Phase-resolved photoacoustic spectroscopy: Application to metallic-ion-doped glasses

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The possibility of using the phase shift of the photoacoustic signal of different constituents of a composite sample for resolving the spectra of the constituents, at a fixed modulation frequency, is discussed. The proposed method is experimentally tested using samples of soda-lime–silica glass doped with binary oxide mixtures.

The considerable interest in the rapid development of photoacoustic spectroscopy[1] (PAS) in recent years was largely due to its potential advantages in the study of optical-absorption spectra together with its capability for depth-profile analysis (i.e., microscopy). PAS also offers additional advantages for the characterization of thermal properties[2,3] and of nonradiative relaxation processes[4-9] in solids. Since the photoacoustic (PA) signal is sensitive only to the heat deposited in the sample, any absorbed energy which is re-radiated as fluorescence does not contribute to the signal, and it is therefore clear that PAS should provide information concerning the balance between radiative and nonradiative relaxation processes in solids. Work along these lines has been reported concerning the investigation of radiationless relaxation processes in crystals[4-6] as well as the measurement of radiative quantum efficiency of doped glasses.[7-9] These studies are usually done using the chopping-frequency dependence of the PA signal.

In this paper we propose an alternative technique using single-modulation-frequency phase detection for resolving the PA spectrum and measuring nonradiative relaxation times in solids. We consider the case in which the PA signal is generated in a sample irradiated by a modulated monochromatic light beam of intensity $I_0 \exp(j\omega t)$. The sample is described by a two-level electronic state that has a nonradiative excited-state lifetime τ and which returns to its ground state with a nonradiative efficiency η. The electronic state has an optical-absorption coefficient $\beta(\lambda)$. At a distance x from the front surface of the sample, the absorbed-energy density $W(x,t)$ is given by

$$W(x,t) = \beta I_0 e^{-\beta x} e^{j\omega t} . \tag{1}$$

This energy is absorbed by the ground state, so that the rate of change of the excited-state energy $E(x,t)$ may be written as

$$\frac{dE(x,t)}{dt} = W(x,t) - \frac{E(x,t)}{\tau} . \tag{2}$$

The photoacoustic signal is the result of the decay of

this excited state to the ground state. The corresponding heat source $Q(x,t)$ resulting from this decay process is

$$Q(x,t) = \frac{\eta}{\tau} E(x,t) = \eta \beta I_0 \frac{e^{-\beta x} e^{j\omega t}}{1 + j\omega\tau} . \tag{3}$$

Equation (3) is the distributed heat source in the sample, which determines the periodic pressure fluctuation in the gas chamber of the PA cell. Using Eq. (3) as the heat source in the thermal-diffusion model of Rosencwaig and Gersho[1] for the generation of the PA signal, and performing some tedious but straightforward calculations, one finds that, for a thermally thick sample, the variable component of the phase ϕ is given by

$$\phi = \tan^{-1}(\omega\tau) - \tan^{-1}\left[\frac{1}{1 + (2\omega\tau_\beta)^{1/2}}\right] , \tag{4}$$

where $\tau_\beta = 1/\beta\alpha_s^2$, with α_s is the thermal diffusivity of the sample. The first term in Eq. (4) corresponds to the nonradiative relaxation contribution and increases with increasing modulation frequency, whereas the second one is the contribution from the thermal diffusion in the optical-absorption depth. This contribution decreases as the modulation frequency increases, i.e., it does not contribute to the phase shift at high modulation frequencies. The physical reasoning of the phase-resolved photoacoustic spectroscopy proposed in this paper may be summarized as follows. For the sake of the argument, we assume that the sample has two absorbing centers A and B with absorption bands at the wavelengths λ_A and λ_B, respectively. These absorbing centers are associated with nonradiative relaxation times τ_A and τ_B, respectively. At a fixed modulation frequency, the PA signal is the resultant of the contributions from these two constituent centers. The heat generated at these absorption centers takes a finite time to diffuse to the sample surface (sample-air interface) and generate the acoustic signal. This time delay is a function of the optical-absorption coefficient, the nonradiative relaxation time (i.e., the time the center takes to generate the heat), and the sam-
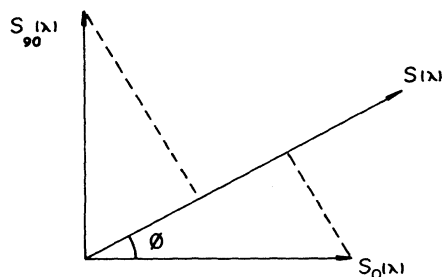
FIG. 1. PA signal at a phase ϕ expressed as a function of the 0° and 90° phase signals.

