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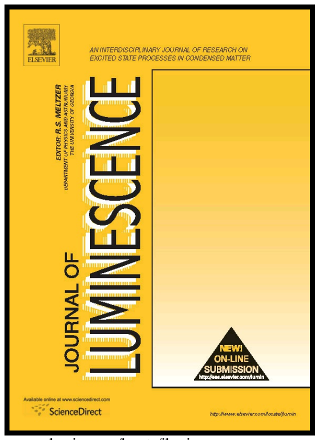

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Judd-Ofelt analysis of Er-doped $CaSc_2O_4$ revisited (revised manuscript)

Şerban Georgescu[a], Angela Ştefan[a,b], OctavianToma[a*]
[a]National Institute for Laser, Plasma and Radiation Physics, 409 Atomiştilor Street, 077125 Măgurele-Ilfov, Romania
[b]University of Bucharest, Faculty of Physics, 405 Atomiştilor Street, 077125 Măgurele-Ilfov, Romania
[*]Corresponding author. Tel.: +40 214574550; octavian.toma@inflpr.ro

Abstract
The Judd-Ofelt analysis of Er^{3+} in $CaSc_2O_4$, presented by the same authors in 2015, is revisited using recently published data concerning the dispersion of the refractive index and taking into account the multisite structure of the luminescent centers. The new Judd-Ofelt parameters are $\Omega_2 = 3.42\times10^{-20}$ cm^2, $\Omega_2 = 1.66\times10^{-20}$ cm^2, and $\Omega_2 = 0.76\times10^{-20}$ cm^2. The energy gap necessary to calculate the common radiative lifetime of the thermalized levels ($^2H_{11/2}$, $^4S_{3/2}$) was measured in a Fluorescence Intensity Ratio experiment and is $\Delta E = 816$ cm^{-1}. We obtained $\tau_{rad}(^2H_{11/2}, {}^4S_{3/2}) = 399$ μs and $\tau_{rad}(^4F_{9/2}) = 390$ μs. The recalculated quantum efficiencies are 0.30 for ($^2H_{11/2}$, $^4S_{3/2}$) and 0.17 for $^4F_{9/2}$.

Keywords: Judd-Ofelt; $CaSc_2O_4$; Er^{3+}; FIR.

1. Introduction

$CaSc_2O_4$ is a promising phosphor. Activated with Er^{3+}, Ho^{3+}, or Tm^{3+} and co-doped with Yb^{3+}, this phosphor demonstrated good upconversion properties [1-7]. The upconversion efficiency of a $CaSc_2O_4$ ceramic sample doped with 1 at. % Er^{3+} and 5% Yb^{3+} was measured by Ştefan et al. [7]. The color of the upconversion emitted light of the $CaSc_2O_4$:Er:Yb changes with ytterbium concentration from green to reddish [7]. Doped with Ce^{3+}, $CaSc_2O_4$ is a bright green emitting phosphor that could replace YAG:Ce^{3+} in white light LED's [8-12]. $CaSc_2O_4$ presents a rigid structure leading to a high quantum efficiency of Ce^{3+} emission and its efficiency decreases slowly with temperature [12, 13].

Due to the low-energy phonons (540 cm^{-1}) [1], the emission of $CaSc_2O_4$ doped with Eu^{3+} can be tuned from white to red, by merely increasing the Eu^{3+} concentration [14].

The $CaSc_2O_4$ crystal has the calcium ferrite structure, space group *Pnam*, D_{2h}^{16}, with three cationic positions: two Sc^{3+} positions with six-fold coordination and one Ca^{2+} position with eight-fold coordination [15]. All these positions have C_s point symmetry. The ionic radius of Sc^{3+} is 0.745Å, while the ionic radius of Ca^{2+} is 1.12Å [16]. Er^{3+} ions (radius 0.89Å in six-fold coordination and 1.003Å in eight-fold coordination [16]) could enter both Sc^{3+} and Ca^{2+} positions. In order for the Er^{3+} ions to enter the Ca^{2+} positions, charge compensation is necessary (random impurities, vacancies) [17-19]. Two luminescent centers involving Er^{3+} in $CaSc_2O_4$ were recently reported by Feng et al. [20], at room temperature: one with Er^{3+} substituting Ca^{2+} and another with Er^{3+} substituting Sc^{3+}. The difference between the two Sc^{3+} centers cannot be observed at room temperature.

The spectroscopic properties (radiative lifetimes, quantum efficiency, branching ratios) of $CaSc_2O_4$ doped with Er^{3+}, Tm^{3+}, or Ho^{3+} were estimated from Judd-Ofelt (JO) analyses on ceramic samples [21-23]. In these analyses, the dispersion of the refractive index was neglected and a constant value $n = 1.9$ was assumed [24].

Recently, the wavelength dependence of the refractive indexes of the orthorhombic $CaSc_2O_4$ single crystal was determined [19] and now it can be used in a revision of the JO analysis of Er-doped ceramic $CaSc_2O_4$

In the present paper, a more accurate value is obtained for the quantum efficiency of the green-emitting levels ($^4S_{3/2}$, $^2H_{11/2}$) using recalculated JO parameters (taking into account the new data regarding the refractive index dispersion given in [19]) as well as more accurate values of the luminescence lifetimes (obtained by taking into account the multi-site structure of the material). Another important refinement of the quantum efficiency is obtained by estimating the energy gap between $^2H_{11/2}$ and $^4S_{3/2}$ thermalized energy levels of Er^{3+}, necessary to calculate the common radiative lifetime of the $^2H_{11/2}$, $^4S_{3/2}$ levels, more accurately using a Fluorescence Intensity Ratio (FIR) experiment. The quantum efficiency of the red emitting level, $^4F_{9/2}$, is also calculated. This value is important for samples strongly co-doped with Yb^{3+}, for which the emission takes place dominantly in red [7]. The lifetime of the $^4I_{13/2}$ level, necessary for the calibration of the absorption spectrum, is here measured taking into account the multicenter structure of $CaSc_2O_4$:Er^{3+} system. The obtained spectroscopic properties are averaged values on the existing luminescent centers.

2. Experiment

The $CaSc_2O_4$ ceramic samples doped with erbium were synthesized by a solid-state reaction. High purity $CaCO_3$, Sc_2O_3, and Er_2O_3 powders were weighed carefully (paying attention to removing the moisture from $CaCO_3$), then mixed in an agate mortar, pressed with a hydraulic press at 10 MP and then annealed in air at 1500^{0}C for 4h. A solid ceramic sample was obtained. The sample was cut and washed in an ultrasonic bath to remove the abrasive particles.

In the FIR experiment, the upconversion luminescence of the ceramic $CaSc_2O_4$:Er(2%) sample was measured in the temperature domain 150 – 300 K using a Horiba 1000M Series II monochromator equipped with an S-20 photomultiplier (EMI 9658B); the signal was recorded using a lock-in amplifier SR830 (Stanford Research Systems).