



## Spectroscopic studies of Nd<sup>3+</sup> and Er<sup>3+</sup> in KGd(WO<sub>4</sub>)<sub>2</sub> single crystals

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### ABSTRACT

Single crystals of KGd(WO<sub>4</sub>)<sub>2</sub> doped with Nd<sup>3+</sup> and Er<sup>3+</sup> ions were grown by the top seeded solution growth method. Detailed analysis of the room-temperature absorption spectra was performed using the conventional Judd–Ofelt theory and actual dependence of the refractive index on the wavelength. In addition to the intensity parameters  $\Omega_2, \Omega_4, \Omega_6$ , the branching ratios and radiative lifetimes were estimated for all possible transitions in the studied spectral region. Those transitions which can be potentially used for laser applications have been identified for both ions.

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### 1. Introduction

Potassium gadolinium tungstate crystals KGd(WO<sub>4</sub>)<sub>2</sub>, abbreviated as KGW, doped with rare earth ions are very attractive solid state laser materials [1]. It was found that KGW activated by trivalent lanthanide ions show high efficiency for stimulated emission at low pumping energies with laser diode excitation [2]. KGW crystals belong to the monoclinic structure with  $C_2/c \equiv C_{2h}^6$  space group at room temperature, which implies strong physical anisotropy. Monoclinic KGW is an optically biaxial crystal. Some linear optical properties of KGW crystals have been already investigated and the orientation of the optical indicatrix with regard to the crystallographic axes was determined [3]. The principal optical axes  $N_g$  and  $N_m$  are in the  $a$ – $c$  plane and  $N_p$  principal axis is parallel to the  $b$  crystallographic axis [3]. Moreover, the dispersion of the refractive indices in the visible and near-infrared regions was measured and the refractive indices variations were described by an infrared-corrected Sellmeier equation [3]. The structure, optical and spectroscopic properties of undoped and lanthanide doped KGW crystals have been intensively studied in the last few years using different experimental techniques [3–11]. In the present work the analysis of the absorption spectra recorded at room temperature was performed by means of the conventional Judd–Ofelt theory; actual dependence of the refractive index on the wavelength and direction, which is essential for anisotropic media, was used in all

calculations of the Judd–Ofelt intensity parameters, branching ratios and radiative lifetimes.

### 2. Crystal growth and crystal structure

KGW:Nd<sup>3+</sup> and KGW:Er<sup>3+</sup> single crystals were obtained by means of the top seeded solution growth (TSSG) method from 25 mol% solutions of KGW in K<sub>2</sub>W<sub>2</sub>O<sub>7</sub> on the [0 1 0] oriented seeds under conditions of low temperature gradients. Owing to mild temperature gradients the KGW single crystals were confined with crystallographic faces. The growth of the pulled up crystals occurred on (0 1 0) plane that formed flat interface. This allowed to avoid a non-uniform distribution of dopants, as it is often encountered when the interface is formed by several crystallographic faces characterized with different distribution coefficients. The detailed description of the used technique can be found elsewhere [12]. The doping concentration of Nd<sup>3+</sup> and Er<sup>3+</sup> ions was 3 and 1 at%, respectively, which amounted to 0.316 and 0.105 mol/l, accordingly.

The lattice parameters of KGW crystals are  $a=10.652$  Å,  $b=10.374$  Å,  $c=7.582$  Å,  $\beta=130.80^\circ$  [13].

In KGW structure the tungsten and oxygen atoms form octahedral anionic complexes with  $C_1$  symmetry. The potassium K<sup>+</sup> and gadolinium Gd<sup>3+</sup> ions occupy the equivalent crystallographic positions having  $C_2$  symmetry with random distribution. The structure of KGW is formed by chains of W<sub>2</sub>O<sub>8</sub><sup>4-</sup> ions along the  $c$ -axis and connected in their corners by WOW oxygen bridge bonds. The dimers W<sub>2</sub>O<sub>8</sub><sup>4-</sup> are formed by two WO<sub>4</sub><sup>2-</sup> ions, which are connected by WOOW double oxygen bridge bonds. Along the  $b$  axis the tungstate–oxygen layers are alternated with