FIG. 3. PA spectra of the Co-Cr sample, at a modulation frequency of 90 Hz, as given by Eq. (4) of the text at several phase angles. At $\phi = -75°$ the spectrum is due only to the Co^{2+} contribution.

ple thermal-diffusion time. In the case of spatial segregation of constituents A and B, as in layered samples, there will be a contribution to the time lag between the signals arising from A and B due to the difference in the corresponding thermal diffusion times for the heat to reach the sample surface. In fact, this aspect was explored in Refs. 10 and 11 to demonstrate the potential of single-frequency phase-resolved photoacoustic microscopy of layered samples. Now, for the case of a spatially homogeneous distribution of absorption centers, the time lag, if any, between the signals from A and B may be mainly attributed to the difference in the nonradiative relaxation times and the characteristic times τ_β of these centers. This difference in the time the heat takes to reach the gas chamber in the PA cell produces a phase shift θ between the two signals. Thus, the actually observed signal S may be viewed as the resultant of two vectors (whose lengths S_A and S_B correspond to the signals from A and B, respectively) with an angle θ between them. Once the angle θ is known, a phase variation at 90°, say, with respect to the signal S_A, should allow only the contribution of component B to be observed and vice versa. In other words, by measuring the phase variation of the PA signal of a composite sample one may, in principle, single out the contributions of the different constituents with different nonradiative relaxa-
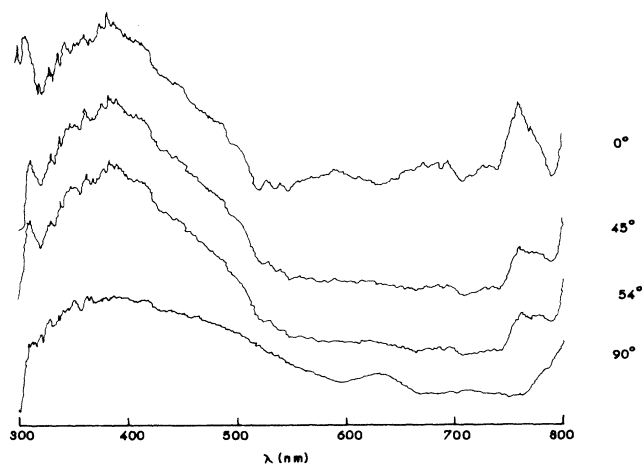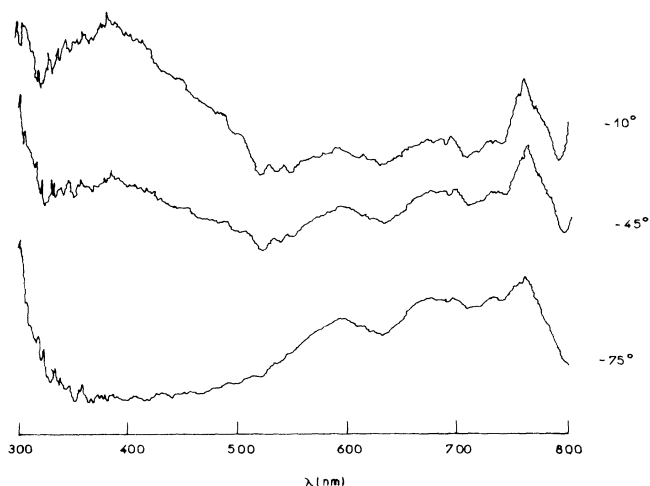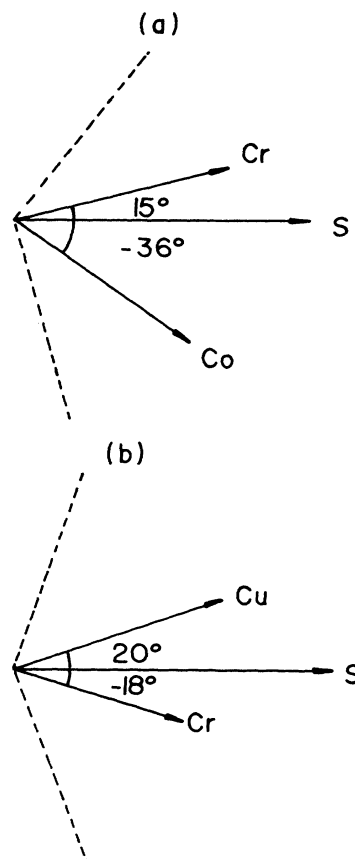

