

Electron paramagnetic resonance studies in $\text{KYb}(\text{WO}_4)_2$

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Abstract

Electron paramagnetic resonance (EPR) studies of $\text{KYb}(\text{WO}_4)_2$ single-crystal have been carried out by means of X-band spectrometer. The EPR spectrum confirms the existence of one Yb center only. For the stoichiometric ytterbium crystal the main z -axis of the g -tensor is located on the $(0\ 1\ 0)$ plane at the angle of $42 \pm 1^\circ$ to the crystallographic a axis in the clockwise direction, while the y - and b -axes are parallel. The EPR spectrum is characterized by a strong anisotropy of the g -factor ($g_z = 6.62 \pm 0.05$, $g_x = 1.039 \pm 0.012$, $g_y = 0.997 \pm 0.012$).

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1. Introduction

The monoclinic double tungstates $\text{KRE}(\text{WO}_4)_2$ (KREW), where RE is the rare earth ion, are interesting compounds which may be used in solid state lasers [1]. The $\text{KRE}(\text{WO}_4)_2$ crystal doped by the Gd, Y, Yb and Lu ions were widely studied, and their laser performances are an active research field nowadays [2,3]. The rare earth double tungstates KREW present a larger broad-band absorption suitable for diode pumping in comparison with other well-known hosts such as YAG and fluorides [4]. The strong anisotropy and non-linear susceptibility make these materials interesting for other optical applications [5,6].

On the other hand, ytterbium-doped laser materials are currently focus of interest due to the high-power diode lasers used as pump sources [7]. The Yb^{3+} ion possesses only two electronic states, leading to the lack of detrimental phenomena, like an excited-state absorption, luminescence concentration quenching and up-conversion

losses. Hence, ytterbium-doped laser crystals have advantages in comparison with the widely used Nd^{3+} -doped laser crystals in $1\ \mu\text{m}$ laser applications. Furthermore, ytterbium-excited emitter state has radiative lifetime longer than that of the Nd^{3+} electronic state [7]. This fact leads to a larger pumping efficiency.

Hence, the stoichiometric ytterbium double tungstate KYbW is an interesting material for thin disk ytterbium laser applications and its laser performance has already been achieved in quasi-CW and CW mode [8–10].

The $4f^{13}$ electrons of ytterbium are less shielded than in other rare earth ions, and thus they have a higher tendency to interact with the lattice and with neighbouring ions [11]. The optical properties of doped crystals are governed by the local site symmetry of the optically active ions and its interactions. The interaction between a paramagnetic doping ion and the magnetic moments of the surrounding nuclei is observed by means of the EPR (electron paramagnetic resonance) spectroscopy as an inhomogeneous broadening of the EPR lines. The g -tensor describes the Zeeman splitting of the lowest Kramer's doublet of the Yb ion [12]. This fundamental information of the

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ytterbium electronic structure in this material is important for both deeper knowledge of this material and its use for further optical applications.

2. Crystal growth, samples preparation and experimental details

We prepared the KYbW single crystals by means of the top-seeded solution growth slow-cooling method as described in previous works [13], with a composition of 11.5/88.5 mol% solute/solvent ($K_2W_2O_7$ was used as a solvent). Saturation temperatures with the described solution were of the order of 1170–1175 K. Parallelepipedic b -oriented seeds were used, and the axial and radial thermal gradients were of about 1 K cm^{-1} . The cooled point was the centre of free surface of solution, where the b -seed is located and the growth process takes place. Slow cooling rates of 0.1 K h^{-1} for 15–20 K and crystal rotation constant at 40 rpm were the other important growth parameters. The applied crystal growth conditions lead to an average growth rate of $(7.5\text{--}0.0) \times 10^{-3} \text{ g h}^{-1}$. After 4 days of growth, the crystals were removed from the solution and cooled down to the room temperature at the rate of 15 K h^{-1} in order to minimise thermal shocks. The growth technology is described in more details in Refs. [8,14]. The ytterbium concentration in the crystals is $6.4 \times 10^{21} \text{ at cm}^{-3}$.

