

# LIFETIME MEASUREMENTS OF THE $^4S_{3/2}$ LEVEL IN ERBIUM PENTAPHOSPHATE MONOCRYSTAL\*

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Lifetime of the main fluorescence level,  $^4S_{3/2}$ , of erbium pentaphosphate monocrystal was measured to be  $380 \pm 20$  ns. Direct excitation to higher energy levels, and also indirect excitation with the use of an infrared beam were applied.

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## 1. Introduction

Erbium pentaphosphate monocrystals ( $\text{ErP}_5\text{O}_{14}$ ) grown by one of us and coworkers [1-3] exhibit an active ions concentration of  $3.78 \times 10^{21} \text{ cm}^{-3}$ . It is well known that at relatively low concentration of  $\text{Er}^{3+}$  in various matrices the media are very suitable for amplification and generation of light, as well as in the process of infrared-to-visible upconversion. However, as the  $\text{Er}^{3+}$  concentration increases, lifetime of the  $^4S_{3/2}$  fluorescence level decreases substantially. Rare-earth pentaphosphate monocrystals present a very characteristic ribbon-like crystal structure that isolates the active ions by optically neutral oxygens. Therefore, we expected that erbium pentaphosphate would be an interesting medium for lasers, and especially for infrared-to-visible upconversion. Let us concentrate on the latter process. Several tens of papers has been already published on that phenomenon. The papers of Danger et al. [4-6] and the references therein could be recommended for an overview of the work performed.

Lifetime of the  $^4S_{3/2}$  fluorescence level plays an essential role in the process of infrared-to-visible upconversion. At low concentration of  $\text{Er}^{3+}$ , the lifetime of the  $^4S_{3/2}$  level amounts to about 0.5 ms, and decreases to about 4  $\mu\text{s}$  at a concentration of  $4 \times 10^{21} \text{ cm}^{-3}$ . Of course, variation of these typical values depends on the host matrix.

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## 2. Experimental

Several mechanisms of excitation of  $\text{Er}^{3+}$  ions are usually considered (see Fig. 1). We have applied nanosecond pulses at  $\lambda = 363$  nm, and sinusoidally modulated beam at 540 nm, to excite the  ${}^4\text{S}_{3/2}$  level directly and via higher energy levels. In the case of an infrared beam at 800 nm excited state absorption and ion-pair cooperative process can be involved.

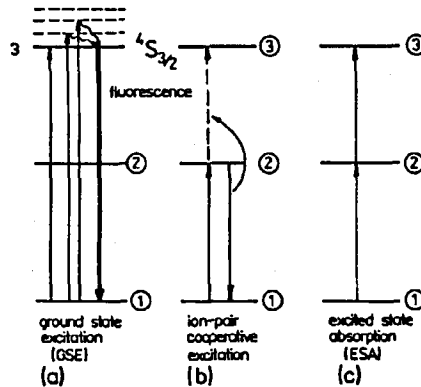


Fig. 1. Illustration of the three main mechanisms of excitation of  $\text{Er}^{3+}$  ions to the  ${}^4\text{S}_{3/2}$  fluorescence level.

Frequency domain method and UV pulse excitation are physically equivalent and should lead to the same results. The aim of applying these two methods was to obtain more reliable experimental results. However, infrared excitation via intermediate level No. 2 (Fig. 1), and especially for ion-pair cooperative process to occur, should lead to a delay in the fluorescence signal as compared to the excitation one [7]. Therefore, it was very interesting to study the decay of the fluorescence after infrared pulse excitation. A brief description of the methods used is given below.

### 2.1. Frequency domain method

The monocrystal is illuminated with light whose intensity is modulated sinusoidally. Because of the finite lifetime of the excited state, the modulated emission is delayed in phase by an angle  $\phi$  relative to the excitation. The observed fluorescence is less modulated (demodulated) relative to the excitation. The lifetime of the level under investigation is [8]

$$\tau_p = \omega^{-1} \tan \phi, \quad (1)$$

where  $\phi$  is the measured phase shift, and  $\omega$  — frequency of the exciting beam. The lifetime can be also calculated using another formula

$$\tau_m = \omega^{-1} \left[ \frac{1}{m^2} - 1 \right]^{1/2}, \quad (2)$$

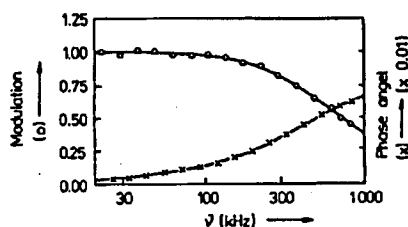


Fig. 2. Demodulation coefficient and phase lag as a function of the frequency of the exciting beam.