FIG. 4. Relative phase angle of the individual contributions to the PA signal at a modulation frequency of 90 Hz for the (a) Co-Cr and (b) Cu-Cr samples.

FIG. 2. PA spectra of the Co-Cr sample, at a modulation frequency of 90 Hz, as given by Eq. (4) at several phase angles. At $\phi = 54°$ the spectrum is due only to the Cr^{6+} ion.

TABLE I. Phase angles of the Co^{2+}, Cu^{2+}, and Cr^{6+} dopants in soda-lime glass samples as determined by PRPAS.

Frequency (Hz)	Co-Cr sample		Cu-Cr sample	
	ϕ_{Co} (deg)	ϕ_{Cr} (deg)	ϕ_{Cu} (deg)	ϕ_{Cr} (deg)
90	−36	15	20	−18
25	−12	25	5	−25

TABLE II. Nonradiative relaxation time τ of Co^{2+} and Cu^{2+} dopant and characteristic thermal-diffusion time τ_β of Cr^{6+} dopant in the soda-lime glass samples.

Frequency (Hz)	Co-Cr sample		Cu-Cr sample	
	τ_{Co} (Ms)	$\tau_{\beta,Cr}$ (ms)	τ_{Cu} (ms)	$\tau_{\beta,Cr}$ (ms)
90	1.3	6.5	0.6	3.8
25	1.4	4.2	0.6	4.2

tion times. The phase-resolved technique we propose in this paper is carried out at a single modulation frequency by simultaneously measuring the in-phase, $S_0(\lambda)$, and the out-of-phase, $S_{90}(\lambda)$, components as a function of wavelength. At a given phase ϕ the PA signal produced in the cell can be written in terms of $S_0(\lambda)$ and $S_{90}(\lambda)$ as (cf. Fig. 1)

$$S(\lambda)=S_0(\lambda)\cos\phi+S_{90}(\lambda)\sin\phi \ . \tag{5}$$

That is, the actual signal is the resultant of S_0 and S_{90} as shown in Fig. 1. Thus, using the experimental data for $S_0(\lambda)$ and $S_{90}(\lambda)$ and carrying out a computer-aided variation of the phase angle ϕ, we search for the phase angles at which only one of the components A or B is present in the computed spectrum. In this way we can single out the phase angles of the individual spectra of the constituents A and B without having to carry out several experimental runs at different modulation frequencies. For the spectroscopically important case of unsaturated optical absorption and a thermally thick sample, when the nonradiative relaxation processes are dominant, the relaxation time is readily obtained from the phase angle from the relation[1,12]

$$\tan\phi=\omega\tau \ . \tag{6}$$

Some caution should be exercised, however, when interpreting the physical meaning of τ. As discussed by Cottrell et al.,[12] the photoacoustically measured relaxation time is not necessarily that appropriate to the level initially excited but rather to the average lifetime of energy contained in a variety of states before becoming heat. Thus, in general, we can have a nonunique relaxation pathway consisting of several successive steps, and the measured lifetime is an average lifetime for heat production. Only when a single level dominates the deexcitation process does the measured lifetime corresponds to that of a particular level. In contrast, when the thermal diffusion in the optical absorption depth is the dominant mechanism for the phase shift, the phase angle is given by

