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Luminescence–structure correlation in $CaYOBO_3:Eu^{3+}$

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Abstract

The spectroscopic properties of europium calcium orthoborate are investigated under site-selective laser excitation in the ${}^5D_0 \rightarrow {}^7F_0$ region. Results show that at least two site distributions are present. Careful analysis of the principal transitions ${}^5D_0 \rightarrow {}^7F_{0-2}$ shows disagreement with the local symmetry description of the sites over which the europium ions are distributed. © 1998 Elsevier Science S.A.

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1. Introduction

The renewal of interest in studying rare-earth-doped borates or oxyborate materials is due to their high UV transparency, their non-linear properties and their exceptional optical damage threshold, which make them attractive for numerous practical applications such as SHG, phosphors for lamps and gas discharge display panels. When activated by Eu^{3+} the calcium oxyborate $CaYOBO_3$ exhibits an intense red luminescence peaking at around 611 nm under UV excitation (254 nm radiation of a Hg lamp). Nevertheless, relatively little is known about the structure and optical properties of this compound [1]. In this paper we report on some optical results using Eu^{3+} as structural probe. The work was completed by an IR study which shows that boron has trigonal coordination.

2. Techniques

X-ray powder diffraction patterns were obtained at room temperature by means of a DATA MP-Siemens D501 diffractometer. The infra-red absorption spectra of the different samples, in the powder form, were recorded on a FTIR spectrophotometer Nicolet type 5 SXC, transformed in the 400 and 4000 cm^{-1} frequency range. Luminescence measurements were performed using a pulsed dye laser (Continuum ND 60) pumped by a Continuum Surelite-SL10 double Nd:YAG laser (10 ns pulse, 0.1 cm^{-1} bandwidth). A mixture of rhodamines 590 and 610 dyes from Exciton was used for excitation into the ${}^5D_0$ level of Eu^{3+}. The 254 nm line of the Hg lamp selected through an Oriel 250 FJ 10-25 interference filter was also used for excitation into the Eu–O charge transfer state. The spectra were recorded using a Jobin Yvon HR 1000 monochromator (focal length 1 m, 1200 grooves mm^{-1} grating and a band pass of 8 Å mm^{-1} slits) and detected by a Hamamatsu R1104 photomultiplier. Data acquisition was performed with an EG&G PAR 162/164 boxcar averager and collected with a digital signal processor IPC-DAS 1600. Luminescence lifetime measurements were made using a Lecroy 9310A, 400 MHz oscilloscope. Sample cooling was provided by a closed cycle He optical Cryomech GB15 cryogenerator allowing the temperature to be varied between 15 and 300 K.

3. Synthesis and structure

Several compositions of doped oxyborates of formulation $CaY_{1-x}Eu_xOBO_3$ were prepared in the solid state by firing intimate stoichiometric mixtures of $CaCO_3$ (Strem 99.9%), Y_2O_3 and Eu_2O_3 (Rhône-Poulenc 99.99%) and H_3BO_3 (Strem 99.9%), first at 600°C for 3 h to allow total decomposition of $CaCO_3$ and H_3BO_3 and then at 1200°C for 16 h. All the materials were checked by X-ray powder diffraction, chemical analysis and infra-red spectroscopy. The powder diagram of $CaY_{1-x}Eu_xOBO_3$ ($0 \leq x \leq 0.25$) indexes an orthorhombic unit cell, as suggested in Ref. [1]. The spectra clearly show that the borate $CaYOBO_3$ could not accommodate more than 25% Eu^{3+}. However, since the crystal structure of $CaYOBO_3$ was only based on a

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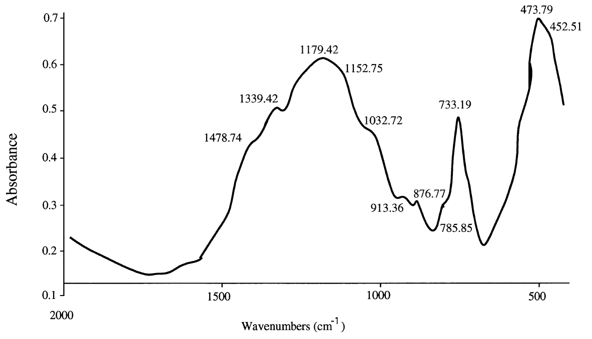

