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Spectroscopy of tetragonal Eu:NaGd$(WO_4)_2$ crystal

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ABSTRACT

We report on growth and detailed spectroscopic study of Eu^{3+}-doped tetragonal sodium gadolinium double tungstate, Eu:NaGd$(WO_4)_2$, a new promising crystal for deep-red lasers. Large-volume crystal doped with 4.9 at.% Eu is grown by Czochralski method along the [001] crystallographic direction. Absorption of Eu^{3+} ions is studied at room temperature (RT) and at 6 K. For the absorption band related to the $^7F_1 \rightarrow {}^5D_1$ transition suitable for pumping of Eu:NaGd$(WO_4)_2$, the maximum cross-section is $\sigma_{abs} = 1.2 \times 10^{-21}$ cm^2 at 535.5 nm with the full width at half maximum (FWHM) of 3.1 nm (at RT, for $E \parallel a$ polarization). For the $^5D_0 \rightarrow {}^7F_4$ transition, the maximum stimulated-emission cross-section is $\sigma_{SE} = 1.6 \times 10^{-21}$ cm^2 at 698.3 nm (RT, $E \parallel c$ polarization). Lifetime of the $^5D_0$ state is 490 ± 10 μs (at RT). Under UV excitation, Eu:NaGd$(WO_4)_2$ provides intense red emission with CIE coordinates ($x = 0.671$, $y = 0.329$).

1. Introduction

Tetragonal sodium double tungstates (DT) and double molybdates (DMo) have the common chemical formula $Na^+R^{3+}(T^{6+}O^{2-}{}_4)_2$ where R = Gd, Y, Lu, La or Bi and T = W (for DT) or Mo (for DMo), when doped with trivalent rare-earth ions, are promising materials for solid-state lasers emitting in the near-IR [1–5]. In particular, efficient laser operation with Nd^{3+} [6], Yb^{3+} [7,8], Tm^{3+} [9,10] and Ho^{3+} ions [11] has been reported. These materials have an important advantage as compared with their monoclinic counterparts where Na^+ is replaced by K^+, i.e. the absence of polymorph phase transition [12], so they can be easily grown by the Czochralski method [13,14]. Sodium DT and DMo normally have a scheelite-like structure. For scheelite, $CaWO_4$, (space group $C^6_{4h} \equiv I4_1/a$), Ca^{2+} has strongly distorted dodecahedral local environment by O^{2-} ions (local symmetry S_4) and W^{6+} ions are located in the center of distorted oxygen tetrahedron. In sodium scheelite-like DT and DMo, Na^+ and R^{3+} ions can be distributed among Ca^{2+} positions statistically, partially or fully ordered [2,13]. This disorder leads to locally variable crystal field acting on the dopant ion which is expressed in the large bandwidth of the spectral lines. Particularly this has determined the interest to tetragonal DT and DMo for the use in femtosecond lasers [15,16].

Eu^{3+} ion is attractive due to intense red emission. It originates from the radiative transitions from the metastable $^5D_0$ state to the lower-lying ^7F_J (J = 0 … 6) multiplets. As the energy gap between the $^5D_0$ state and lower-lying excited-state is rather large, > 12000 cm^{-1}, quantum efficiency for the luminescence from this multiplet is approaching unity. Red Eu^{3+} luminescence is used in red and orange-red phosphors like the commercial yttrium oxide, Eu:Y_2O_3 [17], for applications in tricolour lamps, field emission displays, cathode-ray tubes and solid-state lighting [18–21]. Eu^{3+} ion provides also the possibilities for laser operation in the red (~610 nm, $^5D_0 \rightarrow {}^7F_2$ transition) [22,23] and deep-red (~700 nm, $^5D_0 \rightarrow {}^7F_4$) regions [24]. Such red lasers can be potentially used in medicine. To date, the interest for DT and DMo doped with Eu^{3+} ions was focused on their photoluminesent properties for potential phosphor applications. In this way, tetragonal [25–28] and

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monoclinic [29–32] materials were studied in the form of nanopowders. In particular, Eu-doped sodium DT and DMo, as well as their solid solutions which are possible due to close ionic radii of W^{6+} and Mo^{6+}, have provided intense emission in the red under UV excitation.

