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# Photoacoustic Measurements on Semiconducting Powder Samples

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#### Abstract

Photoacoustic measurements of several semiconducting powder samples have been performed, and the measured band-gap energies obtained are found to be in good agreement with published values. The advantages of the photoacoustic technique are briefly discussed.

### Introduction

Photoacoustic spectroscopy has been applied recently to a wide range of materials of interest. In particular, it has been proved to be a very useful tool in the study of highly light-absorbing samples (Rosencwaig 1975; McClelland and Kinsley 1976; Hordvik and Schlossberg 1977; Wetsel and McDonald 1977). Attempts have also been made to measure the band-gap energies  $E_g$  of some semiconducting samples, and the results are promising (Rosencwaig 1975). In the present preliminary note we report the determination of  $E_g$  for 10 semiconducting powder samples over the energy range of 1–4 eV by the photoacoustic technique. Previously unreported band-gap energies for several materials are presented here, and the merit of the technique is briefly discussed.

# **Photoacoustic Cell Measurements**

The photoacoustic cell was made from a block of brass in which was drilled a hole 65 mm in length and 16 mm in diameter. A window and sample holder were fitted to the ends of the hole. The powder sample was placed in a teflon disc of 10 mm diameter and 1.5 mm depth. A 1 in. (25.4 mm) diameter electret condenser microphone was mounted in a side arm of the hole, and the signal was amplified by a low-noise amplifier and then fed into a lock-in detector. The photoacoustic cell was also fitted with a needle valve and a shutoff valve to allow air or helium gas to be admitted into the cell.

A 150 W xenon lamp was used as the light source. After dispersion by a  $\frac{1}{4}$  m Spex spectrometer, the monochromatic light beam emerging from a 5 mm slit was chopped at a selected frequency and then focused onto the semiconducting powder sample by means of a lens and right-angled prism. A photoacoustic signal of about 0.1 mV was readily obtained with reasonable signal-to-noise ratio for most of the samples. In cases where the photoacoustic signals were weak (for samples such as CdI<sub>2</sub>, BaS, etc.), the cell was filled with helium gas to enhance the signals. This usually increased the gain by a factor of at least two (Wong 1978). Throughout the



Fig. 1. Photoacoustic spectra of semiconducting powder samples of: (a)  $CdI_2$  and  $Sb_2O_3$  and (b) CuI.

Powder sample	Band-gap energy in eV:		Powder	Band-gap energy in eV:	
	Photoacoustic	Optical	sample	Photoacoustic	Optical
BaS	2.84		CdI <sub>2</sub>	3.49	
CuCl	3.26	3·31 <sup>A</sup>	EuS	1.78	1 · 7 <sup>в</sup>
CuI	3.05	3·06 <sup>A</sup>	PbO	2.86	$2 \cdot 6^{A}$
CuO	2.05	1·95 <sup>A</sup>	$Sb_2O_3$	3.42	
Cu <sub>2</sub> O	2.14	$2 \cdot 2^{\mathbf{A}}$	TlBr	2.97	3·02 <sup>A</sup>

Table 1. Band-gap energies of semiconducting powder samples

<sup>A</sup> Value taken from Table 9–16 of Gray (1972). <sup>B</sup> Reflectance data.

experiment the light source was constantly monitored to ensure a constant output level; any residual variation is estimated to give an experimental error of not more than  $\pm 10\%$ .

Since the light output from the xenon-lamp spectrometer system varies over the spectral region of interest, the photoacoustic signal from the sample must be normalized against a totally light-absorbing reference sample. In the present study, the normalization consisted of dividing the photoacoustic signal from the sample by the photoacoustic spectrum of a carbon black sample. To ensure the reliability of this method, two carbon black spectra were recorded: one before the measurement on the semiconducting samples and the other after. Less than 5% variation was found in the carbon black spectra throughout the experiment.

# Results

Figs 1a and 1b show the normalized photoacoustic spectra of the powder samples  $CdI_2$ ,  $Sb_2O_3$  and CuI. The chopping frequency was 50 Hz. The arrows indicate the band-gap energies deduced from the spectra. Band-gap energies for these and other samples are presented in Table 1, where they are compared with values obtained by optical or other means. It is seen that the agreement is fairly good.

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The band-gap energies measured by the present photoacoustic technique differ slightly from those obtained by optical means. For an optical-method determination (i.e. one based on absorption, transmission, reflectance, photoconductance, etc.) the measured band-gap energy corresponds to a direct electronic transition from the top of the valence band to the lower part of the conduction band, with the restriction that the change in momentum  $\Delta k = 0$ . However, the photoacoustic method looks at the radiationless transition from the conduction band to the valence band, and is in fact a calorimetric method. As the actual structure of the conduction and valence bands is complicated (Kittel 1974), it is not unexpected that the present calorimetric  $E_g$  values differ slightly from those determined by optical means.

The photoacoustic method possesses the following advantages when compared with other methods: (i) It requires only a very small amount of powder, usually less than a few milligrams. (ii) No special sample preparation is required, and this makes the method especially suitable for use with highly unstable samples. (iii) It allows almost complete recovery of the sample after the measurement. (iv) The photoacoustic signal can be enhanced readily by replacing the air of the cell by helium gas; this is a unique facility when compared with other means of measurement. (v) There are no light-scattering problems, as the scattered light makes a negligible contribution to the photoacoustic signal.

The photoacoustic technique gives consistent determinations of band-gap energies for all semiconducting samples I have studied. Certain improvements in the present photoacoustic spectrometer are desirable. To improve its resolution, a narrower slit width should be used, though this would reduce substantially the light intensity and hence the photoacoustic signal. A much more intense light source would therefore be required. Also, the use of a double-beam photoacoustic spectrometer might eliminate the laborious point-by-point normalization process presently required.

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