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Journal of Luminescence 92 (2001) 317–322

JOURNAL OF  
LUMINESCENCE

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# The luminescent quantum efficiency of $\text{Cr}^{3+}$ ions in co-doped crystals of $\text{LiNbO}_3:\text{ZnO}$ determined by simultaneous multiple-wavelength photoacoustic and luminescence experiments

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Received 1 May 2000; accepted 19 September 2000

## Abstract

In this paper, the luminescent quantum efficiency of  $\text{Cr}^{3+}$  ions in co-doped crystals of  $\text{LiNbO}_3:\text{ZnO}:\text{Cr}^{3+}$  is determined by using a method based on simultaneous multiple-wavelength measurement of photoacoustic and luminescence signal after pulsed laser excitation. The quantum efficiency found in this lattice was  $(10 \pm 4)\%$ . This result was compared with the value found from the study of the lifetime in terms of the temperature of the luminescent levels involved. In this last case, two non-equivalent crystal sites were found for  $\text{Cr}^{3+}$  ions, and two fluorescence quantum yields were determined. After the estimation of the concentration of each site by electron paramagnetic resonance experiments, the averaged fluorescence quantum yield value was  $(9 \pm 2)\%$  in agreement with the previous result. © 2001 Elsevier Science B.V. All rights reserved.

PACS: 43.35U; 78.55; 78.60

Keywords: Photoacoustic spectroscopy; Luminescent quantum efficiency;  $\text{Cr}^{3+}$ ;  $\text{LiNbO}_3$ 

## 1. Introduction

Lithium niobate is a material that combines excellent electro-optic, acousto-optic and non-linear properties with the possibility of rare earth or transition metal doping. This material can be

used in bulk or it is possible to prepare low-loss optical wave guides [1,2]. Laser action was obtained in different doping ions and more recently self-frequency doubled action was obtained in lithium niobate doped with Nd or Yb [3,4].

The fluorescence quantum efficiency  $\Phi$  of a luminescent material is one of the most relevant parameters to have a complete characterisation of a material. While photoacoustic methods have been extensively used in the quantum efficiency

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determination of gases or liquids [5–7], there are much less examples for solid state materials. Normally, photoacoustic methods use a comparison with one standard material. This procedure is not adequate for quantitative measurements in solid state, because changing the sample may substantially affect the acoustic coupling in the experimental set-up. Some authors have pointed out the possibility of obtaining absolute measurements without standards [8] and this last time an alternative method based on the simultaneous detection of photoacoustic and luminescence signals, after excitation at two different wavelengths, has been proposed by E. Rodriguez et al. [9]. This method called SIMPLE (simultaneous multiple-wavelength photoacoustic and luminescence experiments) relies on the existence of a full non-radiative relaxation, providing an internal reference that can be used for absolute quantum efficiency determination. The harmonics of a Nd:YAG laser were used in the first experiments, with the disadvantage of the necessary coincidence of the Nd:YAG harmonics with the absorption bands of the sample. These difficulties can now be avoided thanks to the appearance of pulsed tunable sources (oscillator parametric MOPO) which can be used for broad excitation in the range 0.4 at 2  $\mu\text{m}$ . This method was applied to the determination of luminescence quantum efficiency of  $\text{Cr}^{3+}$  ions in co-doped  $\text{LiNbO}_3:\text{ZnO}$  crystal. The  $\text{Cr}^{3+}$  ions in this crystal present two broad absorption bands and can be excited with the MOPO. In relation to Zn co-doping, it should be noted that in this way the photorefractive damage of  $\text{LiNbO}_3$  is suppressed and therefore this material is adequate for optoelectronic application.

Additionally, a comparison between this method and values found by luminescence lifetime studies in terms of the temperature is reported in this paper.

