Magnetic Resonance and Dielectric Studies of a Nonlinear $\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$ Single Crystal Doped with Erbium

T. BODZIONY^{a,*}, J. TYPEK^a, M. ORLOWSKI^a, J. MAJSZCZYK^a,
M. WABIA^a, M. BERKOWSKI^b, W. RYBA-ROMANOWSKI^c,
N. GUSKOS^d, V. LIKODIMOS^d AND E.A. ANAGNOSTAKIS^d

^aInstitute of Physics, Technical University of Szczecin
al. Piastów 17, 70-310 Szczecin, Poland

^bInstitute of Physics, Polish Academy of Sciences, Warsaw, Poland

^cInstitute of Low Temperature and Structure Research
Polish Academy of Sciences, Wrocław, Poland

^dSolid State Section, Department of Physics
University of Athens, Athens, Greece

Single crystal of erbium doped $\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$ grown by the Czochralski method have been investigated by electron paramagnetic resonance and dielectric spectroscopy methods. Dielectric permittivity ε measurements performed in 90–440 K temperature range have shown negligible dispersion for 1 kHz – 1 MHz frequencies and a Curie–Weiss type behaviour with $C = 47700$ K and $\theta = -340$ K. Electron paramagnetic resonance studies have revealed the presence of two different paramagnetic, monoclinic centres. The calculated g factor values are: $g_1 = 1.449$, $g_2 = 11.534$, $g_3 = 4.24$ for the main M_1 centre and $g_1 = 1.982$, $g_2 = 4.169$, $g_3 = 4.25$ for the weaker M_2 centre. The temperature dependence of EPR line intensity for centre M_1 and M_2 is quite different — while lines attributed to M_1 could only be observed at low temperatures, below 20 K, lines of M_2 centre persisted up to 200 K. The M_1 centre is connected with Er^{3+} ion entering substitutionally into La^{3+} site, while M_2 is probably connected with $3d$ ions at the same site, unintentionally introduced into the material as an admixture.

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*corresponding author; e-mail: Tomasz.Bodziony@ps.pl

1. Introduction

Rare earth doped semiconductors attract a constant interest due to their applications in light emitting diodes or diode lasers. Erbium doped materials have attracted particular attention because the Er^{3+} intra- $4f$ -shell transition $^4I_{13/2} - ^4I_{15/2}$ near $1.54 \mu\text{m}$ matches the minimum in the absorption of silica-based fiber-optic communication systems. $\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$ (LGT, langataite) and $\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$ (LGN) compounds with $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ (langasite) type structure crystallize in the space group $P321$, consistent with the crystal class 32 [1]. Recent studies of LGT and LGN revealed that these materials are promising for acousto-electronic applications and for design of piezoelectric sensors [2, 3]. In addition they have nonlinear optical properties [3]. When doped with rare earth or transition metal ions LGT and LGN crystals become luminescent media able to generate and amplify light. This ability combined with inherent nonlinear property offers a possibility to design Q -switching and self-frequency doubling laser sources. Luminescence rare earth ions are expected to substitute for La^{3+} ions. These are located in polyhedra with coordination number eight (distorted Thomson cube) among layers ($z = 0$) of $(\text{Ga}, \text{Ta})\text{O}_4$ tetrahedra, having octahedral Ga^{3+} as the nearest neighbours in the plane perpendicular to the c -axis ($z = 0.5$). Tetrahedral Ga^{3+} ions occupy positions with C_2 and C_3 point symmetry and in that latter case they are statistically distributed with Ta^{4+} ions. The resulting inherent structural disorder induces inhomogeneous broadening of spectral bands associated with transitions within $4f^{11}$ configuration of Er^{3+} ions. Due to structural peculiarities erbium doped LGT crystal is expected to be useful for the all-solid-state laser with diode pumping. Recent investigation has concluded that the material is an intermediate gain laser exhibiting advantageous broadening of pump bands [4]. However, an ambiguity appeared when the nature of activator sites have been considered.

The aim of this paper is to report the first dielectric and electron paramagnetic resonance (EPR) results of LGT: Er^{3+} single crystal studies. EPR has proven to be a powerful tool for study of defects in semiconductors due to its possibility to reveal detailed microscopic information concerning the structure of magnetic defects.

2. Experimental

Single crystals of $\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$ were grown by the Czochralski method at the rate not larger than 2 mm/h in an inert (nitrogen) atmosphere. X-ray powder diffraction method has revealed that the crystal has a trigonal structure with the lattice cell parameters $a = 8.2470 \text{ \AA}$, $c = 5.1303 \text{ \AA}$, and $\gamma = 120^\circ$, in agreement with previously published results. The nominal doping concentration of erbium was 1 wt%, but the actual concentration found by the inductive coupled emission spectroscopy was 0.57 wt%. The details of the growth processes are published elsewhere [4, 5].

The samples for EPR studies had the shape of a square parallelepiped ($2.7 \times 2.7 \text{ mm}^2$) with the face perpendicular to the trigonal axis (c -axis) and the thickness was 3.3 mm. The sample was mounted on a rotating support to obtain the angular dependence of the EPR spectra. The EPR experiments were performed on a Bruker E500 spectrometer operating in the X-band microwave frequency, equipped with the TE₁₀₂ cavity with 100 kHz field modulation. The phase sensitive detection was applied to record the derivatives of the absorbed microwave power. The temperature dependence studies in the range of 3.6–300 K were performed using an Oxford Instruments ESP 300 continuous flow liquid-helium cryostat.

