Combined EPR and ODMR study of Ce$^{3+}$ optical emitters in yttrium aluminium garnet

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Abstract. Electron paramagnetic resonance (EPR) was detected in the ground state of Ce$^{3+}$ ions in YAG:Ce single crystals by monitoring the intensity of photoluminescence under non-resonant excitation. The photoluminescence intensity was found to increase strongly in magnetic field at liquid helium temperature. The optically detected magnetic resonance (ODMR) effect was of the order of percents and corresponded to resonance decrease in the luminescence intensity. ODMR correlated with the conventional EPR spectra of Ce$^{3+}$ ions, which occupy the dodecahedral Y$^{3+}$ sites in the YAG crystal lattice. The increase of the PL intensity in magnetic field was concluded to be caused by Boltzmann distribution between spin sublevels of the ground state of Ce$^{3+}$ ions. The ODMR tend to equalize the populations of levels in resonance and results to a decrease of PL intensity. Different types of Ce$^{3+}$ centres characterized by the presence of nearby antisite defects were observed, which should be taken into account in applications of single ion spectroscopy based applications of YAG:Ce.

1. Introduction

Rare-earth doped crystals with the garnet structure play an important role in quantum electronics. Interest in garnet crystals with the Ce$^{3+}$ activator has significantly increased in recent years due to the increasing potential for their use as high-performance scintillators in many fields, including positron emission tomography imaging [1, 2] and high energy physics [3]. Ce$^{3+}$ doped phosphors with the garnet structure are widely used in white light-emitting diodes [4].

Recent publications on the application of garnet crystals doped with rare earth elements for quantum computing open up new possibilities in this direction. It was declared that rare-earth-doped crystals are excellent hardware for quantum storage of optical information [5]. Coherent properties of rare-earth single-spin qubits in yttrium aluminium garnets (YAG) have been demonstrated [6]. Hyperfine coupling to aluminium nuclear spins suggests that cerium electron spins can be exploited as an interface between photons and long-lived nuclear spin memory. Additional functionality of these materials is added by their wave-guiding properties allowing for on-chip photonic networks. Combined with high brightness of Ce$^{3+}$ emission and a possibility of creating photonic circuits out of the host material, this makes cerium spins an interesting option for integrated quantum photonics.
Obviously, progress in these fields depends in many respects on the degree of understanding of the spectroscopic properties of the considered crystals and, on this basis, the development of methods for producing crystals with desired parameters. One of the most powerful direct methods to investigate the properties of materials is electron paramagnetic resonance (EPR) [7, 8], which makes it possible to determine the chemical and charge states of an impurity centre, its local symmetry, the composition of the nearest environment, the structure of energy levels, the specific features of the interaction with the crystal lattice, etc.

For single spin manipulation one needs to use optically detected magnetic resonance (ODMR) techniques [9, 10]. ODMR is “trigger detection” in that the absorption of a resonance microwave photon triggers a change in emission (absorption) of an optical photon due to the selective feeding of the magnetic sublevels. A giant gain in sensitivity appears since the energy of an optical quantum is by several orders of magnitude higher as compared with a microwave one, and it becomes possible to detect a very small number of spins down to a single spin. ODMR of Ce\(^{3+}\) ions in garnets was studied via the magnetic circular dichroism (MCD) in absorption [11, 12]. In Ref. 12 EPR of Ce\(^{3+}\) ions in \(\text{Y}_3\text{Al}_5\text{O}_{12}\) has been observed via MCD and the MCD bands at 227, 270, 338 nm and at 458.5 nm have been definitely attributed to Ce\(^{3+}\).

In the present paper, we report results of joint ODMR and EPR study of YAG:Ce single crystals. EPR of the ground state of Ce\(^{3+}\) ions was detected by monitoring the photoluminescence intensity and correlated with conventional EPR spectra. Several types of Ce\(^{3+}\) centres characterized by the presence of nearby defects were observed by EPR.

2. Experimental details

In this work, we investigated \(\text{Y}_3\text{Al}_5\text{O}_{12}\) single crystals doped with cerium at concentrations of 0.1 to 0.2 at %. The crystals were grown from the melt by vertical directed crystallization [13, 14] in an \(\text{Ar}/\text{H}_2\) atmosphere with the use of molybdenum containers and seed crystals oriented along the crystallographic axis [001]. The EPR studies were performed on the samples with specified activator concentrations which were cut from the regions without facet growth forms and light-scattering inclusions in the form of rectangular parallelepipeds 1.5 \(\times\) 2 \(\times\) 5 mm\(^3\) in size.

The EPR experiments were carried out by using X-band (9.3 GHz) JEOL EPR spectrometer equipped with a helium gas-flow cryostat, which was manufactured in the laboratory and provided temperature control within the range of 4–300 K. The EPR spectra of a residual paramagnetic impurity of Mo\(^{3+}\) were used to control the sample orientation in the magnetic field. It was found that the long sample edge (the rotation axis) was turned by 24° from the crystal axis [100] and rotation about it corresponded to polar angles \(\phi = 24°\) and \(\theta = 0°\) to 360°.

