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THE APPLICATION OF TWO-BEAM PHOTOACOUSTIC SPECTROSCOPY TO STUDY ULTRAVIOLET LIGHT-INDUCED PHOTOCHEMICAL AGEING OF ZnS PHOSPHOR POWDER

L. EAVES and P. E. SIMMONDS*
Department of Physics, University of Nottingham, University Park, Nottingham NG7 2RD, England

This paper describes a new application of the photoacoustic (PA) effect[1] in the characterization of powdered ZnS(Mn,Cu) which is the active phosphor material in electroluminescence cells[2-5]. In addition to applying conventional PAS to obtain the optical absorption spectrum of this material, we have exploited a simple double beam arrangement in which a probe light beam is used to monitor the pronounced darkening effect that occurs on the surface of the powder following illumination with near ultraviolet radiation in the presence of moisture. The technique is a convenient and, in principle, a quantitative method of determining the dependence of the rate of darkening on the wavelength of the UV irradiation. The induced change in the absorption spectrum (i.e. the change in 'colour') is measured with the conventional PA arrangement. The two-beam PA technique appears to be of general applicability for studying processes of this type.

The PA technique is now well-established as a method of studying the optical absorption spectra of materials in forms (e.g. powders, suspensions, gels) that are not amenable to study with conventional transmission methods. In addition to its spectroscopic applications, the technique has also proved to be a convenient means of monitoring changes in the physical properties of materials, e.g. during phase transitions. The technique can also be employed as a probe of surface and sub-surface structural variations of solids. These applications are discussed in a recent review[1]. The application which we describe here examines a change in the physical property of the phosphor powder, namely the UV light-induced darkening, by monitoring the PA signal produced by a second probe beam of broad-band red light.

Light-induced darkening on ZnS can occur as a bulk effect in single crystals due to the change in the charge state of impurities following capture of free carriers. In its new charge state the impurity gives rise to optical absorption in the visible part of the spectrum. The effect is observed only at low temperatures and can be reversed either by warming or by suitable optical irradiation[6]. A second light-induced darkening process[7] occurs at the surface of both micro-crystalline powder and single crystals in the presence of moisture. It is thought to arise from a photolysis effect in which near-band gap radiation produces free carriers which induce a chemical reaction between the ZnS and water contamination leaving a precipitate of Zn in the surface layer. This degradation changes the colour of the Mn-doped powder from light pastel green to dark grey in the areas that have been exposed to the UV light. The effect cannot be reversed by subsequent heating or irradiation, although bleaching has been observed under very special conditions[7]. The deleterious effect of this process on the ZnS in the powder panels is diminished by encapsulation to exclude water vapour from the atmosphere.

The arrangement used to study the dependence of the darkening on the wavelength of the UV radiation is shown schematically in Figure 1. Light from a 250 W Xenon arc lamp is dispersed through a ¼m grating monochromator with 0.3 μm blaze grating and is focussed (Beam 1) onto the ZnS powder enclosed in a photoacoustic

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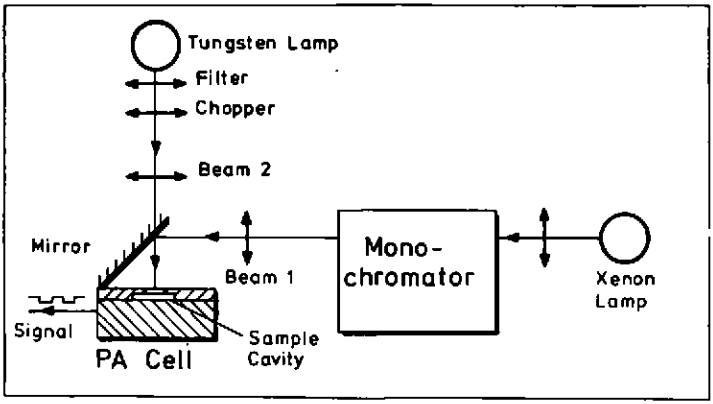
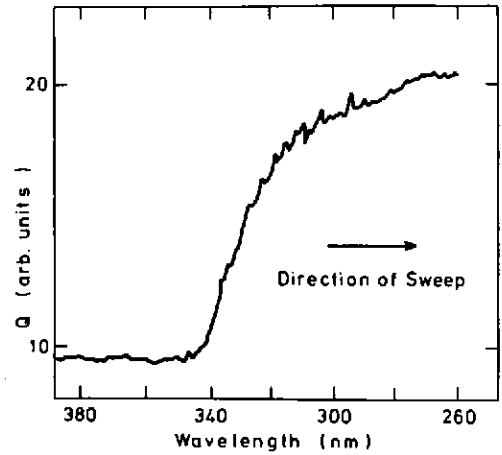


FIGURE 1: Schematic diagram of two-beam arrangement. Darkening induced by Beam 1 is monitored by PA signal produced by Beam 2. The mirror is arranged to allow the two beams to superimpose on the sample.

cell that we have used previously for studying PA spectra of various semiconductors[8]. This light beam is not chopped. A second beam of filtered light from a tungsten halogen lamp ($\lambda > 0.6$ μm) is also focussed onto the powder and its intensity is modulated with a mechanical chopper (15 Hz). This beam (Beam 2) is used as a probe to monitor any change in the optical absorption of the powder by measuring the amplitude of the PA signal which it induces. Figure 2 shows the variation of the PA signal generated in this manner as the wavelength of the incident UV radiation (Beam 1) is decreased. A sharp increase in the long wavelength PA signal is seen with UV irradiation at a wavelength near 345 nm (3.6 eV). At this wavelength the optical absorption as measured in the conventional PA arrangement also increases sharply due to excitation across the intrinsic band gap. The threshold wavelength (345 nm) for strong light-induced darkening is essentially independent of scanning rate for rates up to an order of magnitude slower than shown in Figure 2 (12 nm minute^{-1}). The decreasing slope of the PA response at shorter wavelengths results partly from the reduced light intensity for $\lambda < 340$ nm and partly from the approaching saturation of the PAS signal (i.e. the specimen eventually becomes black).



