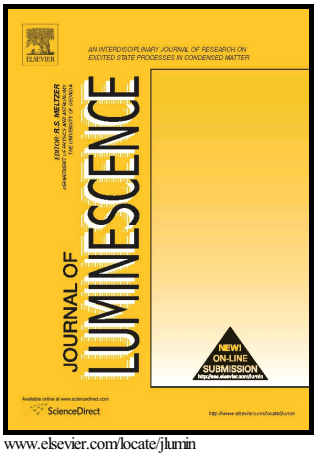

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Judd-Ofelt analysis of Eu^{3+} and Er^{3+} doped in ceramic $BaGd_2ZnO_5$

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Abstract
Judd-Ofelt (JO) analyses are performed on the efficient upconversion oxide phosphor Er^{3+}:$BaGd_2ZnO_5$ as well as on the tunable phosphor Eu^{3+}:$BaGd_2ZnO_5$. The refractive index of $BaGd_2ZnO_5$ found using the luminescence spectrum of Eu^{3+} is $n = 2.17$. The JO parameters for Eu:$BaGd_2ZnO_5$ are $\Omega_2 = 9.71\times10^{-20}$ cm^2 and $\Omega_4 = 6.15\times10^{-20}$ cm^2. The JO parameters of Er^{3+}:$BaGd_2ZnO_5$ are $\Omega_2 = 2.77\times10^{-20}$ cm^2, $\Omega_4 = 1.61\times10^{-20}$ cm^2, and $\Omega_6 = 0.60\times10^{-20}$ cm^2. The energy gap (ΔE = 879 cm^{-1}) between $^2H_{11/2}$ and $^4S_{3/2}$ energy levels of Er^{3+} was obtained from a Fluorescence Intensity Ratio experiment. For the Er^{3+}:$BaGd_2ZnO_5$, the calculations yielded the transition probabilities, branching ratios, radiative lifetimes, and quantum efficiency of the excited energy levels of Er^{3+} involved in upconversion.

Key words. $BaGd_2ZnO_5$; Judd-Ofelt; Eu^{3+}; Er^{3+}.

1. Introduction

The materials which present upconversion (UC) luminescence have multiple applications in biology and medicine (as biomarkers), in improving the photon harvesting in solar cells, displays, solid-state lasers and temperature sensors. Recently, upconversion luminescence was used to put in evidence the Curie transition in $BaTiO_3$ ceramics [1]. The main shortage of these materials is the rather low efficiency of the UC, mainly for low pump intensities.

The best known UC material is the hexagonal $NaYF_4$ doped with Er^{3+} and Yb^{3+}. Its maximum efficiency (visible emitted power divided to IR absorbed power) is ~4% [2]. Recently, higher efficiency (5.2%) was reported in an oxide material: $BaGd_2ZnO_5$ doped with Er^{3+} and Yb^{3+} [3]. Another promising UC oxide, $Ba_5Gd_8Zn_4O_{21}$:Er^{3+}:Yb^{3+}, proved to be more efficient, at low pump intensities, than hexagonal $NaYF_4$:Er:Yb [4].

According to the published papers, these zincate oxides have low-energy phonons (generally considered to be around 360 cm^{-1} [5, 6]), comparable with $NaYF_4$ [7]. The Raman spectrum of $BaEu_2ZnO_5$, a material very close to $BaGd_2ZnO_5$, was measured by Taboada et al. [8]: though the maximum phonon frequency is 595 cm^{-1}, the temperature dependence of $^5D_0$ and $^5D_1$ luminescence intensity suggests that phonons of about 340 cm^{-1} are involved in the non-radiative transitions of Eu^{3+} in $BaGd_2ZnO_5$. Quite similar results were obtained in BaY_2ZnO_5, a material isomorph with $BaGd_2ZnO_5$: a maximum phonon frequency of 590 cm^{-1} [9]. A different result was reported for BaY_2ZnO_5 in [3]: a phonon spectrum extended up to 966 cm^{-1}. However, a fact that supports the manifestation of only low-energy phonons in the Eu^{3+}-doped samples is the obtaining of the bluish luminescence of Eu^{3+} [10, 11] in these materials doped with low concentrations of Eu^{3+}; the bluish luminescence originates on the $^5D_1$, $^5D_2$, and $^5D_3$ levels, which are separated from the lower energy levels by small gaps. Given the above, these materials have the advantage (over fluorides) of being more chemically stable and can be obtained by solid-state reactions in air, sol-gel methods or combustion.

Color tunability of Eu^{3+} luminescence from blue to red through white was also obtained in Eu:$BaGd_2ZnO_5$ [10] and in its isomorph Eu^{3+}:BaY_2ZnO_5 [11] by changing the dopant concentration.

Recently, polymorphic phase transition in potassium-sodium niobate ferroelectric ceramics was evidenced in Eu^{3+} luminescence [12].

Usually, the JO parameters are obtained from absorption spectra, but the JO analysis of materials doped with Eu^{3+} can be performed using the luminescence spectrum instead of the absorption spectrum [13, 14]. The luminescence spectrum of Eu^{3+} can be calibrated using the pure magnetic-dipole character of $^5D_0 \rightarrow {}^7F_1$ transition. The probability of this transition depends only on the refractive index of the material. Although the measurement of the refractive index of such ceramic materials is a difficult experimental task, an estimation of the refractive index (without dispersion) can be performed knowing the luminescence lifetime of $^5D_0$ [15, 16]. Due to the very large energy gap between $^5D_0$ and $^7F_6$ (~ 12000 cm^{-1}), the decay, for low Eu^{3+} concentrations, is practically radiative.

The highly efficient upconverting oxide materials discussed above are part of a series of materials presenting optical anisotropy, with good luminescence properties when doped with rare-earth ions, but which are very difficult to be obtained as single crystals or transparent ceramics. These materials can be obtained easily as ceramic samples; thin ceramic samples can transmit light. In order to characterize such materials, in a series of recent papers [17-21], we extended the JO analysis method to ceramic samples which, due to their granular structure, scatter the transmitted light. The first problem, encountered when measuring absorption spectra of samples scattering the transmitted light, is the 'effective' thickness of the sample, which is not known. To calibrate the absorption spectra for materials with granular structure, additional information is necessary. In [17, 20] we used the magnetic-dipole contribution to the $^3H_6 \rightarrow {}^3H_5$