Optical spectroscopy and magnetic behaviour of Sm^{3+} and Eu^{3+} cations in $Li_6Eu_{1-x}Sm_x(BO_3)_3$ solid solution

Rekia Belhoucif [a, b, *], Matias Velázquez [c], Olivier Plantevin [d], Patrick Aschehoug [e], Philippe Goldner [e], George Christian [d]

[a] Faculté de Physique, Laboratoire d'Électronique Quantique, USTHB, BP 32 El alia, 16111, Bab Ezzouar, Alger, Algeria
[b] Faculté des Sciences, Département de Physique, UMBB, Route de la Gare Ferroviaire, 35000, Boumerdes, Algeria
[c] CNRS, Université de Bordeaux, ICMCB, 87 avenue du Dr. A. Schweitzer, 33608, Pessac cedex, France
[d] CSNSM UMR 8609, CNRS-Université d'Orsay, Bât. 108, 91405, Orsay Campus, France
[e] PSL Research University, Chimie ParisTech -CNRS, Institut de Recherche de Chimie Paris, 75005 Paris, France

ARTICLE INFO

ABSTRACT

A new borate solid solution series of powders, $Li_6Eu_{1-x}Sm_x(BO_3)_3$ (LSEBx, x = 0.35, 0.5, 0.6, 1), were synthesized by solid-state reaction, characterized and their luminescent properties were investigated. The absorption spectra indicate that absorption takes place mainly from the Sm^{3+} $^6H_{5/2}$ ground state, with a strong band at 405 nm. The photoluminescence spectra reveal that the Eu^{3+} red emission intensity strongly depends on the Sm^{3+} content x. Judd–Ofelt theory was applied to experimental data for the quantitative determination of phenomenological parameters Ωi (i = 2, 4, 6) Judd Ofelt parameters, radiative transition rates and emission quantum efficiency. Owing to the energy transfer from Sm^{3+} to Eu^{3+} the intense red light detected at 613 nm at room temperature under UV or blue light excitation, was improved by ~35% as compared with Sm^{3+}-free samples. This energy transfer was confirmed by faster decay times of Sm^{3+} as energy donors. Moreover, the energy transfer between Sm^{3+} and Eu^{3+} is unidirectional and irreversible, implying that the energy transfer wastage between Sm^{3+} and Eu^{3+} is very low. Magnetic susceptibility (χ) measurements of LSEBx were carried out in the temperature range 2 −320 K and are used to compare calculated and experimental energy levels.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Rare earth ions find many applications as activators and sensitizer in solid state and crystal lasers, infrared quantum counters [1–3] as well as infrared to visible converters [4–6]. Energy transfer between ions in solids can be accomplished either radiatively or nonradiatively and the mechanism and kinetics involved have been extensively addressed [7,8]. The non-radiative energy transfer [9] pertains to the case of resonance of the ion donor and ion-acceptor transitions, when there is at least partial overlap of the donor luminescence lines and of the acceptor absorption lines. Experiments, however, have revealed cases of effective non-radiative energy transfer between ions even when there was no overlap of the donor and acceptor transitions [10]. Apparently these processes occur with phonons taking part. It is of considerable interest to investigate experimentally the characteristic features of nonresonant transfer: its efficiency, its dependence on the frequency of the phonons that take part in the transfer process, the transfer rates, the mechanism of transfer, levels responsible for transfer, etc.

In this work, we chose to investigate mixed Sm^{3+}/Eu^{3+} pairs because of the practical importance of Eu^{3+} as a phosphor and possibly a laser active cation [11,12]. The relatively large absorption of some of the Sm^{3+} bands permits a good pumping to the Eu^{3+} levels at a wavelength ≈ 400 nm assuming an efficient energy transfer. The luminescence from the Sm^{3+} $^4G_{5/2}$ level may be quenched by both cross-relaxation between Sm^{3+} ions and energy transfer from Sm^{3+} donor ions to Eu^{3+} acceptor ions. For at least three reasons, this configuration is particularly suitable for an experimental investigation of the Sm-Eu energy-transfer process. Firstly, both the Sm^{3+} $^4G_{5/2}$ and the Eu^{3+} $^5D_0$ states have slow intrinsic decay rates over the temperature range 10−300 K [13]. Secondly, the energy-transfer rate from Sm^{3+} to Eu^{3+} is comparable

