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Simultaneous multiple-wavelength photoacoustic and luminescence experiments: A method for fluorescent-quantum-efficiency determination

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In this work, a method for fluorescent-quantum-efficiency determinations is presented. The method is based on the simultaneous measurement of photoacoustic and luminescent signals, after pulsed-laser excitation at different wavelengths. This method is applied to the case of Eu^{2+} ions in KCl where a luminescent quantum efficiency of 100% is obtained.

INTRODUCTION

In the evaluation of the physical properties of a luminescent material, the quantum efficiency (Φ) is obviously one of the most relevant parameters. Nevertheless, its determination is not straightforward, and although several methods exist, they do not fulfill the requirements needed for all the materials.

Photoacoustic spectroscopy, where the thermal energy generated after optical excitation is detected, constitutes a widely accepted method. In its most extended version,[1] the pressure modulation of the gas in the sample chamber is detected by using a microphone. The signal, synchronously detected with the modulated optical excitation, is proportional to the amount of heat generated in the nonradiative relaxation of the energy absorbed by the sample.

The photoacoustic method has been extensively used in the investigation of gases and liquid materials[2,3] where it becomes relatively easy to relate the photoacoustic signal of the sample with that of a standard material with known quantum efficiency. In the case of solid materials, this comparison is not so easy because of the fact that changing the sample affects the acoustic coupling with the sensors, introducing gross errors.

The solution to this problem would lie in the possibility of absolute quantum-efficiency determinations, without the comparison with standards, avoiding the change of the sample. This solution will be possible if an absolute internal reference is provided.

Although such an internal reference may be found in some cases,[4,5] generalization to the majority of solid-state materials is not obvious.

In the present work, we propose a procedure where the photoacoustic signal is detected after excitation at several wavelengths, with at least one of them having a relaxation of known quantum efficiency. This method is potentially suitable to study several impurities where it is possible to excite atomic levels leading to a 100% nonradiative relaxation, which can be used as the internal reference.

Pulsed-laser excitation provides additional advantages. In fact, one of the drawbacks of the photoacoustic methods is the relatively poor temporal response (typically milliseconds) which constitutes a severe limitation when systems having different relaxation times are studied. The use of pulsed lasers, with pulse widths in the range of a few nanoseconds, allows a better discrimination of the different deexcitation channels.

Finally, let us indicate that the simultaneous detection of photoacoustic and luminescent signals will be a further improvement which not only completes the information required to obtain the spectroscopic parameters, but also can be used to reach a higher experimental accuracy, as will be shown later.

This method is applied to study Eu^{2+} ions in KCl, which meets the conditions required. Additionally, this choice allows the comparison between this method and previous photoacoustic measurements obtained under modulated broadband lamp excitation.[6,7]

EXPERIMENTAL SETUP

The experimental setup used in this work is shown in Fig. 1. A pulsed Nd:YAG laser with the capability of generating up to the fourth harmonics is used as excitation. The laser (Quanta Ray DCR-2) gives pulses of 10 ns width, and it was used at a repetition rate of 15 Hz.

A rectangular mask of dimensions 1×3 mm^2 was used to define the area of the sample illuminated, and the fraction of energy reaching the sample was measured by using a calibrated thermal detector with a wide spectral response (Scientec 364).

The sample (X), in the form of rectangular slabs $10\times5\times1$ mm^3 in size, were cleaved from a crystal boule grown, by the Czochralski method, in the Crystal Growth Laboratory of the Universidad Autónoma de Madrid.

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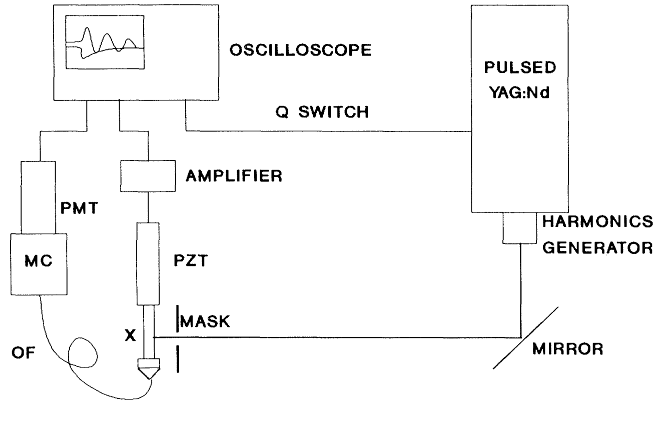

FIG. 1. Experimental setup used for the simultaneous measurement of photoacoustic and luminescent signals. PMT, photomultiplier tube; MC, monochromator; OF, optical fiber; PZT, piezoelectric transducer; and *X*, crystal.

