



ELSEVIER

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Optical Materials 20 (2002) 301–304



www.elsevier.com/locate/optmat

The luminescent quantum efficiency of Cr^{3+} ions in $\text{Cs}_2\text{NaAlF}_6$ single crystals

G.A. Torchia^{a,*}, D. Schinca^a, N.M. Khaidukov^b, J.O. Tocho^a

^a *Departamento de Física, Centro de Investigaciones Ópticas (CONICET-CIC), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 1900 La Plata, Argentina*

^b *Institute of General and Inorganic Chemistry, 117907 Moscow, Russia*

Received 23 April 2002; accepted 25 June 2002

Abstract

The luminescent quantum efficiency of Cr^{3+} ions in single fluoride crystal $\text{Cs}_2\text{NaAlF}_6$ was determined by using the simultaneous multiple-wavelength photoacoustic and luminescent experiments method, based on the generation of photoacoustic and luminescence signals after pulsed laser excitation. The luminescent quantum yield for the most important transition between the ${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$ vibronic levels was found to be $68 \pm 3\%$. This value agrees with that obtained from the ratio of the lifetimes of the corresponding transition at different temperatures.

© 2002 Elsevier Science B.V. All rights reserved.

PACS: 43.35U; 78.55; 78.60

Keywords: Photoacoustic spectroscopy; Luminescent quantum efficiency; Cr^{3+} ; $\text{Cs}_2\text{NaAlF}_6$

1. Introduction

The search for new solid-state tunable laser sources in the visible and near infrared has generated strong interest on different kind of materials doped with rare earth or transition-metal ions. Active research has been conducted in host materials such as LiNbO_3 , and alkali halides (KCl, NaCl, KBr), fluorides (KZnF_3 , $\text{Cs}_2\text{NaAlF}_6$, $\text{Cs}_2\text{NaGaF}_6$), garnets (CGGO,SGGO) and glasses [1–11].

For the case of the transition-metal ions of the group of iron, it is well known that the external 3d unfilled shell produces electronic transitions that give rise to intense luminescence. Since the active 3d-electrons are outside the core of the ions, the effect of the electric field is stronger than in the case of rare-earth ions. Optical transitions can originate both sharp and broad emission bands depending on the symmetry of the involved states and the dynamic and static environment around the active ions in the crystal.

Broad bands are due to the strong coupling between the ions and the lattice vibrations, so the phonon coupling is very important in order to obtain a large spectral range when manufacturing tuneable lasers. But the extent of the crystal

* Corresponding author. Present address: Departamento de Física de Materiales C-IV, Universidad Autónoma de Madrid, 28049 Cantoblanco, Madrid, Spain. Tel.: +34-91-397-4770; fax: +34-91-397-8579.

E-mail address: gustavot@ciop.unlp.edu.ar (G.A. Torchia).

phonon frequencies in these materials enhances non-radiative transitions, thus reducing the possibility of laser applications. For this reason, it is important to choose materials that have phonon frequencies much less than the energy gap of the transition in the crystal. Fluoride crystals are very attractive for visible laser transitions since they have a cut-off frequency lower than 600 cm^{-1} .

Cr^{3+} ion in fluoride crystals have been investigated by several research groups [6,7] since laser action in $\text{KZnF}_3:\text{Cr}^{3+}$ was first obtained [8]. In this work we explore the optical properties of Cr^{3+} ion in $\text{Cs}_2\text{NaAlF}_6$. This crystal has the hexagonal perovskite structure with lattice parameters $a = 6.18\text{ \AA}$ and $c = 29.87\text{ \AA}$. The Na^+ and Al^{3+} cations are ordered and octahedrally surrounded by F^- anions. In this material, the Cr^{3+} ions replace substitutionally the Al^{3+} ions.

