

## Photoacoustic measurement of the thermal diffusivity of $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ alloys

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A simple open photoacoustic cell method is demonstrated for obtaining the thermal diffusivity of  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$  alloys. It is based upon the measurement of the acoustic signal as a function of the modulation frequency in the region where the sample is thermally thick. The dependence of the measured values of the thermal diffusivity as a function of the alloy composition is also discussed.

Alloys IV-VI are well known for generating and detecting infrared radiation in the 8- to 14- $\mu\text{m}$  atmospheric window and beyond. In particular,  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$  alloys have been grown in our laboratory in the last six years, and the subsequent fabrication of infrared detectors and lasers has been reported in Ref. 1. The complete optical and thermal characterization of these crystals is of utmost importance for the controlled manufacturing of infrared detectors and lasers since power dissipation in optoelectronic devices is an important mechanism in limiting the device performance, especially in the case of semiconductor diode lasers.

Among the several physical parameters to be monitored, the thermal diffusivity  $\alpha (=k/\rho c; k$  is the thermal conductivity,  $\rho$  is the density, and  $c$  is the specific heat) is a particularly important parameter. Its measurement allows us to obtain the thermal conductivity once the density and the specific heat are known. Apart from this, the importance of  $\alpha$  as a physical parameter to be monitored is also due to the fact that, like the optical absorption coefficient, it is unique for each material. This can be appreciated from the tabulated values of  $\alpha$ , presented by Touloukian *et al.*,<sup>2</sup> for a wide range of materials, such as metals, minerals, food stuffs, biological specimens, and polymers. Of the various methods for measuring the thermal diffusivity,<sup>2,3</sup> the photoacoustic (PA) technique has proven, in recent years, to be one of the simplest and fastest ones. For a review on the photoacoustic measurements of the thermal diffusivity we refer to Ref. 3.

In this paper we report on the photoacoustic measurement of the thermal diffusivity of  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$  alloys as a function of the mole fraction  $x$  of Sn. However, instead of using a conventional closed-cell PA configuration, we propose an alternative scheme called open photoacoustic cell (OPC), as recently discussed in Ref. 4. The schematic cross section of the proposed OPC configuration is shown in Fig. 1(a). It consists of mounting the sample directly onto a circular electret microphone. The typical design<sup>5</sup> of an electret microphone consists of a metallized electret diaphragm (12- $\mu\text{m}$  Teflon with a 500–1000-Å-thick deposited metal electrode) and a metal backplate separated from the diaphragm by an air gap (45  $\mu\text{m}$ ). The metal

layer and the backplate are connected through a resistor  $R$ . The front sound inlet is a circular hole of 2 mm diameter, and the front air chamber adjacent to the metallized face of the diaphragm is roughly 1 mm long. As a result of the periodic heating of the sample by the absorption of modulated light, the pressure in the front chamber oscillates at the chopping frequency, causing diaphragm deflections, which generates a voltage  $V$  across the resistor  $R$ . In other words, the proposed OPC technique consists of using the front chamber of the microphone itself as the usual gas chamber of conventional photoacoustics. In this regard we note that the proposed technique is simply a transmission PA technique. Its advantages over conventional photoacoustic spectroscopy (PAS) is the use of a reduced gas chamber with no further transducer medium needed as in conventional PAS, minimal requirements of experimental arrangement, and no cell machining. The use of a minimal gas chamber considerably increases the signal-to-noise ratio.

Applying the simple one-dimensional thermal diffusion model of Rosencwaig and Gersho<sup>6</sup> to the OPC configuration schematically shown in Fig. 1(b) one gets for the pressure fluctuation  $p$  in the air chamber

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

where  $\gamma$  is the air specific heat ratio,  $P_0$  ( $T_0$ ) is the ambient pressure (temperature),  $I_0$  is the absorbed light intensity,  $f$  is the modulation frequency, and  $l_i$ ,  $k_i$ , and  $\alpha_i$  are the length, thermal conductivity, and thermal diffusivity of material  $i$ , respectively. Here, the subscript  $i$  denotes the sample ( $s$ ) and the gas ( $g$ ) media, respectively, and  $\sigma_i = (1+j)a_i$ , where  $a_i = (\pi f / \alpha_i)^{1/2}$  is the complex thermal diffusion coefficient of material  $i$ . In arriving at Eq. (1) we have assumed that the sample is optically opaque to the incident light and that the heat flux into the surrounding air is negligible. The optical opaqueness condition means that all the light is absorbed at the sample surface at  $z = -l_s/2$ , which is a reasonable assumption for metals and most semiconductors irradiated by visible light. For a thermally thin sample (i.e.,  $l_s a_s \ll 1$ ) Eq. (1) reduces to