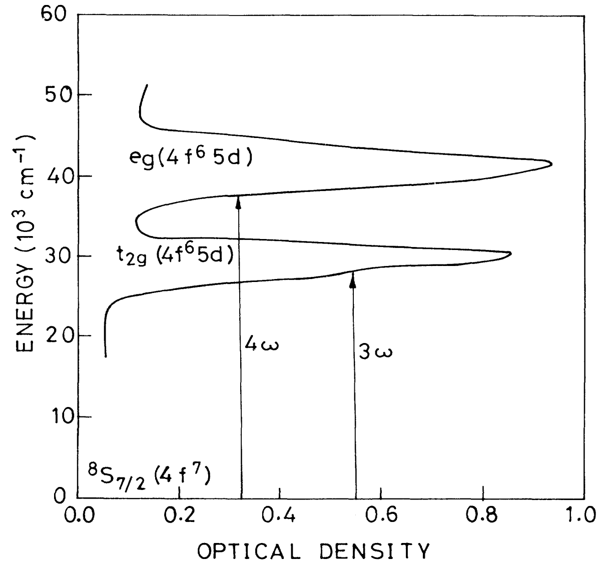

FIG. 2. Matching between the Eu^{2+} absorption bands in KCl and the third (3ω) and fourth (4ω) harmonics of Nd:YAG.

The concentration of Eu^{2+} ions in the crystal, as determined from the absorption spectrum and calibrated cross sections,[8] was 3×10^{18} ions cm^{-3}.

The optical absorption and emission spectrum were previously determined by using a Cary 14 spectrophotometer and a Jobin-Yvon JY3CS spectrofluorimeter.

Photoacoustic signals were detected by using a resonant piezoelectric transducer (PZT), built by S. E. Braslavsky from the Max Planck Institute für Stralenchemie (Mülheim), having a bandwidth of 200 kHz.[9] The samples were glued to the transducer by using cyanoacrilate, which gives the adequate acoustic coupling.

The luminescent signal was simultaneously detected by using an EMI 9558QB photomultiplier tube (PMT). The luminescence was collected with an optical fiber (OF) coupled to the entrance slit of a monochromator (MC) used to select the desired emission wavelength.

The signals from the acoustic transducer and the photomultiplier were conveniently amplified and finally recorded and averaged by using a digital oscilloscope Tektronix 2440.

EXPERIMENTAL RESULTS AND DISCUSSION

As is well known,[10] the absorption spectrum of Eu^{2+} ions in KCl crystals consists of two broad absorption bands attributed to transitions from the $^8S_{7/2}$ ground state of the $4f^7$ configuration to the $4f^65d$ configuration. In cubic symmetry the crystal field splits the d electron into two e_g and t_{2g} components, which correspond to the observed absorption bands (Fig. 2). For sixfold coordination, which is the case for Eu^{2+} ions entering substitutionally for K^+ ions in KCl, the t_{2g} is the low-lying level.

It can be observed from Fig. 2 that the two absorption bands can be reached by excitation with the third (3ω) and fourth (4ω) harmonics of the Nd:YAG laser. The absorbances, for a 1.05-mm-thick sample, were 0.55 and 0.32 at 355 nm (3ω) and 266 nm (4ω), respectively.

After excitation to any of these two bands, a single luminescent band is observed, corresponding to the $t_{2g}\rightarrow4f^7$ transition. It is important to remark that no distinct emission has been detected after excitation to the high-energy (e_g) absorption band, which indicates that the decay process between the e_g and t_{2g} levels is fully nonradiative. This nonradiative transition provides the internal reference needed for an absolute quantum-efficiency determination.

The detailed properties of the Eu^{2+} luminescence are dependent on the host matrix, and for KCl the emission band has its maximum at 422 nm, having a characteristic decay time of 1.3 μs.[6]

The time evolution of the luminescent (L) and photoacoustic (P) signals after pulsed-laser excitation is shown in Fig. 3. It can be observed that the luminescence decays exponentially after a fast rise, coincident with the excitation time, which can be identified by a small jitter in the background line.

The photoacoustic signal, at variance, is delayed from the excitation because of the time the acoustic signal needs to reach the piezoelectric transducer. This fact confirms that the signal comes from real absorption, ruling out the possibility of any contribution from scattered light.

