

Excited state absorption in KCl:Eu²⁺

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ABSTRACT: Non-linear behavior with respect to exciting fluence of both photoacoustic and luminescent signals in KCl:Eu(2+) , excited by laser pulses at 355 nm, were analyzed in terms of excited state absorption (ESA). Measured ESA cross-sections for 355 and 420 nm were found to be $1 \times 10^{(-17)}$ cm² and $2.5 \times 10^{(-18)}$ cm² respectively.

1. INTRODUCTION

There is great interest to search for materials to develop tunable solid-state lasers emitting at shorter wavelengths than the present ones. Divalent europium ions in a strong crystalline field has potential for laser operation in the violet and blue spectral regions^[1]. However, in some crystalline hosts, (like CaF₂), it was found that strong excited state absorption prevented laser action^[2]. Alkali halides can be more appropriate hosts for laser action due to their small Madelung energy at the europium site. In view of this interest, excited state absorption (ESA) measurements have been performed at room temperature in KCl:Eu⁺² using photoacoustic and luminescence methods.

As it is well known^[3], the absorption spectrum of Eu ions in KCl crystals consists in two broad absorption bands attributed to transitions from the ⁸S_{7/2} ground state of the 4f⁷ configuration, to the 4f⁶5d 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. 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 (fig 1). After excitation of these two bands, a single luminescent band is observed, corresponding to the t_{2g} → 4f⁷ transition. Vibronic relaxation provides strong photoacoustic signals for both excitations.

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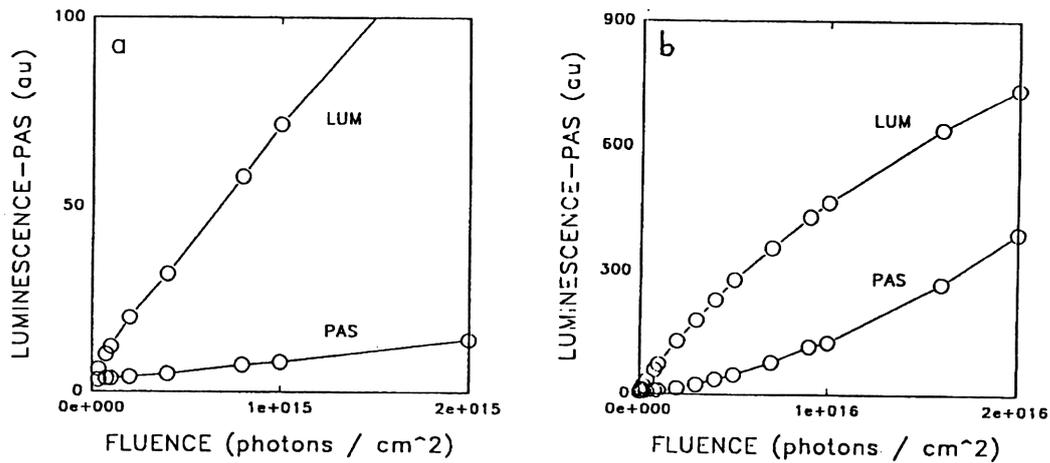


Fig.3: Photoacoustic and luminescence signals, as defined in the text, vs. excitation fluence. (a) linear behaviour at low fluence and (b) non linear behaviour at high fluence.

transition, σ_g and σ_e are the ground and excited state absorption cross sections at 355 nm and q_1 values can be calculated from absorption and luminescence spectra. k_p is a constant that relates the heat to the amplitude of the PAS signal and it was calculated to match the experimental results at low fluence (linear region). The third term arises from ESA. Relaxation after this process is assumed to be 100% non-radiative. Each contribution is represented in fig. 4. Best fit of all points by using eq.(1) was obtained for $\sigma_e(355 \text{ nm}) = 1 \times 10^{-17} \text{ cm}^2$. Luminescence results could not be fitted using this simple model. LUM saturates more strongly than the predictions given by depletion of the ground state due to excited state population.

We concluded that luminescence is reabsorbed within the excited zone. If $\sigma_e(\text{LUM})$ represents the ESA cross section for the luminescence wavelength and L , the length of the excited zone in the direction of observation, LUM can be written as:

$$\text{LUM} = (1 / L \cdot \sigma_e(\text{LUM})) \cdot [1 - \exp(-N_1 L \sigma_e(\text{LUM}))], \quad (2)$$

with:

$$N_1 = N_0 \sigma_g \cdot [\exp(-\sigma_g F) - \exp(-\alpha \sigma_e(355) F)] / (\alpha \sigma_e(355) - \sigma_g),$$

where α represents the fraction of ions going from the higher excited state to metastable states. In reference [4], $\alpha = 0.67$ was calculated. Using eq. 2, the best fit of experimental results of LUM was obtained for $\sigma_e(\text{LUM}) = 2.5 \times 10^{-18} \text{ cm}^2$ (fig.5).

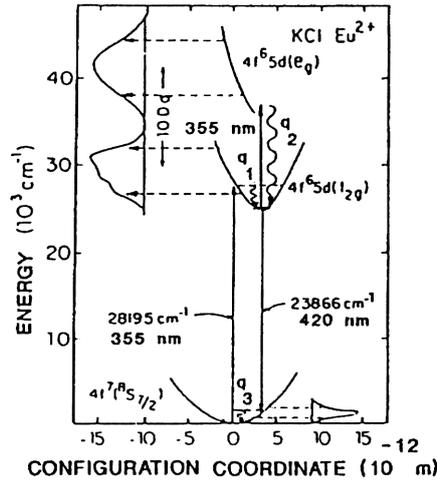


Fig.1: Energy levels of KCl:Eu²⁺. Main excitation and relaxation processes are shown.

