

Short Communication

The use of time-resolved diffuse reflectance spectroscopy to observe transient absorption in transition-metal-ion doped zinc oxide powders

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Transient absorption spectra in doped (copper, cobalt, iron, manganese, nickel) and undoped ZnO powders have been obtained following pulsed sub-bandgap excitation at 532 nm, and the absorption decays have been compared on the basis of their first half-lives. With ultrabandgap excitation at 354 nm, essentially the same transient spectra are obtained, but the 520 nm emission of undoped ZnO is not observed in any of the doped materials, except for Co:ZnO at low cobalt concentrations. The following categories of transients absorption excited at 532 nm can be discerned: (i) an absorption around 400 nm with a first half-life ranging between 10 and 25 μ s which is attributed to the host ZnO lattice; (ii) an absorption, characteristic of the dopant, located at wavelengths slightly longer than those at which the dopant ground state absorbs, which has a much longer first half-life (80 - 100 μ s). In the case of Cu:ZnO, a fast transient absorption, assignable to the dopant, was observed (first half-life, 6 μ s). The production of a transient of category (ii) seems to correlate with the observation of a photocurrent in the doped electrode material when excited at 532 nm.

The use of semiconductors in solar energy research is widespread [1], and one particular aspect of this research that attracts interest is the sensitization of photostable large bandgap materials (*i.e.* with $E_g > 3$ eV) to the visible region of the spectrum. Among the methods of achieving spectral sensitization, the adsorption of a dye onto the semiconductor surface or the doping of the semiconducting material with a suitable impurity are especially popular, and have proven that it is possible to extend the response of a photoelectrochemical device to the more abundant wavelengths of the terrestrial solar spectrum. The mechanism of spectral sensitization by the dye adsorption method is well understood [2], but this is not always the case for sensitization by impurity doping. With this in mind, we have investigated transition-metal-doped zinc oxide samples (which have already been

shown [3] to possess a photoresponse up to 700 nm) by the recently developed technique of diffuse reflectance laser flash photolysis [4]. This technique, which employs diffusely reflected light to monitor a transient absorption following pulsed excitation of the sample, has been successful in detecting triplet-triplet absorption in opaque samples of microcrystalline organic ketones [5, 6], in aluminium sulphonated phthalocyanine dyed into cotton fabric [7] and in polymer-bound rose bengal [8]. We now wish to communicate preliminary results on the detection of transient absorptions in transition-metal-ion doped ZnO powders. The study of these photoinduced transients from non-luminescent centres has been conducted in parallel with a study of the electroluminescent properties of the same materials [9], and we hope that the ability to study non-luminescent centres will contribute significantly to a fuller understanding of the mechanism of impurity sensitization.

Transients are obtained by exciting ZnO powder, doped (approximately 1 at.%) with copper, cobalt, iron, manganese and nickel, at 532 nm (pulse length, 20 ns; 200 mJ pulse⁻¹). Excitation at this wavelength means that no significant electron-hole pair separation occurs across the fundamental band-gap of ZnO. Upon repeated flashing at 532 nm with the full output of the laser, no damage to the surface of the material can be seen and no spectroscopic evidence of photoinduced permanent change is found. Careful inspection of the trace shows that the transient decays back to the pre-pulse level. Figure 1 gives the observed transient difference spectrum for undoped ZnO while Figs. 2, 3 and 4 show the transient difference spectra for the metal-ion-doped oxides — no reliable data could be obtained in the region of excitation owing to the necessity of preventing scattered 532 nm laser light from entering the detection system. The short wavelength portion of Figs. 2 - 4, showing monitoring to the blue of the excitation, reveals that the undoped

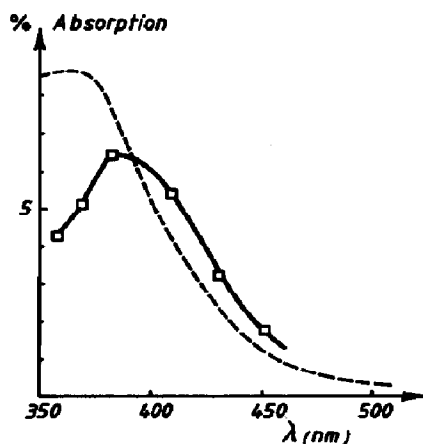


Fig. 1. Ground state diffuse reflectance spectrum *vs.* BaSO₄ (---) and transient difference spectrum (-□-) following pulsed excitation at 532 nm for undoped ZnO powder.