Additionally, illumination using frequencies out of the Eu^{2+} absorption bands (e.g., using the second harmonics of the Nd:YAG laser at 532 nm) gives no detectable photoacoustic signal. Therefore the signal detected after excitation at 3ω and 4ω can be unequivocally related to processes originating after the Eu^{2+} absorption.

The signal consists of a series of compressions and expansions which give rise in the transducer to an oscillating signal (Fig. 3).

The temporal maxima of both luminescent and photoacoustic signals will be taken as a measure of the intensities generated in these processes. (In the case of photoacoustic measurements, the first maximum, which is

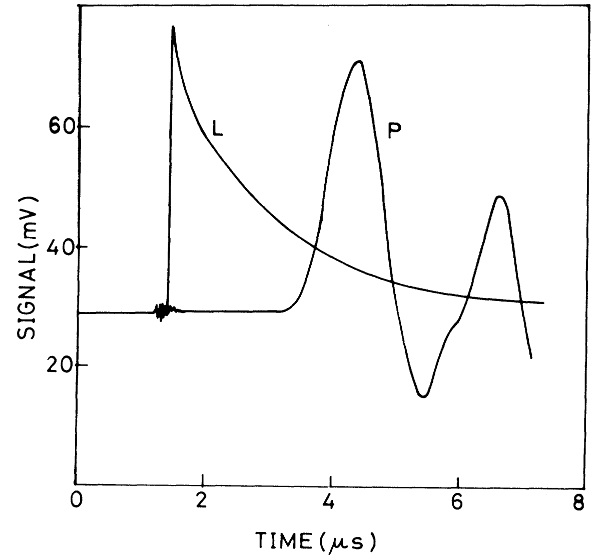

FIG. 3. Temporal response of the luminescent (L) and photoacoustic (P) signals.

the less influenced by reflections, will be taken.)

The dependence of the photoacoustic and luminescent signals ($\lambda_{\mathrm{em}}=422$ nm) with the energy of the laser pulse after (a) 3ω and (b) 4ω excitation is shown in Fig. 4. Both signals follow a linear dependence with the pulse energy, with a slope which is dependent on the spectroscopic parameters governing the different relaxation channels.

In order to quantify the observed results, the simplified energy-level scheme of Fig. 5 shall be used.

The relaxation from the bottom of the lower excited state (t_{2g}) to the $4f^7$ level, with an unknown quantum efficiency Φ, gives two thermal contributions: a first one, q_2, associated with the complementary nonradiative process, which is proportional to its efficiency $(1-\Phi)$; and a second one, q_3, associated with the nonradiative relaxation within the ground state and proportional to the quantum efficiency Φ.

Previously, the thermal contributions of the relaxations within the excited states had to be added.

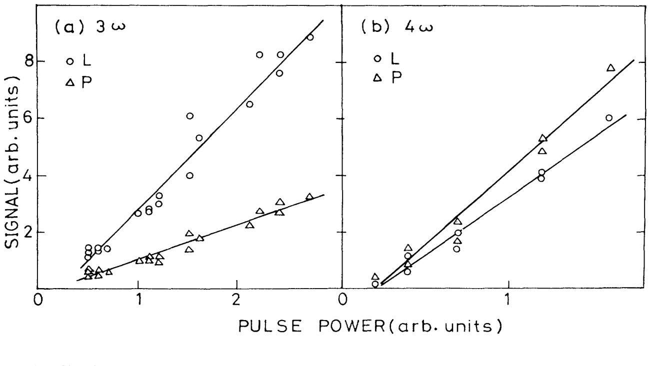

FIG. 4. Dependence of the luminescent (L) and photoacoustic (P) signals with the exciting pulse energy after (a) 3ω and (b) 4ω excitation.