Two oriented plates were cut in order to use them in EPR experiments. A D-5000 Siemens X-ray texture equipped with an Euler cradle Goniometer, was used to orient the samples. Two crystals were cut, one parallel to the (010) plane with $4.5 \times 6.4 \text{ mm}$ along the $c \times a^*$ directions and 1.7 mm in thickness and the other one parallel to the (001) plane with $6.8 \times 3.4 \text{ mm}$ along the $a^* \times b$ directions and 1.4 mm thick. Because of the above-described samples' orientation the rotation of the magnetic field was possible in the plane (010), and then the spectrum with the magnetic field oriented along the axis b was also measured.

The investigations of the EPR spectra were performed by means of a standard X-band spectrometer operating at 9240 MHz. The temperature of the sample was changed using the EPR Oxford Instrument ESR9 continuous-flow cryostat with Intelligent Temperature Controller ITC4. The sample was mounted on a rotating sample holder that allowed to measure the angular dependencies of the EPR spectra.

3. EPR characterization

As was reported previously [14], KYbW is a monoclinic crystal with $C2/c$ space group and $Z = 4$. The unit cell parameters are $a = 10.590(4)$, $b = 10.290(6)$, $c = 7.478(2) \text{ \AA}$ and $\beta = 130.70^\circ(2)$. The double chain of WO_6 along the c direction sharing vertex is conformed by units of two distorted octahedra W_2O_{10} , that is characteristic of all monoclinic KREW tungstates [15–17]. The cation K^+ is

twelve-coordinated by oxygen ions. The potassium polyhedra is a distorted icosahedron.

Yb^{3+} is located at C_2 point symmetry position. Each unit cell contains 4 equivalent ytterbium positions. It is surrounded by 8 oxygens forming distorted antiprism polyhedra (Thompson cub). The four different Yb–O distances have values of 2.198–2.711 Å. The distortion of the polyhedra can be described by the parameter

$$\Delta_d = (1/8) \sum_{n=1}^8 \left\{ \frac{[d(Yb-O)_n - \langle d(Yb-O) \rangle]}{\langle d(Yb-O) \rangle} \right\}^2,$$

[18], and its value is equal to 3.8. The ytterbium polyhedra form a zig-zag chain along the [101] direction share common edges O3–O3' (2.999 Å). The Yb–Yb distances in the same chains are 4.049 (2) and 6.009(2) Å and in the neighbouring chains 6.721(2) Å.

The electronic configuration of trivalent ytterbium ion is $4f^{13}$. The ground state of the free ion is $^2F_{7/2}$. In the C_2 local crystal field symmetry of double tungstate the ground multiplet splits into four Kramers doublets $4 \Gamma_{3,4}$. The experimental energy values of these levels determined by low-temperature emission (at 6 K) are equal to 0, 168, 438 and 555 cm^{-1} [8]. The EPR signals were observed at the lowest doublet.

The studies of the EPR spectra were performed over a wide temperature range from 4.2 to 300 K. However, the results are shown only for 4.2 K. Fig. 1 presents the experimental and fitted angular dependencies of the EPR resonance field in the (010) plane. The EPR spectra can be described by the simple spin Hamiltonian

$$H = g\beta \mathbf{BS},$$

where \mathbf{B} is the induction of an external magnetic field, \mathbf{S} the spin operator, β the Bohr magneton and g the tensor of spectroscopy splitting, which has diagonal form for principal system with the magnetic x and z axes, different from the crystallographic a and c axes in (010) plane.

