Thermal diffusivity of lead iodide


Citation: J. Appl. Phys. 83, 6193 (1998); doi: 10.1063/1.367492
View online: http://dx.doi.org/10.1063/1.367492
View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v83/i11
Published by the American Institute of Physics.

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Thermal diffusivity of lead iodide

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(Received 16 December 1996; accepted for publication 10 February 1998)

The thermal diffusivity and thermal conductivity have been determined for lead iodide PbI₂, at room temperature, using the photoacoustic spectroscopy. The result shows a thermal diffusivity \( \alpha = (25.0 \pm 0.4) \times 10^{-3} \text{ cm}^2/\text{s} \), a value very close to other semiconductors of current technological importance. The electrical conductivity is also measured and discussed. © 1998 American Institute of Physics. [S0021-8979(98)03010-2]

The sensitivity of a modulation frequency in the photoacoustic spectroscopy (PAS) technique has been amply demonstrated in various thermal diffusivity measurements of semiconductors. The fact that the PA signal depends on how the heat diffuses through the sample enables us to measure its thermal properties. Thermal diffusivity, as optical band gap energy, is an important physical parameter to be considered in device modeling. Like the thermal diffusivity, the thermal conductivity is particularly an important parameter to manufacturing devices. The measurement of thermal diffusivity \( \alpha \) allows us to obtain the thermal conductivity \( k \), once the density \( \rho \) and the specific heat \( C_v \) are known. We determine \( k \) by the relation \( k = \alpha \rho C_v \).

A better knowledge of both thermal and optical properties leads to improvements in the whole processes of device fabrication and its optimization.

Recently, we have determined the optical band gap energy of lead iodide PbI₂ by PAS, having so demonstrated the utility of this method to investigate the optical properties of semiconductors. The spectra are obtained directly from the sample and analyzed in respect to the modulator.

PbI₂ is a wide gap semiconductor, with large applicability as a room temperature detector. The detector leakage current (\( I_d \)) is proportional to the conductivity of the material. As good detectors are expected to have low value of \( I_d \), the electrical conductivity of this material would also be highly desirable.

Studying the PbI₂ thermal properties, we have performed the experimental determination for the thermal diffusivity, using PAS techniques. The conventional experimental photoacoustic setup, consisting of a periodically exciting light source and the photoacoustic cell containing the sample and microphone is show schematically in Fig. 1.

The aluminum open-ended cell used is show in Fig. 2. The cylindrical gas cavity has its top closed by a quartz window, the bottom being closed by the sample itself. This cell configuration allows different ways for the sample excitation, i.e., from its front side and also from its rear side. The choice between these possibilities determines the kind of spectrum obtained, transmission or reflection, as well as the suitable model for treatment of the experimental data.

A Kondo 50 W lamp was used as light source and the heating frequency modulated by a HMS 220 mechanical chopper, varied from 20 through 150 Hz. This modulating beam passes through a convergent lens and a water filter. The latter is used to “cool down” the light beam, cutting off the IR spectrum components.

The acoustic signal produced in the gas cavity by the sample is detected by a Sennheiser condensed microphone (model KE 4-211.2) and analyzed in respect to the modulator reference by a lock-in amplifier ITHACO 3961B.

The amplitude and the phase angle of the photoacoustic signal are recorded and interpreted as a function of the chopping frequency.

\[ E_g \approx (2.36 \pm 0.05) \text{ eV} \]

\[ T_\text{chop} = \left( \frac{v}{2\pi} \right) \approx 120 \text{ Hz} \]

\[ I_d \approx 10^{-8} \text{ A} \]

\[ \alpha \approx 5 \times 10^{-3} \text{ cm}^2/\text{s} \]

\[ k \approx 2 \times 10^{-3} \text{ cm}^2/\text{s} \]

FIG. 1. The schematic experiment setup for thermal diffusivity measurements.
For two samples of PbI₂. The thermal conductivity was obtained from the following relation

\[ k = \frac{\rho \alpha_s C_v}{s} \]

where \( k \) is the thermal conductivity, \( \rho \) is the density, \( \alpha_s \) is the thermal diffusivity, \( C_v \) is the specific heat, and \( s \) is the sample thickness.