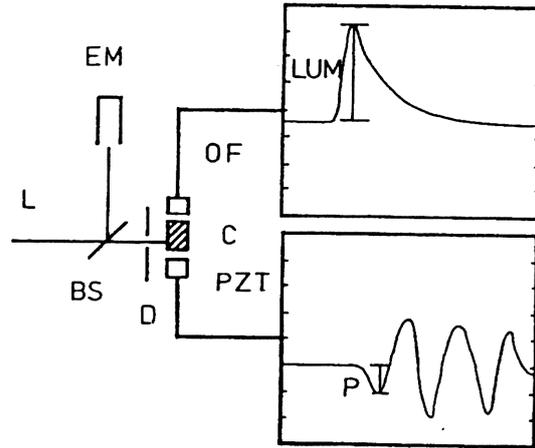


Fig.2: Experimental setup. L laser beam; BS: beam splitter; M:energy meter; D:diaphragm; OF: optic fiber; C: crystal; PZT: piezo transducer; LUM: luminescence signal; P: Photoacoustic signal.

2. EXPERIMENTAL SETUP AND RESULTS

The experimental setup used in this work (fig 2) is similar to that described for the determination of the luminescence quantum yield of this material¹⁴. Excitation at 355 nm was provided by the third harmonic of a Nd:YAG pulsed laser. The sample, in the form of a rectangular slab of 10 by 5 by 1 mm, with absorbance less than 0.1, was fixed to a PZT detector. Luminescence was collected by an optical fiber and analyzed by a monochromator-photomultiplier system. Both signals were amplified and digitized. Laser pulse energy was measured by using a calibrated pyroelectric detector. The first peak of the photoacoustic signal (PAS) and the maximum of the luminescence signal (LUM) were plotted in terms of incident laser fluence, which could be varied by using a half-wave plate polarizer combination. It is clearly seen in fig.3 that both signals depart from linearity. While LUM tends to saturate, PAS has an opposite behavior.

3. DISCUSSION

By the use of the diagram in fig. 1 we can calculate the amount of prompt heat released after the absorption of the excitation laser pulse with fluence F. The PAS signal can be written as:

$$PAS = k_p [(\sigma_g q_1 F) + (\phi q_3 F) + (\sigma_e(355) q_2 F^2)], \tag{1}$$

where ϕ represents the fluorescence quantum yield of the $t_{2e} \rightarrow 4f^7$

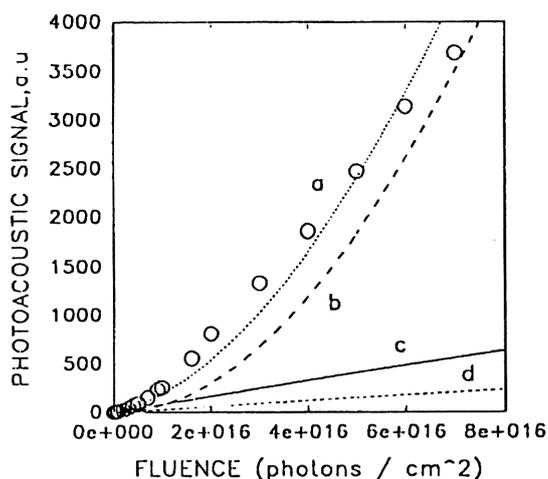


Fig. 4: PAS signal vs. fluence. (○) experimental data. Curve (a): total PAS signal; (b): ESA contribution; (c), (d): linear contributions.

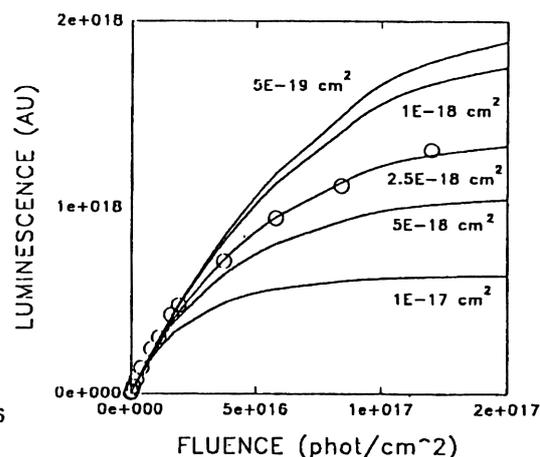


Fig. 5: Luminescence signal vs. fluence. (○): experimental data. Curves represent eq. (2) for different values of $\sigma_e(420)$.

4. CONCLUSIONS

Non linear behaviour of photoacoustic signals in KCl:Eu^{2+} can be explained in terms of ground state depletion due to excited state absorption at the pump wavelength. The calculated value for $\lambda = 355 \text{ nm}$ is in agreement with previously published results^[5].

Excited state reabsorption of luminescence must be included in order to explain the strong saturation of luminescence with pump fluence. The obtained value for $\sigma_e(420 \text{ nm})$ seems to be enough to prevent laser action in KCl:Eu^{2+} . This result is in disagreement with calculations made in ref.[6]. No laser action in this material has been reported yet.

5. ACKNOWLEDGMENTS

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