

## Growth and spectroscopic properties of Sm<sup>3+</sup>:KY(WO<sub>4</sub>)<sub>2</sub> crystal

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### ABSTRACT

A Sm<sup>3+</sup>:KY(WO<sub>4</sub>)<sub>2</sub> crystal was grown by the modified Czochralski technique. Polarized absorption and fluorescence spectra, as well as a fluorescence decay curve, were recorded at room temperature. Radiative properties such as emission probabilities, branching ratios and radiative lifetimes were investigated within the framework of the Judd-Ofelt theory as well as the theory of f-f transition intensities which takes into account the influence of the excited configurations. Emission cross section spectra were determined. <sup>4</sup>G<sub>5/2</sub> fluorescence decay was analyzed within the framework of the Inokuti-Hirayama model. The spectroscopic properties of Sm:KYW crystal were compared with those of other Sm<sup>3+</sup>-doped materials.

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## 1. Introduction

There is increasing interest in finding new solid state media emitting in the visible spectral range. Rare-earth ions with emission in the visible spectral range are attractive for solid state lasers (without any nonlinear frequency conversion) and different applications: medicine (photodynamic therapy [1]), biophotonics, spectroscopy, quantum optics (atom trapping, atomic clocks, sodium guide stars [2]), communication, color displays, high density optical data storage and replacement dye lasers. Sm<sup>3+</sup>-doped materials could be promising for these applications due to its strong orange-yellow fluorescence. Spectroscopic properties have been evaluated for Sm-doped single crystals [3–12], glasses [13,14], ceramics [15] and phosphors [16]. These investigations have shown the Sm<sup>3+</sup> as a promising ion for solid state optical materials. Moreover, laser oscillation in the Sm<sup>3+</sup> doped LiLuF<sub>4</sub> and SrAl<sub>12</sub>O<sub>19</sub> crystals was obtained successfully [17].

The family of potassium double tungstates  $\alpha$ -KRE(WO<sub>4</sub>)<sub>2</sub> (RE = Y and Ln) crystals activated by rare-earth ions is a well-known host

for solid-state lasers [18]. The main advantage of these crystals as a laser media is relatively high values of absorption and emission cross sections of rare-earth dopants. Also, double tungstates can be doped with high concentration of active ions without significant fluorescence quenching because of relatively large distances between the dopants ions [19].

This paper is devoted to the comprehensive spectroscopic characterization of Sm<sup>3+</sup>:KY(WO<sub>4</sub>)<sub>2</sub> (Sm:KYW) as a potential optical material. Polarization dependent absorption and fluorescence spectra were recorded. The conventional Judd-Ofelt theory and theories which take into account the influence of excited configurations were applied to determine the radiative properties of Sm<sup>3+</sup> ions. Fluorescence decay curve of the <sup>4</sup>G<sub>5/2</sub> level was registered and the excited state relaxation dynamics was discussed.

## 2. Experimental details

Sm:KYW crystal was grown by the modified Czochralski technique at low temperature gradient (<1 deg/cm) using the [010]-oriented seed crystal from the potassium ditungstate (K<sub>2</sub>W<sub>2</sub>O<sub>7</sub>) flux [20]. The mass content of the Sm<sup>3+</sup> ions in the KYW crystal was determined using an ICP spectrometer IRIS Intrepid HR Duo (Thermal Elemental) and was found to be 0.434 ± 0.004 wt%. The

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samarium concentration was calculated to be  $1.14 \cdot 10^{20} \text{ cm}^{-3}$  using measured volumetric crystal density of  $6.58 \text{ g/cm}^3$ . The as-grown crystal (see Fig. 1) was clear and had a good optical quality.

KYW is a biaxial crystal, with a monoclinic structure (space group  $C_{2h}^6 -2/m$ ,  $Z = 4$ ). Unit cell parameters for crystallographic setting  $I2/c$  are  $a = 8.05 \text{ \AA}$ ,  $b = 10.35 \text{ \AA}$ ,  $c = 7.54 \text{ \AA}$ ,  $\beta = 94^\circ$ . There are two possible crystallographic settings  $C2/c$  and  $I2/c$  for this space group, however, the last one better describes the crystal habit [18]. Optical properties of KYW crystal are different for directions along the optical indicatrix axes  $N_p$ ,  $N_m$ ,  $N_g$ . Principal axis  $N_p$  coincides with the crystallographic  $\mathbf{b}$  axis ([010]). The other two ones lie in the  $\mathbf{a}-\mathbf{c}$  plane. The principal axis  $N_g$  is rotated at  $19^\circ$  anticlockwise from  $\mathbf{c}$  crystallographic axis. Its orientation was determined using a polarizing microscope POLAM-L213-BE (LOMO).

Samarium ions substitute yttrium ions in the KYW crystal and occupy the  $C_2$  local point symmetry positions. The ionic radius of  $\text{Sm}^{3+}$  ion ( $1.079 \text{ \AA}$ ) is close to one of the  $\text{Y}^{3+}$  ( $1.019 \text{ \AA}$ ) for eight-fold coordination [21]. The separation between Y-Y pairs affects the energy transfer between the dopant ions. For KYW crystal this distance in the  $\text{YO}_8$  chain parallel to the [101] direction is  $0.406(3) \text{ nm}$  and between different chains is  $0.604(2) \text{ nm}$  [18].

For the spectroscopic investigations a sample of Sm:KYW crystal was cut parallel to principal optical plains. The absorption and luminescence spectra of the Sm:KYW crystal were measured at room temperature with light polarized parallel to the three principal optical indicatrix axes. The absorption spectra in polarized light were recorded by a CARY 5000 spectrophotometer with a spectral bandwidth (SBW) of  $0.1 \text{ nm}$  in the UV and visible ranges and  $0.3 \text{ nm}$  in the NIR spectral range.

