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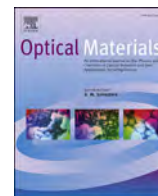


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Spectroscopy of tetragonal Eu:NaGd(WO<sub>4</sub>)<sub>2</sub> crystal

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## ABSTRACT

We report on growth and detailed spectroscopic study of Eu<sup>3+</sup>-doped tetragonal sodium gadolinium double tungstate, Eu:NaGd(WO<sub>4</sub>)<sub>2</sub>, 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<sup>3+</sup> ions is studied at room temperature (RT) and at 6 K. For the absorption band related to the <sup>7</sup>F<sub>1</sub> → <sup>5</sup>D<sub>1</sub> transition suitable for pumping of Eu:NaGd(WO<sub>4</sub>)<sub>2</sub>, the maximum cross-section is  $\sigma_{\text{abs}} = 1.2 \times 10^{-21} \text{ cm}^2$  at 535.5 nm with the full width at half maximum (FWHM) of 3.1 nm (at RT, for *E* || *a* polarization). For the <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>4</sub> transition, the maximum stimulated-emission cross-section is  $\sigma_{\text{SE}} = 1.6 \times 10^{-21} \text{ cm}^2$  at 698.3 nm (RT, *E* || *c* polarization). Lifetime of the <sup>5</sup>D<sub>0</sub> state is 490 ± 10 μs (at RT). Under UV excitation, Eu:NaGd(WO<sub>4</sub>)<sub>2</sub> provides intense red emission with CIE coordinates (*x* = 0.671, *y* = 0.329).

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## 1. Introduction

Tetragonal sodium double tungstates (DT) and double molybdates (DMo) have the common chemical formula Na<sup>+</sup>R<sup>3+</sup>(T<sup>6+</sup>O<sup>2-</sup>)<sub>4</sub>)<sub>2</sub> 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<sup>3+</sup> [6], Yb<sup>3+</sup> [7,8], Tm<sup>3+</sup> [9,10] and Ho<sup>3+</sup> ions [11] has been reported. These materials have an important advantage as compared with their monoclinic counterparts where Na<sup>+</sup> is replaced by K<sup>+</sup>, 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<sub>4</sub>, (space group C<sub>6h</sub><sup>4h</sup> ≡ I<sub>41/a</sub>), Ca<sup>2+</sup> has strongly distorted dodecahedral local environment by O<sup>2-</sup> ions (local symmetry S<sub>4</sub>) and W<sup>6+</sup> ions are located in the center of distorted oxygen tetrahedron. In sodium scheelite-like DT and DMo,

Na<sup>+</sup> and R<sup>3+</sup> ions can be distributed among Ca<sup>2+</sup> 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<sup>3+</sup> ion is attractive due to intense red emission. It originates from the radiative transitions from the metastable <sup>5</sup>D<sub>0</sub> state to the lower-lying <sup>7</sup>F<sub>J</sub> (J = 0 ... 6) multiplets. As the energy gap between the <sup>5</sup>D<sub>0</sub> state and lower-lying excited-state is rather large, > 12000 cm<sup>-1</sup>, quantum efficiency for the luminescence from this multiplet is approaching unity. Red Eu<sup>3+</sup> luminescence is used in red and orange-red phosphors like the commercial yttrium oxide, Eu:Y<sub>2</sub>O<sub>3</sub> [17], for applications in tricolour lamps, field emission displays, cathode-ray tubes and solid-state lighting [18–21]. Eu<sup>3+</sup> ion provides also the possibilities for laser operation in the red (~610 nm, <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub> transition) [22,23] and deep-red (~700 nm, <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>4</sub>) regions [24]. Such red lasers can be potentially used in medicine. To date, the interest for DT and DMo doped with Eu<sup>3+</sup> ions was focused on their photoluminescent 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 nano-powders. 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:KRE(WO<sub>4</sub>)<sub>2</sub> or KREW 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<sup>3+</sup> doping, NaGd(WO<sub>4</sub>)<sub>2</sub> crystal or shortly NGW seems to be very suitable due to closeness of ionic radii of VIII-fold oxygen-coordinated Gd<sup>3+</sup> ( $R_{ion} = 1.053 \text{ \AA}$ ) and Eu<sup>3+</sup> ( $R_{ion} = 1.066 \text{ \AA}$ ). 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 ( $\Delta T/\Delta x < 1.0 \text{ }^\circ\text{C/cm}$ ). The melting temperature for Eu:NGW is 1253 °C. The initial compounds were Na<sub>2</sub>CO<sub>3</sub>, WO<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub> and Eu<sub>2</sub>O<sub>3</sub> (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