Fig. 1. Infra-red spectrum of CaYOBO$_3$:10% Eu^{3+}.

comparison with the X-ray patterns of Y$_2$BeO$_4$ [2], single-crystal X-ray determination is needed to remove any remaining doubts. Following this structural description [2], two equivalent cationic sites corresponding to the Y^{3+} crystallographic sites can be observed in yttrium beryllate, both showing C$_s$ symmetry, which can accommodate the Eu^{3+} dopant. Fig. 1 presents the infra-red spectrum of the 10% Eu^{3+}-doped CaYOBO$_3$. The observed frequencies correspond to the boron–oxygen vibrations and triangular coordination of the boron [3].

4. Luminescence

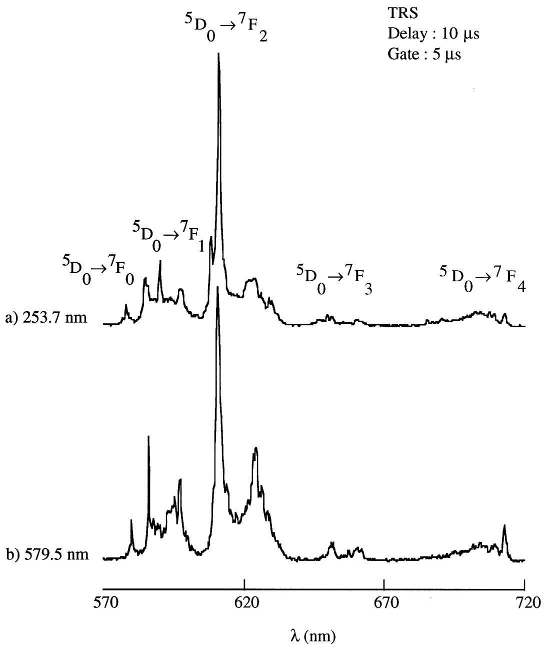

Fig. 2. Emission spectra of CaYOBO$_3$:15% Eu^{3+} at 77 K under (a) UV excitation, (b) visible excitation in the $^5D_0$ level of Eu^{3+}.

The emission spectra were recorded at different temperatures for several concentrations under UV and visible excitation. The spectra obtained are similar and relatively simple showing only transitions from the $^5D_0$ level (Fig. 2). Within the range of compositions of the solid solution, the unit cell volume of CaYOBO$_3$ increases linearly with increasing Eu^{3+} concentration. This unit cell volume variation does not produce any change either in the emission or in the excitation spectra of Eu^{3+}. The fact that only transitions from $^5D_0$ states are observed under UV excitation may be explained by the quenching of the emission from higher excited ^5D_J (J=1–4) levels by efficient multiphonon de-excitation processes associated with lattice vibrations. According to the IR spectrum (Fig. 1) the phonon cutoff is about 1700 cm^{-1} in Ca(Y,Eu)OBO$_3$. Thus relaxation can occur between two successive excited levels resulting in essentially two vibration quanta. The excitation spectra in the $^7F_{0,1} \rightarrow ^5D_0$ wavelength range were recorded at different temperatures by monitoring different emission bands. At low temperature the spectra consist essentially of two bands labelled A and B in Fig. 3, the relative intensities of which vary slightly depending on the monitored emission. The two bands which appear on both the high and low energy side of the $^7F_0 \rightarrow ^5D_0$ excitation bands are attributed to a vibronic side band and $^7F_1 \rightarrow ^5D_0$ absorption band, respectively. The presence of two site distributions in the $^7F_0 \rightarrow ^5D_0$ absorption range with maxima at 578.2 (A) and 579.9 nm (B) confirms that Eu^{3+} introduced into the matrix lie in two crystallographic sites. To examine the details of these site distributions, low temperature emission

