$^5D_0$ luminescence in europium-doped langanite

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The luminescence spectrum of Eu^{3+} in langanite was measured and analyzed. The radiative lifetime (τ_{rad}) of the $^5D_0$ level and the Judd-Ofelt parameters (Ω_2, Ω_4, Ω_6) for Eu^{3+}-doped langanite crystal were obtained from the analysis of the luminescence spectrum. The following values were obtained: τ_{rad} = 1.11 ms, $\Omega_2=7.16\times10^{-20}$ cm^2, $\Omega_4=4.75\times10^{-20}$ cm^2, and $\Omega_6\approx1.66\times10^{-20}$ cm^2.

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1. Introduction

Langanite crystals ($La_3Ga_{5.5}Nb_{0.5}O_{14}$ - LGN) belong to the langasite ($La_3Ga_5SiO_{14}$ - LGS) family and crystallize in the *P321* space group, symmetry class *32* and are isostructural with the calciumgallogermanate ($Ca_3Ga_2Ge_4O_{14}$) [1, 2]. The general formula is $A_3BC_3D_2O_{14}$ where *A* represents the dodecahedral positions (distorted Thompson cubes), *B* – octahedral positions and *C*, *D* – tetrahedral positions. La^{3+} occupies the position *A*. The local symmetry at this site is C_2 [3]. LGN is a partially disordered crystal: the octahedral positions *B* are occupied by two different ions, Ga^{3+} and Nb^{3+} with equal probability. Ga^{3+} occupies the remaining positions (*C* and *D*).

When excited in the near UV (396 nm, transition $^7F_0 \rightarrow {}^5L_6$), Eu^{3+}-doped LGS, LGN, and LGT ($La_3Ga_{5.5}Ta_{0.5}O_{14}$) crystals show bright red luminescence which suggests the possibility to use these materials as red phosphors. Besides, the disorder of these crystals results in wider absorption bands of Eu^{3+}, improving the matching between the absorption lines and the spectrum of the light-emitting diodes.

One important parameter for a luminescent material is the radiative lifetime of the emitting level. Knowing the radiative lifetime, the quantum efficiency of the emitting level is obtained as the ratio between the measured lifetime and the radiative lifetime.

Usually, for trivalent rare-earth ions, the radiative lifetime is obtained from the Judd-Ofelt (JO) analysis based on the absorption spectra [4, 5]. We note that the absorption spectra are measured in absolute units (e.g. absorbance function of wavelength) and do not need further calibrations. On the contrary, the luminescence spectra are measured in relative units and need calibration and correction for the spectral responsivity of the experimental apparatus.

The luminescence spectrum corresponding to the $^5D_0 \rightarrow {}^7F_J$ (J = 0, … 6) transitions of Eu^{3+} allows a simple determination of the JO parameters.

The aim of this paper is the measurement of the radiative lifetime of $^5D_0$, the main emitting level of Eu^{3+}, based on the luminescence spectrum and the determination of the JO parameters for further comparisons.

2. Experimental

Eu-doped langanite was synthesized in our laboratory from high-purity La_2O_3, Ga_2O_3, Nb_2O_5, and Eu_2O_3. The oxides were mixed in an agate balls mill and calcinated at 1500ºC for 24 h. The powder was pressed in pellets 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 LGN were obtained by milling of single crystals. The luminescence of the Eu:LGN was excited in UV with a Xe-Hg arc lamp equipped with suitable filters. The experimental set-up for luminescence measurements contains a 1 m Jarrell-Ash monochromator, an S-20 photomultiplier and a SR 830 lockin amplifier on line with a computer. For decay measurements, the luminescence was excited with the second harmonics of a Nd-YAG laser and analyzed with an Ortec MCS-PCI multichannel scaler card.

To correct the luminescence spectrum for the spectral responsivity of the experimental apparatus we used a tungsten-halogen lamp whose emissivity is close to that of a black body having approximately 3000K.

All the measurements were performed at room temperature.

3. Results and discussion

For Eu^{3+} doped materials, the radiative lifetime of $^5D_0$ can be obtained directly from the luminescence spectrum, without applying the Judd-Ofelt model. The transition $^5D_0 \rightarrow {}^7F_1$ is pure magnetic-dipole and its probability is practically independent of the host material and its value was calculated: $A_{rad}(^5D_0 \rightarrow {}^7F_1) = 15.1n^3$ s^{-1} [6], n being the refraction index. The magnetic-dipole transition is used to calibrate the luminescence spectrum.