The fluorescence quantum efficiency of luminescent materials is one of the most important parameters needed to have a complete characterization of its optical properties. Photoacoustic methods have been extensively used in quantum efficiency determination of gases and liquids [12–14], but less used for solid-state materials. Usually the photoacoustic methods rely on a comparison with a standard sample of known quantum yield. This procedure is not adequate for quantitative measurements in solid materials, because changing the sample may substantially affect the acoustic coupling in the experimental set-up. To avoid these difficulties Rodriguez et al. [15] developed a method to obtain the luminescent quantum efficiency without standard sample. The method is based in the simultaneous detection of luminescence signal (LUM) and photoacoustic signal (PAS) after the excitation at two wavelengths, as a function of incidence power for each wavelength and is called simultaneous multiple-wavelength photoacoustic and luminescent experiments (SIMPLE). This method relies on the existence of a full non-radiative relaxation, providing an internal reference that can be used as absolute quantum efficiency reference.

In a similar way, a multi-wavelength thermal lens method was developed to determine the fluorescence quantum efficiency of solids [16].

By using new optical sources, such as optical parametric oscillator (OPO), it is possible to get tuneable radiation between 0.4 and $2\text{ }\mu\text{m}$ that coincide with the absorption bands corresponding to a large number of materials. In this work, the SIMPLE method was applied to determine the luminescence quantum efficiency (Φ) of Cr^{3+} ions in $\text{Cs}_2\text{NaAlF}_6$ crystal. The result is compared with that obtained using the lifetime dependence with temperature.

2. Experimental

The fluorides were synthesised in the Institute of General and Inorganic Chemistry, Moscow, Russia, by a direct temperature-gradient method as a result of reaction of aqueous solutions of CsF (30–35 mol%) and NaF . The mole ratio CsF/NaF was changed from 4.8 to 5.2 and mixed with appropriate oxide mixtures of Al_2O_3 and Cr_2O_3 (99.995% pure). This procedure was done to get good quality crystals since the growth optimal condition depends on the CsF/NaF ratio [17]. The crystal used in this work was grown by the hydrothermal method with 0.5% the Cr^{3+} at a temperature of about 750 K, a temperature gradient of about 2 K/cm and pressures of 100–150 Mpa [17].

Optical absorption was conducted at room temperature by means of a Beckman DU-65 spectrophotometer. LUM and PAS were measured after excitation with an OPO from GWU, Germany. This source was pumped by a Q-Switch Nd:YAG laser lasing at 355 nm (Surelite II, Continuum) yielding 8 ns of pulse width and a typical output energy of 20 mJ in the used range.

The LUM was detected by a cross-dispersion spectrograph with a CCD camera from Multi-channel Instruments AB (Mechelle 900). To apply the SIMPLE method, the LUM signal was taken at the maximum of the emission band.

The PAS was detected with a resonant ceramic piezoelectric transducer (PZT) having a bandwidth of 200 MHz. In order to obtain better PAS signals the PZT was glued to the sample to improve the acoustic coupling. The PAS was detected and recorded by a digital oscilloscope Tektronik TDS 3032. To use the SIMPLE method, the PAS was

taken as the peak-to-peak of the first arrival ringing wave. These considerations made negligible other contributions originated by reflections on the other faces of the sample. A detailed description of the experimental set-up can be found in Ref. [15].

3. Results and discussion

The Cr^{3+} ions in the fluoride crystal $\text{Cs}_2\text{NaAlF}_6$ show two broad absorption bands corresponding to ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ and ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ vibronic transitions. These bands are centred at about 430 and 620 nm respectively.

Fig. 1 shows the absorption and emission optical spectra for Cr^{3+} ions in $\text{Cs}_2\text{NaAlF}_6$ crystal. Also shown in this figure are the energy levels involved in these optical transitions including all radiative and non-radiative process that are relevant for calculations. The absorption spectrum presents the two optical transitions mentioned above. The emission spectrum consists of single broad luminescence band centred at about 770 nm with a FWHM of 100 nm, independent of the excitation wavelength. We can point out that there is a full non-radiative connection between the ${}^4\text{T}_1$ and ${}^4\text{T}_2$ states because no fluorescence starting in the ${}^4\text{T}_1$ level was observed.