Fluorescence spectra were recorded under an InGaN-laser diode excitation at  $405 \text{ nm}$ . The luminescence emission was collected by a wide-aperture lens and focused onto the entrance slit of a monochromator MDR-23 (SBW =  $0.1 \text{ nm}$ ). The signal was detected with a Hamamatsu C5460-01 APD module connected to a SR830 Standford lock-in amplifier. A Glan-Taylor polarizer was used to separate light polarizations. A gray body light source with a color temperature of  $2900 \text{ K}$  was used to correct the measured spectra with respect to detector response, grating efficiency, and other optical elements.

The decay curve of the upper manifold ( ${}^4G_{5/2}$ ) was registered under pulsed excitation at  $480 \text{ nm}$  by means of an optical parametric oscillator LOTIS TII LT-2214, which was pumped by a third harmonic of the flashlamp-pumped Q-switched Nd:YAG laser LOTIS TII LS-2137. The fluorescence emission at the wavelength of  $649 \text{ nm}$  was imaged by wide aperture lens onto the entrance slit of a monochromator MDR-12. The signal was detected by a fast Hamamatsu photodetector C5460 connected to an oscilloscope with a bandwidth of  $500 \text{ MHz}$ .

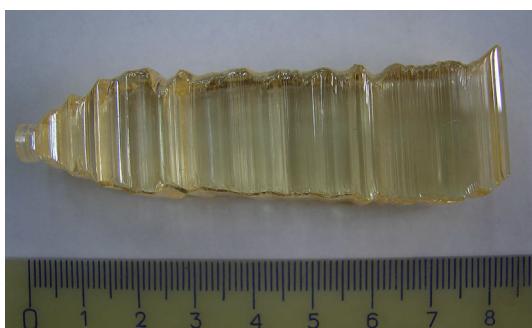


Fig. 1. Sm-doped KYW crystal boule.

### 3. Results and discussion

#### 3.1. Absorption spectra

The polarized dependent absorption spectra of the Sm:KYW were recorded in the  $350$ – $570 \text{ nm}$  and  $970$ – $3100 \text{ nm}$  spectral ranges. The spectra were corrected for the Fresnel losses using the Sellmeier's coefficients for the KYW crystal [18]. The spectra of absorption cross section  $\sigma_{GSA}$  in the visible and NIR spectral ranges are shown in Fig. 2. The absorption bands within the  $4f^5$  samarium configuration can be divided into two groups. The first one, appearing in the NIR region consists of quite intense lines which are assigned to the spin-allowed transitions from the ground state  ${}^6H_{5/2}$  to the excited multiplets  ${}^6H_J$  and  ${}^6F_J$ . Another group located in the UV and visible regions consists of a great number of closely spaced levels. Spin forbidden transitions occur between these levels and the ground state level. Hence the intensities of lines are weak, excepting spin allowed  ${}^6H_{5/2} \rightarrow {}^6P_J$  transitions. It should be noted, that identification of observed absorption bands in the UV–vis spectral range is difficult due to their strong levels overlapping. Assignments of the spectral lines for the excited states from the ground state were performed according to Ref. [22].

The absorption spectra of the Sm:KYW exhibits significant polarization dependence with dominant  $E||N_m$  polarization. The strongest transition  ${}^6H_{5/2} \rightarrow {}^6P_{3/2}$  has a peak value of absorption cross section of  $9.2 \cdot 10^{-20} \text{ cm}^2$  at  $404.6 \text{ nm}$  for  $E||N_m$  polarization. This value is larger than observed in Sm:NaGd(MoO<sub>4</sub>)<sub>2</sub> [6], Sm:GdVO<sub>4</sub> [11], Sm:(Ca,Mg,Zr)GGG [12] Sm,Mg:SRA, [17].

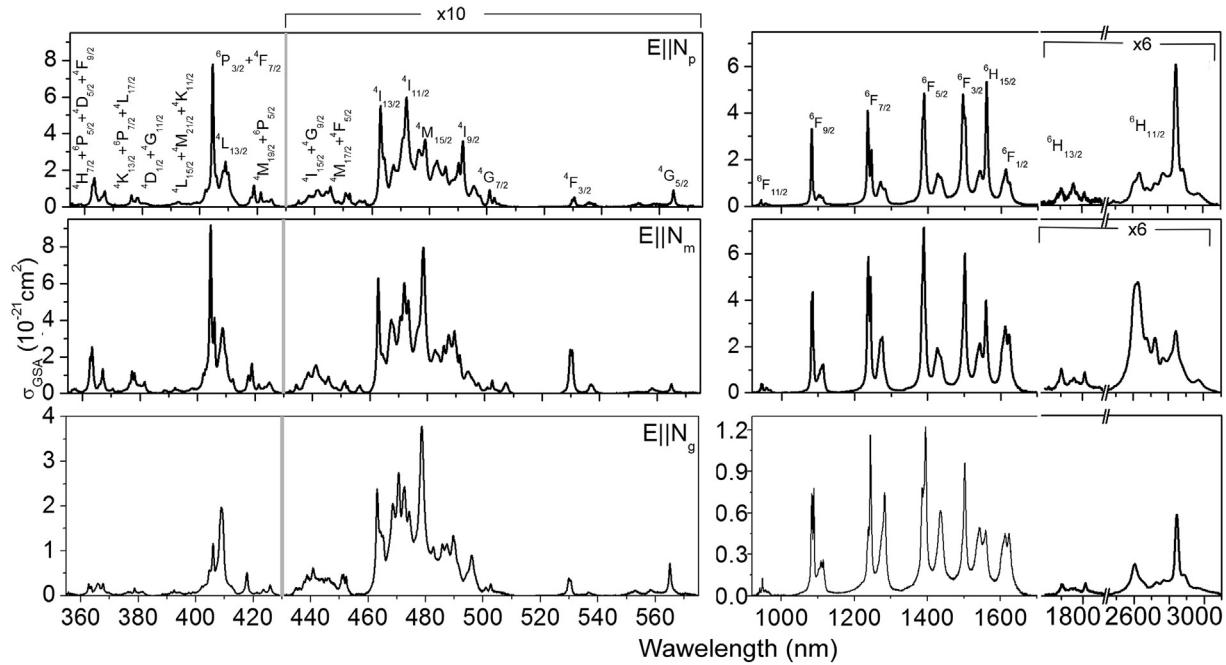
#### 3.2. Analysis of $f-f$ transition intensities

