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Photoacoustic determination of the luminescent quantum efficiencies of F_2^+ and $(F_2^+)_{\text{H}}$ centres in NaCl:OH⁻ crystals

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Received 1 August 1989, in final form 13 November 1989

Abstract. Photoacoustic (PA) measurements of F_2^+ centres in additively coloured NaCl:OH⁻ crystals have been carried out. The 1.06 μm line of a pulsed Nd:YAG laser was used for excitation and the PA signal was detected with a piezoelectric detector.

The F_2^+ centres were produced by photoaggregating samples *in situ*, allowing measurements of the PA signal as a function of the centre concentration to be obtained without altering the experimental geometry. In agreement with previous observations of temperature independence for both lifetime and luminescence intensity, a quantum efficiency of almost 100% was measured.

The relative quantum efficiency of $(F_2^+)_{\text{H}}$ centres was determined by a comparison of the luminescent emissions of both centres at liquid-nitrogen temperature.

1. Introduction

Laser action using F_2^+ and $(F_2^+)_{\text{H}}$ centres has been obtained in several alkali halide matrices [1–3]. By using different hosts, it is possible to cover a broad emission range extending from 0.85 to 4.0 μm , which is of particular interest to the fields of molecular spectroscopy, fibre optic communications and the physics of narrow-band-gap semiconductors [2, 3].

The IR transition $2p\sigma_u \rightarrow 1s\sigma_g$ of the F_2^+ -type centres displays almost ideal properties for laser emission such as a high oscillator strength ($f \approx 0.2$) and the absence of excited-state absorptions [2, 3]. In addition, a luminescent intensity which is independent of temperature from liquid-helium temperature to almost 200 K [4], a decay time which is also temperature independent in the range 85–330 K [5] and the high light-to-light conversion obtained in laser action [3, 4] has led to the assumption of a nearly 100% luminescent quantum efficiency.

Nevertheless, until now no direct determination of the quantum efficiency of F_2^+ or $(F_2^+)_{\text{H}}$ centres has been performed. This could be done by using photoacoustic (PA) techniques [6] as has been proved, first in dye solutions and then in solid materials [7–11]. The present paper reports PA measurements under pulsed excitation of F_2^+ centres in NaCl which allows direct evaluation of the luminescent quantum efficiency of

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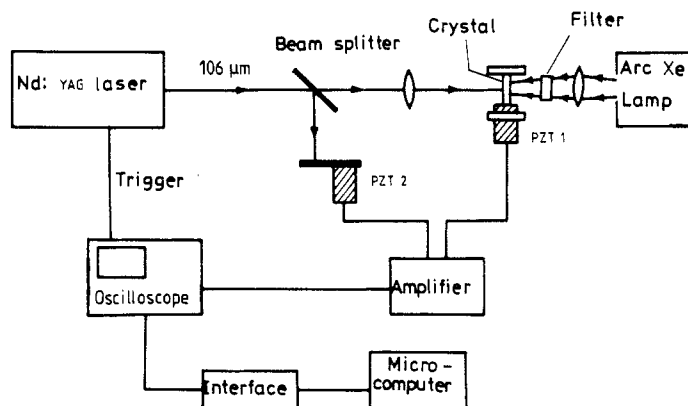


Figure 1. Schematic representation of the experimental set-up for PA measurements.

these centres. Low-temperature (77 K) $F_2^+ \rightarrow (F_2^+)_{\text{H}}$ transformation then also allows a comparative determination of the luminescent quantum efficiency of $(F_2^+)_{\text{H}}$ centres.

2. Experimental methods

NaCl:OH⁻ crystals were grown by the Czochralski method in the Crystal Growth Laboratory of the Universidad Autónoma de Madrid using Suprapur NaCl as the starting material. Samples $10\text{ mm} \times 5\text{ mm} \times 1\text{ mm}$ in size were cut from the boule and additively coloured at 720°C in a heat pipe using sodium vapour at 60 Torr.

PA measurements were made using the experimental set-up shown in figure 1. The $1.06\text{ }\mu\text{m}$ line from a pulsed Nd:YAG laser (10 ns width) is used to excite the $1s\sigma_g \rightarrow 2p\sigma_u$ transition of the F_2^+ centre in NaCl. The PA signal was detected with a piezoelectric transducer coupled to the sample. The transducer was made in the Universidad de La Plata (Argentina) using a lead zirconate titanate (PZT-5A) cylinder, following the scheme described by Patel and Tam [12]. The PA signal of charcoal, taken with a second PZT transducer, was used to account for fluctuations in incident laser intensity.

The signal, suitably amplified, was recorded with a Philips digital oscilloscope model PM-31, triggered by the Nd:YAG laser. The data were recorded through a data acquisition and control adapter linked to an IBM/PS-2 microcomputer.