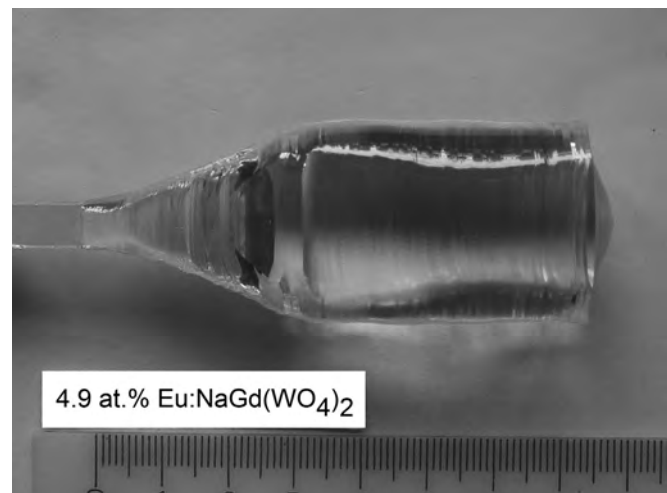


Fig. 1. Image of the as-grown bulk of Eu:NGW crystal.

the melt, the crystal was cooled to room temperature at a rate of 20–30 °C/h.

The as-grown bulk (Fig. 1) had the dimensions of 30 × 30 × 65 mm<sup>3</sup> 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<sub>4</sub>)<sub>2</sub> 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<sup>-1</sup>. 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 × 10<sup>-4</sup> cm<sup>-1</sup>. The Mohs' hardness of Eu:NGW is ~4.7.

Concentration of Eu<sup>3+</sup> 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<sup>3+</sup> in the annealed crystal was 4.9 ± 0.3 at.% which corresponded to an absolute concentration  $N_{Eu} = 3.1 \pm 0.2 \times 10^{20} \text{ cm}^{-3}$  (density of the crystal measured by the hydrostatic method was  $\rho = 7.15 \text{ g/cm}^3$ ). Thus, the segregation coefficient for Eu<sup>3+</sup> ions was  $K = [Eu]_{crystal}/[Eu]_{melt} = 2.45 \pm 0.05$ . The stoichiometric formula for the studied crystal was NaGd<sub>0.951</sub>Eu<sub>0.049</sub>(WO<sub>4</sub>)<sub>2</sub>.

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  $a = b = 5.262 \text{ \AA}$  and  $c = 11.389 \text{ \AA}$  (number of formula units per unit cell,  $Z = 2$ ) which are slightly larger than the parameters for undoped NGW crystal with  $a = b = 5.240 \text{ \AA}$  and  $c = 11.368 \text{ \AA}$ . This agrees with the fact that ionic radius of Eu<sup>3+</sup> is larger than that of Gd<sup>3+</sup>. The unit cell volume for Eu:NGW crystal is  $V = 315.4 \text{ \AA}^3$  and the calculated density is 7.119 g/cm<sup>3</sup> 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  $\alpha_c = 19.1 \times 10^{-6} \text{ K}^{-1}$ , and the anisotropy degree is  $\alpha_c/\alpha_a = 2.1$ . The volumetric thermal expansion is equal to  $\alpha_{vol} = 2\alpha_a + \alpha_c = 37.1 \times 10^{-6} \text{ K}^{-1}$ .

## 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  $E \parallel a$  ( $\sigma$ -polarization) and  $E \parallel c$  ( $\pi$ -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

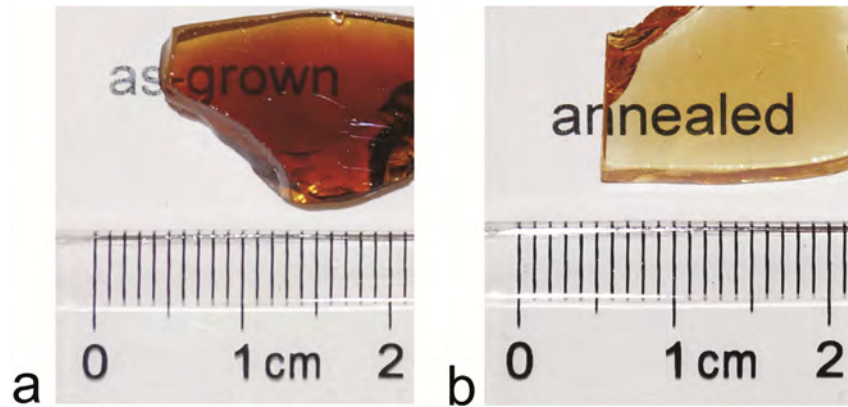


Fig. 2. Images of polished plates from the as-grown crystal (a) and annealed one (b).

(SBW) was 0.02 nm and in the near-IR (1.8 ... 2.8  $\mu\text{m}$ ), the value was  $\text{SBW} = 0.1$  nm. Absorption cross-section was calculated from the absorption coefficient,  $\sigma_{\text{abs}} = \alpha/N_{\text{Eu}}$ . For low-temperature (LT) measurements at 6 K, we used an Oxford Instruments Ltd. cryostat (SU 12 model) with helium-gas close-cycle flow.

Photoluminescence (PL) of Eu:NGW was excited at 355 nm. The spectrum was measured with a lock-in amplifier, monochromator MDR-23 (SBW = 0.2 nm) and a sensitive Hamamatsu C5460-01 photodetector. Glan-Taylor prism was used to separate the  $E \parallel a$  and  $E \parallel c$  polarization states of emission. Spectral sensitivity of the set-up was determined with a halogen lamp with a calibrated spectral power density.