## 2. Experimental set-up

The congruent  $\text{LiNbO}_3:\text{Cr}:\text{Zn}$  crystal used in this work was grown in the Universidad Autónoma de Madrid, by Czochralski's method

in an open atmosphere. The  $\text{Cr}^{3+}$  and  $\text{Zn}^{2+}$  compositions were determined by EXFT (Fluorescence Total X-ray Emission) calibrated with standard samples. The concentrations of chromium and zinc ions in the crystal were 0.1% and 5.3%, respectively; these measurements were normalised at  $\text{Nb}^{5+}$  concentrations. The samples were cut in the form of rectangular slabs of approximate dimensions  $10 \times 5 \times 1 \text{ mm}^3$ . Their faces were carefully polished with diamond powder of 1  $\mu\text{m}$ . Continuous wave and pulsed optical and photoacoustic measurements were performed.

Optical absorption was conducted at room temperature by using an Hitachi U-3501 spectrophotometer. Continuous wave (cw) emission was excited with a multiline Argon laser. The fluorescence spectrum was analysed with a 50 cm focal length monochromator (SPEX 5000 M) with a germanium photodiode followed by lock-in amplification.

Pulsed measurements were made with excitation from an optical parametric oscillator (MOPO-730 by Spectra Physics). This source pumped by a Q-Switch neodymium laser provide pulses of 8 ns (FWHM), of approximately 200 mJ from 450 to 690 nm with a bandwidth of  $0.1 \text{ cm}^{-1}$ .

Pulsed fluorescence (LUM) was detected by using the above mentioned monochromator at fixed wavelength of 950 nm but with a different light detector for better time resolution. A Hamamatsu 751 K AsGaIn phototube was used. For the fluorescence quantum yield determinations by simultaneous multiple-wavelength photoacoustic and luminescence experiments (SIMPLE) method, LUM was taken as the maximum of luminescence time resolved signal.

Photoacoustic signal was achieved with a resonant ceramic piezoelectric transducer (PZT), having a bandwidth of 200 kHz. The piezoelectric detector was coupled to the sample with vacuum grease, to optimise the acoustic coupling. To use the SIMPLE method, photoacoustic signal (PAS) was taken as the peak to peak value of the first arrival wave. These considerations make negligible the other contribution originated by reflections on the other face of the sample.

Both signals, photoacoustic (PAS) and LUM were detected simultaneously and registered by

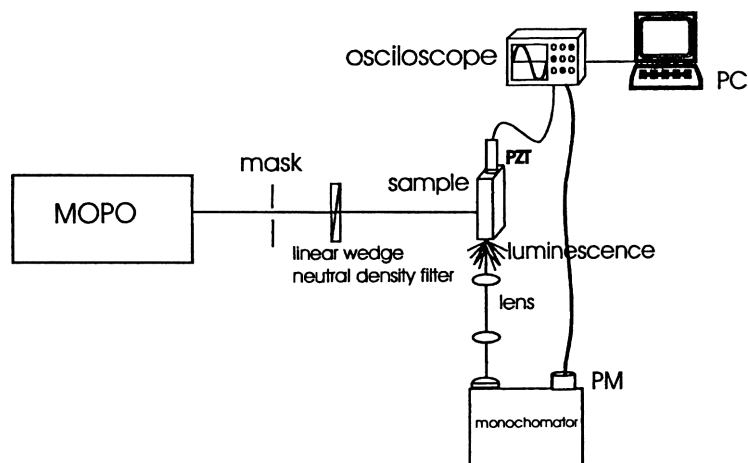


Fig. 1. Experimental set-up used in this work for the measurement of quantum efficiency of  $\text{Cr}^{3+}$  ions in co-doped  $\text{LiNbO}_3:\text{ZnO}:\text{Cr}^{3+}$  crystals by the SIMPLE method.

digital oscilloscope Tektronix 2440. Fig. 1 shows the experimental set-up used in this work.

