W$ ,  $U$ ,  $V$ ,  $E$  and  $q_0$  are complex valued constants,  $b_1$ ,  $b_2$ ,  $b_3$ ,  $W_0$  and  $F$  are real valued constants, and  $s = (1+i)a$ .  $q_0$  and  $W$  represent the complex amplitudes of the periodic temperature at the sample-gas boundary ( $x = 0$ ) and at the sample-backing boundary ( $x = -l$ ) respectively. The quantities  $W_0$ ,  $F$  denotes the d.c. components of the temperature at the sample surface  $x = 0$  and  $x = -l$  respectively. The explicit solution for  $q_0$ , the complex amplitude of the periodic temperature at the solid-gas boundary ( $x = 0$ ) is given by,

$$q_0 = \frac{bI_0}{2K(b^2 - s^2)} \cdot \frac{(r-1)(b+1)e^{sl} - (r+1)(b-1)e^{-sl} + 2(b-r)e^{-bl}}{(g+1)(b+1)e^{sl} - (g-1)(b-1)e^{-sl}} \quad (5)$$

where  $b = \frac{K}{Ka}$ ,  $g = \frac{K}{Ka}$  and  $r = (1-i)\frac{b}{2a}$  (6)

The periodic temperature variation at the sample surface as governed by eq.(5) causes thermal waves to diffuse into the gas. The periodic diffusion produces a periodic temperature variation in the gas as given by the component of the solution (4),

$$q_{a.c.}(x, t) = q_0 e^{-s\alpha} e^{i\omega t} \quad (7)$$

Because of the periodic heating, this boundary layer of gas expands and contracts periodically and thus can be thought of as acting as an acoustic piston on the rest of the gas column, producing an acoustic signal that travels through the entire gas column. The complex envelope of the sinusoidal pressure variation can be given as

$$q = \frac{Yb}{Ka(b^2 - s^2)} \cdot \frac{(r-1)(b+1)e^{sl} - (r+1)(b-1)e^{-sl} + 2(b-r)e^{-bl}}{(g+1)(b+1)e^{sl} - (g-1)(b-1)e^{-sl}} \quad (8)$$

Where,  $Y = \frac{I_0 \rho P_0}{2T_0 l \sqrt{2}}$

If sample is considered as thermally thin ( $m \gg l$ ) the Eqn. (5) becomes

$$q_0 = \frac{bl_0}{2K(b^2 - s^2)} \cdot \frac{(r-1)}{(g+1)} \quad (9)$$

Now if the PA signal normalized (with black carbon powder) and  $q$  be the normalized PA amplitude, then

$$q = \frac{bm}{(bm+1)^2 + 1} \quad (10)$$

After simplification the optical absorption can be given as [13]

$$b = (1/m) \frac{q^2 + q(2 - q^2)^{1/2}}{(1 - q^2)} \quad (11)$$

#### IV. RESULTS

The normalized PA spectra of  $Cu_2GeSe_3$  as a function of incident wavelength at different temperatures between 70 and 300 K are shown in Fig. 1.

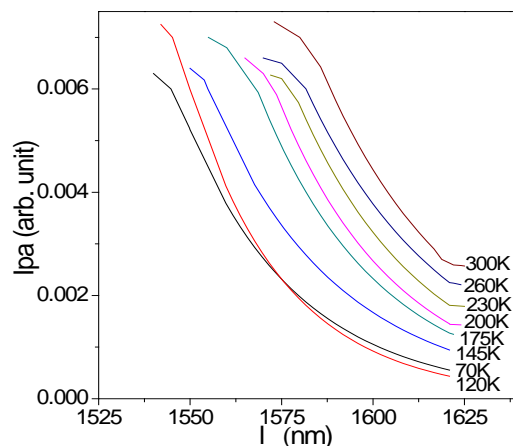


Figure 2. Normalized photoacoustic (PA) spectra of  $Cu_2GeSe_3$  as a function of incident wavelength at different temperatures

The variation of the absorption coefficient of  $\text{Cu}_2\text{GeSe}_3$  with the incident photon energy between 0.76 and 0.81 eV at different temperatures is shown in Fig. 3.

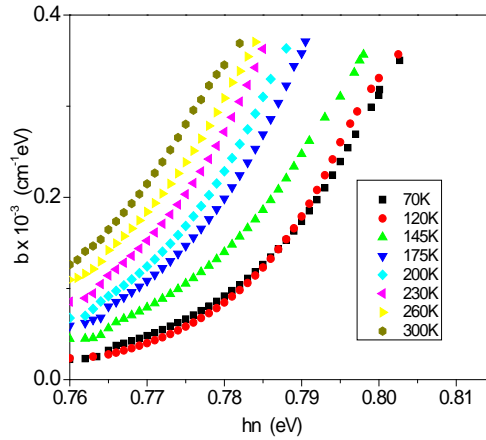


Figure 3. Absorption coefficient ( $b$ ) of  $\text{Cu}_2\text{GeSe}_3$  as a function of incident photon energy.  $b$  is determined using Fig. 1 and Eq. 11.