For time-resolved PL studies, ns optical parametric oscillator Lotis TII LT-2214 tuned to 530 nm was used as excitation source. The decay curves were detected with monochromator MDR-12 (SBW = 1 nm), fast Hamamatsu C5460 photodetector (response time, 40 ns) and a 500 MHz Textronix TDS-3052B digital oscilloscope. The decay from  $^5D_0$  state was monitored at 610 nm and 700 nm, and the characteristic decay time was determined according to a single-exponential law,  $I_{\text{PL}} = I_0 \exp(-t/\tau)$ .

Raman spectra were measured using a Renishaw inVia Raman microscope with a  $\times 50$  objective. The excitation wavelength was 632.8 nm (He–Ne laser). The spectral resolution was  $0.1 \text{ cm}^{-1}$ .

#### 4. Optical spectroscopy

Optical absorption spectrum of the Eu:NGW crystal is shown in Fig. 3 (light polarization is  $E \parallel a$ , RT). The absorption band attribution is performed according to earlier results [36]. The feature of  $\text{Eu}^{3+}$  ion is a small energy gap between the ground state ( $^7F_0$ ) and

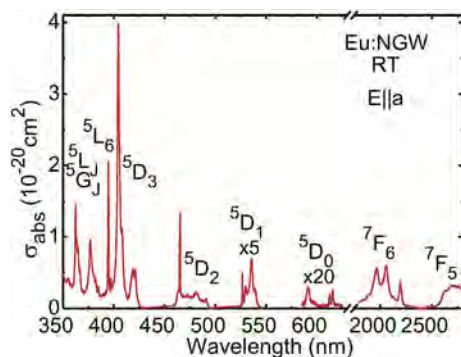


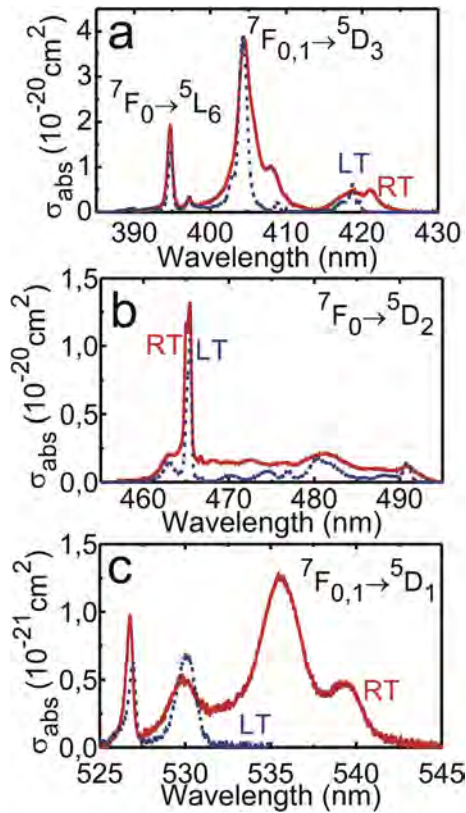
Fig. 3. Absorption cross-section spectrum of Eu:NGW crystal at room-temperature, light polarization is  $E \parallel a$ .

the lower-lying excited state ( $^7F_1$ ),  $\sim 350 \text{ cm}^{-1}$  in DTs. The latter manifold is thermally populated at RT (the fractional population probabilities for  $^7F_0$  and  $^7F_1$  states are  $\sim 0.65$  and  $0.33$ , respectively, as estimated from Boltzmann distribution). Indeed, in the absorption spectrum the transitions from both  $^7F_0$  and  $^7F_1$  states are detected. In the near-IR, characteristic bands of  $\text{Eu}^{3+}$  ions related to the transitions  $^7F_{0,1} \rightarrow ^7F_5$  ( $3500\text{--}3900 \text{ cm}^{-1}$ ) and  $^7F_6$  ( $4500\text{--}5200 \text{ cm}^{-1}$ ) are observed. In the visible, intense absorption bands are related to the transitions to the higher-lying  $^5D_0$  ( $\sim 16800 \text{ cm}^{-1}$ ),  $^5D_1$  ( $\sim 18350 \text{ cm}^{-1}$ ),  $^5D_2$  ( $\sim 21500 \text{ cm}^{-1}$ ),  $^5D_3$  ( $\sim 24700 \text{ cm}^{-1}$ ) and  $^5L_6$  multiplets ( $\sim 25350 \text{ cm}^{-1}$ ). For wavenumbers above  $25500 \text{ cm}^{-1}$ , energy sublevels from the  $^5L_j$ ,  $^5G_j$  and  $^5D_j$  multiplets are partially overlapped and their attribution is complicated.