The whole time-resolved phototube-signal was recorded in order to get the lifetime of the emission level. In this case the sample was cooled from room temperature to liquid helium temperature by using a flux cryostat. PZT was removed for these measurements.

### 3. Results and discussion

The absorption spectrum of  $\text{Cr}^{3+}$  ions in co-doped  $\text{LiNbO}_3:\text{Cr}^{3+}:\text{ZnO}$ , presents two broad absorption bands, centred at 500 nm and 660 nm, when the content of ZnO in the melts is above 7% mol. These bands are associated with the vibronic transitions  ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$  and  ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ , respectively, of  $\text{Cr}^{3+}$  ions in  $\text{LiNbO}_3:\text{ZnO}$  congruent crystals [10].

Fig. 2 shows the absorption and emission spectra obtained by cw excitation. A single luminescence wide band is observed independent of the excitation wavelength; therefore the internal non-radiative relaxation between the  ${}^4\text{T}_1$  and  ${}^4\text{T}_2$  provides a valuable PAS reference for internal calibration. This band is centred at 950 nm with 100 nm of FWHM, corresponding to the vibronic transition of chromium  ${}^4\text{T}_1 \rightarrow {}^4\text{A}_2$  [10]. In the same

figure level diagram is presented, where all radiative and non-radiative processes, corresponding to vibronic transitions of  $\text{Cr}^{3+}$  into a low crystal field symmetry, are included [11].

For the luminescence conditions found in this ion, two excitation bands and one emission band, the fluorescence quantum efficiency by the SIMPLE technique can be determined. In this method, the fluorescence quantum efficiency ( $\Phi$ ) can be calculated from

$$\Phi = \frac{\lambda_{\text{emi}}}{\lambda_{\text{L}}} \frac{A - \lambda_{\text{L}}/\lambda_{\text{H}}}{A - 1}, \quad (1)$$

where  $\lambda_{\text{L}}$  and  $\lambda_{\text{H}}$  represent the wavelengths of low and high energy excitation,  $\lambda_{\text{emi}}$  is the emission wavelength and  $A$  represents the ratio between the slope of the linear fit in the graphics PAS against LUM, for each excitation wavelength at low and high energy,

$$A = \frac{\partial \text{PAS}_{\lambda_{\text{High}}}/\partial \text{LUM}_{\lambda_{\text{High}}}}{\partial \text{PAS}_{\lambda_{\text{Low}}}/\partial \text{LUM}_{\lambda_{\text{Low}}}}. \quad (2)$$

Fig. 3 shows the experimental results for the PAS against the LUM signal. The crystal of  $\text{LiNbO}_3:\text{Cr}^{3+}:\text{ZnO}$  was excited with pulses from the MOPO at 500 nm ( $\lambda_{\text{High}}$ ) for high energy and 650 nm ( $\lambda_{\text{Low}}$ ) for low energy. These results clearly show that the relation PAS vs. LUM for different excitation energies from the MOPO was linear.

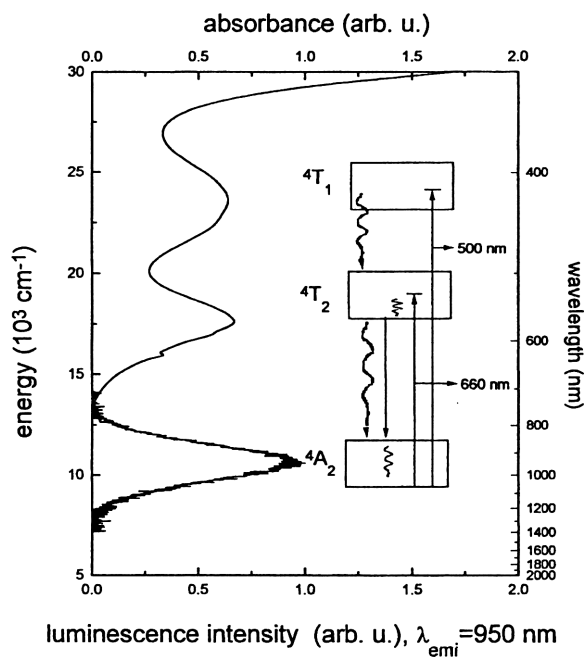


Fig. 2. Absorption and emission (cw) spectra of chromium ions in the LiNbO<sub>3</sub>:ZnO crystal. The level diagram of Cr<sup>3+</sup> ions in this crystal is also presented.