The absorption spectra show that the transition is allowed and direct in nature. In the high absorption region, the absorption coefficient  $b$  for the direct transition is governed by

$$bhn = A(hn - E_g)^{0.5} \quad (12)$$

The direct transition is confirmed from the plot of  $(bhn)^2$  vs  $hn$  for  $\text{Cu}_2\text{GeSe}_3$  at different temperatures between 70 and 300 K as shown in Fig. 4.

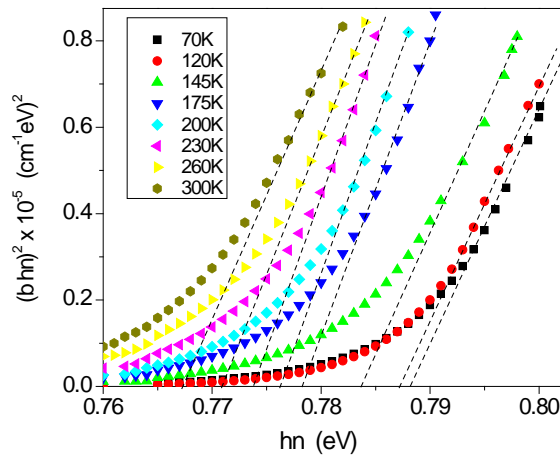


Figure 4. Plot of  $(bhn)^2$  versus  $hn$  for  $\text{Cu}_2\text{GeSe}_3$

The values of the corresponding optical bandgap ( $E_g$ ) are estimated (where the extrapolated dotted lines meet the abscissa) at different temperature. Thus the estimated bandgap as a function of temperature is shown in Fig. 5.

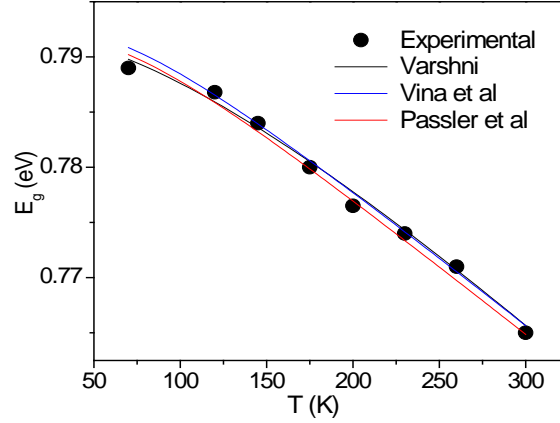


Figure 5. Temperature variation of band gap ( $E_g$ ) of  $\text{Cu}_2\text{GeSe}_3$ . Data is fitted according to Eq. (13), (14), and (16) respectively. The fitting parameters are given in Table 1.

## V. DISCUSSION

A number of models are available to describe the temperature dependence of energy band-gap or more particularly temperature induced band gap shrinkage. Varshni [14] gave the empirical model with the following equation:

$$E_g(T) = E_g(0) - \frac{gT^2}{l+T} \quad (13)$$

where  $E_g(0)$  is the band gap at 0 K,  $g$  is the slope,  $dE_g(T)/dT$  is limiting case of  $T \rightarrow \mu$  and  $l$  is a material specific parameter. This model is a combination of a linear high temperature dependence and a quadratic low temperature asymptote for  $E_g(T)$ .

Based on Bose–Einstein occupation factor for photons, Viña et al. proposed a semi empirical model [15] as

$$E_g(T) = E_g(0) - \frac{A}{\exp(Q_B/T) - 1} \quad (14)$$

where  $A$  represents the strength of the electron–phonon interaction,  $Q_B = \hbar\omega/k_B$  is the characteristic temperature attributed to the effective phonon energy on the temperature scale [15]. Based on electron-phonon interaction, another analytical model is presented by Pässler [16]. According to this model  $E_g(T)$  can be analytically derived from the expression

$$E_g(T) = E_g(0) - \int_0^{\infty} f(\epsilon) z(\epsilon, T) d\epsilon \quad (15)$$

where  $f(\epsilon)$  electron-phonon spectral function and  $Z(\epsilon, T)$  is the average phonon occupation number. Spectral function is of power-law type as  $f(\epsilon) \propto \epsilon^r$  in the energy range from 0 to a cut-off value

$\epsilon_0 = \frac{r+1}{r} k_B Q_B$ . Here  $Q_B$  is average phonon temperature [17] and  $r$  is a scaling parameter which can

be determined from experimental  $E_g(T)$  data fitting. The value of  $r$  is in the range of  $1.2 < r < 1.8$ . In such condition Eq. (3) can be revised as

$$E_g(T) = E_g(0) - \frac{SQ}{2} \left( \frac{e}{k_B T} \right)^{1/p} + \frac{aT}{c} \left( \frac{e}{k_B T} \right)^{1/p} - \frac{1}{Q} \left( \frac{e}{k_B T} \right)^{1/p} \quad (16)$$

where  $p = r+1$  and  $S = - \left( dE_g / dT \right)_{T \rightarrow \infty}$  is high-temperature limit value for the forbidden gap entropy.

