

Energy level scheme of $\text{Eu}^{3+}:\text{La}_3\text{Ga}_5\text{SiO}_{14}$ (langasite)

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In this paper, based on the luminescence and diffuse reflectance spectra measured at room temperature, we present preliminary results concerning the energy level scheme of Eu^{3+} in the partially disordered crystal langasite ($\text{La}_3\text{Ga}_5\text{SiO}_{14}$).

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1. Introduction

One of the main characteristic of a doped material is the energy level scheme of the dopant. Usually, the energy level scheme is obtained from luminescence and absorption spectra. For powders, the absorption spectra can not be measured; instead, excitation and diffuse reflectance spectra are accessible. Finding the energy level scheme in a disordered material (amorphous or partially disordered crystal) is a difficult task even for rare-earth ions: the emission and absorption lines are wider and overlap and a multicenter structure could be present. The aim of this paper is to find the energy level scheme of rare earth ion in a partially disordered crystal. As an example, we have chosen Eu^{3+} in langasite ($\text{La}_3\text{Ga}_5\text{SiO}_{14}$ – LGS).

The structure of langasite crystals is given by the formula $A_3BC_3D_2O_{14}$ where *A* represents the dodecahedral positions (distorted Thompson cubes), *B* – octahedral positions and *C*, *D* – tetrahedral positions [1]. La^{3+} occupies the position *A*. The local symmetry at this site is C_2 [2]. In LGS, the *B* and *C* are occupied by Ga^{3+} . LGS is a partially disordered crystal since the tetrahedral positions *D* are randomly occupied by Ga^{3+} and Si^{4+} . In langasite Eu^{3+} substitutes La^{3+} .

In this paper we present preliminary results concerning the energy level scheme of Eu^{3+} in LGS using luminescence and diffuse reflectance spectra measured at room temperature.

2. Experimental

Eu-doped langasite was synthesized in our laboratory from high-purity La_2O_3 , Ga_2O_3 , SiO_2 , and Eu_2O_3 , according to $(\text{La}_{0.95}\text{Eu}_{0.05})_3\text{Ga}_5\text{SiO}_{14}$ formula. The oxides were mixed in an agate balls mill and calcinated at 1500°C for 24 h. Then the powder was pressed in pallets and the crystals were grown along the *C*-axis in platinum crucibles in nitrogen atmosphere, using the Czochralski method. The powders of Eu^{3+} -doped LGS were obtained by milling of single crystals.

The luminescence of the $\text{Eu}:\text{LGS}$ was excited using a ScienceTech Xe-Hg 350-W lamp with suitable filters. The luminescence spectra were measured at room temperature

using a Horiba Jobin-Yvon 1000M monochromator, an S-20 photo-multiplier and an SR830 lockin amplifier from Stanford Research Systems. The experimental setup for diffuse reflectance measurements was described elsewhere [3].

3. Results and discussion

3.1. Luminescence spectra

The 5D_0 level is not degenerated. Since the local symmetry at the Eu^{3+} position in LGS is low (C_2), the degeneracy is completely removed and in the luminescence transition $^5D_0 \rightarrow ^7F_J$, $2J+1$ lines should be visible. The above affirmation holds if there is only one luminescence center. Taking into account that LGS crystals are partially disordered, more than one luminescence centers could exist. The presence of more than one luminescence centers can be observed easier in the spectrum of $^5D_0 \rightarrow ^7F_0$ transition since this transition takes place between two nondegenerate levels.

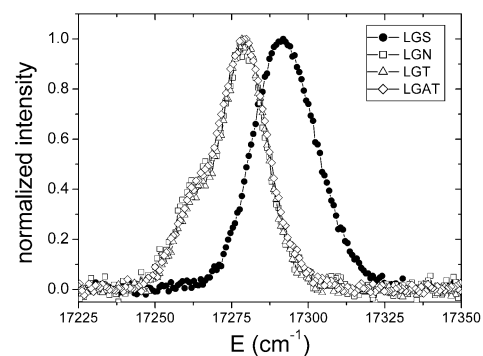


Fig. 1. Luminescence spectrum of $^5D_0 \rightarrow ^7F_0$ transition of Eu^{3+} in LGS powder (solid symbols) and LGN, LGT, and LGAT powders (open symbols).

In Fig. 1 are shown the luminescence spectra of $^5D_0 \rightarrow ^7F_0$ transition of Eu^{3+} in four crystals from the langasite family: LGS, langanite ($\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$ – LGN),

langatate ($\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$ - LGT), and a langatate crystal with aluminum ($\text{La}_3(\text{Ga}_{1-x}\text{Al}_x)_{5.5}\text{Ta}_{0.5}\text{O}_{14}$ - LGAT). We note: (i) the position of this transition in LGS is at higher energy due to the more reduced covalence [4]; (ii) the shape of the luminescence line in LGS is close to a Gaussian while, for the other crystals, a shoulder at lower energy is observed. The reasons for these differences are discussed elsewhere [5]. It results that the assignation of the various transitions between the Stark sublevels of Eu^{3+} in luminescence and absorption spectra and, as a consequence, the building of the energy level scheme of Eu^{3+} is easier in LGS. In the following, we will consider only one center (or quasicenter [6]) formed by Eu^{3+} in LGS.