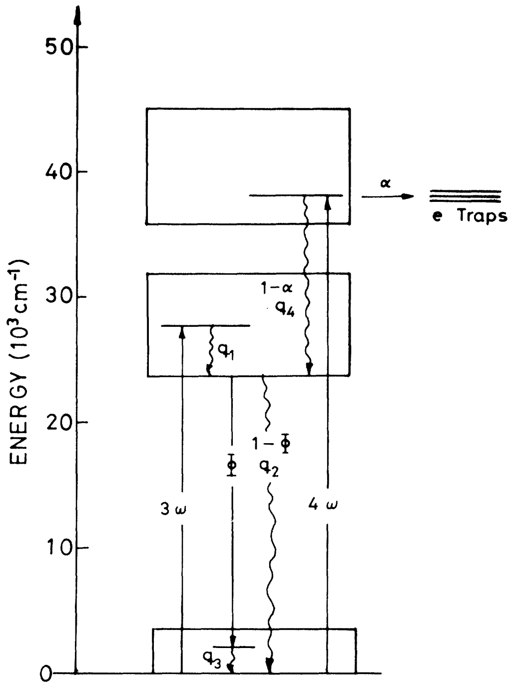

FIG. 5. Schematic energy diagram indicating the different contributions to the photoacoustic and luminescent signals.

After excitation to the t_{2g} level, at a frequency 3ω, the nonradiative relaxation within the t_{2g} level gives a thermal contribution q_1, and in the case of excitation at a frequency 4ω to the upper energy level e_g, a first nonradiative relaxation from this level to the bottom of the low-lying t_{2g} level produces a thermal contribution q_4.

At this point it is necessary to consider an important effect which has not been mentioned yet. This is the participation of other excited states in the dynamics of Eu^{2+} deexcitation.

It has been observed, in accordance with previous results of other authors[6,7] that the luminescence after e_g excitation is smaller than after t_{2g} excitation. This fact has been explained considering the participation of an additional deexcitation channel, associated with some excited state having a long lifetime.[6,7]

The participation of a long-lived excited state has been confirmed, with the detection of an afterglow emission (with the normal Eu^{2+} spectrum) after pulsed excitation to the e_g level.[11,12]

Several additional experimental results, including the detection of UV-excited photoconductivity[13] and thermoluminescence,[14] again with the Eu^{2+} emission spectrum,[15] lead to the conclusion that, after excitation to the high-energy absorption band, some Eu^{2+} ions are ionized and the electrons stabilized at suitable traps. The slow liberation from these traps and Eu recombination produces the afterglow emission or thermoluminescence if they are thermally released.

Therefore a fraction of the Eu^{2+} ions does not decay immediately to the t_{2g} level (and then to the ground state) after e_g excitation. This fraction will be designated by α (Fig. 5).

This fact is also in accordance with the detection of a dephased component in the photoacoustic signal after modulated lamp excitation.[6,7]

The main result, in connection with the present experiments, is that the recombination of these ions takes place at a time scale much longer than the times involved in the pulsed experiments here presented (μs), and therefore they do not contribute to the observed signals.

Taking into account this loss, the photoacoustic signals (per absorbed photon) generated after excitation at frequencies 3ω or 4ω can be written as

$$P(3\omega)=K_P[q_1+(1-\Phi)q_2+q_3\Phi]N_a(3\omega)\ , \tag{1a}$$

$$P(4\omega)=K_P(1-\alpha)[q_4+(1-\Phi)q_2+q_3\Phi]N_a(4\omega)\ , \tag{1b}$$

where $N_a(3\omega,4\omega)$ indicates the number of absorbed photons at the corresponding wavelength and K_P represents an instrumental constant depending on the coupling and photoacoustic response.

Because of the factor $(1-\alpha)$, which adds a new parameter, the sole comparison of photoacoustic signals at two different wavelengths [Eqs. (1a) and (1b)] cannot give enough information to determine the quantum efficiency.

Additional information is needed, which can be obtained performing simultaneous luminescence measurements.

The dependence of the luminescent signal with the number of absorbed photons can be expressed as

$$L(3\omega)=K_L\Phi N_a(3\omega)\ , \tag{2a}$$

$$L(4\omega)=K_L(1-\alpha)\Phi N_a(4\omega)\ , \tag{2b}$$

where now K_L represents an experimental constant which depends on all the efficiencies involved in the collection of luminescence and the consequent transformation in an electrical signal, including the spectral response of the experimental setup.

It is important to remember that, irrespective of the excitation wavelength, the luminescence appears at a fixed wavelength, and therefore K_L is independent of the particular wavelength used for excitation.

From Eqs. (1) and (2), it is readily obtained that

$$\frac{\partial P(4\omega)/\partial N_a(4\omega)}{\partial P(3\omega)/\partial N_a(3\omega)}=\frac{\partial L(4\omega)/\partial N_a(4\omega)}{\partial L(3\omega)/\partial N_a(3\omega)}\,\frac{q_4+(1-\Phi)q_2+q_3\Phi}{q_1+(1-\Phi)q_2+q_3\Phi}\ , \tag{3}$$

which directly relates the quantum efficiency Φ with the experimentally determined magnitudes, that is, the slopes of photoacoustic and luminescent signals vs the number of absorbed photons, and the q_i values which are directly obtained from the spectroscopic information.