* Corresponding author. Faculté de Physique, Laboratoire d'Électronique Quantique, USTHB, BP 32 El alia, 16111, Bab Ezzouar, Alger, Algeria.
E-mail address: faizabelhoucif@gmail.com (R. Belhoucif).

to the intrinsic decay rates of the isolated ions [13]. Thirdly, both the Sm^{3+} $^4G_{5/2}$ and the Eu^{3+} $^5D_0$ states may be separately excited in the region 17000-18000 cm^{-1} and the emission from these states may be studied with minimum spectral overlap.

In this work, we studied the luminescence behaviour of the Eu^{3+} and Sm^{3+} ions in the LSEBx solid solution, which was synthesized by solid-state reaction. We focused on the spectroscopic properties of Sm^{3+} in order to confirm the energy transfer from Sm^{3+} to Eu^{3+}. Among Eu^{3+}-activated phosphors, those containing a high Eu^{3+}-concentration without concentration quenching are desirable for host materials under near UV excitation in order to emit strong red light [14]. Therefore, we selected $Li_6RE(BO_3)_3$ as a host material that has an anionic borate BO_3^{3-} group. The borate are better hosts for examining the effects of chemical environments on the optical properties of the rare earth ions, due to their high transparency, low melting point, high thermal stability, chemical and mechanical stability [15−19] and allows the high probability of electric dipole f-f transitions of rare earth (RE) in the host material and can contain a high RE concentration without concentration quenching, compared to other host materials [20]. The magnetic susceptibility behaviour was also studied and found to depend strongly on the Eu^{3+}/Sm^{3+} concentration ratio. The populations of the first excited states become significant and Eu^{3+} and Sm^{3+} cations do not entail a Curie law or Curie−Weiss law behaviour of the LSEB compounds.

2. Experimental

A series of $Li_6Eu_{1-x}Sm_x(BO_3)_3$ (x = 0, 0.35, 0.5, 0.6, 1) powders were synthesized by solid state reaction. The starting materials, Li_2CO_3 (4N), Eu_2O_3 (4N), Sm_2O_3 (4N) and H_3BO_3 (4N) were weighed according to the stoichiometric ratio, mixed in an agate mortar, transferred to crucibles and then thermally treated in air in successive stages at 300 °C for 24 h, 500 °C for 24 h, separated by intermediate grindings. As-prepared powder was pressed into a pellet and then sintered at 750 °C for 48 h. X-ray diffraction was used to confirm the structure of the material and to make sure no impurity phases were present.

Diffuse reflectance spectra (DRS) of the sintered polycrystalline LSEBx pellet samples were measured by means of an UV−vis−NIR spectrophotometer (Model Cary 5000). Photoluminescence spectra were recorded by means of a spectrometer (Triax 320 Horiba Jobin-Yvon) equipped with both laser diodes and pulsed xenon lamps as the light source. Photomultiplier tubes (PMT) (Hamamatsu R928 and R955) were used as detectors in the visible and NIR regions. The decay profiles from the $^5D_0$ excited state to its lower lying energy levels have been recorded by monitoring the excitation and emission wavelengths at 405 and 611 nm, respectively. Decay measurements were recorded using a tunable optical parametric oscillator pumped by a Nd:YAG Q-switched laser (Ekspla NT342B-SH) with 6 ns pulse length, a Jobin-Yvon HR250 monochromator and a photomultiplier tube. The magnetic susceptibility measurements were carried out in a Quantum Design SQUID MPMS XL magnetometer. The sample was first finely grinded and next pressed into a pellet to eliminate as much as possible preferential reorientation effect. The diamagnetic contribution to the susceptibility has been measured with a pure $Li_6Y(BO_3)_3$ pellet [21]. The estimated experimental value is about -1.3×10^{-5} (in CGS emu units). All the data were corrected for this diamagnetic contribution, which is extremely small in comparison to the observed susceptibilities. The temperature dependence of the magnetic susceptibility for powder samples was investigated under field-cooled (FC) mode over the temperature range 5−355 K under a magnetic field of $\mu_0H = 5$ mT.