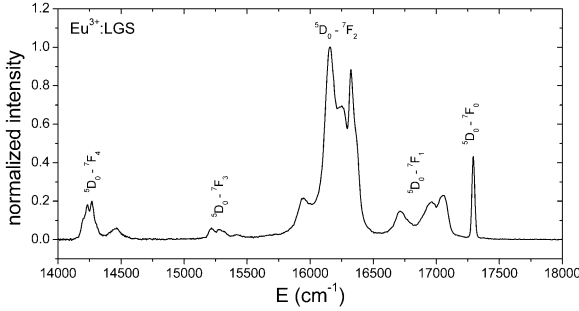


Fig. 2. Luminescence spectrum of Eu^{3+} in LGS corresponding to ${}^5D_0 \rightarrow {}^7F_0$, 7F_1 , 7F_2 , 7F_3 , and 7F_4 transitions.

In Fig. 2 is given the luminescence spectrum of Eu^{3+} in LGS corresponding to ${}^5D_0 \rightarrow {}^7F_0$, 7F_1 , 7F_2 , 7F_3 , and 7F_4 transitions. Three luminescence lines are clearly observed in the magnetic-dipole transition ${}^5D_0 \rightarrow {}^7F_1$ and five in the electric-dipole transition ${}^5D_0 \rightarrow {}^7F_2$. Seven lines should be observed in ${}^5D_0 \rightarrow {}^7F_3$ transition and nine lines in ${}^5D_0 \rightarrow {}^7F_4$ one. In fact, we observed only three luminescence lines in ${}^5D_0 \rightarrow {}^7F_3$ transition and four in ${}^5D_0 \rightarrow {}^7F_4$. The results are given in Table 1. The intensities of the ${}^5D_0 \rightarrow {}^7F_5$, 7F_6 transitions are too low to allow the determination of the energy levels.

3.2. Diffuse reflectance spectra

Working with powders, instead to measure the absorption, we measured the diffuse reflectance. The diffuse reflectance spectrum of $\text{Eu}:\text{LGS}$ powder, in rapport with the white etalon (BaSO_4), is given in Fig. 3. The baseline of the diffuse reflectance spectrum is tilted towards high energies due to the presence of point defects involving oxygen [8-10].

We note that the transitions beginning from 7F_0 and 7F_1 are observed in absorption since these levels are populated at room temperature; the transition ${}^5D_0 \rightarrow {}^7F_2$ is observed in luminescence because the 7F_2 level is not populated.

The diffuse reflectance spectrum from Fig. 3 can be transformed in a kind of absorption spectrum with the Kubelka-Munk relation [7]

$$\frac{k}{s} = \frac{(1-R)^2}{2R} \quad (1)$$

where k is the absorption coefficient, s is the scattering coefficient and R is the reflectance. The result is shown in Fig. 4. Before the application of transformation (1) the baseline of the reflectance spectrum was extracted.

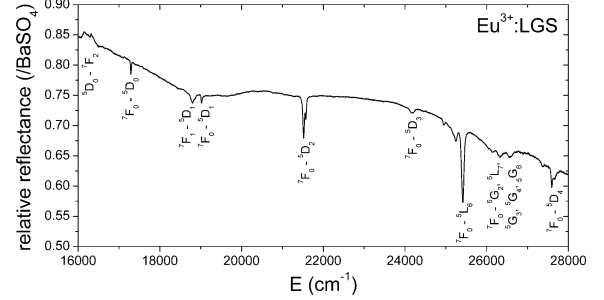


Fig. 3. Diffuse reflectance spectrum of $\text{Eu}:\text{LGS}$ in rapport with 'white' BaSO_4 . The main absorption lines are indicated. The luminescent transition ${}^5D_0 \rightarrow {}^7F_2$ is also shown.

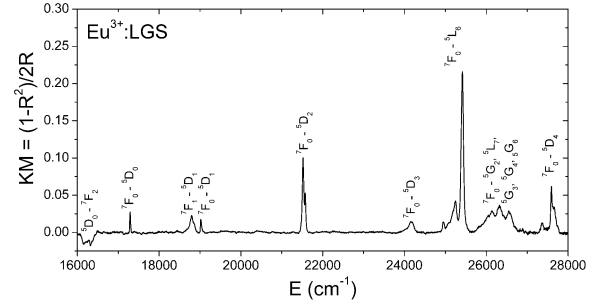


Fig. 4. Absorption (Kubelka-Munk) spectrum of $\text{Eu}:\text{LGS}$. The baseline was extracted. The luminescent transition ${}^5D_0 \rightarrow {}^7F_2$ appears negative.

All three Stark sublevels of 5D_1 were tentatively identified in ${}^7F_0 \rightarrow {}^5D_1$ transition (the results are given in Table 1) but only two (instead of five) in ${}^7F_0 \rightarrow {}^5D_2$.

Table 1. Energy levels of Eu^{3+} in LGS observed at room temperature.

Eu^{3+} level	Energy (cm^{-1})
7F_0	0
7F_1	238, 341, 575
7F_2	927, 968, 1041, 1139, 1348
7F_3	15216, 15279, 15320
7F_4	14199, 14230, 14271, 14458
5D_1	19016, 19027, 19041
5D_2	21519, 21573
5L_6	24952, 25080, 25184, 25245, 25414

At room temperature, the transition ${}^7F_0 \rightarrow {}^5D_3$ is not resolved. The transition ${}^7F_0 \rightarrow {}^5L_6$ is better resolved and in Table 1 we introduced the results (5 Stark sublevels from 13).

4. Conclusions

Due to the peculiar structure of the partially disordered langasite crystal, the multicenter structure is not resolved in the luminescence and absorption lines. This simplifies the identification of the transitions. Using luminescence and diffuse reflectance spectra part of the of the energy level scheme of Eu^{3+} in LGS are obtained.

At room temperature, the luminescence and absorption lines show a significant homogeneous broadening. In order to better resolve the structure of the luminescence and absorption lines, low temperature measurements should be performed. Such work is now in progress.

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