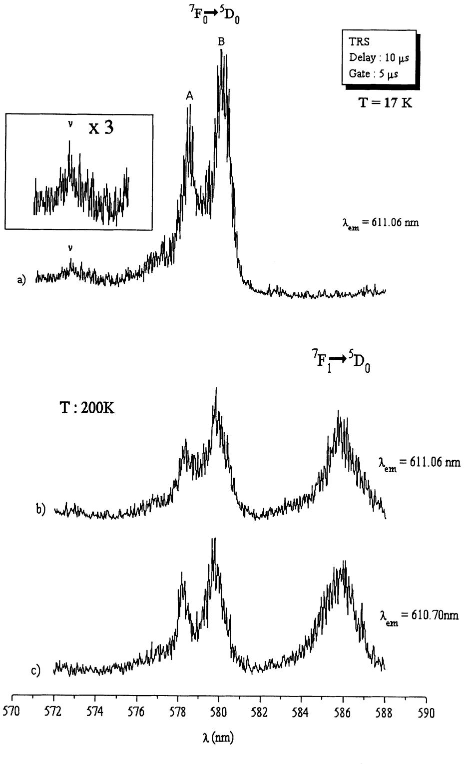

Fig. 3. Excitation spectra of CaYOBO$_3$:15% Eu^{3+} at (a) 17 K, (b,c) 200 K. A and B refer to the two site distributions in which the europium ions are located (see text).

spectra were recorded upon selective excitation. Fig. 4 shows the $^5D_0 \rightarrow {}^7F_{1,2}$ emission spectra recorded at 77 K for CaYOBO$_3$:15% Eu^{3+}. The observation of vibronic side bands (ν) in these emission spectra indicates the rather strong vibronic coupling of the $^5D_0$ level. The self emission features of each site can then be identified. On the other hand, all the emissions exhibit exponential luminescence decay with a time constant of 2 ms at 15 K in the overall range of Eu^{3+} concentration. Such an observation excludes a possible site-to-site energy transfer. The oxyborate structure has two types of sites available for cation substitution both with C$_s$ symmetry following the structural description. The expected splitting for the J manifolds of Eu^{3+} in the C$_s$ site is: 1, 3, 5, 7 and 9 for $J=0$, 1, 2, 3 and 4, respectively. While for the A excited spectra it seems possible to accredit such symmetry since the related $^5D_0 \rightarrow {}^7F_{1,2}$ emissions show at least 1, 3 and 4 peaks, the B excited emission spectra show less than the expected peaks notably for the $^5D_0 \rightarrow {}^7F_1$ transition. Moreover, the splitting of the $^7F_1$ manifolds of Eu^{3+}, which is directly proportional to the crystal field strength [4], is different for the two sites in the case of CaYOBO$_3$:Eu^{3+}. On the other hand, the B excited emission spectra show more pronounced vibronic sidebands, notably in the case of the electric dipole transition $^5D_0 \rightarrow {}^7F_2$. All these observations are in contradiction with similar environments for the two sites. To elucidate the contradictions, a structural determination was undertaken from a single crystal prepared by a flux evaporation process using a protocol described elsewhere [5]. The complete structure determination is in progress.

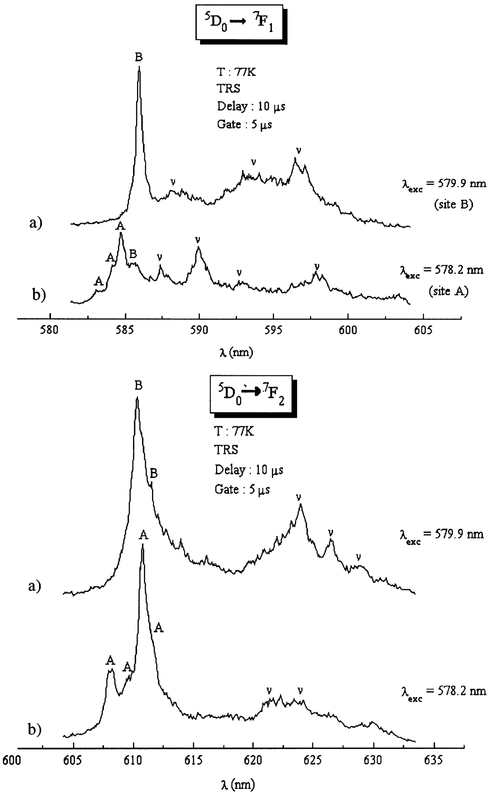

Fig. 4. $^5D_0 \rightarrow {}^7F_{1,2}$ emission spectra of CaYOBO$_3$:15% Eu^{3+} under selective excitation: (a) excitation at 578.2 nm, (b) excitation at 579.9 nm.

Acknowledgements

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