The area corresponding to a transition $i \rightarrow j$ in the luminescence spectrum is proportional with the radiative transition probability, the population of the initial level, N_i and the photon energy $h\upsilon_{ij}$ averaged on the luminescence band [6]

$$Area(i \rightarrow j) \propto A_{rad}(i \rightarrow j) N_i h\nu_{ij} \quad (1)$$

One problem is finding this averaged value. Using $E = \upsilon/c$ instead of υ, we can define the averaged value $\widetilde{E}$ as

$$\widetilde{E} = \int I(E) E\, dE / \int I(E) dE \quad (2)$$

where $I(E)$ is the intensity of the luminescence spectrum for a given E value.

We can express the ratio of the radiative transition probability $A_{rad}(^5D_0)$ and $A_{rad}(^5D_0 \rightarrow {}^7F_1)$ (denoted as A_{01}) as

$$\frac{A_{rad}\left(^5D_0\right)}{A_{01}} = 1 + \frac{\widetilde{E}_{01}}{\int_{01} I(E) dE} \sum_{i=2}^{6} \frac{\int_{0i} I(E) dE}{\widetilde{E}_{0i}} \quad (3)$$

where the integrals are performed on the luminescence bands associated with $^5D_0 \rightarrow {}^7F_i$ transitions (i = 1,...,6).

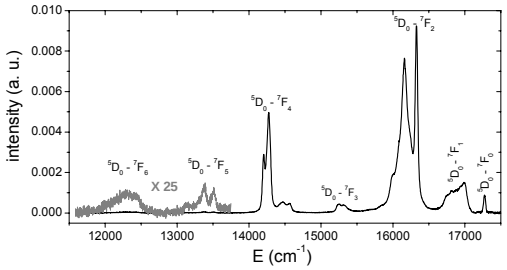

Fig. 1. Fluorescence spectrum of the $^5D_0 \rightarrow {}^7F_J$ transitions (J = 0, 1, ... 6) in Eu-doped LGN. The superposing transitions originating from $^5D_1$ and $^5D_2$ levels were eliminated adjusting the reference phase of the lock-in amplifier. The spectrum was corrected for the spectral sensitivity of the experimental setup.

The luminescence spectrum given in Fig. 1 corresponds to the $^5D_0 \rightarrow {}^7F_J$ (J = 0, … 6) transitions. The superposing transitions originating from $^5D_1$ and $^5D_2$ levels were eliminated adjusting the reference phase of the lock-in amplifier. Applying Eq. (3), $A_{rad}(^5D_0) = 7.85 \times A_{rad}(^5D_0 \rightarrow {}^7F_1)$. For the LGN powder, the values of n were averaged on the orientations: $n = (2n_o + n_e)/3$, where n_o and n_e represent the ordinary, respectively extraordinary refraction indices. With the values of the index of refraction given in [7], n = 1.966; it results $A_{rad}(^5D_0)$ = 901 s^{-1} and $\tau_{rad}(^5D_0)$ = 1.11 ms.

The luminescence decay of the $^5D_0$ level is shown in Fig. 2. Because the second harmonics of the Nd:YAG laser is resonant with the transition $^7F_1 \rightarrow {}^5D_1$, the kinetics of $^5D_1$ level is present in Fig. 2 as a risetime. The decay of $^5D_0$ is exponential with the lifetime $\tau_{exp}(^5D_0)$ = 1.05 ms. It results η = 0.95. The experimental lifetime of $^5D_1$, as obtained from the risetime, is $\tau_{exp}(^5D_1)$ = 67 μs.

The value of the radiative lifetime is very close to the experimental one. This result is expected due to the large gap between $^5D_0$ and $^7F_6$ levels, of approximately 12000 cm^{-1}, as results from Fig. 1. Due to this large gap, the probability of the multiphonon transitions is very low and the decay of $^5D_0$ is practically pure radiative.