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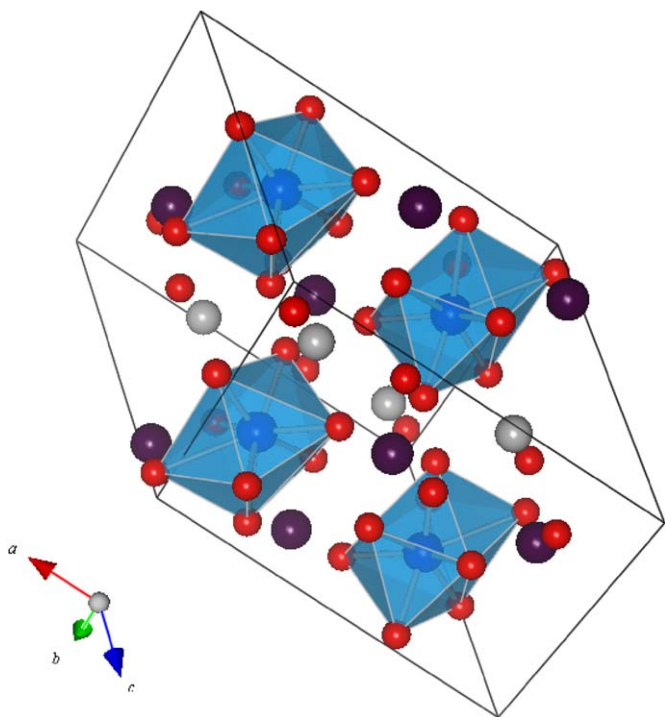


Fig. 1. One unit cell of KGd(WO<sub>4</sub>)<sub>2</sub> crystal. Tungstate ions are in black, potassium ions in grey, gadolinium ions are at the centers of the oxygen polyhedra.

the cationic layers created by K<sup>+</sup> and Gd<sup>3+</sup> ions. In the rare earth ions doped KGW crystals the Gd<sup>3+</sup> ions can be substituted by Nd<sup>3+</sup> and Er<sup>3+</sup> ions [3,5]. Fig. 1 shows one unit cell of KGW crystal with coordination polyhedra around Gd<sup>3+</sup> ions.

### 3. Experimental spectroscopic results

The room-temperature absorption spectra of KGW:Nd<sup>3+</sup> and KGW:Er<sup>3+</sup> crystals were recorded using the Cary 400 spectrophotometer in the spectral range from 300 to 800 nm. The absorption spectra were recorded for three possible orientation of the samples: when the electric field vector of the incident light is parallel to the *a*, *b* axes and *c*\* direction (perpendicular to the *ab* plane) of the crystal. Figs. 2 and 3 show the absorption spectra of KGW:Nd<sup>3+</sup> and KGW:Er<sup>3+</sup> crystals, respectively, as a function of the wavelength. As seen from these figures, there exists considerable anisotropy of absorption, both from the point of view of intensities of the absorption bands and positions of their maxima (the latter one is due to the dependence of the absorption intensities on polarization (symmetry selection rules), which can affect slightly the barycenters of the absorption bands in the polarized spectra). Nd<sup>3+</sup> and Er<sup>3+</sup> ions absorption in the spectral region below 300 nm is overlapping with strong host absorption, and thus is not shown in figures.

Both ions are the Kramers' ions, having three (Nd<sup>3+</sup>) and eleven (Er<sup>3+</sup>) f-electrons. So, all energy levels remain to be at least doubly degenerated in the absence of a magnetic field.

The absorption spectrum of KGW:Nd<sup>3+</sup> is very rich (Fig. 2) and most of the bands exhibit some structure caused by the crystal field splitting of the *J*-manifolds. The dominant absorption bands located at about 750 and 600 nm are associated with absorption transitions from the <sup>4</sup>I<sub>9/2</sub> ground state to the <sup>4</sup>F<sub>7/2</sub>+<sup>4</sup>S<sub>3/2</sub> and <sup>4</sup>G<sub>5/2</sub>+<sup>2</sup>G<sub>7/2</sub> states, respectively. Two broad lower intensity bands at 530 and 350 nm are ascribed to the transitions to the groups of the <sup>2</sup>K<sub>13/2</sub>+<sup>4</sup>G<sub>7/2</sub> and <sup>4</sup>D<sub>3/2</sub>+<sup>4</sup>D<sub>5/2</sub> levels, respectively. The absorp-