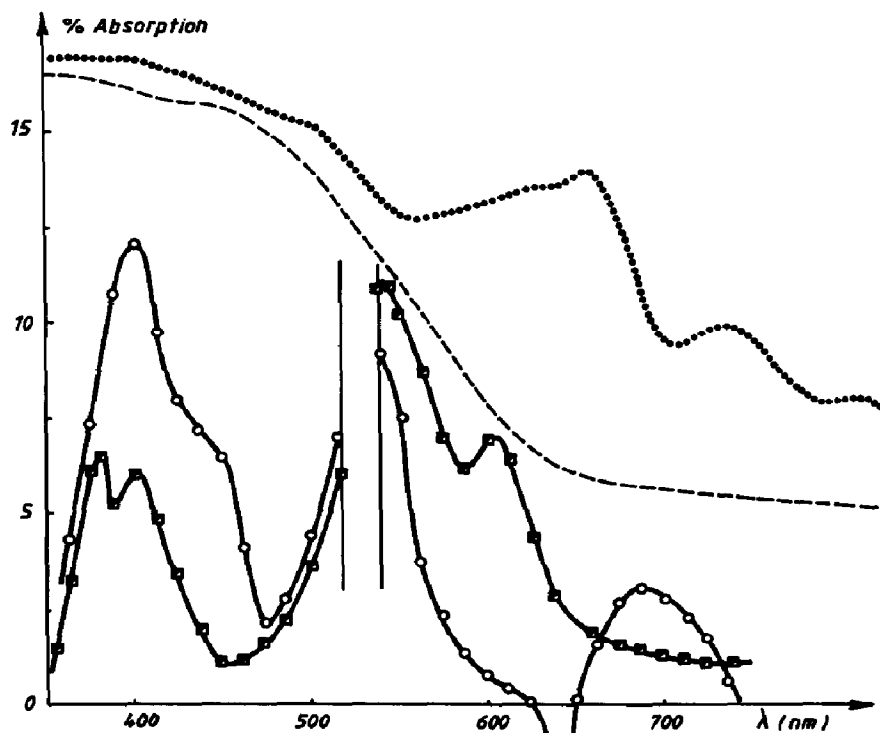


Fig. 2. Ground state diffuse reflectance spectra vs. BaSO_4 of Ni:ZnO (.....) and Mn:ZnO (---), and transient difference spectra following pulsed excitation at 532 nm for Ni:ZnO (—○—) and Mn:ZnO (—■—) powders.

material possesses a transient absorption centred at 380 nm; Mn:ZnO has a similar spectrum, whereas iron and nickel dopants shift the maximum to 400 nm, and in Cu:ZnO or Co:ZnO the maxima are found at longer wavelengths (460 nm and 470 nm respectively). With reference to the longer wavelength region of Figs. 2 - 4, in which spectra at wavelengths to the red of the excitation are depicted, it is interesting to note that the difference spectra are negative in the region 590 - 660 nm for Co:ZnO and Ni:ZnO where there is ground state absorption. The time-resolved transient difference spectrum for Co:ZnO has isosbestic points at 580 and 650 nm where the positive-negative change-over occurs (Fig. 4); this indicates that ground state depletion, transient production and decay are directly related. In addition, transient absorption decay restores the Co^{2+} to its original concentration. This also means that the real absorption spectrum of the transient species is different from that depicted in Fig. 4. Note that an increase in the cobalt concentration causes an increase in both the transient absorption at 690 nm and the ground state depletion, which provides further evidence that both phenomena are related to the presence of Co^{2+} . Since the kinetics of the transient absorption decay could not be fitted by a simple rate law, no reliable rate constants were available. However, the first half-life, *i.e.* the time taken by the signal to decrease to half ($\Delta I^0/2$) of the maximum value at

