Optical determination of the direct bandgap energy of lead iodide crystals

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Optical determination of the direct bandgap energy of lead iodide crystals

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The optical bandgap energy of lead iodide PbI_2, grown by Bridgman's method, is obtained by photoacoustic spectroscopy. Due to its potential applications, as a room temperature, semiconductor material detector, which may be used as a photocell, or as a x- and γ-ray radiation detector, the physical properties of PbI_2 have attracted much attention. We computed, by different methods the bandgap energy. We found the energy in a range $2.301 \pm 0.038 \leqslant \langle E_g \rangle \leqslant 2.359 \pm 0.037$ eV. © *1996 American Institute of Physics.* [S0003-6951(96)04439-7]

Lead iodine, PbI_2, is an intrinsic wide bandgap semiconductor ($E_g > 2$ eV) composed by elements with large atomic number ($Z_{Pb} = 82$ and $Z_I = 53$). This material has been the subject of many investigations due to specific technological features, for instance, its large applicability, at room temperature, as photocell, and x- and γ-ray detector.[1–6] PbI_2 is more attractive than other similar materials, such as HgI_2, because of its lower vapor pressure and lack of a destructive phase transition, which shows up at temperature around 130 °C for Hg_2.[1,2,5,7–9]

This work reports on the optical absorption of PbTz in the region of the fundamental band edge. From the analysis of the data the bandgap energy, E_g, is obtained. This parameter is of great importance in electronic and optoelectronic design. A photoacoustic spectroscopy (PAS) technique has been used for the measurements PAS has attracted much attention as useful nondestructive method for studying the optical properties of semiconductors.[8,10–15] The spectra are obtained directly from the heat generated in a sample, due to nonradiative absorption processes.

In the present investigation, the starting material for crystal growth was prepared using Merck resublimed iodine and lead powder (100 mesh), both 99.9% purity.

The elements were reacted in a vacuum sealed quartz ampoule (2 mm thickness, 18 mm inner diameter, and 25 cm length), with the weight ratio obeying the stoichiometric composition of PbI_2, resulting in a total mass of ~50 g.

The sealed ampoule was subjected to a temperature of 430 °C during 48 h to synthesize a homogeneous compound. Since the element iodine has a large vapor pressure, the furnace was heated very slowly (50 °C/day) in order to allow a considerable time for reaction. If Pb and I_2 are reacted under a higher heating rate, the released exothermic energy might heat the uncombined I_2, leading to the possibility of an explosion at the ampoule due to excessive pressure.

For single crystal preparation a tipped-end quartz ampoule (10–8 mm diam, ~200 mm length), loaded with reacted PbI_2 (~10 g) and sealed under vacuum of $\sim 10^{-5}$ Torr, was placed in a furnace for growth by vertical Bridgman's method.

After heating, the upper furnace (starting ampoule position) is maintained at about 40 °C above the melting point (408 °C) of the compound, and then, the crystal growth is performed by dropping the ampoule at a rate of about 2 mm/h through a freezing gradient of 10 °C/cm.

The growth resulted in a PbI_2 single crystal (~30 mm length, 8 mm diam) with the *c*-axis oriented perpendicular to the growth axis.

The experimental apparatus for PAS measurements is shown in Fig. 1. A 230 W tungsten lamp and a 100 W mercury lamp are used as light sources. The latter is used as a calibration source. The reflective beam passes through a collimator, a plane reflection gratings, a set of lens, and a mechanical chopper (with a modulation frequency varying between 15 to 90 Hz), producing a monochromating light focused onto a sample holder assembly which is inside the photoacoustic cell.

The PA signal produced is processed by using a preamplifier and a lock-in amplifier. The resultant PA spectra are recorded in a computer, which simultaneously displays the wavelength/energy dependent absorption intensity as shown in Fig. 2

To obtain the optical bandgap energies, we have applied the following methods.

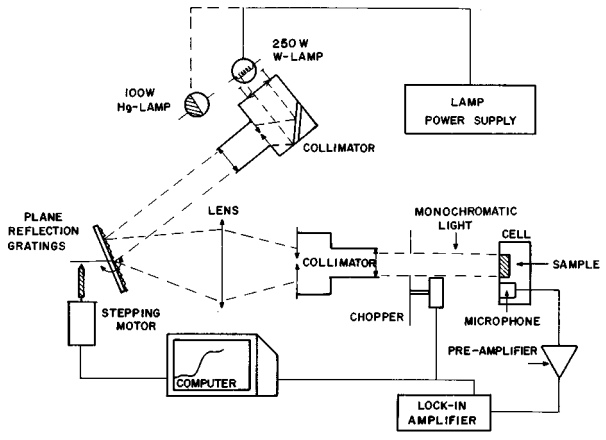

FIG. 1. The schematic experiment setup of the photoacoustic spectroscopy.