where  $m = \frac{B/A}{b/a}$ ;  $B/A$  is the modulation coefficient of the observed fluorescence, and  $b/a$  stands for the exciting light. If the decay is single exponential, then  $\tau_m = \tau_p = \tau$ , where  $\tau$  is the fluorescence lifetime. We applied light from an argon ion laser ( $\lambda = 488$  nm) whose frequency was varied from 1 to 800 kHz. The fluorescence was observed in the "green" band around 540 nm. A typical display of the phase lag and the modulation factor is shown in Fig. 2.

### 2.2. UV pulse excitation

Nanosecond UV pulses ( $\lambda = 363$  nm) were used to excite the sample, and the fluorescence was observed at 551 nm. The photon counting method was applied to measure the decay signal (Fig. 3).

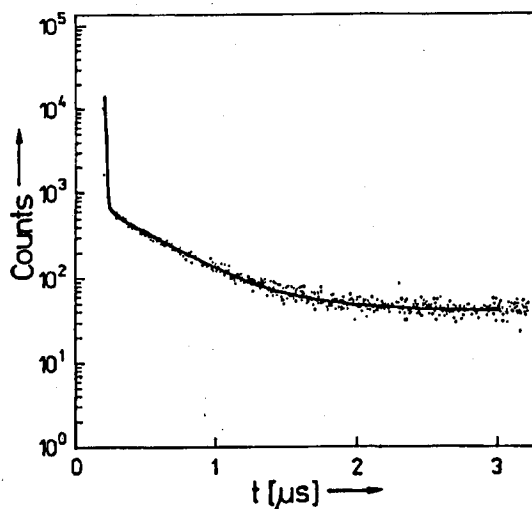


Fig. 3. Fluorescence decay from the  $^4S_{3/2}$  level. Excitation wavelength,  $\lambda = 363$  nm.

## 2.3. Infrared exciting pulses

A tuned titanium-sapphire laser was used to excite the sample with infrared pulses ( $\lambda = 800$  nm), each of 350 fs in duration. The light beam was focused within the sample. In this way, the green upconversion signal was clearly visible. Decay of the fluorescence light is shown in Fig. 4.

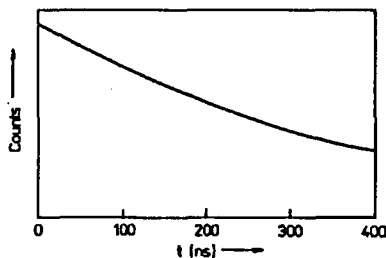


Fig. 4. Fluorescence decay from the  ${}^4S_{3/2}$  level in  $\text{ErP}_5\text{O}_{14}$  monocrystal. Excitation wavelength,  $\lambda = 800$  nm.

## 3. Conclusions

The results obtained are summarized in Table. Differences in the measured values are due to various method applied, however, the result  $\tau = 380 \pm 20$  ns is firmly established. Such a short lifetime of the  ${}^4S_{3/2}$  level excludes the ion-pair upconversion pumping (in the case of an infrared beam), and points to strong concentration quenching. Ion-pair cooperative process that is usually responsible

TABLE

Results of measurements of the lifetime.

Excitation	Fluorescence	Lifetime $\tau$ [ns]
Directly to the ${}^4S_{3/2}$ and to higher levels. "Frequency domain" method, $\lambda_{\text{exc}} = 488$ nm, $\nu = 1 \div 800$ kHz	In the "green" at $\lambda = 540$ nm	380
Directly to the ${}^4S_{3/2}$ level and to higher levels. Nanosecond pulses at $\lambda = 363$ nm	In the "green" at $\lambda = 551$ nm	400
Sequences of infrared femtosecond pulses ( $\lambda = 800$ nm). Excited state absorption	In the "green" at $\lambda = 540$ nm	365

for upconversion seems to be completely washed out, because we did not observe any delay between the fluorescence signal and the excitation pulse.

As pointed out by Dieke in 1961 [9], an increase in concentration of active rare-earth ions causes broadening of the energy levels and leads to a decrease in fluorescence lifetime, sometimes even to extinguish the fluorescence completely.