In order to maintain the experimental geometry, the F_2^+ centres were created, starting with freshly quenched samples, by *in situ* F-light illumination from a 100 W arc Xe lamp filtered through a CuSO_4 solution 1 cm thick.

A similar procedure was followed to transform the F_2^+ into $(F_2^+)_{\text{H}}$ centres, which is effectively accomplished at 77 K [13–15].

Luminescence measurements have been performed under Xe lamp excitation using Jobin-Yvon H-20 and H-25 monochromators for excitation and emission, respectively, and using a Judson IR Ge detector.

3. Experimental results and discussion

The absorption spectrum of NaCl:OH⁻ crystals consists of the OH⁻ band and oxygen- and hydrogen-related bands in the UV with the F and F-aggregate bands in the visible and near IR [13, 14].

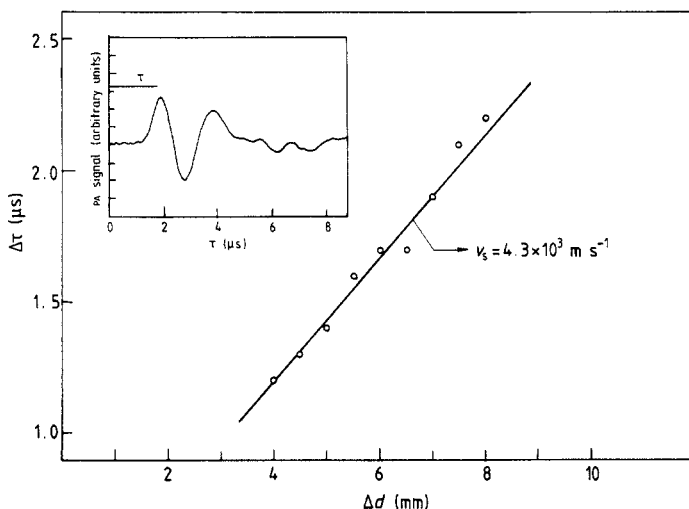


Figure 2. Dependence of the change $\Delta\tau$ in delay time on the change Δd in the laser beam-transducer separation. The inset shows a typical PA signal.

In well quenched samples, the visible and near-IR spectrum consists mainly of the F band and additional weaker bands associated with F_2 , F_3 and F_3^+ centres, the intensities of these additional bands being strongly dependent on the colouration pressure. This pressure also determines the magnitude of a weak absorbing background extending into the IR which is due to a variety of small colloidal aggregates [14].

For colloid radii between 25 and 400 Å, the extinction coefficient shows a distinct resonance, but for smaller radii the spectrum flattens; the scattering cross section falls to zero and the extinction is completely due to absorption [16].

In order to obtain F_2^+ laser emission, the colloidal absorption background has to be maintained low enough to minimise the losses at the F_2^+ emission wavelength. The requirement for a low background together with a reasonably high concentration of F_2^+ centres sets the optimum colouration pressures in the range 20–25 Torr [14]. The slightly higher colouration pressures used in this work produce a slightly higher background absorption but a much higher relative F_2^+ -centre concentration.

This background absorption produces a PA signal after pulsed Nd:YAG excitation, which is shown in figure 2. The signal begins at a well defined delay time τ after the occurrence of the laser pulse. This delay time is found to be linearly dependent on the distance d between the laser beam and the transducer surface. By moving the cell with a micrometer stage, d can be varied by several millimetres and τ is observed to change by several microseconds. The relation between the change Δd in distance and the change $\Delta\tau$ in delay is shown in figure 2. The slope in this figure gives the propagation velocity v_{exp} of the signal, $4.3 \times 10^3 \text{ m s}^{-1}$, which is in agreement with the calculated ultrasonic velocity, in the $\langle 100 \rangle$ direction, at room temperature in NaCl: $v_{\text{calc}} = (c_{11}/\rho)^{1/2} = 4.7 \times 10^3 \text{ m s}^{-1}$, where $c_{11} = 0.486 \times 10^{11} \text{ N m}^{-2}$ is the elastic constant in the $\langle 100 \rangle$ direction and $\rho = 2.17 \times 10^3 \text{ kg m}^{-3}$ is the density of NaCl [17]. Thus we are detecting a true PA signal generated from the colloidal absorption of the laser pulse which can be used as an internal reference to be compared with the PA signal of the F_2^+ centres.

If the crystal is now illuminated in the F band, the F_2^+ band appears (figure 3). The concentration of F_2^+ centres increases linearly at first and reaches a maximum value after

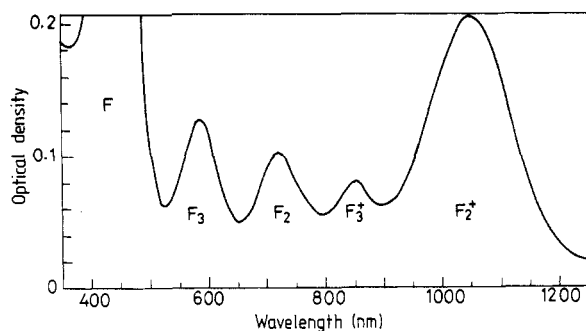


Figure 3. Optical absorption spectrum for additively coloured NaCl:OH⁻ crystals at 77 K after the photoaggregation process which leads to the formation of F₂⁺ centres.

around 30 min illumination, followed by a slow decrease for longer irradiation times. In this work, illumination times have been chosen which are short enough to ensure that the conversion is restricted to the linear part of the process, thus avoiding the formation of higher aggregates.