The UV absorption edge of the Eu:NGW crystal is at  $\lambda_{\text{UV}} = 325 \text{ nm}$  ( $E_g \sim 3.8 \text{ eV}$ ) and it is almost independent from the polarization, as determined from the Tauc plot. This determines smaller transparency region of NGW in UV as compared with monoclinic KGW crystal with  $\lambda_{\text{UV}} = 290 \text{ nm}$ . This is typical for all tetragonal DTs and DMos and causes weak yellow-green coloration of undoped samples, while undoped monoclinic DTs are clear.

The details of absorption bands of Eu:NGW crystal related to the transitions  $^7F_{0,1} \rightarrow ^5L_6$ ,  $^5D_3$  and  $^5D_2$  (blue region) and  $^7F_{0,1} \rightarrow ^5D_1$  (green region) are analyzed in Fig. 4 at RT and LT (light polarization  $E \parallel a$ ). For LT, the spectra are shown in a.u. The UV pumping of Eu-doped DT typically causes the color center formation and darkening of the sample that can prevent laser operation [35]. Thus, only the absorption bands in the visible will be considered.

The intense band peaked at 394.5 nm ( $\sigma_{\text{abs}} = 1.9 \times 10^{-20} \text{ cm}^2$ ) is ascribed to the  $^7F_0 \rightarrow ^5L_6$  transition. It can be used for pumping of Eu:NGW by blue InGaN laser diodes emitting in the vicinity of  $\sim 400 \text{ nm}$ . The full width at half maximum (FWHM) for this band is 0.8 nm which is almost 3 times larger than that of monoclinic Eu:KGW [37]. The feature of Eu:NGW is the anomalously strong absorption at 400–420 nm which is attributed to the  $^7F_{0,1} \rightarrow ^5D_3$  transitions. Second relevant band in the blue contains two very narrow (FWHM  $\approx 0.3 \text{ nm}$ ) peaks at 465.0 and 465.4 nm (for  $E \parallel a$ , while for  $E \parallel c$  only second peak is detected) and the maximum  $\sigma_{\text{abs}}$  is  $1.3 \times 10^{-20} \text{ cm}^2$  at 465.4 nm. Eu:NGW can be pumped into this band by a frequency-doubled optically pumped semiconductor lasers. The band, related to the transition  $^7F_1 \rightarrow ^5D_1$ , was previously used for pumping of  $\text{Eu}^{3+}$ -doped monoclinic DT with green frequency-doubled Nd lasers [24,33]. This band is determined by broad local peak at 535.5 nm with  $\sigma_{\text{abs}} = 1.2 \times 10^{-21} \text{ cm}^2$  and FWHM = 3.1 nm. The weaker band related to  $^7F_0 \rightarrow ^5D_1$  transition contains local peaks at 526.7 and 529.8 nm and demonstrates small FWHM,  $< 0.4 \text{ nm}$ , so it is not suitable for pumping.



**Fig. 4.** Details of the absorption bands related to the  $7F_{0,1} \rightarrow 5D_3$  and  $5L_6$  (a),  $7F_0 \rightarrow 5D_2$  (b) and  $7F_{0,1} \rightarrow 5D_1$  (c) transitions of  $\text{Eu}^{3+}$  ions in NGW crystal at room-temperature (RT) and 6 K (LT), light polarization is  $E \parallel a$ . The spectrum for LT is shown in a.u.

**Table 1**

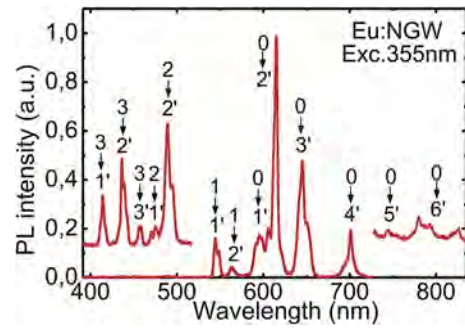
Peak absorption cross-sections,  $\sigma_{\text{abs}}$ , the corresponding wavelengths,  $\lambda_{\text{peak}}$ , and full widths at half maximum of the absorption peak,  $\Delta\lambda$ , for  $7F_1 \rightarrow 5D_1$  transition of  $\text{Eu}^{3+}$  ions in double tungstate crystals.

Transition	Crystal <sup>a</sup>	Polar.	$\lambda_{\text{peak}}$ , nm	$\Delta\lambda$ , nm	$\sigma_{\text{abs}}$ , $10^{-20}$ cm <sup>2</sup>
$7F_1 \rightarrow 5D_1$	Eu:NaGd(WO <sub>4</sub> ) <sub>2</sub>	<i>a</i>	535.5	3.08	0.12
	Eu:KGd(WO <sub>4</sub> ) <sub>2</sub>	<i>m</i>	534.3	0.66	0.89
	Eu:KY(WO <sub>4</sub> ) <sub>2</sub>	<i>m</i>	534.3	0.59	1.71
	Eu:KLu(WO <sub>4</sub> ) <sub>2</sub>	<i>m</i>	534.2	0.66	0.95

<sup>a</sup> Results for monoclinic DT are in accordance with [35,37,38].