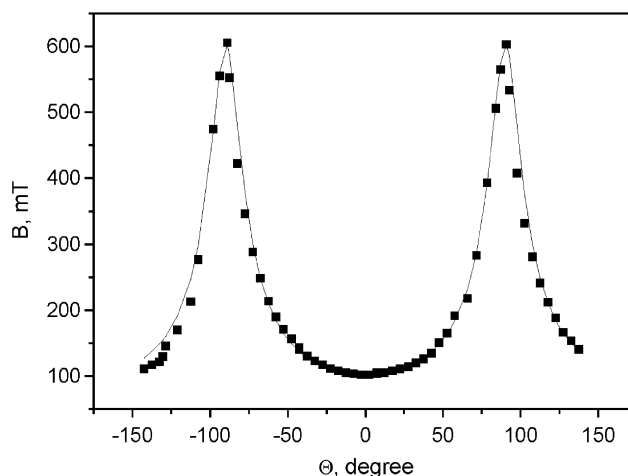


Fig. 1. Angular dependence of the resonant field for $KYb(WO_4)_2$ in the ac plane ($T = 4.2 \text{ K}$). The angle $\theta = 0^\circ$ corresponds to x axis. Squares—experimental data points, solid line—fit according to formula g_{eff} .

The EPR spectrum shows only one broad absorption line. Its resonance field strongly depends on the direction of magnetic field relative to the crystallographic axes. The EPR spectrum of Yb^{3+} ion in the $\text{KYb}(\text{WO}_4)_2$ crystal is found to be strongly anisotropic. In monoclinic crystals, one of the principal directions in the EPR spectrum is always directed along the crystallographic b axis ($[0\ 1\ 0]$, C_2 axis). It will be marked as the y axis, and the corresponding main value of the g tensor is g_y . In these crystals the directions of the principal components of the g factor in the $(0\ 1\ 0)$ plane (perpendicular to the b axis) do not coincide with the crystallographic a and c axes. We have observed similar behavior for another physical properties [19]. For this reason, the principal values and directions of the g tensor in the $(0\ 1\ 0)$ plane were determined experimentally using the angular dependence of the spectra in this plane. The direction, in which g factor reaches a maximum value is marked as the z axis, as in previous works [20,21], and the direction in which g factor reaches a minimum value is marked as the x axis. The solid line in Fig. 1 is a result of fitting according to a well-known expression:

$$g_{\text{eff}}^2 = g_z^2 \cos^2 \Theta + g_x^2 \cos^2 \phi \sin^2 \Theta + g_y^2 \sin^2 \phi \sin^2 \Theta,$$

where Θ and ϕ are the Euler angles of magnetic field direction in the xyz coordinates (Θ is the angle between the z axis and the direction of magnetic field, ϕ is the angle between the x axis and the crossline of the xy and zH plane).

The determined main values of g tensor are $g_z = 6.62 \pm 0.05$; $g_x = 1.039 \pm 0.012$; $g_y = 0.997 \pm 0.012$. The angle between the magnetic z axis (associated with the main value g_z) and the crystallographic a axis is $(42 \pm 1)^\circ$ in clockwise direction. Fig. 2. shows the main directions of the g tensor components relative to the crystallographic axes. Fig. 3. presents the EPR lines for magnetic field oriented along the x -, y - and z -axes. The EPR line widths are equal to $\Delta B_z = 97$ mT, $\Delta B_x = 152$ mT and $\Delta B_y = 186$ mT at the temperature of 4.2 K.

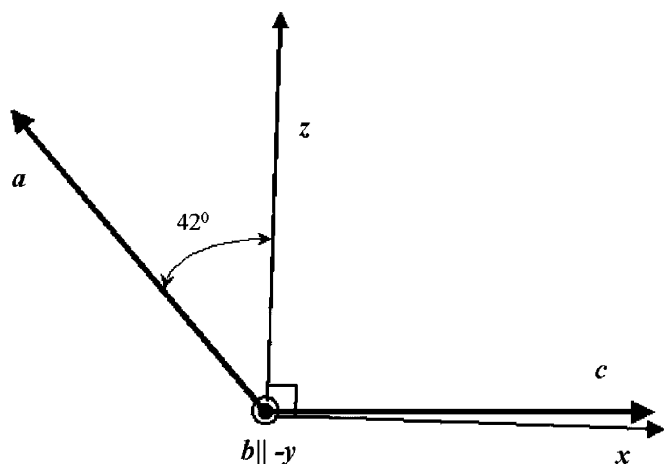


Fig. 2. Orientation of g tensor in relation to crystallographic axes.