To determine the transition intensities of  $\text{Sm}^{3+}$  ion in KYW crystal the Judd-Ofelt theory [23,24] was applied. The detailed description of the Judd-Ofelt analysis can be found in many papers but here we provide basics of this procedure. Measured absorption spectra were used to calculate experimental oscillator strengths  $f_{exp}$  between manifolds with quantum numbers  $J$  and  $J'$ :

$$f_{exp}(JJ') = \frac{mc^2}{\pi e^2 N_0 \bar{\lambda}^2} \int \overline{\alpha_{JJ'}(\lambda)} d\lambda, \quad (1)$$

where  $\overline{\alpha_{JJ'}(\lambda)} = [\alpha_{Np}(\lambda) + \alpha_{Nm}(\lambda) + \alpha_{Ng}(\lambda)]/3$  is the polarization averaged absorption coefficient,  $\bar{\lambda}$  is the weighted mean wavelength,  $N_0$  is the concentration of  $\text{Sm}^{3+}$  ions. It should be noticed, that contribution of the magnetic dipole (MD) transitions ( $\Delta J = 0, \pm 1$ ) from the ground state level to the several excited state levels was taken into account and, consequently, the electric dipole (ED) oscillator strengths  $f_{exp}^{ed}$  were obtained. The values of the double reduced-matrix elements  $||U^{(t)}||$  were calculated from the intermediate coupling approximation using the free-ion parameters for samarium ion in glasses [25]. The values of experimental and calculated ED absorption oscillator strengths  $f_{exp}^{ed}$  and  $f_{J0}^{ed}$ , respectively, and the root mean square deviation are given in Table 1. Three phenomenological intensity parameters  $\Omega_t$  were evaluated by the least-square fitting procedure and are presented in Table 2.

The influence of the excited configurations on the absorption and luminescence spectral characteristics in the case of  $\text{Sm}^{3+}$  ions may be significant [26]. It was shown [26], that applying the theory of  $f-f$  transition intensities, which takes into account the influence of  $4f^{N-1}5d$  excited configuration, improves the agreement of the calculated results with the experimental data. Thus, to determine the radiative properties of  $\text{Sm}^{3+}$  ion in KYW crystal we applied the theory of  $f-f$  transition intensities for the system with the



**Fig. 2.** Polarized ground absorption cross sections of Sm:KYW. Please note the different scales.

**Table 1**  
Experimental ( $f_{\text{exp}}^{\text{ed}}$ ) and calculated ( $f^{\text{ed}}$ ) oscillator strength.

Transition ${}^6H_{5/2} \rightarrow$	Wavelength range (nm)	$\bar{\lambda}$ (nm)	$f_{\text{exp}}^{\text{ed}}, 10^{-6}$	$f_J^{\text{ed}}, 10^{-6}$	$f_{MJO}^{\text{ed}}, 10^{-6}$	$f_{ICI}^{\text{ed}}, 10^{-6}$
${}^6H_{11/2}$	2400–3100	2744	1.406	1.188	1.166	1.347
${}^6H_{13/2}$	1780–2130	1957	0.292	0.347	0.342	0.389
${}^6F_{1/2} + {}^6H_{15/2} + {}^6F_{3/2} + {}^6F_{5/2}$	1325–1700	1443	15.083	15.082	15.084	15.084
${}^6F_{7/2}$	1180–1320	1251	6.5	6.509	6.509	6.504
${}^6F_{9/2}$	1035–1145	1092	3.535	3.572	3.578	3.532
${}^6F_{11/2}$	920–980	953	0.478	0.561	0.565	0.531
${}^4G_{5/2}$	545–575	561	0.086	0.076	0.078	0.079
${}^4F_{3/2}$	526–540	531	0.146	0.017	0.018	0.02
RMS deviation				$0.11 \cdot 10^{-6}$	$0.13 \cdot 10^{-6}$	$0.1 \cdot 10^{-6}$

**Table 2**  
Intensity parameters ( $\mathcal{Q}_t$ ) for  $\text{Sm}^{3+}$ -doped crystals.

Crystal	$\mathcal{Q}_2 (10^{-20} \text{ cm}^2)$	$\mathcal{Q}_4 (10^{-20} \text{ cm}^2)$	$\mathcal{Q}_6 (10^{-20} \text{ cm}^2)$	Refs.
Sm:KYW (JO)	10.63	7.16	3.074	This work
Sm:KYW (MJO)	11.567	7.722	3.303	
Sm:KYW (ICI)	14 $R_2 = 0.052 \cdot 10^4 \text{ cm}$	7.49 $R_4 = 0.016 \cdot 10^4 \text{ cm}$	1.11 $R_6 = -0.467 \cdot 10^4 \text{ cm}$	
Sm:NaGd(MoO <sub>4</sub> ) <sub>2</sub>	8.65	4.4	1.96	[6]
Sm:LiNbO <sub>3</sub>	2.11	4.5	1.45	[8]
Sm:CaNb <sub>2</sub> O <sub>6</sub>	8.02	5.37	1.45	[9]

intermediate configuration interaction [27] (denoted as the ICI approximation). The line strength of the ED transition from initial  $J$  manifold to some terminal  $J'$  manifold, in this case, can be evaluated by the formula:

parameters related to the configuration interaction.