It is evident from figure 3 that the F₂⁺ centres can be excited with the 1.06 μm line of the Nd:YAG laser. Consequently, the PA signal should also increase with increasing illumination time, partially owing to the Stokes shift (the F₂⁺ emission peaks at 1.45 μm) and partially because of a possible non-radiative de-excitation of the centres.

The PA signal can be expressed as

$$V = KN_0 h\nu_0 [(1 - 10^{-OD_c}) + (1 - 10^{-OD})(1 - \Phi\nu/\nu_0)] \quad (1)$$

where K is a constant which depends on the geometry and the response of the system, N_0 is the number of incident photons of frequency ν_0 which are re-emitted at frequency ν , OD and OD_c are the optical densities at 1.06 μm of the F₂⁺ centres and the colloids, respectively, and Φ is the luminescent quantum efficiency of the F₂⁺ centres, defined as the ratio of the number of emitted to the number of absorbed photons.

At the concentrations used in this work, the approximation $1 - 10^{-OD} = OD$ holds, and it is readily obtained from equation (1):

$$V/V_0 = 1 + (1 - \Phi\nu/\nu_0)OD/OD_c \quad (2)$$

where $V_0 = KN_0 h\nu_0/OD_c$ is the PA signal in the absence of F₂⁺ centres.

The PA signal as function of the optical density of the F₂⁺ centres at 1.06 μm is given in figure 4 (open circles). The data correspond to the average over 20 individual shots and the error bars represent $\pm\sigma$, σ being the standard deviation.

It can be seen that the PA signal follows a linear dependence, in accordance with equation (2). A set of theoretical lines where the quantum efficiency Φ is taken as a parameter is also given. The best fit of the experimental data by using equation (2) shows that the quantum efficiency of the F₂⁺ centres is very close to 100% ($\Phi = 1.02 \pm 0.07$).

Unfortunately, this procedure cannot be used to determine the luminescent quantum efficiency of (F₂⁺)_H centres as these centres are unstable above 200 K [14, 15]. Therefore the quantum efficiency can only be obtained at low temperatures where the photoaggregation process cannot be performed.

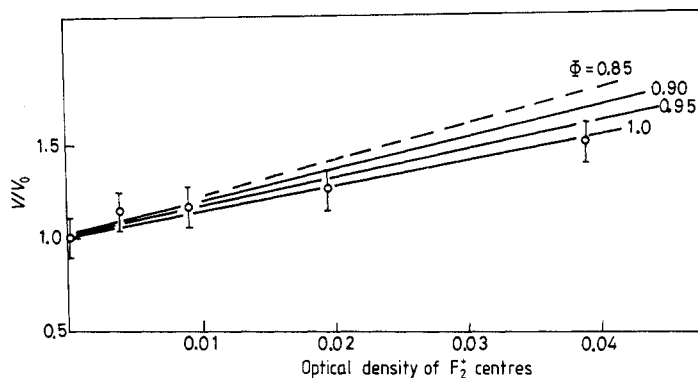


Figure 4. Relative PA signal as function of the F_2^+ optical density. A set of theoretical lines, according with equation (2), has been drawn using different quantum efficiencies.

In order to determine the quantum efficiency, the possibility of $F_2^+ \rightarrow (F_2^+)_H$ transformation by low-temperature F-light illumination [14, 15, 18] can be explored. By performing this transformation in the same cryostat used to measure the low-temperature photoluminescence of the F_2^+ centres, it is possible to compare both luminescences without introducing any change in geometry. A quantitative determination of the quantum efficiency of the luminescence of the $(F_2^+)_H$ centres, relative to that of the F_2^+ centres, is then possible.

Following this procedure, it has been found that, at liquid-nitrogen temperature, the luminescence of the $(F_2^+)_H$ centres (the total area under the emission spectrum) is 0.97 (± 0.04) times that of the F_2^+ centres. This demonstrates that the $(F_2^+)_H$ centres have essentially the same quantum efficiency as the F_2^+ centres. Therefore the oxygen impurities which are linked to this defect do not affect its quantum efficiency although they are very important in increasing the stability of the centre [14], confirming its superior characteristics as laser-active centres.

Acknowledgments

The authors wish to acknowledge stimulating discussions with Professor F Jaque and Dr J García-Solé as well as financial support from Comisión Interministerial de Ciencia y Tecnología, Spain.

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