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

I.e., the amplitude of the PA signal decreases as  $f^{-1.5}$  as one increases the modulation frequency. In contrast, at high modulation frequencies, such that the sample is thermally thick (i.e.,  $l_s a_s \gg 1$ ), one gets

$$p \approx \frac{\gamma P_0 I_0 (\alpha_g \alpha_s)^{1/2}}{\pi T_0 l_g k_s} \frac{e^{-l_s \sqrt{\pi f / \alpha_s}}}{f} e^{j(\omega t - \pi/2 - l_s a_s)} \quad (3)$$

Equation (3) means that, for a thermally thick sample, the amplitude of the PA signal is basically dominated by an exponential decrease with the modulation frequency as  $(1/f) \exp(-a\sqrt{f})$ , where  $a = l_s (n/\alpha_s)^{1/2}$ . The thermal diffusivity  $\alpha_s$  can then be obtained, in the thermally thick region, by an experimental data fitting from the coefficient  $a = l_c (\pi/\alpha_c)^{1/2}$  in the argument of the exponential  $\exp(-a\sqrt{f})$ . It should be emphasized that in the frequency range of our measurements the microphone frequency response is such that it increases with increas-

ing modulation frequency. Thus, the preexponential factor in the above expression ( $\sim 1/f$ ) is essentially canceled. The frequency response was measured using a 25  $\mu\text{m}$ , thick Al foil coated with a black paint and the He-Ne laser as the pumping beam. Above 50–60 Hz the recorded PA signal behaved as  $f^{-1.5}$  as predicted by Eq. (2) for a thermally thin sample. The frequency response  $\chi(f)$  was then obtained by writing the detected signal  $S$  as  $S = \chi f^{-1.5}$ . In Fig. 2 we show the microphone response  $\chi$  as a function of the modulation frequency.

The measurements were made on plate-shaped  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$  samples illuminated by a 2.15-mW He-Ne laser modulated by a rotating blade chopper. For these samples, the large optical absorption coefficient at the He-Ne laser wavelength ensures us the optical opaque condition implicit in Eq. (1). The output microphone signal was fed into a lock-in amplifier and recorded as a function of the modulation frequency. The samples were prepared by melting elemental lead, tin, and tellurium in weighed proportions in evacuated 15-mm quartz tubing, as described in Ref. 1. The materials used were 69 grades obtained from Cominco American. The crystals were grown by lowering the capsule through a Bridgman furnace. The lowering rate was 1.5 cm/day. The upper portion of the furnace was set at 930  $^\circ\text{C}$  and the lower portion at 895  $^\circ\text{C}$ . The finished crystals were sectioned into 1-mm slices. The tip, end, and middle slices from each crystal were analyzed by density measurements to determine the lead-to-tin ratio. The resulting values were used to plot a composition versus distance curve for each crystal. Slices were selected from each crystal to cover the range of composition used in this work. Laue diffraction analysis was used to assure that the sample was a single crystal. The samples thicknesses varied from 260 to 450  $\mu\text{m}$  after polishing. In Fig. 3 we show the semi-log plot of the PA signal amplitude as a function of  $\sqrt{f}$  for typical samples, namely,  $x=0$  and  $x=0.2$ . According to Eq. (3) the thermal diffusivity is obtained from the slopes  $a$  of these curves as  $\alpha = \pi(l/a)^2$ . In Fig. 4 we show the results of our measurements of  $\alpha$  as a function of the alloy composition  $x$ . The values of  $\alpha$  found for both PbTe and SnTe are in good agreement