Additionally, we applied the modified Judd-Ofelt theory (MJO) [28]. In this case, only the excited configuration of the opposite parity makes a significant contribution, and the line strength can be

$$S_{\text{calc}}^{\text{ed}}(J') = \sum_{t=2,4,6} \mathcal{Q}_t \left[ 1 + 2R_t (E_J + E_{J'} - 2E_f^0) \right] \cdot \left| \langle 4f^n | S L J | U^{(t)} | 4f^n | S' L' J' \rangle \right|^2, \quad (2)$$

here  $E_J$  and  $E_{J'}$  are the energies of the combined multiplets,  $E_f^0$  is the average energy of  $4f^n$  configuration and  $R_t$  are additional

obtained from the following equation:

$$S_{\text{calc}}^{\text{ed}}(J') = \sum_{t=2,4,6} \Omega_t \left[ 1 + 2\alpha(E_J + E_{J'} - 2E_f^0) \right] \cdot \left| \left\langle 4f^n [SL] J \middle| U^{(t)} \middle| 4f^n [S'L'] J' \right\rangle \right|^2. \quad (3)$$

The values of the experimental and the calculated ED absorption oscillator strengths  $f_{\text{exp}}^{\text{ed}}$  and  $f_{\text{calc}}^{\text{ed}}$ , respectively, are given in [Table 1](#).

The obtained intensity parameters  $\Omega_t$  for Sm:KYW are listed in [Table 2](#) and compared with ones for other samarium doped crystals. The high value of the parameter  $\Omega_2$  suggests the high degree of covalency of the bonds between rare earth ions and their ligands [[29](#)].

Obtained intensity parameters were used to calculate ED radiative transition probabilities  $A_{\text{ed}}$ . Several transitions from the upper  ${}^4G_{5/2}$  level to the lower multiplets fulfill the selection rules for MD transitions. MD radiative transition probabilities  $A_{\text{md}}$  can be calculated separately and added to the ED transition probabilities. The total radiative transition probability can be expressed as [[22](#)]:

$$A_{\Sigma}(JJ') = \frac{64\pi^4 e^2}{3h(2J+1)\lambda^3} \left[ \frac{n(n^2+2)^2}{9} S_{\text{ed}} + n^3 S_{\text{md}} \right]. \quad (4)$$

The calculated luminescence branching ratios for  $J' \rightarrow J$  transitions  $\beta_{JJ'} = A(J'J)/\sum A(J'J)$  and the radiative lifetime  $\tau_{\text{rad}} = 1/\sum A(J'J)$  are presented in [Table 3](#).

As can be seen from [Table 3](#) there is no significant difference in the results obtained by using the three theories (JO, MJO and ICI approximation) for Sm:KYW crystal, in contrast with the Sm:LiNbO<sub>3</sub> crystal [[26](#)]. It indicates a small effect of the excited configurations on the absorption spectra in our case.

### 3.3. Fluorescence properties

Polarized fluorescence spectra of Sm:KYW in the range of 540–970 nm were recorded under excitation at 405 nm and corrected to the spectral response of the luminescence set-up. Overview of polarization averaged fluorescence spectrum is presented in [Fig. 3](#). The observed emission bands are related to the radiative transitions from  ${}^4G_{5/2}$  manifold to the lower lying levels. Manifold to manifold branching ratios for the transitions from the upper state the  ${}^4G_{5/2}$  to the lower lying states are found from:

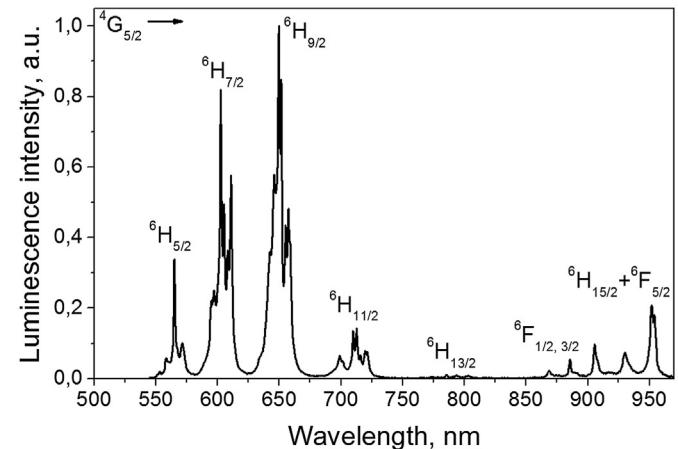
$$\beta_{JJ'} = \frac{\int \lambda I_{JJ'}(\lambda) d\lambda}{\sum_J \int \lambda I_{JJ'}(\lambda) d\lambda} \quad (5)$$

here  $I_{JJ'}(\lambda)$  is the spectral density fluorescence power in arbitrary units. The experimental averaged values of  $\beta_{JJ'}$  over three polarizations with respect to calculated ones are presented in [Table 4](#). It can be seen that measured and calculated values are in a good agreement. It is evident that almost 90% emitted energy is distributed in the visible spectral range. In the case of Sm:KYW, Sm:NaGd(MoO<sub>4</sub>)<sub>2</sub> [[6](#)] and Sm:CaNb<sub>2</sub>O<sub>6</sub> [[7](#)] almost the half of the emitted energy belongs to the  ${}^4G_{5/2} \rightarrow {}^6H_{9/2}$  transition. But for the most of Sm<sup>3+</sup>-doped materials, the transition is  ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$  has the highest intensity [[2,5,7,8,10–17](#)].