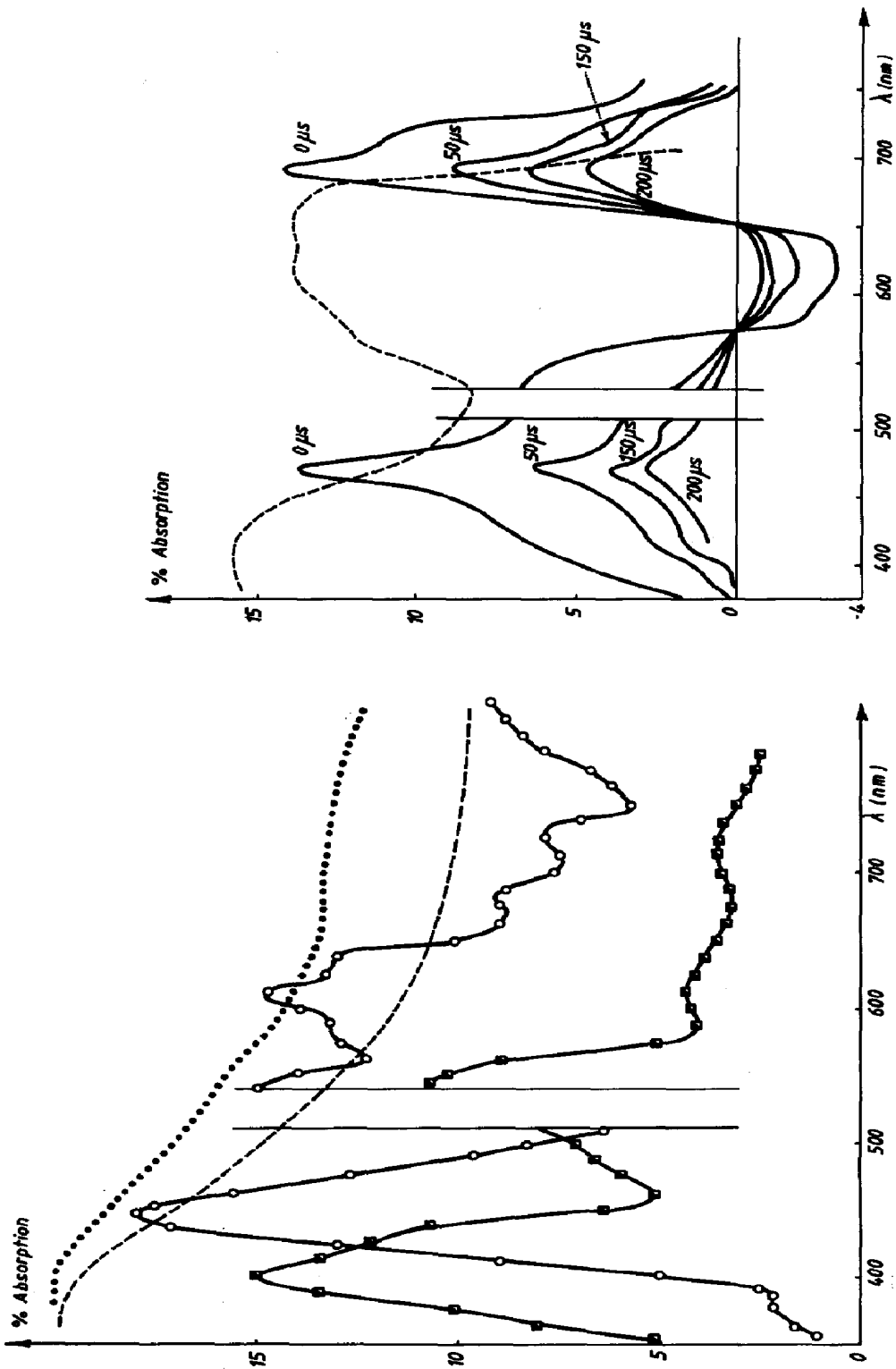


Fig. 3. Ground state diffuse reflectance spectrum vs. BaSO_4 of Cu:ZnO (.....) and Fe:ZnO (---), and transient difference spectra following pulsed excitation at 532 nm for Cu:ZnO (—○—) and Fe:ZnO (—■—) powders.

Fig. 4. Time-resolved transient difference (—) spectrum and ground state diffuse reflectance (---) spectrum of Co:ZnO powder vs. BaSO_4 .