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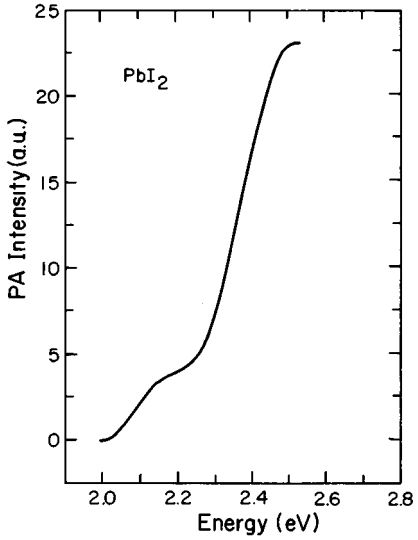

FIG. 2. Room temperature PA intensity spectrum of PbI_2 as a function of photon energy. First measurement.

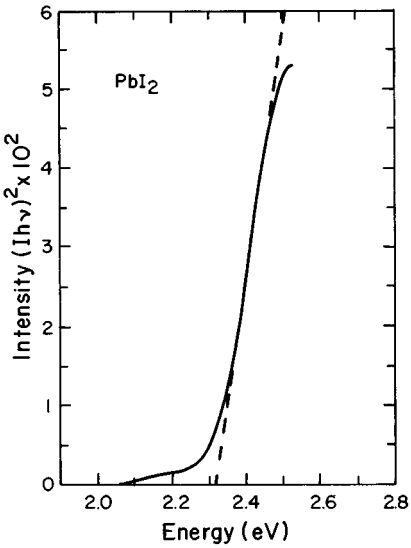

FIG. 3. Intensity $(Ih\upsilon)^2$ of PbI_2 as a function of photon energy near the fundamental absorption edge at room temperature. The dashed line crosses the energy axis at 2.317 ± 0.033 eV, corresponding to the first measurement of Table I.

TABLE I. Values of the bandgap energy for the direct transition (E_g^{dt}) and derivative (E_g^{dv}) methods, respectively, $\langle E_g\rangle$ stands for the computed average. NM is the number of measurements.

NM	E_g^{dt} (eV)	E_g^{dv} (eV)
1	2.317 ± 0.033	2.377 ± 0.031
2	2.312 ± 0.044	2.358 ± 0.042
3	2.267 ± 0.041	2.329 ± 0.041
$\langle E_g\rangle$	2.301 ± 0.038	2.359 ± 0.037

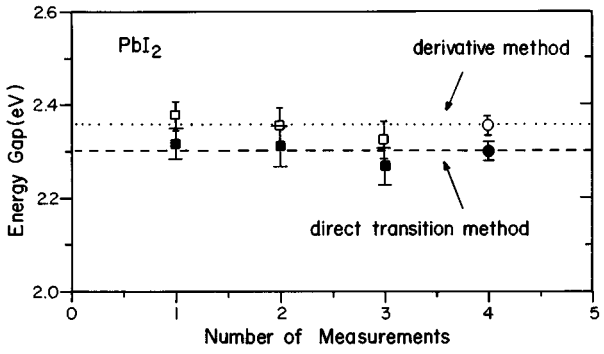

FIG. 4. Bandgap energy dependence on the repeated measurements of PbI_2, for derivative and direct transition methods, respectively. The open and full circles correspond to the averaged values of them.

(1) The first makes use of the relation for allowed direct transitions[8,16,17]

$$Ih\upsilon = A(h\upsilon - E_g^{dt})^{1/2}, \tag{1}$$

where I is the absorption intensity, A a coefficient, and $h\upsilon$ is the photon energy. The value of E_g^{dh} has been obtained by the extrapolation of the best-fit line between $(Ih\upsilon)^2$ and $h\upsilon$ up to the point where it crosses the ordinate axis, as shown in Fig. 3.

(1) In the second, we have evaluated the derivative of the intensity signal near the fundamental absorption edge, leading to E_g^{dv}.

To improve accuracy, we have repeated the measurements three times and calculated the respective errors each time. The final result was obtained by averaging over these three independent results. In Table I, we show the bandgap energies for all situations described above.

Figure 4 shows the bandgap energy as a function of Number of Measurements, NM. The open and full squares with error bars correspond to the derivative and direct transition method, respectively. The open and full circles correspond to the average of the respective methods.

In summary, we have investigated through the PAS technique, and different methods, the optical bandgap energy, of PbI_2. This semiconductor has shown to have a pronounced E_g, above 2 eV, proving to be an excellent material for detecting devices at room temperature.

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