The absorption spectra of ZnS (Mn = 0.4%, Cu = 0.05% expressed in atomic percentages of the Zn concentration) and of undoped ZnS as

FIGURE 2: Increase of PA signal Q produced by probe Beam 2 ($\lambda \gtrsim 600$ nm) as the wavelength of the UV irradiation (Beam 1) is decreased. PA signal monitors light-induced darkening.

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measured using the photoacoustic technique are shown in Figure 3. The PA response, Q, is ratioed against that for carbon black Q_C. In addition to the

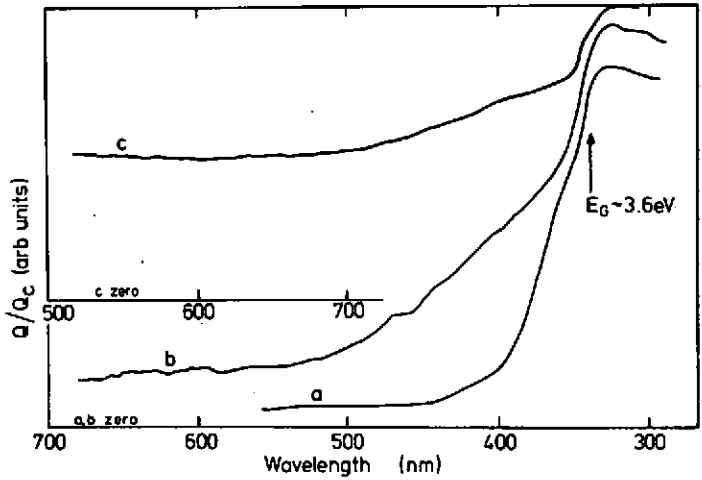

FIGURE 3: Conventional PA spectrum Q/Q_C of ZnS powders: (a) undoped ZnS; (b) ZnS (0.4% Mn, 0.05% Cu) before UV irradiation showing Mn^{2+} absorption bands; (c) ZnS(Mn,Cu) after UV irradiation showing essentially grey spectral response. The spectra are normalized against that of the carbon black response Q_C.

strong near-band edge absorption with an onset near 345 nm (3.6 eV), the doped sample also shows a broad Mn-related[8-10] absorption band with a threshold at around 540 nm (2.3 eV). The overall shape of the absorption curve for the powder appears similar to that reported in Reference 9 for a single crystal doped with a comparable concentration of Mn.

The PA spectrum of the heavily doped (0.4%) powder, taken after about 20 minutes' irradiation with UV light of wavelength near 345 nm, is also shown in Figure 3. The modulation of the normalized signal near the band gap energy is much reduced as a result of the substantial light-induced increase in absorption for wavelengths between 1,000 and 400 nm. For wavelengths beyond 1.2 μm the UV light-induced component of the absorption decreases slowly towards a negligible value for $\lambda \gtrsim 2.4$ μm.

The rate at which photo-darkening occurs for a given intensity of incident UV radiation apparently depends on the Mn doping level and on the condition of the ZnS powder. As can be seen from Figure 4, unintentionally-doped and relatively lightly doped (e.g. 0.05% Mn) material shows no detectable effects of exposure to the unfocussed output of the Xenon lamp over a period of many minutes. The monochromator was removed for these measurements, otherwise the arrangement was that shown in Figure 1.

The darkening rate of doped material is found to be strongly reduced after the powder is left in a warmed (90°C) drying chamber or under high vacuum (< 10^{-3} torr) for several hours. Exposure to a normal laboratory atmosphere restores the ability to induce the effect. In order to induce any observable darkening

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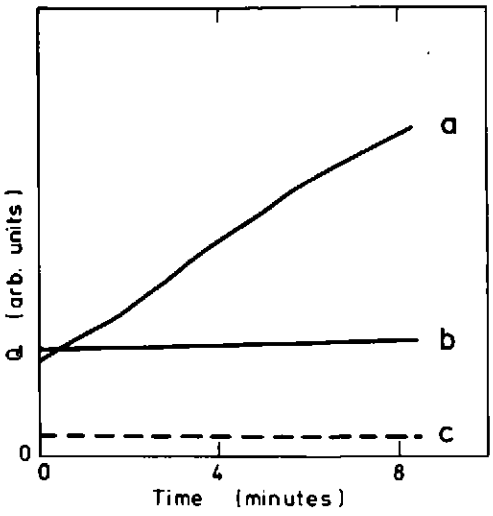

FIGURE 4: Photo-incuded darkening as measured by the PA response Q versus time for 3 ZnS powders: (a) ZnS (0.4% Mn, 0.05% Cu), after long exposure to normal atmosphere; (b) ZnS (0.4% Mn, 0.05% Cu) after drying and short (∿ 5 minutes) exposure to air; (c) undoped, untreated ZnS, no detectable increase in Q after further 45 minutes.

of undoped, undried powder, high-intensity irradiation with the strongly focussed broad-band output of the UV lamp is required. The darkening is accelerated when the powder is irradiated through a quartz window against which it is pressed lightly.

It is known[5] that the electroluminescence of the ZnS phosphor includes a significant UV contribution during a short period (∿ 1 μs) after the application of the voltage pulse. Thus, light-induced darkening may be a factor in the ageing of panels unless all traces of residual moisture are removed from the powder. The PA method appears to be a simple means of investigating photochemical reactions of this type.

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*On leave from the University of Wollongong, New South Wales, Australia.