After a linear fit for experimental points  $\Lambda = 1.35 \pm 0.05$  was determined. By using the expression (1), the fluorescence quantum efficiency of Cr<sup>3+</sup> ions in co-doped LiNbO<sub>3</sub>:ZnO crystal was calculated as  $\Phi = 10 \pm 4\%$ .

The fluorescence quantum yield can be estimated through the analysis of the lifetime of the emission level in terms of the temperature. If sufficiently low temperature values can be achieved,  $\Phi$  can be calculated from

$$\Phi(T) = \frac{\tau_{\text{exp}}(RT)}{\tau_{\text{exp}}(LT)}, \quad (3)$$

where the non-radiative transitions probability at low temperature (LT) was taken as null.

Fig. 4 shows the time resolved luminescence signals at low temperature (a) and room temperature (b) of chromium ions in lithium niobate doped with ZnO. Fluorescence was excited by 650 nm pulses and detected at 950 nm. Bi-exponential decay can be attributed to the presence of two non-equivalent sites for Cr<sup>3+</sup> in LiNbO<sub>3</sub>.

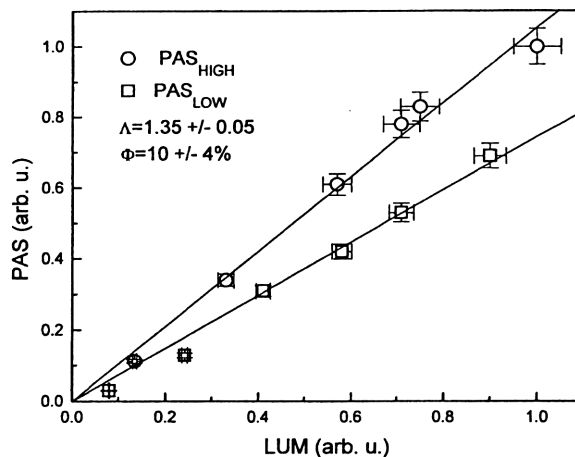


Fig. 3. Photoacoustic (PAS) and luminescence (LUM) signals for different MOPO excitation powers corresponding to different wavelengths.

The fitting gives  $(8 \pm 2) \mu\text{s}$  and  $(19 \pm 2) \mu\text{s}$  for the lifetime of Cr<sup>3+</sup> at LT and  $(0.4 \pm 0.1) \mu\text{s}$  and  $(2.3 \pm 0.2) \mu\text{s}$ , at room temperature for both sites. Faster relaxation can be attributed to Cr<sup>3+</sup> in lithium sites because the lifetime is similar to the measured one in LiNbO<sub>3</sub> without doping. Other lifetimes correspond to Cr<sup>3+</sup> in niobium sites; this site is induced by the high concentration of Zn<sup>2+</sup> used in the sample. By using these lifetime values in the expression (3) quantum efficiencies of  $10 \pm 2$  and  $4 \pm 1\%$  for Cr<sub>(Nb<sup>5+</sup>)</sub><sup>3+</sup> and Cr<sub>(Li<sup>+</sup>)</sub><sup>3+</sup>, respectively, were obtained.