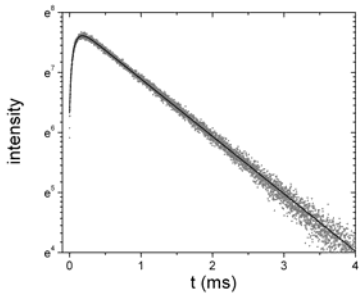

Fig. 2. Kinetics of the luminescence of $^5D_0$ level of Eu^{3+} in LGN excited with the second harmonics of the Nd:YAG laser.

Though the value of the radiative lifetime of the $^5D_0$ level was obtained without making appeal to the JO theory, estimation of the JO parameters could be of interest for comparison with other rare-earth doped materials.

In the frame of the JO theory, the electric-dipole transition probability between the initial state $|i\rangle = |[SL]J\rangle$ and the final state $|f\rangle = |[S'L']J'\rangle$ is given by:

$$A_{if}^{ed} = \frac{64\pi^4 e^2 \widetilde{E}^3}{3h(2J_i+1)} n \left[\frac{(n^2+2)^2}{9}\right] \times \sum_{t=2,4,6} \Omega_t \left|\left\langle i \left\| U^{(t)} \right\| f \right\rangle\right|^2 \quad (4)$$

The sum in Eq. (1) contains the JO intensity parameters Ω_2, Ω_4, Ω_6 and the squares of the reduced matrix elements of the unitary operators $U^{(2)}$, $U^{(4)}$, and $U^{(6)}$ whose values are practically independent of the host. Their values for Eu^{3+} can be found in [8, 9]. For the transitions originating in $^5D_0$ level, the only non-vanishing matrix elements are $\left|\left\langle {}^5D_0 \left\| U^{(2)} \right\| {}^7F_2 \right\rangle\right|^2$ = 0.0033, $\left|\left\langle {}^5D_0 \left\| U^{(4)} \right\| {}^7F_4 \right\rangle\right|^2$ = 0.0023 and $\left|\left\langle {}^5D_0 \left\| U^{(6)} \right\| {}^7F_6 \right\rangle\right|^2$ = 0.0003. Thus, the intensity of the electric-dipole transition $^5D_0 \rightarrow {}^7F_2$ depends only of Ω_2, that of $^5D_0 \rightarrow {}^7F_4$ only of Ω_4 while

the intensity of $^5D_0 \rightarrow {}^7F_6$ depends only of Ω_6. Therefore, the luminescence spectrum of Eu^{3+} allows a simple determination of the Judd-Ofelt parameters.

The terms entering Eq. (3) are (with short notations): A_{02}/A_{01}= 4.863, A_{04}/A_{01}= 1.673, and A_{06}/A_{01}= 0.055. It results: A_{02}= 537 s^{-1}, A_{04}= 192 s^{-1}, and A_{06}= 6.3 s^{-1}. Using Eq. (4), the values of the JO parameters are $\Omega_2=7.16\times10^{-20}$ cm^2, $\Omega_4=4.75\times10^{-20}$ cm^2, and $\Omega_6\approx1.66\times10^{-20}$ cm^2, ($\Omega_2 > \Omega_4 > \Omega_6$). The errors on Ω_6 are larger due to the very low intensity of $^5D_0 \rightarrow {}^7F_6$ transition (see Fig. 1). Interestingly, for erbium-doped langatate ($La_3Ga_{5.5}Ta_{0.5}O_{14}$), whose structure is similar with the structure of LGN, the JO parameters are $\Omega_2=7.34\times10^{-20}$ cm^2, $\Omega_4=2.52\times10^{-20}$ cm^2, and $\Omega_6=1.06\times10^{-20}$ cm^2 (also, $\Omega_2 > \Omega_4 > \Omega_6$) [10], comparable with the JO parameters obtained in this paper. The same order of the JO parameters was found for erbium-doped LGS: $\Omega_2=7.05\times10^{-20}$ cm^2, $\Omega_4=1.53\times10^{-20}$ cm^2, and $\Omega_6=0.73\times10^{-20}$ cm^2 [11].

4. Conclusions

The radiative lifetime of the $^5D_0$ level of Eu^{3+} in LGN was measured from the luminescence spectrum. Its value is close to the experimental one due to the large gap between $^5D_0$ and $^7F_6$ which precludes multiphonon de-excitation.

The Judd-Ofelt parameters obtained from the luminescence spectrum are comparable with those obtained in literature for erbium-doped langatate and langasite.

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