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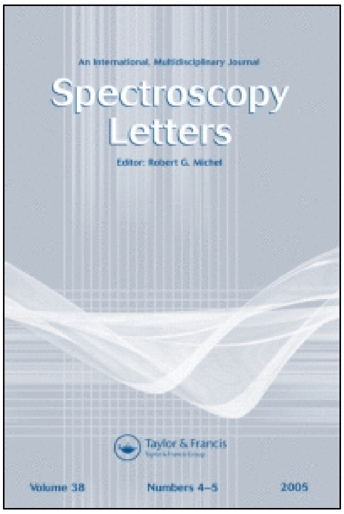

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Photoacoustic Spectroscopy of Strongly Absorbing Solids: Bismuth Tri-Iodide

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PHOTOACOUSTIC SPECTROSCOPY OF STRONGLY ABSORBING SOLIDS: BISMUTH TRI-IODIDE

Key Words: Photoacoustic Spectroscopy, Bismuth Tri-Iodide

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INTRODUCTION

We found a need to optically characterize bismuth tri-iodide, BiI_3, which has been used in antireflective thin film coatings on potassium chloride laser windows. We received a 7mm thick, 18mm diameter disc shaped sample of BiI_3 which exhibited a dark gray, glassy, metallic appearance. Several commercial spectrophotometers in the laboratory showed it to be opaque from 0.3μm to 50μm. We therefore decided to see if relevant optical data could be obtained on the sample using an in-house built photoacoustic spectrometer.

Photoacoustic spectroscopy[1-5] (PAS) is a recently developed technique for obtaining spectra of solids which are similar to optical absorption spectra. The main advantage of the method is that spectra can be obtained from a wide variety of samples...powders, amorphous solids, opaque materials, smears, gels, etc. Many of these types of samples do not yield meaningful results in conventional optical spectrophotometers. Thus PAS offers special advantages when opaque and/or highly scattering samples are to be studied.

The basic principle of the technique is the radiationless conversion into heat pulses of periodically interrupted light impinging on a sample. A gas in contact with the sample is periodically heated producing pressure changes detectable as sound. If the gas volume is enclosed and has a sensitive microphone detector in it, signals can be obtained using phase sensitive detection. Very elaborate theories[6-9] have been developed to describe the production of PAS signals. The main point we wish to show here is that absorption edges can be routinely obtained from materials which otherwise require elaborate sample preparation procedures.

EXPERIMENTAL

The PAS spectrometer used has a single beam type schematically similar to those described elsewhere.[1-5] The light source is a 900 watt xenon lamp in a Schoeffel Instrument Company housing with a Christie Electric Corporation power supply. The monochromator is a Jarrel-Ash Model 82-410 Quarter-Meter Monochromator with a Model 82-462 Omni Drive. This yields spectra from 200nm to 1000nm. A Princeton Applied Research (PARC)

Model 5204 Lock-In Analyzer was used with an Ithaco Model 167 Preamplifier for signal detection. The chopper was a PARC Variable Frequency Light Chopper Model 192 with a 20 blade chopper wheel. This offered chopping frequencies from 50Hz to 2kHz. The chopping frequency was measured by a Hewlett Packard Model 5304A Electronic Timer/Counter. The detector microphone was a GenRad Type 1961-9601 Random Incidence Response 1-inch Electret-Condenser Microphone. Signals were recorded on a Hewlett-Packard Model 7046A $X\text{-}Y_1\text{-}Y_2$ Recorder.

The photoacoustic signal is directly proportional to the light intensity incident on the sample.[6-9] When making wavelength dependent studies, a calibration of the xenon lamp spectral intensity is needed. This is achieved by making a carbon black sample using a sooty gas torch flame deposit on an Al_2O_3 platelet. It is assumed to be a flat black absorber so that its spectrum reflects that of the xenon lamp and associated optics. The relative spectral features of the resulting carbon spectrum closely follow that of published xenon spectra.

The BiI_3 disc was placed at the end of a PAS cell resting on a gray rubber gasket. The entrance window of the cell was of CaF_2. A clamp held the window and sample in place. The lock-in phase was set at 500nm and the wavelength was swept from 300 to 800nm. The chopping frequency used was 316.8Hz, the d. c. prefilter time constant was 1.1 second, the output time constant was 1 second, and the sweep rate was 40nm/minute. The carbon spectrum was taken at 111.6Hz chopping frequency with a d. c. prefilter time constant of 0.1 second, an output time constant of 0.3 second, and a sweep rate of 100nm/minute. The spectra were digitized on a Tektronix 4954 digitizing tablet and displayed on a Tektronix 4014-1 graphics terminal. Computer programs were written to divide point-by-point so that normalized results were obtainable. In this case the carbon black signal was used as the reference in the denominator.