Table 1. Fitting parameters for the  $E_G(T)$  data of  $\text{Cu}_2\text{GeSe}_3$  according to Eqs. (13), (14), and (16).

$E_G(0)$ (eV)	$g$ (meV/K)	$l$ (K)	$A$ (meV)	$S$ (meV/K)	$p$	$Q_B$ (K)
0.79 2	0.16	240	---	---	---	---
0.79 2	---	---	26.3	---	---	206
0.79 2	---	---	---	0.125	2.7	170

Theoretical curve fittings are shown in Fig. 5. In the three models, the values of  $E_g(0)$  are the same,  $E_g(0) \sim 0.792$  eV. In the data fitting modeled due to Varshni, band-gap shrinkage falls linearly at the rate of 0.16 meV/K ( $= g$ ) at higher temperature. The value of  $l$  is 240 K which is comparable with Debye temperature  $q_D$  [18]. The effective phonon temperature  $Q$  is related to  $q_D$  as  $Q : \frac{2}{3} q_D$  [16]. Taking  $q_D \sim 240$  K, the value of  $Q$  is estimated as 160 K which is more close to the value listed in Table 1 according to Pässler model. With Pässler model, the effective phonon energy,  $e_{\text{effective}} = k_B Q$  and the cut-off phonon energy,  $e_0 = \frac{p}{p-1} k_B Q$  are estimated as 14.7 meV and, 23.3 meV respectively. The cut-off phonon energy is comparable with the minimum optical phonon energy in ternary compounds and it is quite reasonable to assume that the temperature

## VI. CONCLUSION

Photoacoustic spectroscopy (PAS) is a good tool for the determination of optical properties of solids. In the process of modulated beam being incident on the sample, the periodic heat flow from the interior of the sample to the surrounding gas is modeled to create an acoustic piston on the rest of the gas column, producing an acoustic signal. The information contained in the acoustic signal is helpful for the determination of optical properties of solids. As an example,  $A_2B^{IV}C_3^{VI}$  type ternary compound,  $\text{Cu}_2\text{GeSe}_3$  shows very good optical properties estimation. At different temperature optical absorption spectra has been obtained in the range of 0.76–0.81 eV. PAS demonstrates high accuracy in determining temperature induced band gap shrinkage (BGS) in narrow bandgap compound  $\text{Cu}_2\text{GeSe}_3$ . The electron-phonon interaction has been taken into consideration to explain the band gap shrinkage. Data fitting was obtained by the empirical and semi-empirical models of Varshni, Varshni, and Pässler. The result obtained in PAS is in good agreement with different theoretical BGS

models.

#### REFERENCES

- [1] A. G. Bell, *Am. J. Sci.*, 20 (1880) 305-324.
- [2] A. G. Bell, *Philos. Mag.* 11 (1881) 510-528.
- [3] B. K. Sarkar, A. S. Verma, R. C. Gupta, K. Singh, *Int. J. Thermophys.*, 31 (2010) 620–629.
- [4] L. A. Kulakova, B. A., Matveev, B. T. Melekh, *J. Non Cryst. Sol.*, 266-269 (2000) 969 – 972.
- [5] L. K. Samanta, *Phys. Status Solidi A*, 100 (1987) K93 – K97.
- [6] J. J. Lee, C. S. Yang, Y. S. Park, K. H. Kim, W. T. Kim, *J. Appl. Phys.*, 86 (1999) 2914 – 2916.
- [7] M. Onoda, X. A. Chen, A. Sato, H. Wada, *Mater. Res. Bull.*, 35 (2000) 1563 – 1570.
- [8] L. V. Piskach, O. V. Parasyuk, Y. E. Romanyuk, *J. Alloys Compd.*, 299 (2000) 227 – 231.
- [9] G. Marcano, C. Rincón, L. M. de Chalbaud, D. B. Bracho, *J. Appl. Phys.*, 90 (2001) 1847 -1853.
- [10] B. K. Sarkar S. Chatterjee, R. K. Mukherjee, B. K., Chaudhuri, *J. Mater. Sci. Lett.*, 16 (1997) 1499-1502.
- [11] A. Rosencwaig, *Opt. Commun.*, 7 (1973) 305-308.
- [12] A. Rosencwaig, A. Gersho, *J. Appl. Phys.*, 47 (1976) 64-69.
- [13] B. K. Sarkar, B. K. Chaudhuri, *Int. J. Thermophysics*, 26 (2005) 295-303.
- [14] Y. P. Varshni, *Physica*, 34 (1967) 149-154.
- [15] L. Viña, S. Logothetidis, M. Cardona, *Phys. Rev. B.*, 30 (1984) 1979-1991.
- [16] R. Pässler, *Phys. Status Solidi B*, 200 (1997) 155-172.
- [17] R. Pässler, *Phys. Status Solidi B*, 216 (1999) 975-1007.
- [18] L. I. Berger, *Semiconductor materials*, 1997, CRC Press, Inc.