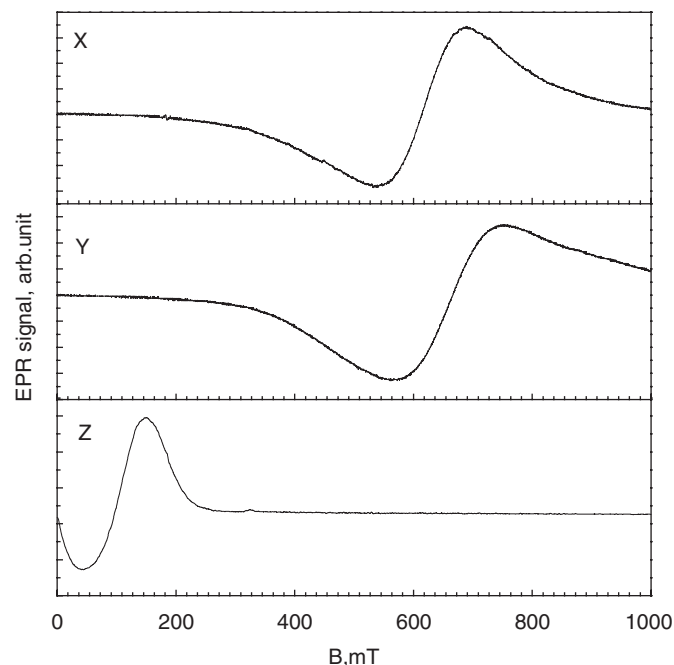


Fig. 3. The EPR spectra for magnetic field oriented along the x , y and z directions ($T = 4.2$ K).

The peculiarity of EPR spectra in $\text{KYb}(\text{WO}_4)_2$ is an asymmetry of the absorption line widths observed for different orientations. It is not exactly clear now, why it occurs, however, we can make some suppositions. The strong hyperfine interactions could produce the resonance line asymmetry. The isotopic abundance of the ytterbium nucleus is 14.3% for ^{171}Yb (nuclear spin $I = 1/2$), and 16.13% for ^{173}Yb (nuclear spin $I = 5/2$). The nuclear spin of other isotopes is zero. The isotope with $I = 5/2$ has both the magnetic momentum and the large quadrupole momentum which can essentially influence hyperfine interaction, which results in mixing of various states. The spin–spin interactions (magnetic dipolar and exchange interactions) between the ytterbium ions can also have significant contribution to the asymmetry of EPR line widths. The main axes of the tensors describing the hyperfine and spin–spin interactions do not coincide with the main axes of the g tensor because of the crystal low symmetry. It is confirmed by the results of the studies of diluted $\text{Yb:KY}(\text{WO}_4)_2$ crystal. All the above-mentioned reasons can determine the profile of the observed EPR spectra. In our opinion, the main reason of the asymmetry and of the broadening of the EPR lines are the spin–spin interactions. The shape of EPR spectra of $\text{KDy}(\text{WO}_4)_2$ and of $\text{RbNd}(\text{WO}_4)_2$ crystals confirm this supposition [22,23].

It should be noted that the absorption resonance lines broaden with increasing temperature, and at temperatures above 40 K the EPR spectrum is not possible to observe, due to strong spin–phonon interaction.

The investigations of the EPR spectra in the $\text{KY}(\text{WO}_4)_2$ single crystal doped with ytterbium, especially for a small concentration of the ytterbium ions, will allow to study the

hyperfine and spin–spin interactions in more details as well as to clarify the reasons of the occurrence of the absorption lines asymmetry.

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