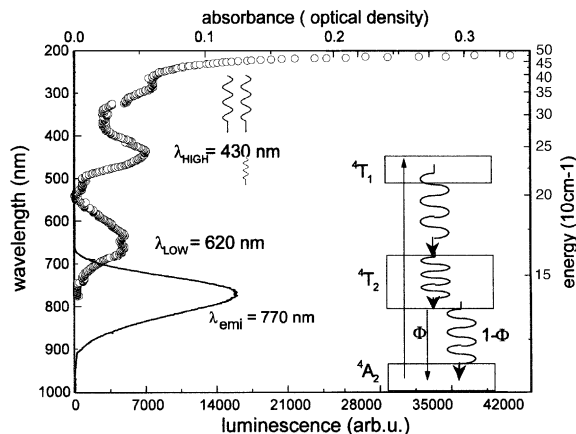


Fig. 1. Absorption and emission spectra of the Cr^{3+} ions $\text{Cs}_2\text{NaAlF}_6$. The inset shows the energy corresponding with all transitions.

As it was demonstrated in Ref. [15], the luminescent quantum efficiency 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 λ_{H} and λ_{L} represent the wavelengths used to excite the high and low energy bands respectively, λ_{emi} is the emission wavelength and A represents the ratio between the slope of the linear fit in the PAS vs. LUM plot 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. 2 shows the PAS vs. LUM diagram achieved in our crystal. This diagram is constructed with pairs of data corresponding to the amplitude of the acoustic signal and the peak of the luminescence intensity recorded for different laser pulse energies. As it can be seen, there is a good linear fit for each set of point data; the corresponding A was 1.97 ± 0.05 . By using expression (1), the luminescence quantum efficiency of Cr^{3+} ions in $\text{Cs}_2\text{NaAlF}_6$ crystal was $\Phi = (68 \pm 3)\%$.

The fluorescence quantum yield can also be estimated through the analysis of the lifetime of the involved emission levels in terms of the temperature. At sufficient low temperatures, when the non-radiative relaxation process can be assumed

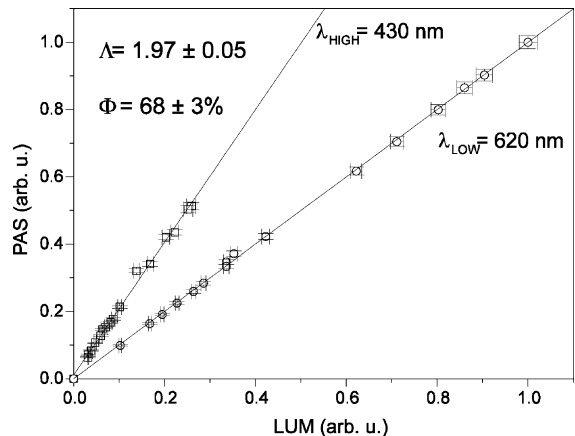


Fig. 2. PAS vs. LUM signals for the two excitation wavelengths for different incident OPO power.

to be negligible, the fluorescence quantum yield can be estimated from

$$\Phi = 100 \times \frac{\tau_{\text{exp}}(\text{room temperature})}{\tau_{\text{exp}}(\text{low temperature})}. \quad (3)$$

At room temperature, the emission band lifetime was measured in Ref. [6] as 180 μs while at 77 K the same authors have measured 260 μs . By using Eq. (3), the calculated fluorescence quantum yield results $\Phi = (69 \pm 3)\%$, for a 10% accuracy in lifetimes and assuming that 77 K is low enough to stabilize the lifetime.