The comparison of peak absorption cross-sections of  $\text{Eu}^{3+}$  ions related to the  $7F_1 \rightarrow 5D_1$  transition in  $\text{Eu}^{3+}$ -doped DT is presented in Table 1. Monoclinic DT offer one order of magnitude higher  $\sigma_{\text{abs}}$  (as compared with Eu:NGW) which is attributed to their low-symmetry structure. However, FWHM of the absorption band for Eu:NGW is 6 times larger than that for monoclinic DT [38] which can reduce the requirements for pump wavelength. The latter factor strongly reduced efficiency of Eu lasers based on monoclinic crystals [33,34]. In particular, for 20 mm-long 5 at.% Eu:NGW, absorption at ~534 nm is ~35%. Further improvement of pump efficiency for Eu:NGW can be done by growing of highly doped (>20 at.% Eu) crystals. This is possible due to the closeness of ionic radii of  $\text{Gd}^{3+}$  and  $\text{Eu}^{3+}$  (moreover, the stoichiometric NaEu(WO<sub>4</sub>)<sub>2</sub> crystal can exist in the tetragonal phase [39]).

Photoluminescence (PL) of Eu:NGW crystal was excited in the UV at 355 nm. The used excitation wavelength allowed population of metastable  $5D_0$  and higher-lying  $5D_1$ ,  $5D_2$  and  $5D_3$  states. For these multiplets, in contrast to the  $5D_0$  one, the energy gap to the lower-lying state is relatively small (~1000–2000 cm<sup>-1</sup>) which, however,



**Fig. 5.** Photoluminescence (PL) spectrum of Eu:NGW crystal at room temperature, numbers on the graph denote  $5D_j \rightarrow 7F_j$  (shortly  $J \rightarrow J'$ ) transitions of  $\text{Eu}^{3+}$  ions, excitation wavelength is 355 nm.

is enough wide to prevent domination of multi-phonon non-radiative relaxation over the radiative transitions and, hence, the emission from these states is observed. The PL spectrum of Eu:NGW is shown in Fig. 5 together with the interpretation of observed emission bands related to the  $5D_j \rightarrow 7F_j$  (shortly  $J \rightarrow J'$ ) transitions. The bands with the maxima at ~580, 595, 614, 645, 700, 745 and 780 nm are related with the  $0 \rightarrow 0'$ ,  $1'$ ,  $2'$ ,  $3'$ ,  $4'$ ,  $5'$  and  $6'$  transitions, respectively. The most intense band is at ~614 nm ( $0 \rightarrow 2'$ ) and it determines red color of the PL. CIE 1931 (*Commission internationale de l'éclairage*) coordinates for PL of Eu:NGW crystal are  $x = 0.671$  and  $y = 0.329$ . The dominant wavelength in the emission spectrum is  $\lambda_d = 608$  nm with the purity  $p = 99\%$ . A comparison of color coordinates of PL from single- and nano-crystalline Eu-doped DT and DMO is presented in Table 2.

It should be noted that no signs of blue  $\text{Eu}^{2+}$  emission were detected for Eu:NGW crystals (both as-grown and annealed). Thus, we conclude that all Eu ions in the NGW crystal are trivalent.

$\text{Eu}^{3+}$  is known for its hyper-sensitive purely electric-dipole, ED, transition  $5D_0 \rightarrow 7F_2$  that is the indicator of the symmetry of the ion site. If the site has no inversion center, this transition will be dominant over the  $5D_0 \rightarrow 7F_1$  magnetic dipole, MD, one [18,43]. The ratio of integral intensities of the above mentioned emission bands, is called the asymmetry parameter  $R$  [44]:

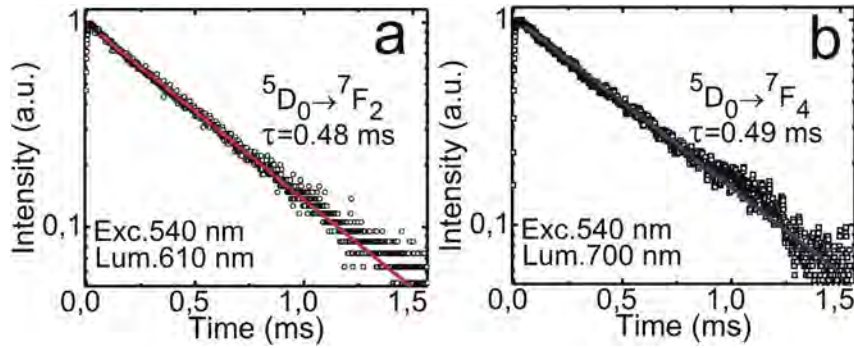
$$R = \frac{I_{\text{ED}}(5D_0 \rightarrow 7F_2)}{I_{\text{MD}}(5D_0 \rightarrow 7F_1)}. \quad (1)$$

For Eu:NGW,  $R = 3.4$  (a prevalence of ED transition). This is consistent with the fact that  $\text{Eu}^{3+}$  ions replaces  $\text{Gd}^{3+}$  ones located in distorted  $S_4$  sites without inversion center. The value of  $R$  for

**Table 2**

Color coordinates  $x$ ,  $y$  (in accordance with *Commission internationale de l'éclairage*, CIE 1931, color space) for photoluminescence of  $\text{Eu}^{3+}$ -doped DT and DMO compounds (C – single-crystal, P – nanocrystalline powder).