The stimulated emission (SE) cross sections  $\sigma_{\text{SE}}$  for the most intense transitions  ${}^4G_{5/2} \rightarrow {}^6H_J$  ( $J = 5/2, 7/2, 9/2$  and  $11/2$ ) were calculated by the Füchtbauer–Ladenburg formula [[30](#)]:

$$\sigma_{\text{SE}}^{\alpha}(\lambda) = \beta \frac{\lambda^5}{8\pi c n^2 \tau_{\text{rad}}} \frac{3I^{\alpha}(\lambda)}{\int [I^{Np}(\lambda) + I^{Nm}(\lambda) + I^{Ng}(\lambda)] \lambda d\lambda}, \quad (6)$$

here  $I^{\alpha}(\lambda)$  is the spectral density of fluorescence power ( $\alpha = N_m, N_p$  and  $N_g$  polarizations),  $\tau_{\text{rad}}$  is the radiative lifetime of the  ${}^4G_{5/2}$  level,  $\beta$  is the branching ratio of the corresponding transition. The obtained SE-spectra are displayed in [Fig. 4](#) for the wavelength range between 555 nm and 730 nm. The highest cross section was found



**Fig. 3.** Polarization averaged fluorescence spectra of Sm:KYW crystal.

**Table 3**

The calculated radiative probabilities ( $A_{\Sigma}$ ), fluorescence branching ratios ( $\beta$ ) in Sm:KYW crystal.

Transition ${}^4G_{5/2} \rightarrow$	$\bar{\lambda}$ (nm)	$A_{\Sigma}$ (JO) ( $s^{-1}$ )	$A_{\Sigma}$ (MJO) ( $s^{-1}$ )	$A_{\Sigma}$ (ICI) ( $s^{-1}$ )	$\beta_{\text{calc}}$ (JO)	$\beta_{\text{calc}}$ (MJO)	$\beta_{\text{calc}}$ (ICI)
${}^6H_{5/2}$	560	57.98	59.34	60.29	0.0048	0.0465	0.0471
${}^6H_{7/2}$	595	331.13	344.29	300.96	0.2725	0.2697	0.2349
${}^6H_{9/2}$	640	529.81	558.74	601.47	0.436	0.4377	0.4695
${}^6H_{11/2}$	701	111.42	117.32	106.9	0.0917	0.0919	0.0834
${}^6H_{13/2}$	772	15.17	16	8.5	0.0125	0.0125	0.0066
${}^6F_{1/2}$	869	13.17	14.13	16.62	0.0108	0.011	0.013
${}^6H_{15/2}$	877	27.44	28.68	61.74	0.0226	0.0225	0.0248
${}^6F_{3/2}$	887	0.92	0.98	0.44	0.0008	0.0008	0.0004
${}^6F_{5/2}$	923	99.34	103.32	121.9	0.0818	0.0833	0.0952
${}^6F_{7/2}$	1007	13.09	13.89	13.3	0.0108	0.0109	0.0104
${}^6F_{9/2}$	1131	14.69	15.91	18.4	0.0121	0.0125	0.0144
${}^6F_{11/2}$	1343	0.89	0.92	0.59	0.0007	0.0008	0.0005
$\tau_{\text{rad}}$ ( $\mu\text{s}$ )					823	783	780

**Table 4**

Measured ( $\beta_{Jf}$ ) and calculated ( $\beta_{calc}$ ) branching ratios for the  ${}^4G_{5/2}$  level in Sm:KYW crystal.

Transition ${}^4G_{5/2} \rightarrow$	Wavelength range, nm	$\beta_{calc}$ (J-O)	$\beta_{calc}$ (MJO)	$\beta_{calc}$ (ICl)	$\beta_{Jf}$
${}^6H_{5/2}$	545–580	4.8	4.6	4.7	5.8
${}^6H_{7/2}$	580–625	27.3	27	23.5	26.2
${}^6H_{9/2}$	625–678	43.6	43.8	46.9	43.9
${}^6H_{11/2}$	685–737	9.2	9.2	8.3	8.1
${}^6H_{13/2}$	765–810	1.2	1.3	0.7	0.8
${}^6F_{1/2, 3/2, 5/2} + {}^6H_{15/2}$	865–970	11.6	11.8	13.3	15.2

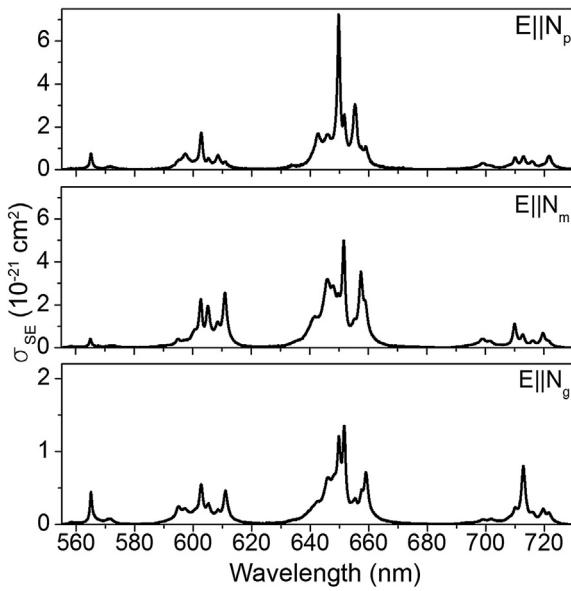


Fig. 4. Stimulated emission cross sections spectra of Sm:KYW crystal.

to be  $7.2 \cdot 10^{-21} \text{ cm}^2$  ( $\lambda = 649.7 \text{ nm}$ ) for  $N_p$  polarization and  $5.2 \cdot 10^{-21} \text{ cm}^2$  ( $\lambda = 651.6 \text{ nm}$ ) for  $N_m$  polarization. In Table 5 we compare obtained in this study emission spectroscopic parameters of Sm:KYW crystal with ones of other Sm-doped materials.