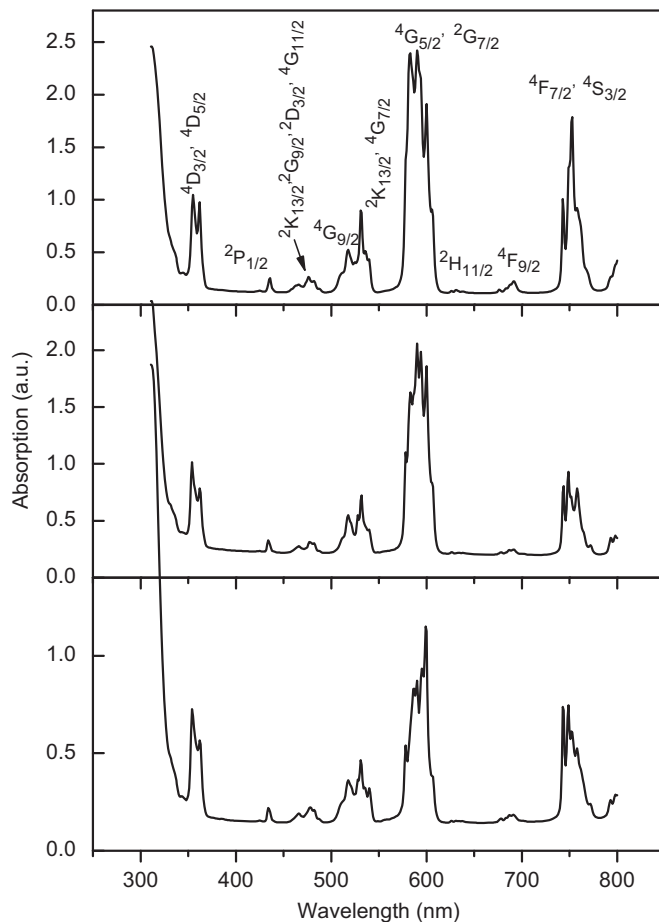


Fig. 2. The room-temperature absorption spectra of KGW:Nd<sup>3+</sup>. The incident light's electric field vector is parallel to the *c*\* direction and *a*, *b* axes (from the top to the bottom). Absorption peaks assignment in the two lowest figures is the same as in the upper figure.

tion spectrum of KGW:Er<sup>3+</sup> (Fig. 3) exhibits two strong absorption bands located at about 525 and 380 nm, related to the absorption from the <sup>4</sup>I<sub>15/2</sub> ground state to the <sup>2</sup>H<sub>11/2</sub> and <sup>4</sup>G<sub>11/2</sub> manifolds, respectively. The remaining bands of lower intensities in both spectra are assigned as shown in Figs. 2 and 3.

### 4. Judd–Ofelt analysis

#### 4.1. KGW:Nd<sup>3+</sup>

Detailed analysis of the absorption spectra recorded at room temperature was performed using the conventional Judd–Ofelt theory [14,15] and actual dependence of the refractive index on the wavelength [3]. The oscillator strength  $f_{calc}$  of an electric-dipole transition between two states  $|4f^N(\alpha'S'L)J\rangle$  and  $|4f^N(\alpha SL)J\rangle$  of an ion with *N* f-electrons is given by the following equation [14,15]:

$$f_{calc} = \frac{8\pi^2 m c \sigma}{3h(2J+1)} \chi \sum_{\lambda=2,4,6} \Omega_{\lambda} \left| \langle 4f^N(\alpha'S'L)J' \| U^{(\lambda)} \| 4f^N(\alpha SL)J \rangle \right|^2 \quad (1)$$

where *m* is the electron's mass, *c* stands for the speed of light, *h* is the Planck's constant,  $\sigma$  is the barycenter of the absorption band (in cm<sup>-1</sup>), *J* is the value of the total angular momentum of the ground manifold (9/2 in the case of Nd<sup>3+</sup> and 15/2 in the case of Er<sup>3+</sup>) and  $\chi = (n^2 + 2)^2 / 9n$  is the local field correction factor. The

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