RESULTS AND DISCUSSION

The normalized BiI_3 spectrum obtained by the above procedure is shown in Figure 1. It shows an absorption edge around 650nm. Some similar related results have appeared in the literature for specially prepared samples. Evans[10] has reported a room temperature absorption edge of around 0.62μm for a single crystal sample 0.35μm thick and for an evaporated film. Tubbs[11] studied thin films of thickness 200-600Å. He found the room temperature absorption edge around 0.62μm for a thin film and slightly greater than 0.63μm for a thicker film. Lowering the temperature shifts the edge to shorter wavelengths. With a 0.1mm thick

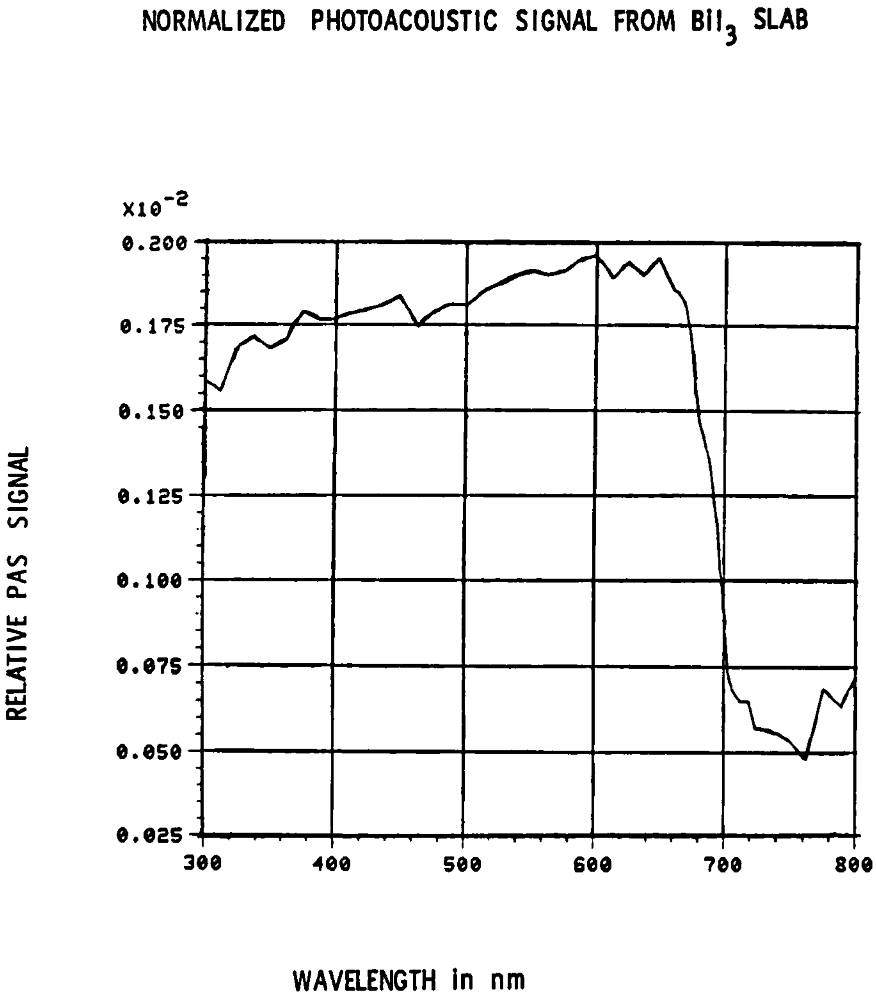

FIG. 1

sample, Shekhmameter[12] found the absorption increasing rapidly beginning near 616nm at 4.2 °K. His samples were too absorbing to see the edge. Vashchenko and

Timofeev[13,14] used reflection spectra because they claim preparing properly thin samples created technically insurmountable problems and found an edge at 2.0 eV or 0.62μm at 293 °K. Komatsu and Kaifu[15] have done more careful measurements along the same lines and find an edge at 1.97 eV or 0.630μm. Schieber et al[16] prepared crystals after four or five cycles of vapor phase purification. They found an absorption edge around 0.69μm on a 0.076mm thick sample. The results obtained here are in general agreement with values obtained with very thin samples necessary for other optical absorption techniques. In conclusion we can say that by using photoacoustic spectroscopy one can routinely obtain absorption edges on highly absorbing materials without resorting to any special sample preparation procedures.

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REFERENCES

1. A. Rosencwaig, Phys. Today, 28(9) 23 (Sept. 1975).
2. A. Rosencwaig, Anal. Chem., 17(6) 592A (May 1975).
3. A. A. King & G. F. Kirkbright, Laboratory Practice, 25 377 (1976).
4. A. Rosencwaig, Rev. Sci. Inst., 48 1133 (1977).

5. A. Rosencwaig, "Solid State Photoacoustic Spectroscopy" in Optoacoustic Spectroscopy and Detection, edited by Yoh-Han Pao (Academic Press, N.Y. 1977), Chapter 8, pp. 193-239.

6. A. Rosencwaig & A. Gersho, J. Appl. Phys. 47 64 (1976).

7. H. E. Bennett & R. A. Forman, Appl. Opt. 14 3031 (1975); 15 1313, 2405 (1976); 16 2834 (1977); J. Appl. Phys. 48 1432 (1977).

8. L. C. Aamodt, J. C. Murphy & J. G. Parker, J. Appl. Phys. 48 927 (1977).

9. F. A. McDonald & G. C. Wetsel, Jr., J. Appl. Phys. 49 2313 (1978).

10. B. L. Evans, Proc. Roy. Soc. A289 275 (1966).

11. M. R. Tubbs, J. Phys. Chem. Solids 29 1191 (1968).

12. R. I. Shekhmametev, Phys. Stat. Sol. b66 371 (1974).

13. V. I. Vaschenko & V. B. Timofeev, Soviet Physics Solid State 9 1242 (1967).

14. V. I. Vaschenko & V. B. Timofeev & I. N. Antipov, Opt. & Spect. 22 440 (1967);[Opt. & Spect. 22 813 (1967].

15. T. Komatsu & Y. Kaifu, J. Phys. Soc. Japan 40 1062 (1976).

16. M. Schieber, T. J. Davies, W. F. Schnepple, P. T. Randtke & R. C. Carlston, J. Appl. Phys. 45 5371 (1974).

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