Compound	Form	$x$	$y$	Ref.
Tetragonal				
Eu:NaGd(WO <sub>4</sub> ) <sub>2</sub>	C	0.671	0.329	This work
Eu:NaGd(WO <sub>4</sub> ) <sub>2</sub>	P	0.661	0.339	[40]
Eu:NaGd(MoO <sub>4</sub> ) <sub>2</sub>	P	0.664	0.335	[41]
Eu:NaY(WO <sub>4</sub> ) <sub>2</sub>	P	0.570	0.350	[28]
Eu:NaLa(WO <sub>4</sub> ) <sub>2</sub>	P	0.660	0.340	[41]
		0.320	0.300	[42]
Eu:KLa(WO <sub>4</sub> ) <sub>2</sub>	P	0.652	0.625	[27]
Eu:LiLa(WO <sub>4</sub> ) <sub>2</sub>	P	0.649	0.349	[27]
Monoclinic				
Eu:KGd(WO <sub>4</sub> ) <sub>2</sub>	C	0.664	0.336	[37]
Eu:KY(WO <sub>4</sub> ) <sub>2</sub>	C	0.670	0.329	[38]
Eu:KLu(WO <sub>4</sub> ) <sub>2</sub>	C	0.672	0.328	[35]



**Fig. 6.** Decay of red luminescence of  $\text{Eu}^{3+}$  ions in NGW at 610 nm,  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition, (a) and 702 nm,  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$  transition, (b); excitation wavelength is 530 nm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$\text{Eu}:\text{NGW}$  is lower than for  $\text{Eu}:\text{KGW}$  ( $R \approx 10$ ) [37] as in the latter case  $\text{Eu}^{3+}$  ions are located in the  $\text{C}_2$  sites with lower symmetry.

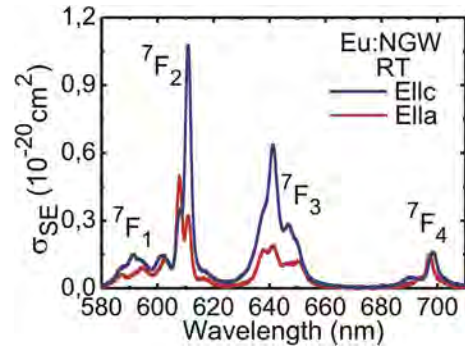
The PL decay curves for  $\text{Eu}:\text{NGW}$  crystal are shown in Fig. 6. The measurements were performed for the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  (at 610 nm) and  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$  (700 nm) emission channels. The decay curves are clearly single-exponential. The luminescence decay time  $\tau$  is equal to  $480 \pm 10 \mu\text{s}$ . A comparison of decay times for  $\text{Eu}^{3+}$  emission in DT and DMO is presented in Table 3. The value of  $\tau$  for  $\text{Eu}:\text{NGW}$  is similar to that of monoclinic DT (430 ... 510  $\mu\text{s}$ ) [37,38]. For  $\text{Eu}$ -doped DT and DMO nanopowders, wider range of decay times was reported, from  $\sim 0.5$  to  $\sim 1$  ms, depending on the crystal composition and  $\text{Eu}$  doping level (cf. Table 3).

To calculate the stimulated-emission (SE) cross-sections,  $\sigma_{\text{SE}}$ , for  $\text{Eu}:\text{NGW}$  we have used the Füchtbauer–Ladensburg (F-L) equation [48]:

$$\sigma_{\text{SE}}^i(\lambda) = \frac{\lambda^5}{8\pi n_i^2 \tau c} \frac{W_i(\lambda)}{1/3 \sum_{i=a,c} \int \lambda W_i(\lambda) d\lambda}. \quad (2)$$

Here,  $W_i(\lambda)$  is the measured spectral power density of luminescence for  $E \parallel a$  and  $E \parallel c$  oscillation states,  $\lambda$  is the light wavelength,  $n_i$  is the refractive index corresponding to  $i$ -th polarization,  $\tau$  is the lifetime of the emitting state ( ${}^5\text{D}_0$  level of  $\text{Eu}^{3+}$ ),  $c$  is the speed of light, and averaging is performed as  $1/3(2f_a + f_c)$  where  $f$  is the integrated luminescence power density. This is related to the fact as for  $\text{Eu}:\text{NGW}$ , light polarization along [100] and [010] axes are identical (both corresponds to  $E \parallel a$  polarization).

The results on SE cross-sections for  $\text{Eu}:\text{NGW}$  crystal are shown in Fig. 7. For  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$  transition (deep-red emission), the peak  $\sigma_{\text{SE}}$



**Fig. 7.** Stimulated-emission cross-sections ( $\sigma_{\text{SE}}$ ) spectra of  $\text{Eu}:\text{NGW}$  crystal for light polarizations  $E \parallel a$  and  $E \parallel c$ .

