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Spectroscopic and photoluminescence characterization of Eu^{3+}-doped monoclinic $KY(WO_4)_2$ crystal

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ABSTRACT

Monoclinic 2 at% Eu-doped $KY(WO_4)_2$ is grown by top-seeded solution growth method. Polarization-resolved absorption and stimulated-emission cross-section spectra are determined for this crystal. Spectroscopic properties of Eu:$KY(WO_4)_2$ are modeled within conventional Judd–Ofelt theory, as well as theory of f–f transition intensities for systems with anomalously strong configuration interaction, yielding absorption oscillator strengths, luminescence branching ratios and radiative lifetime of $^5D_0$ state. The impact of excited-state absorption from this state on possibility of laser operation is discussed. Photoluminescent properties of Eu:$KY(WO_4)_2$ are determined. This crystal provides intense red emission with CIE coordinates $x=0.670$, $y=0.329$.

1. Introduction

Trivalent europium ions, Eu^{3+}, doped into crystalline and glassy materials, possess important applications in tricolor fluorescent lamps, field emission displays, cathode-ray tubes and solid-state lightning technologies. Europium-based phosphors allows one to obtain intense red emission near ~612 nm related with $^5D_0 \rightarrow {}^7F_2$ transition within $4f^6$ electronic shell. Today main commercial host for Eu^{3+} is yttrium oxide Y_2O_3 [1,2]; however, the search of novel inorganic hosts is still in progress. Particularly, europium-doped potassium and sodium double tungstates (DT) and double molybdates (DMo) are recognized as perspective red phosphors [3,4].

Eu^{3+} ion is also suitable for generation of red laser emission on above mentioned channel. Laser action was realized for the first time in bulk Y_2O_3 [5] and liquid chelat [6] at cryogenic temperature, later similar experiment was performed with Eu:YVO_4 [7]. Room-temperature (RT) lasing was obtained with Eu:GaN [8] and Eu:polymer [9] thin films. Recently, 25 at% Eu-doped potassium gadolinium DT, $KGd(WO_4)_2$, was introduced as novel bulk dielectric material for pulsed room-temperature Eu^{3+} lasing [10]. Specifically, it was realized on $^5D_0 \rightarrow {}^7F_4$ transition centered at ~702 nm.

Monoclinic DTs with common formula $KRE(WO_4)_2$ (KREW, with RE=Y, Gd, Lu) doped with variety of trivalent rare-earth ions are well-known materials for efficient solid-state lasers [11]. However, the spectroscopic and laser properties of Eu-doped monoclinic DTs are far from complete description. Under Eu doping, these ions enter positions of "passive" RE^{3+} ones, so no $Eu^{3+} \rightarrow Eu^{2+}$ reduction occurs. Recently, crystalline structure, cryogenic and RT absorption and PL properties were reported for 1.5–5 at% Eu:KLuW [12]. In Ref. [13], absorption and stimulated-emission cross-section spectra were evaluated for KGdW with higher Eu content, 10 at%. Bulk $KYb_{0.8}Eu_{0.2}W$ crystal was studied in Ref. [14]; however, main attention was paid to cooperative energy transfer between Yb^{3+} pairs and single Eu^{3+} ions. Some information about spectroscopic properties of Eu:KGdW, Eu:KYbW, KEuW and Eu:KGd(W/Mo) nanocrystalline phosphors was presented in Refs. [3,15–18].

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Thus, important representative of monoclinic DTs family, Eu:KYW, is still uncharacterized.

In the present paper, we aimed to perform detailed spectroscopic investigation of 2 at% Eu:KYW, for the first time, to our knowledge. Polarization-resolved absorption and stimulated-emission cross-section spectra were evaluated; Judd–Ofelt theory and theory adopted for systems with anomalously strong configuration interaction were applied for determination of absorption oscillator strengths (including excited-state absorption processes), luminescence branching ratios and radiative lifetime of $^5D_0$ state. In addition, PL properties of Eu:KYW were thoroughly studied.

2. Experimental

Europium-doped potassium yttrium double tungstate Eu:KYW melts at ~1080 °C and near this temperature it has an orthorhombic structure (β-phase) similar to one of disordered double molybdates [19]. At the temperature of ~1020 °C this crystal undergoes phase transition to low-temperature monoclinic α-phase. Such α-Eu:KYW crystal in the present paper was grown from the flux under low thermal gradients (below 0.1 °C/cm); potassium ditungstate $K_2W_2O_7$ was used as a solvent. Seed crystals were oriented along [0 1 0] crystallographic axis. Content of Eu^{3+} ions was 2 at% (N_{Eu} = 1.26 × 10^{-20} cm^3, crystal density ρ = 6.501 g/cm^3); growth rate was 3–5 mm/day. Obtained ~150 g boule was ~60 mm along growth direction, with ~20 × 20 mm^2 edge face, Fig. 1. The background losses in the transparence region were below 0.005 cm^{-1}.