Some further rearrangement, provided that $(3\hbar\omega-q_1-q_3)$ is just the energy of the emitted photons (see Fig. 5), leads to an explicit expression for the quantum efficiency:

$$\Phi=\frac{3\omega}{\omega_{\mathrm{em}}}\,\frac{\Lambda-\frac{4}{3}}{\Lambda-1}\ , \tag{4}$$

where ω is the fundamental frequency of the Nd:YAG emission, ω_{em} the frequency of Eu^{2+} emission, and

$$\Lambda=\frac{\partial P(4\omega)/\partial N_a(4\omega)}{\partial P(3\omega)/\partial N_a(3\omega)}\,\frac{\partial L(3\omega)/\partial N_a(3\omega)}{\partial L(4\omega)/\partial N_a(4\omega)}\ . \tag{5}$$

From a linear least-squares fitting of the data of Fig. 4 and the spectroscopic data (ω_{em}), a value $\Phi\approx 1.04\pm 0.24$ is obtained.

The main source of uncertainty comes from the measurement of the absorbed power and then in the evaluation of the number of photons absorbed, $N_a(3\omega,4\omega)$.

Therefore it is possible to improve the accuracy making a direct comparison of the photoacoustic and luminescent signals, avoiding the measurements of the absorbed power. This procedure takes advantage of the fact that both P and L are taken simultaneously for each excitation energy.

These results are given in Fig. 6 for 3ω and 4ω excitation. Comparing this figure with Fig. 4, it is apparent how the experimental indetermination has been reduced.

From Eqs. (1) and (2), we obtain again expression (4), where now

$$\Lambda=\frac{\partial P(4\omega)/\partial L(4\omega)}{\partial P(3\omega)/\partial L(3\omega)}\ , \tag{6}$$

and therefore the comparison of the two slopes of the lines in Fig. 6 gives directly the value of the luminescent quantum efficiency Φ, which is now evaluated with a smaller uncertainty. After a least-squares fitting of the data of Fig. 6, a value $\Phi=1.04\pm 0.06$ is now obtained.

This result indicates that the nonradiative deexcitation channels for the t_{2g} level are practically irrelevant.

This is consistent with the agreement between the calculated and experimental values of the t_{2g} lifetime[6,7] and

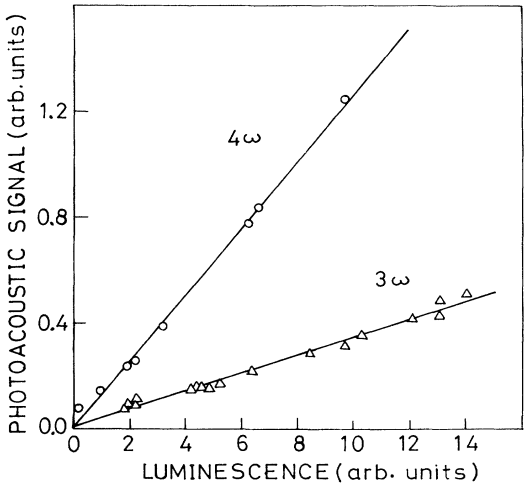

FIG. 6. Direct comparison of the photoacoustic and luminescent signals simultaneously generated after 3ω and 4ω excitation.

with the reported[16] independence of the Eu^{2+} luminescence with temperature up to 400 K, although a smaller value ($\Phi \approx 0.6$) obtained by using modulated broadband lamp excitation and a multiparameter fitting has been previously reported in the literature.[7]

The discrepancy between the present results and those reported in Ref. 7 could be related to the differences in temporal resolution of both methods.

Pulsed techniques provide a better temporal resolution than modulated experiments, which could have some contribution in the photoacoustic signal arising from the slow release of electrons from the traps. This would produce an additional heat, causing the apparent reduction in the quantum efficiency.

Let us finally indicate that at high-pulse-energy excitation, a departure from linearity of either photoacoustic and luminescence signals has been observed.

A full characterization and interpretation of these nonlinearities is in progress.

Let us conclude by indicating that the method here employed is adequate to determine precisely luminescent quantum efficiencies in many solid-state systems, where the appearance of fully nonradiative transitions is quite common, providing then an internal reference for absolute determination.

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