### Table I

<table>
<thead>
<tr>
<th>Thickness (µm)</th>
<th>( \alpha_s ) (10⁻³ cm²/s)</th>
<th>( k ) (10⁻³ W/cm K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>24.8 ± 2.0</td>
<td>26.8 ± 4.3</td>
</tr>
<tr>
<td>250</td>
<td>25.0 ± 0.4</td>
<td>27.1 ± 0.9</td>
</tr>
</tbody>
</table>

For the transmission arrangement, corresponding to the rear-side excitation of a thermally thick sample, the thermoacoustic phase contribution is given by Eq. (1):

\[ \Phi = \Phi_0 + \arctan \left[ \frac{L_s \left( \pi / \alpha_s \right) f}{1 / 2} \right] - 1, \]  

where \( \Phi_0 \) is the initial phase, \( \alpha_s \) is the thermal diffusivity, \( L_s \) is the sample thickness (\( L_s = 200 \) and 250 µm), and \( f \) is the chopping frequency. These parameters are determined by a numerical least-squares fitting procedure.

In Fig. 3 we show the rear-PA intensity as a function of the chopping frequency \( f \) for the PbI₂ sample. It is shown that the PA intensity is proportional to \( f^{-x} \), for our best set of measurements \( x = -0.930 ± 0.004 \). In Fig. 4 we show the chopping frequency dependence of the rear-signal phase. The solid curve represents the best fit of the data to Eq. (1). The room temperature thermal diffusivities of PbI₂ were measured for two different samples of 200 and 250 µm, respectively. The values obtained were \( \alpha_s = (24.8 ± 2.0) \times 10⁻³ \) cm²/s and \( \alpha_s = (25.0 ± 0.4) \times 10⁻³ \) cm²/s, respectively. The better error bar, associated with the second sample, is due in part to the thickness difference, but also to the fact that we have covered its back side with a carbon-black layer. This procedure enhances the PA signal stability, but is not recommended for too thin samples.

Using the values for PbI₂ for \( \alpha_s, \rho = 6.16 \) g/cm³ and \( C_v = 0.0421 \) cal/g/K at 300 K, from Refs. 16 and 17, respectively, one gets the value of \( k \) displayed in Table I.

The \( \alpha_s \) is a physical parameter characteristic of each material. Beyond its intrinsic importance, its determination gives also our best value is one order of magnitude higher than for HgI₂ (\( \alpha_s ≈ 10⁻³ \) cm²/s), which has a wider band gap than for HgI₂. The value of \( \alpha_s \) to the PbI₂ may also be compared to the values of the very narrow band gap semiconductors PbTe (\( E_g ≈ 0.3 \) eV) and SnTe (\( E_g ≈ 0.2 \) eV). Their thermal diffusivities are \( \alpha_s = 14.2 \times 10⁻³ \) cm²/s and \( \alpha_s = 26.2 \times 10⁻³ \) cm²/s, respectively. Recently, the PA measurements of the thermal diffusivity have been done for other materials of current technological importance such as ZnSe, Te₁₋ₓ and Ge:Sb:Te alloys. For the ZnSe, Te₁₋ₓ wide band gap alloys with \( 0 ≤ x ≤ 1 \) and \( 2.12 ≲ E_g ≲ 2.63 \) eV, the values of \( \alpha_s \) are around 16.0 \( 10⁻³ \) cm²/s. Our value of \( \alpha_s = (25.0 ± 0.4) \times 10⁻³ \) cm²/s for PbI₂ is closely related to \( \alpha_s = (27.0 ± 1.4) \times 10⁻³ \) cm²/s of the Ge₁₅Sb₂₉Te₅₆ alloy.

Using a voltage divider technique, the electrical conductivity of the PbI₂ samples with gold contacts was also measured. A stable dc voltage source (HP3478A) and a multimeter (HP3478A) were used in the measurement. The value of the electrical conductivity at room temperature is about \( 5 \times 10⁻¹¹ \) Ω⁻¹ cm⁻¹, which recognize PbI₂ as a good material with potential to be used as, for instance, ionizing radiation detector.

The authors (N.V.) and (A.F.S.) would like to acknowledge financial support of the Brazilian National Research Council (CNPq-Brazil).