**Table 4**

Peak stimulated-emission cross-sections,  $\sigma_{\text{SE}}$ , the corresponding wavelengths,  $\lambda_{\text{peak}}$ , for  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  and  ${}^7\text{F}_4$  transition of  $\text{Eu}^{3+}$  ions in double tungstate crystals.

Transition	Crystal <sup>a</sup>	Polar.	$\lambda_{\text{peak}}$ , nm	$\sigma_{\text{SE}}$ , $10^{-20} \text{ cm}^2$
${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$	$\text{Eu}:\text{NaGd}(\text{WO}_4)_2$	$c$	610.9	1.08
	$\text{Eu}:\text{KGd}(\text{WO}_4)_2$	$m$	613.6	2.78
	$\text{Eu}:\text{KY}(\text{WO}_4)_2$	$m$	613.4	4.02
	$\text{Eu}:\text{KLu}(\text{WO}_4)_2$	$m$	613.7	3.95
${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$	$\text{Eu}:\text{NGd}(\text{WO}_4)_2$	$c$	698.3	0.16
	$\text{Eu}:\text{KGd}(\text{WO}_4)_2$	$m$	702.1	3.02
	$\text{Eu}:\text{KY}(\text{WO}_4)_2$	$m$	702.6	1.34
	$\text{Eu}:\text{KLu}(\text{WO}_4)_2$	$m$	703.5	1.78

<sup>a</sup> Results for monoclinic DT are in accordance with [35,37,38].

**Table 3**

Lifetime of the  ${}^5\text{D}_0$  emitting state of  $\text{Eu}^{3+}$  ions in DT and DMO compounds (C – single-crystal, P – nanocrystalline powder).

Crystal	Form	$\tau({}^5\text{D}_0)$ , ms	Ref.
Tetragonal			
$\text{Eu}:\text{NaGd}(\text{WO}_4)_2$	C	0.49	This work
	P	0.58	[27]
$\text{Eu}:\text{NaGd}(\text{MoO}_4)_2$	P	0.57	[45]
$\text{Eu}:\text{NaY}(\text{WO}_4)_2$	P	0.5–0.7	[28,40,46]
$\text{Eu}:\text{NaLu}(\text{MoO}_4)_2$	P	0.54	[47]
$\text{Eu}:\text{NaLu}(\text{WO}_4)_2$	P	0.57	[27,47]
$\text{Eu}:\text{NaLa}(\text{WO}_4)_2$	P	0.6–1.1	[27,43]
$\text{Eu}:\text{KLa}(\text{WO}_4)_2$	P	0.65	[27]
$\text{Eu}:\text{LiLa}(\text{WO}_4)_2$	P	0.63	[27]
Monoclinic			
$\text{Eu}:\text{KGd}(\text{WO}_4)_2$	C	0.51	[37]
$\text{Eu}:\text{KY}(\text{WO}_4)_2$	C	0.43	[38]
$\text{Eu}:\text{KLu}(\text{WO}_4)_2$	C	0.45	[35]

values are very similar for light polarizations  $E \parallel a$  and  $E \parallel c$ ,  $\sim 1.5 \times 10^{-21} \text{ cm}^2$ . The peak wavelengths  $\lambda_{\text{peak}}$  are 697.2 and 698.3 nm, respectively. These values are much lower than that for monoclinic  $\text{Eu}:\text{DT}$  (cf. Table 4). In addition,  $\lambda_{\text{peak}}$  for  $\text{Eu}:\text{NGW}$  is also shorter: for  $\text{Eu}:\text{KGW}$ , laser operation was achieved at  $\sim 702$  nm. For the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition (red emission), the anisotropy of SE cross-sections is more profound. For light polarization  $E \parallel a$ , the spectrum contains intense peak centered at 610.9 nm with  $\sigma_{\text{SE}} = 1.08 \times 10^{-20} \text{ cm}^2$ . For  $E \parallel c$ , this emission band splits to two components peaked at 607.9 nm and 610.9 nm and the maximum  $\sigma_{\text{SE}} = 0.51 \times 10^{-20} \text{ cm}^2$ . The anisotropy degree for this transition is  $\sigma_{\text{SE}}(a) : \sigma_{\text{SE}}(c) \approx 2:1$ . Thus, for this transition, the linearly polarized laser output is expected.

The study of spectroscopic properties of  $\text{Eu}:\text{NGW}$  indicates that both principal light polarizations,  $E \parallel a$  and  $E \parallel c$ , can be useful for potential laser applications. To access both of them, the crystal should be cut perpendicular to the [001] axis which is usually

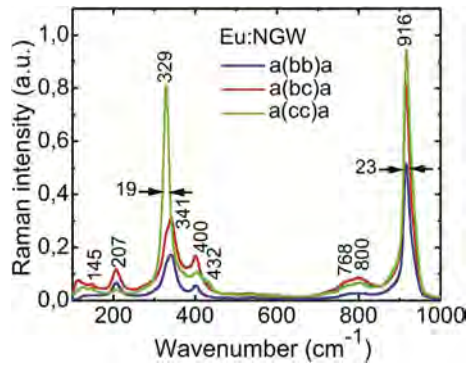


Fig. 8. Polarized Raman spectra of Eu:NGW crystal for the  $a(bb)a$ ,  $a(bc)a$  and  $a(cc)a$  geometries: excitation wavelength is 632.8 nm,  $a$  and  $b$  axes are identical for NGW.

denoted as  $a$ -cut. In addition, for NGW, particularly this crystal cut is beneficial in terms of weaker thermo-optic effects [49].