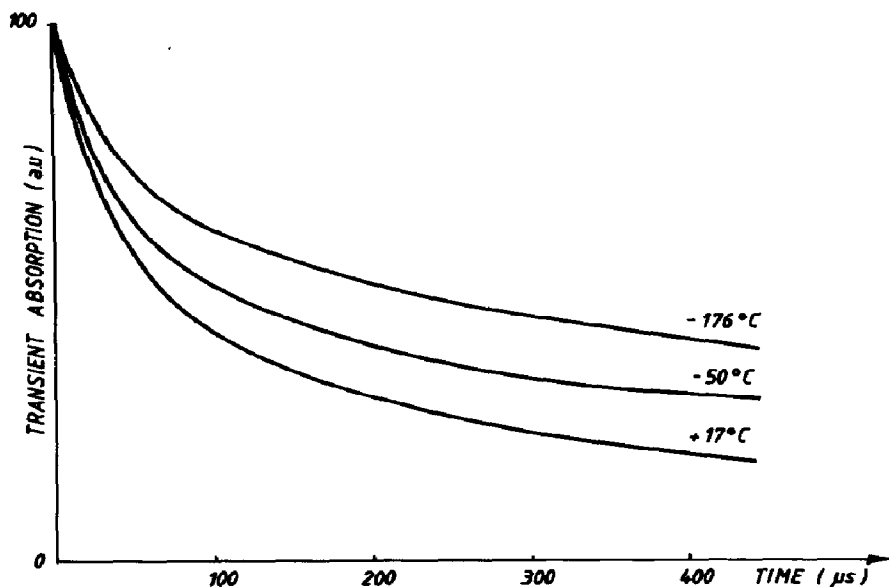


Fig. 5. Transient absorption decay of Co:ZnO monitored at 690 nm: $\lambda_{\text{exc}} = 532 \text{ nm}$; time base, $50 \mu\text{s}$ division⁻¹.

time zero (ΔI^0), has been used to give a guide to the temporal behaviour of the transients. This permits a rapid and easy comparison between different transient species created either in the same material or in ZnO containing different dopants. Figures 5 and 6 give a guideline to the reaction kinetics in the case of Co:ZnO at different temperatures (Fig. 5) and in the case of neat ZnO before (Fig. 6, curve a) and after (Fig. 6, curve b) sintering at 1200°C . Thus, from the half-lives given in Table 1, it is evident that at least two different transient species can be generated in a given material upon laser excitation. The absorption observed around 400 nm may be a transient arising from the host lattice, since it is a feature common to every sample.

Further evidence supporting the effect of metal-ion dopants on the behaviour of ZnO comes from studying the emission excited by pulsed laser light of wavelength 354 nm (50 mJ pulse^{-1}). The broad emission centred on 520 nm which is observed by ultrabandgap excitation in undoped ZnO powder is either very weak or undetectable in the metal-ion-doped oxides. The 520 nm emission is assigned to either the recombination between photoformed electrons in the conduction band and oxygen anion vacancies near the surface of ZnO [10] or to a donor-acceptor pair mechanism [11]. The inclusion of the metal-ion dopant reduces the 520 nm emission of the sample and creates centres from which only a transient absorption is detectable.

The assignment of the transient absorption in the metal-ion-doped powders is not yet fully established. However, it must be pointed out that a transient absorption with a similar half-life is observed at 690 nm for Co:ZnO with excitation at either 532 or 354 nm. The latter wavelength, absorbed mainly by the host lattice, provides excitation across the bandgap of

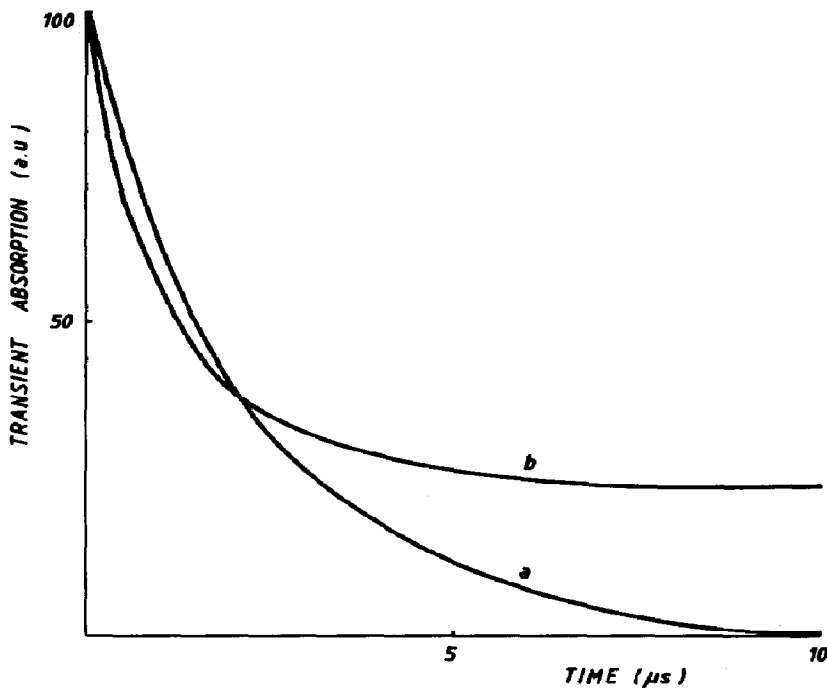


Fig. 6. Transient absorption decay of neat ZnO monitored at 405 nm: $\lambda_{\text{exc}} = 254$ nm; time base, $1 \mu\text{s}$ division⁻¹. Curve a, untreated; curve b, sintered at 1200 °C.