#### 3.4. Fluorescence dynamics

The fluorescence lifetime of the  ${}^4G_{5/2}$  manifold was measured at 650 nm ( ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$  transition) under excitation at 480 nm. Fig. 5 shows a semilog plot of  ${}^4G_{5/2}$  fluorescence decay curve, which has a non-exponential character due to the contribution of nonradiative cross-relaxation processes [31]. For Sm<sup>3+</sup> ions the following resonance cross-relaxation mechanisms are possible:  ${}^4G_{5/2} + {}^6F_{5/2} = {}^6H_{5/2} + {}^6H_{11/2}$  and  ${}^4G_{5/2} + {}^6F_{11/2} = {}^6H_{5/2} + {}^6F_{5/2}$ . Additionally, phonon-assisted cross-relaxation processes can occur. The decay curve can be fitted by the Inokuti-Hirayama (IH) model [32] for dipole–dipole energy transfer mechanism using the following expression:

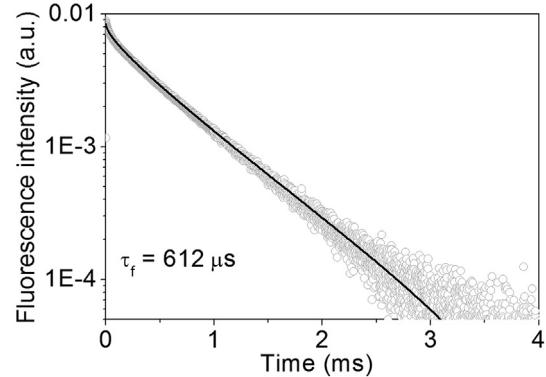


Fig. 5. Fluorescence decay curve of the  ${}^4G_{5/2}$  multiplet of Sm:KYW crystal. The solid line represents fitted decay assuming dipole-dipole interactions.

$$I(t) = I_0 \exp(-t/\tau_0 - \gamma\sqrt{t}) \quad (7)$$

here  $\tau_0$  is an intrinsic lifetime of donor ions in the absence of an energy transfer. The parameter  $\gamma$  determines disordered static energy transfer and can be found by the following formula:

$$\gamma = \frac{4\pi^{3/2}}{3} N_0 R_0^3 \quad (8)$$

here  $R_0$  is the critical transfer distance at which the nonradiative energy transfer rate becomes equal to the spontaneous emission rate [32]. The fitting procedure provides  $\gamma = 18.2 \text{ s}^{-1/2}$  and  $\tau_0 = 0.78 \text{ ms}$ . The comparable values of  $\tau_{rad}$  and  $\tau_0$  show that there is no sufficient energy migration among the donors and we have dominantly the static disordered decay in this case [33]. The critical distance  $R_0$  was derived as 0.84 nm and the average distance between samarium ions  $R_{av} = (4\pi N_0/3)^{-1/3}$  was estimated to be 1.3 nm. Since the critical distance  $R_0$  has a lower value than  $R_{av}$  it is expected that cross-relaxation processes which depopulate  ${}^4G_{5/2}$  level in the Sm<sup>3+</sup>(1.8 at%):KYW crystal are inefficient. The donor-acceptor energy transfer parameter  $C_{DA} = R_0^6 \tau_0^{-1}$  was evaluated to be  $4.6 \cdot 10^{-52} \text{ m}^6 \text{s}^{-1}$ .

Mean fluorescence lifetime  $\tau_f$  was estimated to be 612  $\mu\text{s}$  by the formula:

**Table 5**

Emission spectroscopic properties of some Sm<sup>3+</sup>-doped crystals.

Crystal	$N_{Sm}$ ( $10^{20} \text{ cm}^{-3}$ )	$\lambda_{peak}$ (nm)	$\sigma_{SE}$ ( $10^{-21} \text{ cm}^2$ )	$\tau_{meas}$ ( $\mu\text{s}$ )	$\tau_{rad}$ ( $\mu\text{s}$ )	$\eta$ %	Refs.
Sm:Gd <sub>2</sub> SiO <sub>5</sub>	0.48	601	3.54	1.74	1.78	98	[5]
Sm:NaGd(MoO <sub>4</sub> ) <sub>2</sub>	1.69	646	3.13	0.56	0.98	57	[6]
Sm:SrAl <sub>12</sub> O <sub>19</sub>	1.5	593	1.3	2.33	2.76	84	[7]
Sm:LiNbO <sub>3</sub>	1.2	603	2.5	0.84	1.12	75	[8]
Sm:CaNb <sub>2</sub> O <sub>6</sub>	1.8	657	3	0.73	0.78	94	[9]
Sm:LuLiF <sub>4</sub>	0.74	605	1.2	2.65	4.6	58	[10]
Sm:KYW	1.14	650	7.2	0.612	0.78	78	This work

$$\tau_f = \frac{\int tI(\lambda)d\lambda}{\int I(\lambda)d\lambda}. \quad (9)$$

The calculated radiative and experimentally determined emission lifetimes allow estimating the quantum yield of fluorescence which is about 78%. Table 5 lists the values of fluorescence lifetime and quantum efficiency  $\eta$  of the  $^4G_{5/2}$  multiplet of several Sm<sup>3+</sup>-doped crystals. The obtained results allow making a conclusion, that Sm(1.8 at%):KYW crystal has the quantum yield comparable to ones for other Sm-doped crystals.