Fluorescence quenching may be also caused by nonradiative phonon assisted processes. According to Auzel [10], the probability of non-radiative transition can be written in the following form:

$$W_{NR} = W_0 \exp(-\alpha \Delta E),$$

where  $W_0$  and  $\alpha$  are constants, and  $\Delta E$  is the energy gap between the fluores-

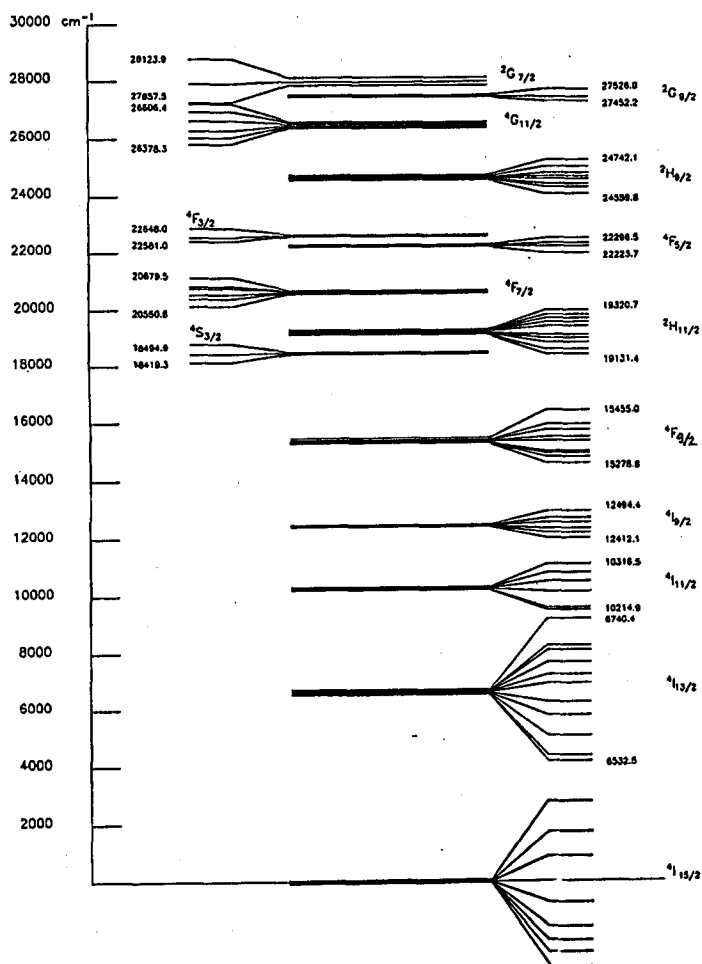


Fig. 5. Energy level diagram of  $\text{Er}^{3+}$  in  $\text{ErP}_5\text{O}_{14}$  monocrystal.

cence level and the nearest lower lying level. In the case of  $\text{ErP}_5\text{O}_{14}$  monocrystals this energy gap amounts to  $2964\text{ cm}^{-1}$  (see Fig. 5). On the other hand, Raman and infrared measurements performed by Kaczmarek and Jendrzyszczak [11], and Kaczmarek and Kaczmarowski [12] revealed the following strongest vibrations:  $1311$ ,  $1171$ ,  $725$  and  $679\text{ cm}^{-1}$  (Raman), and  $1300\text{ cm}^{-1}$  (IR). Neither two-phonon nor three-phonon transition for the  $1300\text{ cm}^{-1}$  vibration will be in resonance with the  $2964\text{ cm}^{-1}$  energy gap. Other multiphonon transitions are less probable. It is thus reasonable to conclude that interaction between active ions, due to their high concentration, is mainly responsible for the fluorescence quenching observed. At high concentration there can be some overlap between  $4f$  configuration of one ion and the  $5d$  configuration of its next neighbour. Concentration quenching in stoichiometric rare-earth crystals was discussed by Lempicki [13]. He proposed a diffusion model for the quenching, assuming that excitation energy of an active ion diffuses to some energy sinks around this ion. The quenching rate he obtained was linearly proportional to concentration. Recent results on infrared-to-visible upconversion in erbium doped fibers [14] indicate that at very low concentration of  $\text{Er}^{3+}$  ions ( $\approx 1000$  ppm), one can obtain up to  $15\text{ mW}$  of visible light (at  $544\text{ nm}$ ) when pumping with an infrared beam (at  $800$  or  $970\text{ nm}$ ) of  $400\text{ mW}$ . One has to conclude that only media containing very low concentration of  $\text{Er}^{3+}$  ions are suitable for practical application in lasers and as infrared-to-visible upconverters.

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