$$\tan\phi=-\frac{1}{1+(2\omega\tau_\beta)^{1/2}} \ . \tag{7}$$

To demonstrate the usefulness of the proposed phase-resolved photoacoustic spectroscopy (PRPAS) we have applied it to the spectroscopy of doped glasses. The spectrometer consisted of a 1000 W xenon arc lamp whose beam, after being mechanically chopped, is focused on a monochromator. The monochromator output beam is then directed into a conventional PA cell in which a quarter-inch Brüel and Kjaer condenser micro-

phone is mounted in one of the walls. The microphone output signal is then fed into two lock-in amplifiers connected in parallel, with signals adjusted to be in phase. One of the lock-in signals is then shifted to be 90° out of phase with the other. The in-phase and quadrature signals are recorded as a function of wavelength. After recording the two spectra at a fixed modulation frequency, the resulting spectrum at a given phase ϕ is computed using Eq. (5).

Two samples were used soda-lime−silica glass doped with Co and Cr (the Co-Cr sample) and with Cu and Cr (the Cu-Cr sample). They were prepared from standard-grade chemicals, in the form of disks of 12 mm diameter and 800 μm thickness. The doping concentrations in each sample were 0.4 wt % CoO and 0.16 wt % CrO_3 for the Co-Cr sample, and 0.4 wt % CuO and 0.4 wt % CrO_3 for the Cu-Cr sample. Control samples of single-oxide doped glasses were also produced for checking the resolved spectra.

In Figs. 2 and 3 we show the resulting spectra at several phase angles for the Co-Cr sample, at a modulation frequency of 90 Hz. The signal at 54° (Fig. 2) exhibits only the Cr^{6+} spectrum with its characteristic absorption band at 380 nm, whereas in Fig. 3 at −75° the spectrum corresponds only to the contribution of Co^{2+}, with its typical peaks at 590 and 760 nm and a broad absorption band between 650 and 700 nm. The assignment of these individual spectra to the corresponding dopant contributions was experimentally checked using single-doped CrO_3- and CoO-glass samples. Since the signal at 54° is due only to the Cr absorption, it is of course perpendicular to the Co signal. We thus conclude that the Co signal would be at an angle of −36° with respect to S_0. Similarly, as the signal at −75° in Fig. 3 is due only to the Co absorption, we conclude that the Cr signal should be at an angle of 15°. These results are depicted in Fig. 4(a), which shows that the actually measured signal S is the resultant of the isolated Co and Cr signals with an angle of approximately 51° between them. The same procedure was also applied to the case of the Cu-Cr sample, and the resulting phase-resolved angles for the Cr and Cu contributions were found to be −18° and 20°, respectively, as shown in Fig. 4(b).

To further check the dominant contributions to the phase shift, we have also carried out the same measurements at a smaller modulation frequency, 25 Hz. As previously discussed, the nonradiative processes contribute to the phase shift in such a way as to increase the phase shift with increasing modulation frequency, whereas the thermal-diffusion contribution is such that it decreases the phase shift on increasing the modulation

frequency. In Table I we summarize our results for the dopant-ion phase angles in both samples. The modulation-frequency dependence of the phase shifts of both Co^{2+} and Cu^{2+} ions is a clear indication that the nonradiative relaxation is the dominant contribution to the phase shifts. In contrast, the Cr^{6+} phase shifts in both samples increase with decreasing modulation frequency indicating thermal diffusion as the dominant contribution. Using the data of Table I together with Eqs.

(6) and (7), we calculated the nonradiative relaxation τ for the Co^{2+} and Cu^{2+} ions, and the characteristic diffusion time τ_β for the Cr^{6+} ion. The results are summarized in Table II. Taking the average value of τ_β for the Cr^{6+} ion as 4.7 ms and using $\alpha_s = 0.005$ cm^2/s for the soda-lime glass base, we can estimate the optical-absorption coefficient of the 380-nm Cr^{6+} band to be 206 cm^{-1}.

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