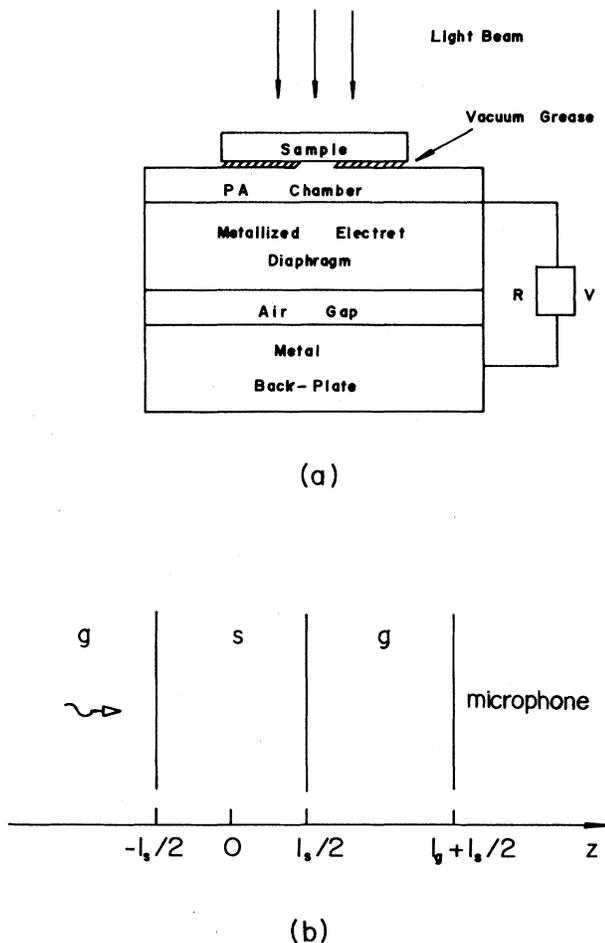


FIG. 1. (a) Proposed open photoacoustic cell (OPC) using the front air chamber of a common electret microphone as the transducer medium; (b) schematic open-photoacoustic-cell geometry.

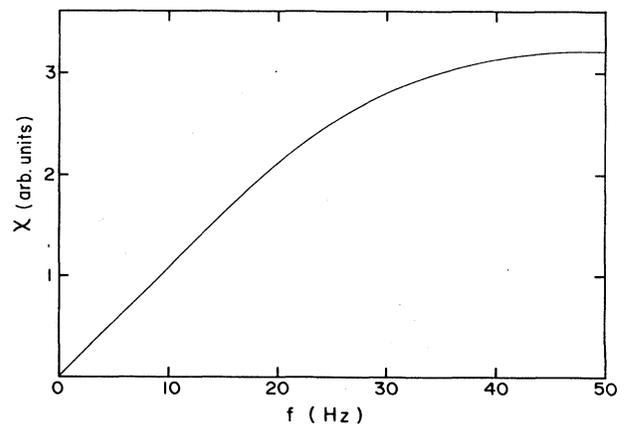


FIG. 2. Microphone response as a function of the modulation frequency.

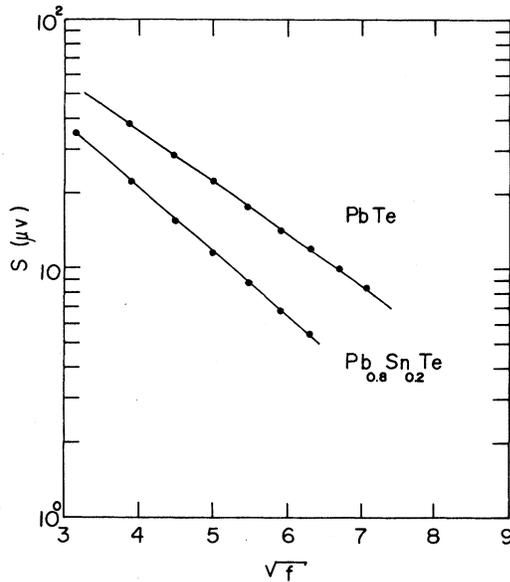


FIG. 3. Microphone output voltage as a function of the square root of the modulation frequency for a 330- $\mu\text{m}$ -thick PbTe sample and a 430- $\mu\text{m}$ -thick  $\text{Pb}_{0.8}\text{Sn}_{0.2}\text{Te}$  sample.