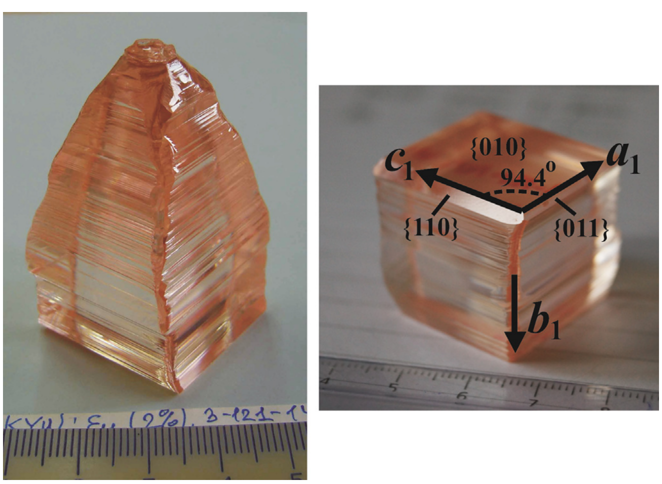

Fig. 1. As-grown crystal boule of 2 at% Eu:KY(WO_4)$_2$ (left image); habit of endface of this boule (right image): $\boldsymbol{a}_1$, $\boldsymbol{b}_1$ and $\boldsymbol{c}_1$ are the crystallographic axes, *I2/c* setting.

The crystal had weak rose coloration. With 2 at% of Eu, even large-volume boule was free of cracks and inclusions that is required for potential laser experiments (at higher Eu content, numerous cracks were observed in the as-grown crystal).

KYW is monoclinic (space group C^6_{2h}–*C2/c* [19]; however, for description of obtained habit of crystal boule, crystallographic setting *I2/c* is more applicable). Lateral sides of central (prismatic) part of the boule are determined by {1 1 0}, {0 1 1} faces and {1 0 0}, {0 0 1} pinacoids. The endface of the boule is mainly determined by well-developed pinacoid {0 1 0} that is surrounded with four relatively small {1 1 0}, {0 1 1} ones, see Fig. 1 (right image).

KYW is optically biaxial and its optical properties are described within the frame of optical indicatrix axes, namely N_p, N_m and N_g [20]. N_p axis coincides with crystallographic $\boldsymbol{b}$ axis, while N_m and N_g are positioned in the $\boldsymbol{a}$–$\boldsymbol{c}$ plane. For investigation of absorption and PL, one cubic sample with dimensions 7(N_p) × 11(N_m) × 10 (N_g) mm^3 was prepared, with all of the faces polished. For determination of UV absorption edge, two 90 μm-thick polished slabs were prepared. They were cut in the N_p–N_g and N_m–N_g planes.

Polarized absorption spectra were measured on Varian CARY 5000 spectrophotometer in the UV, visible (0.3–0.7 μm, spectral bandwidth, SBW, was 0.06 nm) and near-IR (1.8–2.8 μm, SBW = 0.1 nm). Photoluminescence (PL) was excited by focused radiation of 30 mW InGaN laser diode emitting near 400 nm. PL was collected in the direction perpendicular to the excitation one by a wide-aperture lens. The spectrum was registered by means of lock-in amplifier and monochromator MDR-23 (SBW ~ 0.5 nm) with a Hamamatsu C5460-01 photodetector attached to its output slit. Glan–Taylor polarizer was placed before the input slit of monochromator.

For time-resolved PL studies, optical parametric oscillator Lotis TII LT-2214 tuned to 534 nm was used as an excitation source; the duration of excitation pulse was ~20 ns. PL was collected by wide-aperture lens and re-imaged to the input slit of monochromator MDR-12; then it was detected with fast Hamamatsu C5460 photodetector (40 ns response time) and 500 MHz Textronix TDS-3052B digital oscilloscope.

3. Results and discussion

Overview of absorption spectrum of 2 at% Eu:KYW crystal is presented in Fig. 2. The feature of Eu^{3+} ions is the close location of lower-lying excited multiplets, $^7F_1$ and $^7F_2$, to the ground-state one, $^7F_0$ (the energy gap is around 300 and 1000 cm^{-1}). The probability of their thermal population is high (0.33 and 0.02, as

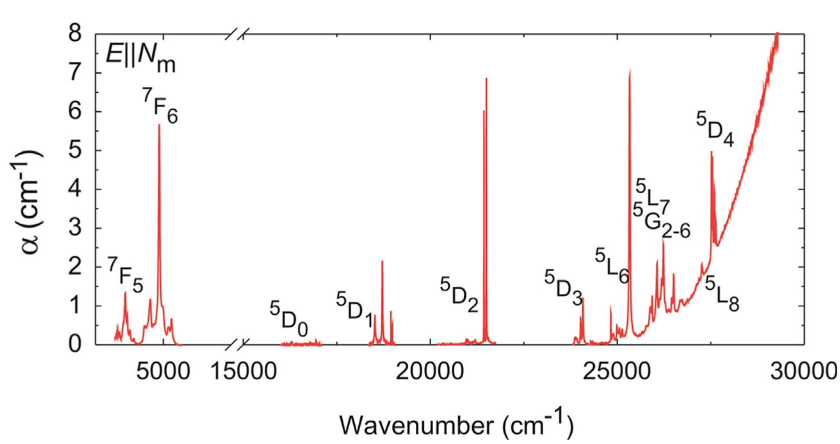

Fig. 2. Absorption spectrum of 2 at% Eu:KY(WO_4)$_2$ crystal (light polarization is $\boldsymbol{E}$||N_m).