The concentration of Cr<sup>3+</sup> ions in both sites was estimated by Electron Paramagnetic Resonance (EPR) technique. The inset of Fig. 4 shows the EPR spectrum at RT for LiNbO<sub>3</sub>:Cr<sup>3+</sup>:ZnO (5.3%) obtained with the magnetic field applied perpendicular to the *c* axis of the crystal with 100 kHz modulation frequency. The two lines of resonance at 1800 and 3500 G were associated with Cr<sub>(Li<sup>+</sup>)</sub><sup>3+</sup> and Cr<sub>(Nb<sup>5+</sup>)</sub><sup>3+</sup>, respectively [12]. From the ratio of areas of this spectrum, the concentration ratio of  $[\text{Cr}_{(\text{Nb}^{5+})}^{3+}]/[\text{Cr}_{(\text{Li}^{+})}^{3+}]$  equal to 4 was calculated.

As the total quantum efficiency luminescence  $\Phi$  is proportional to the concentration times the quantum efficiency for each chromium site in the crystal,  $\Phi$  is equal to  $(9 \pm 2)\%$ , in agreement with the values found by SIMPLE method.

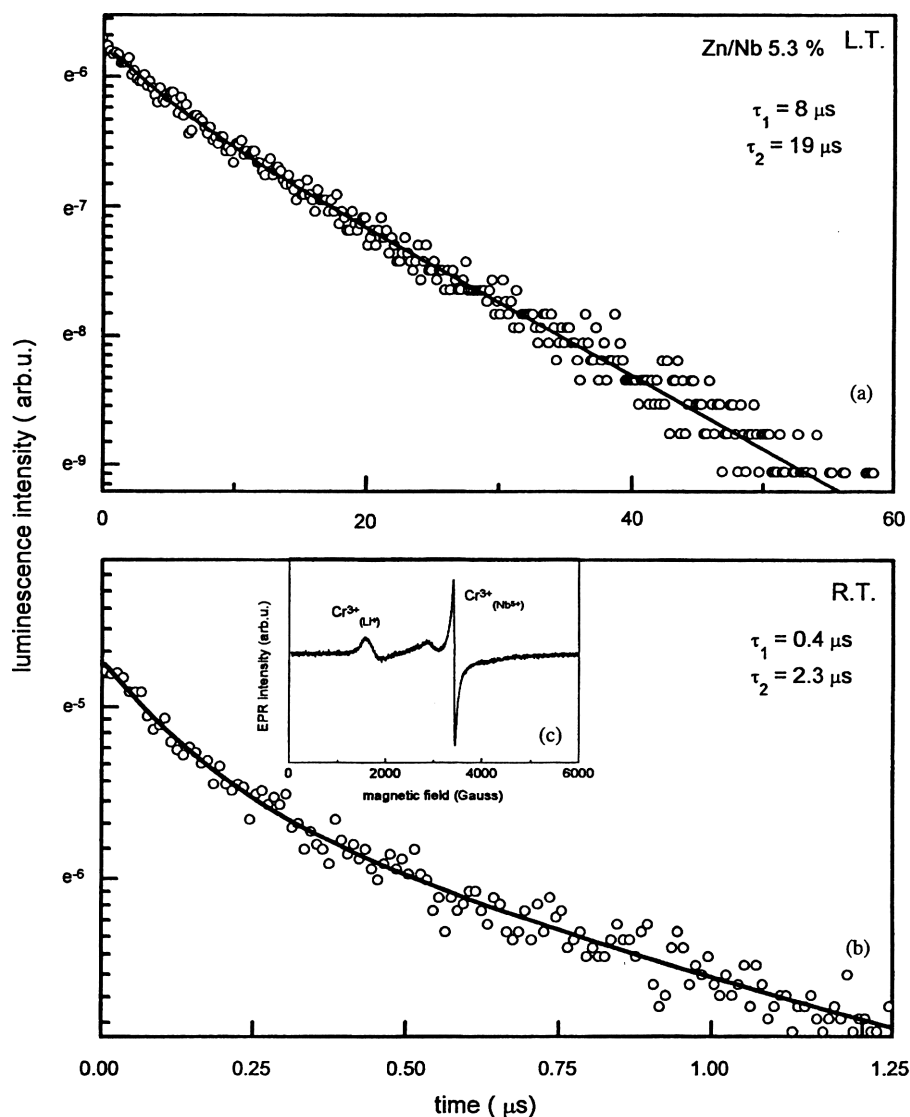


Fig. 4. Logarithmic plots for time resolved fluorescence (950 nm emission, 650 nm excitation) at low temperature (a) and room temperature (b). Bi-exponential fittings are also shown. The two lifetimes are associated to the two centres presented in the crystals. In the inset the EPR spectrum at RT is shown.

#### 4. Conclusions

In this work, the fluorescence quantum efficiency of Cr<sup>3+</sup> ions in co-doped LiNbO<sub>3</sub>:ZnO:Cr<sup>3+</sup> congruent crystal was obtained. By using SIMPLE method the unresolved crystal sites value was (10 ± 4)%, while by lifetime measurements and weighting the two non-equivalent sites found in

this crystal, the total fluorescence quantum yield was estimated as (9 ± 2)%. Despite the fact that this last method is only approximate because several simplifications must be assumed to justify its validity, the values obtained are comparable. It can be affirmed that the quantum efficiency  $\Phi$  for the Cr<sup>3+</sup> ions in ZnO co-doped LiNbO<sub>3</sub> congruent crystal is not more than 10%.