#### 4. Conclusions

We report on modified Czochralski growth and spectroscopic study of a 1.8 at% Sm<sup>3+</sup>-doped KY(WO<sub>4</sub>)<sub>2</sub> crystal. The spin allowed GSA-transition at 404.6 nm possesses a peak value of absorption cross sections of  $9.2 \cdot 10^{-20} \text{ cm}^2$  for  $E||N_m$  polarization. The highest stimulated emission cross sections of  $7.2 \cdot 10^{-21} \text{ cm}^2$  and  $5.2 \cdot 10^{-21} \text{ cm}^2$  were found in the orange spectral range at 649.7 nm ( $N_p$ -polarization) and 651.6 nm ( $N_m$ -polarization), respectively. To the best of our knowledge, Sm:KYW has the highest values of  $\sigma_{GSA}$  and  $\sigma_{SE}$  among known Sm-doped materials. The  $f-f$  transition intensities were calculated by applying the conventional and the modified Judd-Ofelt theories as well as the theory for the system with the intermediate configuration interaction. Based on these calculations the radiative lifetime of the upper state  $^4G_{5/2}$  was derived to be about of 0.78 ms. The fluoresce lifetime and quantum efficiency of the  $^4G_{5/2}$  multiplet were found to be 0.61 ms and 78%, respectively.