Laser action was achieved with monoclinic potassium double tungstates, Eu:K*RE*$(WO_4)_2$ or K*RE*W with *RE* = Gd [33] and Y [34] and the feasibility of laser operation with Eu:KLuW was also discussed [35]. However, power scaling of those lasers was limited due to the low pumping efficiency resulting from narrow absorption bands and limited crystal size. These drawbacks can be overcome by using tetragonal sodium DT which can offer broad spectral bands together with easy Czochralski growth of large bulk samples. For Eu^{3+} doping, $NaGd(WO_4)_2$ crystal or shortly NGW seems to be very suitable due to closeness of ionic radii of VIII-fold oxygen-coordinated Gd^{3+} (R_{ion} = 1.053 Å) and Eu^{3+} (R_{ion} = 1.066 Å). Thus, the aim of the present paper was to grow large-volume Eu:NGW crystals and to study their spectroscopic properties relevant for laser operation (i.e., transition cross-sections and lifetime of the emitting state).

2. Crystal growth

The studied Eu:NGW crystal was grown by the conventional Czochralski method in the conditions of low axial and radial thermal gradients ($\Delta T/\Delta x < 1.0$ °C/cm). The melting temperature for Eu:NGW is 1253 °C. The initial compounds were Na_2CO_3, WO_3, Gd_2O_3 and Eu_2O_3 (4N purity, Sigma–Aldrich) taken in stoichiometric composition. The Eu content in the growth charge was 2 at.%. The crystal was grown on [001]-oriented seed. The seed was oriented with X-ray diffraction (XRD).

A platinum crucible 70 × 120 mm in dimensions, tightly covered with an inverted funnel shaped platinum lid having a narrow tube (diameter: 15 mm), was mounted in a three-zone furnace with three temperature controllers (PIT-3). This lid served as a radiation screen and as a diffusion lock for volatile substances which prevented excessive evaporation and decomposition of the melt. The lid installation strongly reduced the thermal instabilities during the growth process. Electronic feedback was provided by a sensitive weighting system (precision of 10 mg in the 1 kg range). The pulling rate was ~2 mm/day. The growth rate in terms of crystal weight was 1 g/day in the beginning of the process and 20 g/day when the crystal diameter reached its maximum value. After separation from the melt, the crystal was cooled to room temperature at a rate of 20–30 °C/h.

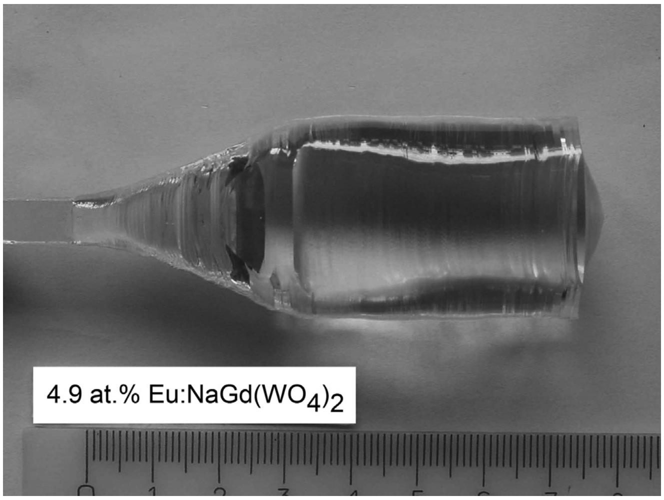

Fig. 1. Image of the as-grown bulk of Eu:NGW crystal.