Photoluminescence (PL) spectra were measured at a temperature between 1.8 and 300 K. A deuterium arc lamp as well as a semiconductor laser (\(\lambda = 405\) nm) were used as excitation sources. A photomultiplier in combination with a grating monochromator was used for light detection.

ODMR measurements were performed on ODMR spectrometer operating in Q-band (35 GHz) providing the magnetic field up to 4.5 T and microwave power up to 0.5 W. The sample was placed in the centre of the cylindrical microwave cavity \(H_{011}\) with optical access for excitation and emission light. ODMR spectra were recorded in the temperature range between 1.8 and 4.2 K by monitoring the intensity of luminescence. No modulation of the microwaves was applied because of long spin–lattice relaxation times of the investigated paramagnetic centres.

3. Experimental results and discussion

Figure 1 shows the PL spectrum of YAG:Ce (0.1%) single crystal recorded at a temperature of 1.8 K. The broadband phonon-assisted emission of the Ce\(^{3+}\) ions is observed, a sharp zero-phonon line at 489 nm [5] characteristic for Ce\(^{3+}\) ions is not visible in the figure because of its low intensity and not high enough resolution. The laser line (405 nm) which was used for the excitation of PL is depicted in the left part of Figure.
Figure 1. The photoluminescence spectrum of the Ce\(^{3+}\) ions in YAG:Ce (0.1%) single crystal. The laser line (405 nm) which was used for excitation of PL is marked by an arrow. Open circles display the dependence of the Ce\(^{3+}\) ODMR signal amplitudes on the detection wavelength.

In magnetic field at a temperature of 1.8 K, the intensity of the total PL of the YAG:Ce single crystal was found to increase. Application of 35 GHz microwaves resulted in appearance of a number of anisotropic resonance signals (ODMR signals) corresponding to a decrease in PL intensity as one can see in Figure 2 which shows the magnetic field dependences of the relative PL intensity in the YAG:Ce single crystal at \(\lambda = 570\) nm for several orientations of the sample in magnetic field. The dips on these dependences correspond to EPR in the ground state of Ce\(^{3+}\) ions. The dependence of the ODMR amplitude on the detection wavelength is shown in Figure 1 by open circles. It coincides with the PL spectrum of Ce\(^{3+}\) ions.

Figure 2. The magnetic field dependences of the relative PL intensity at a wavelength of 570 nm recorded in the YAG:Ce single crystal at a temperature of \(T = 1.8\) K in the presence of 35.1 GHz microwave field. The curves 1 to 4 correspond to different orientations of the crystal in magnetic field: spherical coordinates are \(\varphi = 24^\circ\) and \(\theta = 85^\circ\) (1), 75° (2), 65° (3), and 55° (4).

Figure 3 shows the angular variations of the 35.1 GHz ODMR (a) and 9.3 GHz EPR (b) spectra recorded in the YAG:Ce single crystal with rotation of the sample corresponding to \(\varphi = 24^\circ\) and \(\theta = -5^\circ \div 95^\circ\). Top axes display the effective g-factor values in the same scale for (a) and (b). In the EPR spectra (b), lines from Mo\(^{3+}\) impurity ions were also detected in addition to Ce\(^{3+}\).

Cerium has only even isotopes with a zero nuclear magnetic moment \((I = 0)\). The angular dependences of the EPR spectra are well described by the spin Hamiltonian of orthorhombic symmetry in the form...
\[ \hat{H} = \mu_B S \cdot \mathbf{g} \cdot \mathbf{B}, \]  
where \( \mu_B \) is the Bohr magneton, \( S \) is the effective spin \((S = 1/2)\), \( \mathbf{B} \) is the vector of the external magnetic field, and \( \mathbf{g} \) is the \( g \)-factor tensor.

In the YAG single crystals, the rare-earth ions occupy as a rule dodecahedral sites of the crystal lattice, thus replacing the \( Y^{3+} \) ions. In this position (c-sites), the \( Y^{3+} \) ions are coordinated by eight oxygen ions with local symmetry \( D_2 \) as shown in Figure 3 (c) and form 6 nonequivalent positions. The principal directions of the local magnetic axes of the \( \text{Ce}^{3+} \) ion are oriented in such a way that the \( x \) axes are along one of the crystallographic directions \( <001> \) and the directions of the axes \( y \) and \( z \) coincide with the \( <011> \) directions. The corresponding Euler angles for one centre in the dodecahedral position are as follows: \( \alpha = 90^\circ \), \( \beta = 135^\circ \) and \( \gamma = 90^\circ \). The orientations of other five \( \text{Ce}^{3+} \) centres are obtained by the symmetry operations in the YAG crystal lattice. From the experimental orientation dependences of the EPR line positions, the following parameters of the \( g \)-tensor have been obtained: \( g_x = 2.74 \pm 0.05 \), \( g_y = 1.87 \pm 0.05 \), and \( g_z = 0.91 \pm 0.05 \) in agreement with the data reported in [15]. The calculations were performed with a special computer program developed by V. Grachev [16].
In the EPR spectra of YAG:Ce single crystals, along with the main intense lines of Ce$^{3+}$ ions located in the c-sites, additional lines of approximately two orders of magnitude lower intensity were observed as shown in the inset in Figure 3 (b). These lines have similar angular dependences and can be attributed to Ce$^{3+}$ centres the immediate vicinity of which is distorted by a defect. From the analysis of the angular and temperature dependences of EPR spectra, as well as the average values of the g-factors the satellite lines have been ascribed to the Ce$^{3+}$ with nearby antisite defects [17].