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#### References

- [1] B.J. Chen, L.F. Shen, E.Y.B. Pun, H. Lin, Sm<sup>3+</sup>-doped germanate glass channel waveguide as light source for minimally invasive photodynamic therapy surgery, *Opt. Express* 20 (2011) 879–889.
- [2] L.A. Thompson, C.A. Gerdner, Experiments on laser guide stars at Mauna Kea Observatory or adaptive imaging in astronomy, *Nature* 328 (1987) 229–231.
- [3] D. Pugh-Thomas, Spectroscopic properties and Judd–Ofelt analysis of BaY<sub>2</sub>F<sub>8</sub>: Sm<sup>3+</sup>, *J. Opt. Soc. Am. B* 31 (2014) 1777–1785.
- [4] J.B. Gruber, M.E. Hills, M.P. Nadler, M.R. Kokta, C.A. Morison, Absorption spectra and energy levels of Sm<sup>3+</sup>:Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>, *Chem. Phys.* 113 (1987) 175–186.
- [5] A. Strzep, R. Lisiecki, P. Solarz, G. Dominik-Dzik, W. Ryba-Romanowski, M. Berkowski, Optical spectra and excited state relaxation dynamics of Sm<sup>3+</sup> in Gd<sub>2</sub>SiO<sub>5</sub> single crystal, *Appl. Phys. B* 106 (2012) 85–93.
- [6] J. Huang, J. Huang, Y. Lin, X. Gong, Y. Chen, Z. Luo, Y. Huang, Spectroscopic properties of Sm<sup>3+</sup>-doped NaGd(MoO<sub>4</sub>)<sub>2</sub> crystal for visible laser application, *J. Lumin.* 187 (2017) 235–239.
- [7] C. Gheorghe, L. Gheorghe, A. Achim, S. Hau, R.D. Avram, Optical properties of Sm<sup>3+</sup> doped strontium hexaaluminate single crystals, *J. Alloys Compd.* 622 (2015) 296–302.
- [8] G. Dominik-Dzik, Sm<sup>3+</sup>-doped LiNbO<sub>3</sub> crystal, optical properties and emission cross-sections, *J. Alloys Compd.* 391 (2005) 23–32.
- [9] A. Strzep, W. Ryba-Romanowski, R. Lisiecki, X. Xu, J. Xu, J. Di, Spectroscopic characterization of CaNb<sub>2</sub>O<sub>6</sub> single crystal doped with samarium ions, *J. Lumin.* 151 (2004) 123–129.
- [10] G.Q. Wang, X.H. Gong, Y.F. Lin, Y.J. Chen, J.H. Huang, Z.D. Luo, Y.D. Huang, Polarized spectral properties of Sm<sup>3+</sup>:LiLuF<sub>4</sub> crystal for visible laser application, *Opt. Mater.* 37 (2014) 229–234.
- [11] X. He, L. Zhang, G. Chen, Y. Hang, Crystal growth and spectral properties of Sm:GdVO<sub>3</sub>, *J. Alloys Compd.* 467 (2009) 366–369.
- [12] W. Zhou, Q. Zhang, J. Xiao, J. Luo, W. Liu, H. Jiang, S. Yin, Sm<sup>3+</sup>-doped (Ca,Mg,Zr)GGG crystal: a potential reddish-orange laser crystal, *J. Alloys Compd.* 491 (2010) 618–622.
- [13] R. Vijaya, V. Venkatramu, P. Babu, C.K. Jayasankara, U.R. Rodríguez-Mendoza, V. Lavin, Spectroscopic properties of Sm<sup>3+</sup> ions in phosphate and fluorophosphate glasses, *J. Non-Cryst. Solids* 365 (2013) 85–92.
- [14] Sk. Mahamuda, K. Swapna, M. Venkateswarlu, A.S. Rao, S. Shakya, G.V. Prakash, Spectral characterizations of Sm<sup>3+</sup> ions doped Oxy-fluoroborate glasses for visible orange luminescent applications, *J. Lumin.* 154 (2014) 410–424.
- [15] C. Gheorghe, A. Lupei, F.M. Voicu, C. Tiseanu, Emission properties and site occupation of Sm<sup>3+</sup> ion doped Lu<sub>2</sub>O<sub>3</sub> translucent ceramics, *J. Alloys Compd.* 588 (2014) 388–393.
- [16] Yu-C. Li, Yen-H. Chang, Yu-F. Lin, Yee-S. Chang, Yi-J. Lin, Synthesis and luminescent properties of Ln<sup>3+</sup> (Eu<sup>3+</sup>, Sm<sup>3+</sup>, Dy<sup>3+</sup>)-doped lanthanum aluminum germanate LaAlGe<sub>2</sub>O<sub>7</sub> phosphors, *J. Alloys Compd.* 439 (2007) 367–375.
- [17] D.-T. Marzahl, P.W. Metz, C. Kränel, G. Huber, Spectroscopy and laser operation of Sm<sup>3+</sup>-doped lithium lutetium tetrafluoride (LiLuF<sub>4</sub>) and strontium hexaaluminate (SrAl<sub>12</sub>O<sub>19</sub>), *Opt. Express* 23 (2015) 21118–21127.
- [18] A.A. Kaminskii, A.F. Konstantinova, V.P. Orekhova, A.V. Butashin, R.F. Klevtsova, A.A. Pavlyuk, Optical and nonlinear laser properties of the  $\chi^{(3)}$ -active monoclinic  $\alpha$ -KY(WO<sub>4</sub>)<sub>2</sub> crystals, *Cryst. Rep.* 46 (2001) 665–672.
- [19] P. Klopp, U. Griebner, V. Petrov, X. Mateos, M.A. Bursukova, M.C. Pujo, R. Sole, J. Gavaldà, M. Aguiló, F. Güell, J. Massons, T. Kirilov, F. Diaz, Laser operation of the new stoichiometric crystal KYb(WO<sub>4</sub>)<sub>2</sub>, *Appl. Phys. B* 74 (2002) 185–189.
- [20] A.A. Pavlyuk, Ya.V. Vasiliev, L.Yu. Kharchenko, F.A. Kuznetsov, Low thermal gradient technique and method for large oxide crystals growth from melt and flux, *Proc. Asia Pac. Soc. Adv. Mater.* (1993) 164–171. APSAM-92, Shanghai, China.
- [21] R.D. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, *Acta Crystallogr. Sect. A* 32 (1976) 751–767.
- [22] W.T. Carnall, H. Crosswhite, H.M. Crosswhite, Energy Level Structure and Transition Probabilities in the Spectra of the Trivalent Lanthanides in LaF<sub>3</sub> – Annual Report, Argonne National Laboratory, 1975.
- [23] B.R. Judd, Optical absorption intensities of rare-earth ions, *Phys. Rev.* 127 (1962) 750–761.
- [24] G.S. Ofelt, Intensities of crystal spectra of rare-earth ions, *J. Phys. Chem.* 37 (1962) 511–520.
- [25] C.K. Jayasankar, E. Rukmini, Optical properties of Sm<sup>3+</sup> ions in zinc and alkali zinc borosulfate glasses, *Opt. Mater.* 8 (1997) 193–205.
- [26] E.B. Dunina, A.A. Kornienko, Influence of excited configurations on the intensities of electric-dipole transitions of rare-earth ions, *Opt. Spectrosc.* 116 (2014) 706–711.
- [27] A.A. Kornienko, A.A. Kaminskii, E.B. Dunina, Dependence of the line strength of f-f-transitions on the manifold energy. II. Analysis of Pr<sup>3+</sup> in KPrP<sub>4</sub>O<sub>12</sub>, *Phys. Status Solidi B* 157 (1990) 267–273.
- [28] R.T. Genova, I.R. Martin, U.R. Rodriguez-Mendoza, F. Lahoz, A.D. Lozano-Gorrin, P. Nunez, J. Gonzalez-Platas, V. Lavin, Optical intensities of Pr<sup>3+</sup> ions in transparent oxyfluoride glass and glass-ceramic. Applications of the standard and modified Judd-Ofelt theories, *J. Alloys Compd.* 380 (2004) 167–172.
- [29] S.A. Davis, F.S. Richardson, Hypersensitivity in the absorption spectra of Erbium (III) complexes in aqueous solution, *Inorg. Chem.* 23 (1984) 184–189.
- [30] S.A. Payne, L.L. Chase, L.K. Smith, W.L. Kway, W.F. Krupke, Infrared cross-section measurements for crystals doped with Er<sup>3+</sup>, Tm<sup>3+</sup>, and Ho<sup>3+</sup>, *IEEE J. Quant. Electron.* 28 (1992) 2619–2630.
- [31] A.G. Avanesov, T.T. Basiev, Yu.K. Voron'ko, B.I. Denker, G.C. Maksimova, V.A. Myzina, V.V. Osiko, V.S. Fedorov, Investigation of spatial distribution impurities solids by the method of kinetic luminescent spectroscopy, *Sov. Phys. JETP* 57 (1983) 596–604.
- [32] M. Inokuti, F. Hirayama, Influence of energy transfer by the exchange mechanism on donor luminescence, *J. Phys. Chem.* 43 (1965) 1978–1989.
- [33] Yu.K. Voronko, T.G. Mamedov, V.V. Osiko, A.M. Prokhorov, V.P. Sakun, I.A. Shcherbakov, *Sov. Phys. JETP* 44 (1976) 251–261.