In a previous experiment by E. Rodriguez and co-worker a quantum efficiency of 5% was found but for  $\text{LiNbO}_3:\text{Cr}^{3+}$ , without ZnO co-doping [13]. Despite the fact that in that case the accuracy was much lower due to the reduced excitation range accessed with a dye laser, the value is in good agreement with the value found here for the luminescence quantum yield of  $\text{Cr}^{3+}$  in Li sites.

The SIMPLE method in pulsed regime has been proved as a reliable technique for the determination of fluorescence quantum efficiency in a wide range of  $\Phi$  values and for different ions in several crystal lattices.

## References

- [1] B. Herreros, G. Lifante, *Appl. Phys. Lett.* 72 (1998) 531.
- [2] W. Solher, *Advanced Integrated Optics in LiNbO3* Proceedings of the 11th Annual Conference On European Fibre Communications and Networks (EFOC&N'93), 1993.
- [3] D. Jaque, J.A. Sanz-Garcia, J. Capmany, J. Garcia Sole, *Appl. Phys. B.* 70 (2000) 483.
- [4] E. Montoya, J. Capmany, L.E. Bausá, T. Kellner, A. Dening, G. Haber, *Appl. Phys. Lett.* 74 (21) (1999) 3113.
- [5] C.K.N. Patel, A.C. Tam, *Rev. Mod. Phys.* 53 (1981) 517.
- [6] A.C. Tam, *Rev. Mod. Phys.* 58 (1986) 381.
- [7] H. Vargas, L.C.M. Miranda, *Phys. Rep.* 161 (2) (1988) 43.
- [8] D.J. Dunstan, *J. Phys. D.* 25 (1992) 1825.
- [9] E. Rodriguez, J.O. Tocho, F. Cussó, *Phys. Rev. B* 47 (21) (1993) 14049.
- [10] G.A. Torchia, J.A. Sanz-García, J. Díaz-Caro, T. Han, F. Jaque, *Chem. Phys. Lett.* 288 (1998) 65.
- [11] B. Henderson, *Imbush Optical Spectroscopy of Inorganic Solids*, Oxford Science Publications, Oxford, 1989.
- [12] J. Diaz-Caro, J. Garcia-Solé, D. Bravo, J.A. Sanz-García, F.J. López, F. Jaque, *Phys. Rev. B* 54 (18) (1996) 13042.
- [13] E. Rodriguez, L. Nuñez, J.O. Tocho, F. Cussó, *J. Lumin.* 58 (1994) 353.