The as-grown bulk (Fig. 1) had the dimensions of 30 × 30 × 65 mm^3 and it was oriented along the [001] axis, as confirmed by XRD. The bulk consisted of ~20 mm-long pyramidal part and prismatic one with a circular cross-section which was uniform over the crystal length thus indicating good control of thermal instabilities at the solid–liquid interface. The end facet of the crystal was flat corresponding to the {001} plane. As Eu:NGW crystal was grown in air atmosphere, the oxygen vacancies result in the formation of color center in the as-grown crystal, as described previously for the $NaLa(MoO_4)_2$ crystal [13]. Indeed, the as-grown Eu:NGW crystal was dark red-brown colored, as shown in Fig. 2(a). The inspection of the absorption spectrum revealed broad band spanning from ~350 to 650 nm with a maximum at ~410 nm and peak absorption of ~15 cm^{-1}. To reduce the number of these vacancies, the as-grown crystal was annealed in the air at 850 ± 50 °C for 72 h with a slow heating and cooling (<20 °C/h). After the annealing, the crystal became transparent with a slight yellow coloration due to Eu doping, Fig. 2(b) (the coloration of annealed undoped crystal was slightly greenish). The annealing also served for reduction of stresses in the as-grown bulk which allowed cutting of the crystal without producing additional cracks. The annealed crystal was of high optical quality. It did not contain inclusions and air bubbles, as well as cracks. The optical losses in the transparency region (at ~1 μm) were determined with the ISO-standard laser calorimetry to be $< 0.5 \times 10^{-4}$ cm^{-1}. The Mohs' hardness of Eu:NGW is ~4.7.

Concentration of Eu^{3+} ions was determined with Energy Dispersive X-ray (EDX) spectroscopy using a Vega II LMU electron microscope equipped with an Inca Energy 350 X-ray microanalyzer. The atomic percent of Eu^{3+} in the annealed crystal was 4.9 ± 0.3 at.% which corresponded to an absolute concentration $N_{Eu} = 3.1 \pm 0.2 \times 10^{20}$ cm^{-3} (density of the crystal measured by the hydrostatic method was ρ = 7.15 g/cm^3). Thus, the segregation coefficient for Eu^{3+} ions was $K = [Eu]_{crystal}/[Eu]_{melt} = 2.45 \pm 0.05$. The stoichiometric formula for the studied crystal was $NaGd_{0.951}Eu_{0.049}(WO_4)_2$.

The structure of the Eu:NGW crystal (tetragonal, space group $I4_1/a$) was confirmed with XRD. The unit cell parameters for the 4.9 at.% Eu:NGW are $a = b = 5.262$ Å and $c = 11.389$ Å (number of formula units per unit cell, $Z = 2$) which are slightly larger than the parameters for undoped NGW crystal with $a = b = 5.240$ Å and $c = 11.368$ Å. This agrees with the fact that ionic radius of Eu^{3+} is larger than that of Gd^{3+}. The unit cell volume for Eu:NGW crystal is $V = 315.4$ $Å^3$ and the calculated density is 7.119 g/cm^3 which agrees with the experimental value. Thermal expansion of Eu:NGW crystal was studied in the temperature range of 20–200 °C with a horizontal dilatometer Netzsch 402PC. The resulted values are $\alpha_a = 9.0$ and $\alpha_c = 19.1 \times 10^{-6}$ K^{-1}, and the anisotropy degree is $\alpha_c/\alpha_a = 2.1$. The volumetric thermal expansion is equal to $\alpha_{vol} = 2\alpha_a + \alpha_c = 37.1 \times 10^{-6}$ K^{-1}.

3. Experimental

From the annealed Eu:NGW, the 3 mm-thick plates were cut and polished for spectroscopic study with respect to the [100] and [001] axes. Eu:NGW is a negative uniaxial crystal. Its optical axis is parallel to the [001]-axis. The refractive indices of undoped NGW crystal are $n_o = 1.945$ and $n_e = 1.935$ at ~1 μm [2]. The prepared samples provided access to polarizations $E \parallel a$ (σ-polarization) and $E \parallel c$ (π-polarization).

Room-temperature (RT) absorption spectrum of Eu:NGW was measured with Varian CARY-5000 spectrophotometer. In the visible and UV ranges (300 … 650 nm), the spectral bandwidth