Phases identification was performed using room temperature X-ray powder diffraction with a Bruker Nonius PHILIPS PW 3710 diffractometer using Cu ($\lambda = 0.71073$ Å) radiation, operating at 40 kV and 15 mA. The scanning speed for phase determination was 0.2°/min. The XRD data of the $Li_6Eu_{1-x}Sm_x(BO_3)_3$ powders with different x-values reveal a single-phase without any secondary phase (see Fig. 1-a); all the peaks were assigned within the $P2_1/c$ monoclinic space group of $Li_6Eu_{1-x}Sm_x(BO_3)_3$ (in good agreement with those reported in JCPDS file 425557 to 425564 [21]). The lattice parameters over the whole range of Sm^{3+} cations substitution for Eu^{3+} ones in $Li_6Eu_{1-x}Sm_x(BO_3)_3$ ($0 \le x \le 1$) were estimated from the XRD data shown in Fig. 1-b, and treated by the Le Bail method. The crystal structure remains unchanged with varying Sm^{3+}-concentrations. It was found that very close ionic radii between Eu^{3+} (CN = 8, r = 1.066 Å) and Sm^{3+} (CN = 8, r = 1.079 Å) [22] ions resulted in very slowly changing lattice parameters. This is a direct experimental evidence of the fact that there is a complete solid solution range with full Sm^{3+} substitution for the Eu^{3+} ions in the lattice.
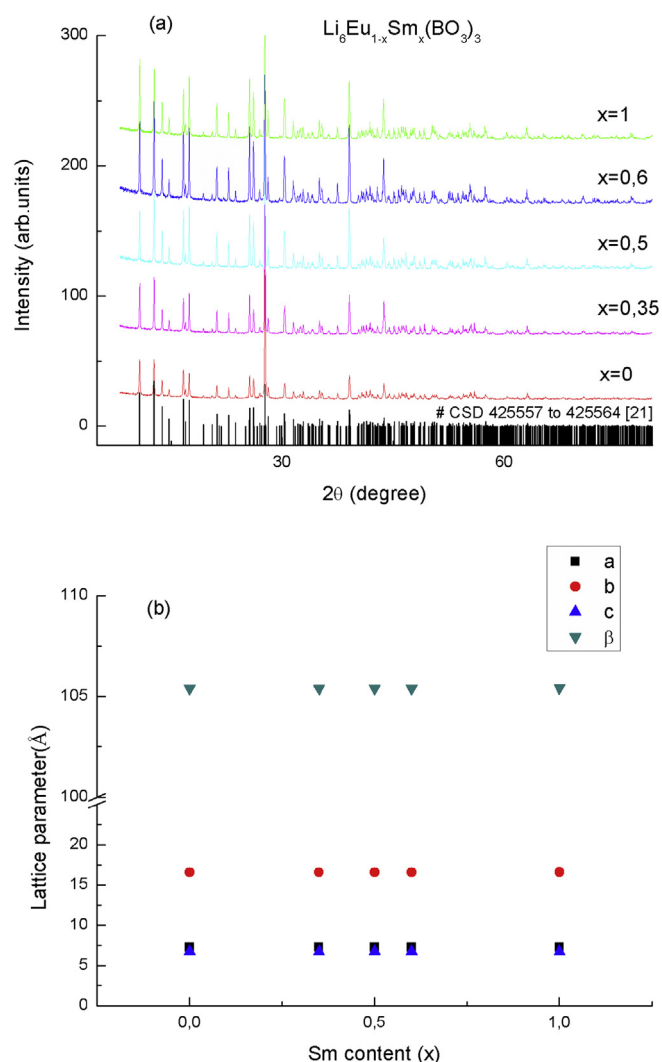
Fig. 1. Powder XRD patterns of $Li_6Eu_{1-x}Sm_x(BO_3)_3$ (x = 0, 0.35, 0.5, 0.65,1) (a). Variations with the Sm^{3+}-concentration of the monoclinic lattice parameters *a, b, c* and β in the $Li_6Eu_{1-x}Sm_x(BO_3)_3$ solid solution (b).