with the ones we get from the literature.<sup>7-10</sup> For example, in the case of PbTe, using the known values<sup>8,9</sup> of the thermal conductivity, density, and specific heat, namely,  $k=0.017$  W/cm,  $\rho=8.16$  g/cm<sup>3</sup>,  $c=0.14$  J/g, one gets  $\alpha=0.015$  cm<sup>2</sup>/s, which is in reasonably good agreement with our value of 0.014 cm<sup>2</sup>/s. Also shown in Fig. 4, by the dashed curve, is the effective thermal diffusivity we would expect for a homogeneous binary mixture of PbTe

and SnTe. According to the theory of binary mixtures,<sup>11,12</sup> the effective thermal diffusivity may be written, in the first approximation, as

$$\alpha_{\text{eff}} = \frac{(1-x)k_1 + xk_2}{(1-x)\rho_1c_1 + x\rho_2c_2}$$

Here, the subscripts 1 and 2 refer to PbTe and SnTe, respectively. Using  $\rho_1=8.16$  g/cm<sup>3</sup>,  $c_1=0.14$  J/g K,  $\rho_2=6.44$  g/cm<sup>3</sup>,  $c_2=0.41$  J/g K, together with the experimental values of  $\alpha_1=0.0142$  cm<sup>2</sup>/s and  $\alpha_2=0.0262$  cm<sup>2</sup>/s, we have calculated  $\alpha_{\text{eff}}$  as represented by the dashed curve in Fig. 4. This model tells us that the thermal diffusivity would increase monotonically from the value of PbTe as the SnTe content increases. In contrast, the behavior of  $\alpha$ , as shown in Fig. 4, is that up to  $x=0.12$  the thermal diffusivity tends to decrease, except for an initial kink at  $x=0.02$ . Above  $x=0.12$ , the thermal diffusivity exhibits a peak at  $x=0.2$  and then rises up to the value of 0.0262 cm<sup>2</sup>/s at  $x=1.0$ . This behavior resembles closely the one exhibited by the lattice thermal conductivity of  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$  alloys reported by Machonis and Cadoff.<sup>7</sup> These authors, using cation-rich alloy single crystals annealed at 150°C below the melting during two weeks, observed that the lattice thermal conductivity decreases as more SnTe is added to the PbTe, reaching a minimum around  $x=0.30$  composition, whereas for the SnTe-rich alloy composition ( $x>0.50$ ) the lattice thermal conductivity increases up to a value of 0.038 W/cm K for the SnTe. The data of these authors for the lattice thermal conductivity  $k_L$  are reproduced in Fig. 5. Here, we note that at  $x=0.4$  composition,  $k_L$ 's exhibit a peak and then rise monotonically towards the  $x=1.0$  composition value. The similarity between these data is quite remarkable. Both data showed a minimum

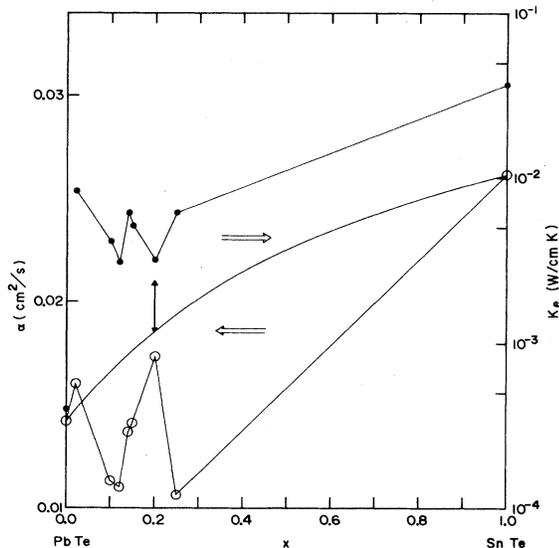


FIG. 4. Thermal diffusivity  $\alpha$  and electronic thermal conductivity  $k_e$  of our samples, obtained from the photoacoustic and Hall effect data, respectively, as a function of their composition  $x$ . The dashed-line curve represents the effective thermal diffusivity behavior one would expect for a binary mixture of PbTe and SnTe.