TABLE 1

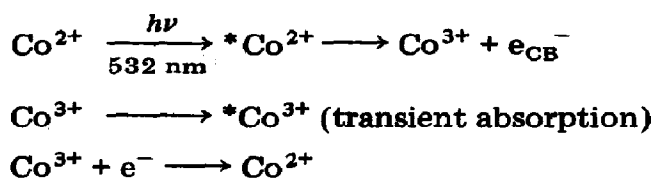
Maximum absorption λ_{max} and half-life $\tau_{1/2}$ of the observed transients in 1 at.% transition-metal-doped ZnO

	<i>Mn:ZnO</i>	<i>Fe:ZnO</i>	<i>Co:ZnO</i>	<i>Ni:ZnO</i>	<i>Cu:ZnO</i>
λ_{max} (nm)	380, 600	400	470, 690	400, 680	460, 660, 670
$\tau_{1/2}$ (μs)	$\left\{ \begin{array}{l} 22 \\ (380)^{\text{a}} \end{array} \right.$ $\left\{ \begin{array}{l} 107 \\ (600)^{\text{a}} \end{array} \right.$	$\left\{ \begin{array}{l} 10 \\ (400)^{\text{a}} \end{array} \right.$	$\left\{ \begin{array}{l} 33 \\ (470)^{\text{a}} \end{array} \right.$ $\left\{ \begin{array}{l} 80 \\ (690)^{\text{a}} \end{array} \right.$	$\left\{ \begin{array}{l} 25 \\ (400)^{\text{a}} \end{array} \right.$ $\left\{ \begin{array}{l} 100 \\ (680)^{\text{a}} \end{array} \right.$	$\left\{ \begin{array}{l} 20 \\ (460)^{\text{a}} \end{array} \right.$ $\left\{ \begin{array}{l} 6 \\ (660)^{\text{a}} \end{array} \right.$ $\left. \left. \left\{ \begin{array}{l} 5 \\ (870)^{\text{a}} \end{array} \right. \right\} \right.$

^aMonitoring wavelength.

ZnO, but the main features of the spectrum in the region 550 - 750 nm are unchanged. When exciting at 532 nm, a strong absorption at 430 nm overlaps the peak at 470 nm. Since the excited states of metal ions have very short lifetimes, at least in solution, we do not expect the observed transient absorptions to occur from such states, although the possibility of a valence band to dopant, or dopant to conduction band, transition must not be excluded. It is possible that the transient absorption takes place from the

oxidized or reduced metal-ion centre, this species having been generated through electron transfer from donor or acceptor sites. With Co:ZnO, excitation at 532 nm can induce a d-d transition [12] in Co^{2+} which leads to the corresponding excited state $^* \text{Co}^{2+}$ which, in turn, releases an electron into the conduction band of ZnO [13]. Since Co^{3+} cannot be stabilized in the ZnO lattice [13], this species could be responsible for the transient absorption in the range 550 - 700 nm; the involvement of this cobalt ion in both ground state and transient absorption is further implied by the observation that the size of the ground state depletion and the transient absorption both increase as the percentage of cobalt in Co:ZnO increases. A similar effect is observed with the photocurrent, which also increases with the concentration of cobalt when irradiating a cobalt-doped ZnO electrode in a photoelectrochemical cell [14]. The following scheme may be put forward to explain the role of cobalt:



Through the release of an electron into the conduction band, this scheme assumes a relationship between the transient absorption and the photocurrent. Indeed, those materials which are known [14] to be photoconductive at the excitation wavelength of 532 nm are precisely those which exhibit a long-lived transient absorption in the region close to their ground state absorption (namely Co:ZnO, Mn:ZnO and Ni:ZnO). In the case of Cu-ZnO where no photocurrent is produced on excitation at 532 nm [14], a different transient is observed, which decays more quickly than in the cobalt-, manganese- and nickel-doped oxides. In Fe:ZnO, the transient absorption appears to be of the ZnO-lattice type. These observations suggest that further studies of transient absorption in doped opaque semiconducting electrode materials may assist in understanding the process of spectral sensitization, and we hope to present a full discussion of the assignment of these absorptions and their relationship to photocurrent sensitization in a forthcoming publication.

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