Figure 4 presents the electronic level structure of Ce$^{3+}$ ion in a YAG crystal [5, 18, 19]. The positions of the Ce$^{3+}$ ion states relative to the conduction and valence bands are shown in the left panel. The configuration of Ce$^{3+}$ is $4f^1$ so the ground term is $^2F$. The spin-orbit coupling splits this term into $^2F_{5/2}$ and $^2F_{7/2}$ sub-terms. The separation between these levels is about 2200 cm$^{-1}$ for the free ion. The energy levels of the lowest sub-term of the Ce$^{3+}$ ion are $^2F_{5/2}$. In a crystal field, the sixfold degeneracy will be lifted (the number of levels is given by $2J+1$). The separation between the adjacent $J$ levels due to the spin-orbit coupling exceeds the splitting of the ground-state levels due to the crystal field by at least an order of magnitude. Since the crystal fields will be slightly different for the different environment of cerium ions, there will be a difference in the parameters of the anisotropic g-factor for Ce$^{3+}$ centres with defects in the immediate vicinity. In the YAG single crystals, the above disturbances of the regular lattice can manifest themselves as extrinsic (non-equivalent) substitutions of Y$^{3+}$ ions for Al$^{3+}$ ions in octahedral sites (a-sites) or as substitutions of Al$^{3+}$ ions for Y$^{3+}$ ions in the c-sites, so called “antisite” defects. The formation of such defects is possible within the limits of 4–6% during the growth of single crystals from the melt.

As was recently shown rare-earth-doped YAG crystals are excellent hardware for quantum storage of optical information. Coherent properties of single rare-earth spin qubits were demonstrated, where ODMR of a single Ce$^{3+}$ ion in YAG ceramic crystals was recorded via the intensity of photoluminescence. To force the creation of an nonequilibrium population of spin sublevels in the ground state of cerium ions resonant circularly polarized optical excitation was used in [5], which changed the emission intensity of Ce$^{3+}$ determined by thermalized populations of the ground-state spin sublevels. This happened because the strongest transition between the ground 4$f^1$ and the optically excited 5$d^1$ spin doublets under $\sigma^+$ circularly polarized excitation is the a spin flip transition 4$f^1$(spin down) ↔ 5$d^1$ (spin up). The other 3 transitions are almost 3 orders of magnitude weaker. However, the decay back to the ground state is equally probable. This results in efficient pumping of the ion into 4$f^1$ spin-up state and a reduction of the intensity of the phonon-assisted Ce$^{3+}$ emission [5].

In our experiments, excitation of PL was non-resonant and was not specifically polarized but we did observe an increase in the emission intensity with magnetic field and resonance decreases of the order of a percent at magnetic fields corresponding to EPR in the ground state of Ce$^{3+}$ ions. It can be assumed that there is a link between the ground state spin polarization and he PL intensity. The resonant microwave transitions, which tend to equalize the Boltzmann populations of the ground state spin sublevels can result in a drop of the luminescence intensity. Further studies are under way which should clarify the details of the mechanism which could couple the spin polarization of the ground state and the emission intensity and exclude the unintentional polarization effects. ODMR of excited
state of Ce$^{3+}$ did not observed in our experiments, probably because of short lifetime and short spin relaxation time in excited state.

### 4. Conclusions

An increase of the photoluminescence intensity with magnetic field and anisotropic ODMR signals corresponding to resonant decreases of the PL intensity were found in YAG:Ce single crystals at liquid helium temperature. The ODMR spectra correlated with the conventional EPR spectra of the ground state of Ce$^{3+}$ ions, which substitute for the Y$^{3+}$ ions and occupy the dodecahedral sites (c-sites) in the crystal lattice. In our experiments, excitation of the Ce$^{3+}$ luminescence was non-resonant and was not specifically polarized but we did observe the effect of the ground state spin polarization of on the emission intensity. These effects are definitely connected with the Boltzmann population distribution in the ground state of cerium ions but further studies are required to clarify the details of the mechanism which couples the ground state spin polarization and the emission intensity.

Several different types of Ce$^{3+}$ centres with slightly different parameters, which are characterized by the presence of nearby defects (antisite defects) were observed by EPR. This should be taken into account in applications using single Ce$^{3+}$ ions in YAG.

### Acknowledgments

This work has been supported by Russian Science Foundation under Agreement #14-12-00859 and Russian Foundation for Basic Research under grant # 13-02-00821

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