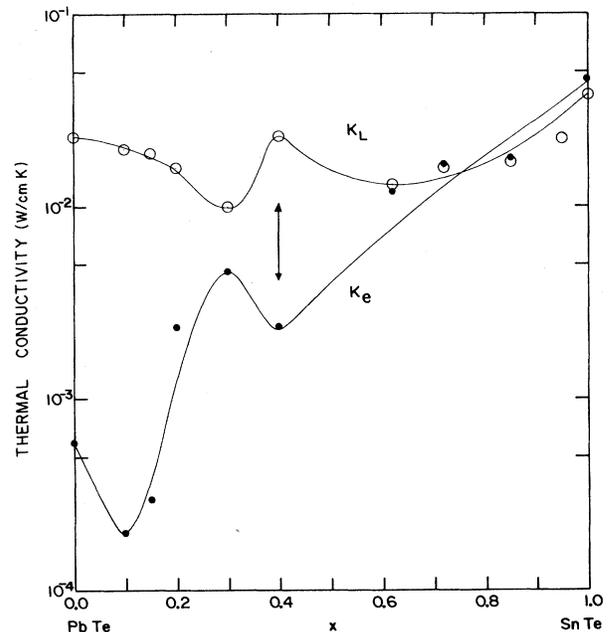


FIG. 5. Lattice and electronic thermal conductivities of the annealed  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$  samples studied in Ref. 7.

in the PbTe-rich region, and when entering the SnTe-rich region they exhibited a kink before rising monotonically towards the corresponding SnTe value. The main difference between these results is that in the case of our samples the minimum in  $\alpha$ , before the peak at  $x=0.20$ , occurred at  $x=0.12$ . In contrast, the lattice thermal conductivity from Ref. 7 exhibited a minimum at  $x=0.30$  and a peak at  $x=0.40$ . In other words, there is an approximately constant shift  $\Delta x$  of 0.20 in the positions of the extrema of these two data. These differences may be attributed to defects in the samples resulting from the different sample preparation methods employed and the fact that in Ref. 7 the samples undergo an annealing process.

To understand the observed behavior of  $\alpha$  on the composition we have calculated the electronic thermal conductivity  $k_e$ . As is well known, the thermal conductivity of a solid is due to the heat transport by both phonons and carriers. In the case of semiconductors, the carrier concentration is generally small compared with that in a metal. The lattice contribution  $k_L$  to the thermal conductivity  $k = k_L + k_e$  of a semiconductor should therefore be larger than the electronic contribution  $k_e$ . However, in doped crystals the electronic contribution may be appreciable. Using the values measured by Hall effect of the electrical conductivity of our samples we have calculated the electronic thermal conductivity from the Wiedemann Franz law, namely,

$$k_e = \chi \left( \frac{k_B}{e} \right)^2 \sigma T.$$

Here,  $\chi$  is a constant having a value of 2 for acoustic phonon scattering and  $\pi^2/3$  for the fully degenerate case. In our calculations we have assumed  $\chi=2$ , as has been found<sup>7</sup> to be the case for PbTe. The electronic thermal conductivity  $k_e$  so obtained is shown in Fig. 4. This figure shows that after an initial rise,  $k_e$  decreases,

reaches a minimum at  $x=0.12$ , and then rises as  $x$  approaches unity. Except for the behavior around the peak at  $x=0.20$ , the dependence of the thermal diffusivity on the alloy composition may be attributed to the electronic contribution to the thermal conductivity. At  $x=0.20$  the electronic thermal conductivity decreases at the same time that  $\alpha$  exhibits a peak. This suggests that the peak in  $\alpha$  at  $x=0.20$  may be due to a kink in the lattice thermal diffusivity. In fact, the same behavior was observed in the case of the annealed samples of Ref. 7, as shown in Fig. 5. We note from this figure that at the point at which  $k_L$  exhibits a peak, namely,  $x=0.40$ , the electronic thermal conductivity also exhibited a minimum.

The results presented in this paper lead to two main conclusions. The first one regards the capability of the photoacoustic technique as a simple and straightforward way of measuring the thermal diffusivity. Furthermore, the use of the proposed OPC method has some advantages over the conventional PA techniques, such as, the use of a minimal gas chamber, and, consequently, an increased signal-to-noise ratio, as well as a greater adaptability to practical restrictions imposed by experimental system requirements, especially when minimal preparation is required. The second point regards the sensitivity of the thermal diffusivity on the sample preparation. In the case of the samples used in Ref. 7, the minimum in the thermal conductivity and, consequently, on the thermal diffusivity occurred around the  $x=0.30$  composition. These samples were annealed at 150°C below the melting during a minimum of two weeks. In our case, the minimum occurred well within the PbTe-rich region, at a  $x=0.12$  composition. Our samples did not undergo any further thermal treatment after the crystal growing process. In fact, the effects of compositional and microstructural variables as well as processing conditions on the thermal diffusivity of several samples, ranging from polymers<sup>4</sup> to glasses<sup>13</sup> and ceramics,<sup>14</sup> are well known.

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