Both monoclinic and tetragonal DTs are well-known Raman-active media [50,51] also offering the possibility of self-Raman conversion [52]. Raman spectra of Eu:NGW are shown in Fig. 8 for  $a(bb)a$ ,  $a(bc)a$  and  $a(cc)a$  geometries. The strongest Raman peak of the stretching vibration of the  $(\text{WO}_4)_2^-$  anion, the  $\nu_1(A_g)$  mode according to the scheelite  $I_4/a$  symmetry, is centered at  $916 \text{ cm}^{-1}$  and its bandwidth is  $\sim 23 \text{ cm}^{-1}$ . Raman spectra are strongly polarized; for an  $a$ -cut crystal, polarization  $E \parallel c$  is of interest for Raman conversion. The assignment of Raman active modes for Eu:NGW crystal is presented in Table 5, in accordance with [51].

Further work on  $\text{Eu}^{3+}$ -doped sodium DT should be focused on growth of highly-doped ( $>20 \text{ at.}\%$  Eu) NGW crystals and laser operation in the deep-red ( $\sim 698 \text{ nm}$ ) and red ( $\sim 611 \text{ nm}$ ) spectral regions. The use of different “passive” ions like  $\text{La}^{3+}$  or  $\text{Bi}^{3+}$  can induce the transition cross-section increase and, thus, the study of Eu:NRW crystals with  $R = \text{Y, Lu, La}$  or  $\text{Bi}$  or Eu:NaRMO crystals seems to be very interesting. The growth of  $\text{Eu}^{3+}$ -doped sodium DT along the  $[100]$  direction can be useful for preparation of long  $a$ -cut laser elements.

## 5. Conclusion

We report on Czochralski growth and spectroscopic study of tetragonal  $\text{Eu}^{3+}$ -doped sodium double tungstate,  $\text{NaGd}(\text{WO}_4)_2$  (Eu:NGW). By providing low axial and radial temperature gradients ( $<1.0^\circ \text{C/cm}$ ) we were able to stabilize the growth process and produce large-volume bulk of very high optical quality. The Eu doping concentration was as high as 4.9 at.% but the results indicate

good prospects for growing of highly-doped Eu:NGW crystals. In addition, annealing in air was found to be crucial to diminish the oxygen vacancies resulting in dark red-brown coloration of the as-grown bulk.

Although absorption and stimulated-emission cross-sections for  $\text{Eu}^{3+}$  ions in NGW are lower than those of  $\text{Eu}^{3+}$ -doped monoclinic double tungstates, Eu:NGW offers wider absorption bands which can be favorable for increased pump efficiency. In particular, for the transition  ${}^7F_1 \rightarrow {}^5D_1$  which can be used for pumping with green frequency-doubled Nd lasers,  $\sigma_{\text{abs}} = 1.2 \times 10^{-21} \text{ cm}^2$  at 535.5 nm while FWHM of the corresponding absorption band is 3.1 nm. In the deep-red region, the laser operation with Eu:NGW is expected at  $\sim 698 \text{ nm}$  and the corresponding stimulated-emission cross-section is  $\sigma_{\text{SE}} = 1.6 \times 10^{-21} \text{ cm}^2$  (at RT, for  $E \parallel c$  polarization). Under UV excitation at 355 nm, Eu:NGW provides intense red emission with color coordinates  $x = 0.671$ ,  $y = 0.329$  (CIE 1931 color space).

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Table 5

Assignment of Raman active modes for Eu:NaGdW crystal.

Mode <sup>a</sup> , $\text{cm}^{-1}$			Assignment <sup>b</sup>
$a(bb)a$	$a(bc)a$	$a(cc)a$	
916 s	916 s	916 s	$\nu_s(\text{WO}_4)$
800 w	800 w	800 w	$\nu_{\text{as}}(\text{WO}_4)$
768 w	768 w	768 w	
		432 w	–
400 w	400 m	400 w	$\delta_{\text{as}}(\text{WO}_4)$
341 m	341 m	329 s	$\delta_s(\text{WO}_4)$
207 w	207 m	207 w	$L(\text{WO}_4)$
	145 w	145 w	$T(\text{Na}^+/\text{Gd}^{3+})$
125 w	114 w	125 w	$T(\text{WO}_4)$

<sup>a</sup> s – strong, m – medium, w – weak.

<sup>b</sup>  $\nu_s$ ,  $\nu_{\text{as}}$  – stretching modes;  $\delta_s$ ,  $\delta_{\text{as}}$  – bending modes;  $L$  – librational modes;  $T$  – translational modes.

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