4. Conclusions

In this work, the fluorescence quantum efficiency of Cr^{3+} ions in $\text{Cs}_2\text{NaAlF}_6$ crystal was obtained. By using SIMPLE method the fluorescence quantum efficiency was $(68 \pm 3)\%$, while by lifetime measurements from the literature the fluorescence quantum yield was estimated to be $(69 \pm 3)\%$. The coincidence justify the validity of the assumption that 77 K is low enough to make the non-radiative transitions negligible in this crystal.

This relatively high value for the quantum efficiency is in agreement with the fact that the localised respiratory phonons in fluoride crystals have low energy and many of them are necessary to fill the transition gap in a multi-phonon non-radiative process. Despite that, reduction from the ideal 100% luminescence quantum efficiency in the fluoride crystals can be attributed to some coupling between the electron and the phonons of the bulk modes of vibration (Raman phonons) as it was suggested for Cr^{3+} ions in LiNbO_3 crystal [18]. Further experimentations are needed to get a full description of the phonon spectra of this crystals.

Acknowledgements

G.A. Torchia is a CONICET (Argentina) fellowship holder. D. Schinca is member of CICBA (Argentina). This work was partially supported by UNLP (Argentina) grant X11/239 and by AN-PCYT (Argentina) grant 1403.

References

- [1] R. Nevado, F. Cusso, G. Lifante, F. Caccavale, C. Sada, F. Segato, *J. Appl. Phys.* 88 (1/11) (2000) 6183.
- [2] D. Jaque, J.A. Sanz-García, J. Capmany, J. Garcia Sole, *Appl. Phys. B* 70 (2000) 483.
- [3] E. Montoya, J. Capmany, L.E. Bausá, T. Kellner, A. Diening, G. Haber, *Appl. Phys. Lett.* 74 (21) (1999) 3113.
- [4] G.A. Torchia, J.A. Sanz-García, J. Díaz-Caro, T. Han, F. Jaque, *Chem. Phys. Lett.* 288 (1998) 65.
- [5] D.C. Shinca, J.O. Tocho, E. Rodriguez, F. Cussó, *J. Phys. IV C7* (1994) 409.
- [6] L.P. Sosman, A.D. Raveres Jr., R.J.M. da Fonseca, T. Abritta, N.M. Khaidukov, *Solid State Commun.* 114 (2000) 661.
- [7] R.J.M. Da Fonseca, A.D. Tavares Jr., P.S. Silva, T. Abritta, N.M. Khaidukov, *Solid State Commun.* 110 (1999) 519.
- [8] U. Braunch, Q. Durr, *Optics Commun.* 49 (1984) 61.
- [9] M. Grinberg, P.I. Macfarlane, B. Henderson, K. Holliday, *Phys. Rev. B* 52 (1995) 3917.
- [10] M. Grinberg, K. Holliday, *J. Lumin.* 92 (2001) 277.
- [11] D. Welch, R. Craig, W. Streifer, D. Scifres, *Electron. Lett.* 26 (1990) 1481.
- [12] C.K.N. Patel, A.C. Tam, *Rev. Mod. Phys.* 53 (1981) 517.
- [13] A.C. Tam, *Rev. Mod. Phys.* 58 (1986) 381.
- [14] H. Vargas, L.C.M. Miranda, *Phys. Report* 161 (2) (1988) 43.
- [15] E. Rodriguez, J.O. Tocho, F. Cussó, *Phys. Rev. B* 47 (21) (1993) 14049.
- [16] S.M. Lima, A.A. Andrade, R. Lebullenger, A.C. Hernades, T. Catunda, M.L. Baeso, *Appl. Phys. Lett.* 78 (21) (2001) 3220.
- [17] P.A. Tanner, L. Yulong, N.M. Edelstein, K.M. Murdoch, N.M. Khaidukov, *J. Phys.: Condens. Matter* 9 (1997) 7817.
- [18] G.A. Torchia, O. Matinez-Matos, P. Vaveliuk, J.O. Tocho, *J. Phys.: Condensed Matter* 13 (30) (2001) 6577.