Samples for dielectric measurements were cut out from the single crystal boule perpendicular to the c -axis. They had a shape of a disc (1 mm thick, 2 cm² surface) and were coated with silver paint electrodes. Dielectric permittivity ϵ_{33} (along the axis with the biggest value) was measured as a function of frequency by the impedance analyser HP 4192A in the 1 kHz – 1 MHz range. The temperature dependence of ϵ_{33} was carried out, in the 90–440 K range (at 2 K step), in a liquid nitrogen chamber with the temperature control better than 0.1 K.

3. Results and discussion

Figure 1 presents the results of dielectric measurements. No dielectric anomaly could be observed in the whole studied temperature range. The dispersion of the dielectric permittivity ϵ in the 1 kHz – 1 MHz range is negligible. The decrease in ϵ_{33} with the temperature increase could be described by the Curie–Weiss law, $C/(T - \theta)$, with $\theta = -340 \text{ K}$ and the Curie constant $C = 47770 \text{ K}$. The value of Curie constant is of the same order as for lithium niobate crystal. The obtained value of $\epsilon_{33} = 75$ at $T = 300 \text{ K}$ for erbium doped crystal is roughly the same as for the undoped crystal, $\epsilon_{33} = 76.5$ [6]. No piezoelectric effect could be detected for the investigated samples, thus the Er³⁺ admixture do not change significantly the local crystal structure (for the 32 group the piezoelectric modulus $d_{33} = 0$). In electric fields up to 35 kV/m the nonlinear effects could not be observed.

The observed EPR spectra in Er doped LGT crystal were composed of many lines, whose positions varied with orientation, in the range of magnetic fields from 20 mT to 500 mT. The intensities of the EPR lines were strongly orientation and temperature dependent and most of the lines were unobservable above 20 K. As an example of the obtained spectra at the temperature of $T = 6.4 \text{ K}$, Fig. 2 shows the EPR lines for the magnetic field along the crystallographic c -axis (Fig. 2a), and a -axis (Fig. 2b). In order to characterize the local site symmetry of paramagnetic centres responsible for the observed lines, their angular variation was determined for rotation of the magnetic field in the crystallographic ac -plane (Fig. 3a) and ab -plane (Fig. 3b). With the magnetic field along the c -axis the spectrum consisted of four lines, the most intense (designated as I in Fig. 2a) at $B_{1c} = 464.4 \text{ mT}$. This line was significantly anisotropic and has a peak-to-peak linewidth of $\Delta B_I = 44 \text{ mT}$. When the direction of the magnetic field was rotated

Fig. 1. Temperature dependence of the dielectric permittivity ϵ_{33} (left axis) and ϵ_{33}^{-1} (right axis) at 10 kHz for LGT:Er³⁺ single crystal. The solid line is the best fit to the Curie-Weiss law.

Fig. 2. EPR spectrum of Er doped LGT crystal measured at 6.4 K. The applied magnetic field is oriented: (a) parallel to the crystallographic c -axis ($\theta = 0^\circ$); (b) along the crystallographic a -axis ($\theta = 90^\circ$, $\varphi = 0^\circ$).

away from the c -axis, in the ac -plane, the line shifted towards lower magnetic fields, reaching the minimum field value $B_{1a} = 73.0$ mT along the a -axis. A similar behaviour was observed for a much weaker line, designated as II in Fig. 2. It moved, from $B_{2c} = 339.5$ mT to $B_{2a} = 158.7$ mT, for magnetic field along the crystallographic c - and a -axis, respectively. The line, labelled as III in Fig. 2, did not show any significant position change ($B_{3c} = 158.7$ mT) as the magnetic field was rotated in the ac -plane, but small splitting could be noticed. The resonance line second in the intensity, labelled IV in Fig. 2a, did not much change its position when the magnetic field was rotated in the ac -plane, but instead has split into three components (see Fig. 3). The splitting seem to be the largest for θ around 30° , although it could not be followed for the whole range of angles due to overlapping with the line I (θ is an angle between the magnetic field and the c -axis). The main feature of the angular variation diagram in the crystallographic ab -plane is the splitting

of the merged lines I and IV into three components (Fig. 3b). Two components showed regular oscillations with the period of 120° as the angle φ was varied (φ is an angle between the magnetic field in the ab -plane and the a -axis). For the lines II and III, which have merged when the magnetic field was aligned along a -axis, a small splitting into at least two components in the ab -plane was detected. Thus the behaviour of lines II and III resembles the behaviour of lines I and IV. Due to the slight misorientation of the sample the merging of lines along the a -axis was not complete.

Fig. 3. Angular dependence of the EPR lines of LGT:Er³⁺ for the applied magnetic field in the ab -crystallographic plane (a) and ac -crystallographic plane (b). Data were obtained at 9.345 GHz and 6.4 K. Different symbols represent different resonance lines in the EPR spectra.

With the help of EPR it is relatively easy to determine the point group symmetry of the observed centres and to restrict the number of possible models for defect complexes. A closer inspection of both angular dependence graphs allows us to formulate the conclusions concerning the symmetry of different magnetic centres responsible for the observed resonance lines. For the lines I and IV a centre of the monoclinic symmetry is responsible, which would be designated as M_1 . The twofold axis of that centre is parallel to the crystallographic a -axis. As the behaviour of lines II and III is similar to lines I and IV, yet another monoclinic centre, labelled as M_2 , should be invoked.

To gain a deeper knowledge of the observed paramagnetic centres the temperature dependence of the integrated line intensities (defined as the product of line amplitude and the square of peak-to-peak linewidth) were measured. Although all centres followed the same Curie-law type of paramagnetic behaviour, $I = C/T$, the Curie constants were quite different for the centre M_1 as compared to centre M_2 (Fig. 4). It follows that these two types of centres are formed by different paramagnetic ions. As the EPR lines connected with the centre M_2 might be observed at a relatively high temperatures, $T > 100$ K, they could not be attributed to Er^{3+} ions. This centre probably arise from the unintentional admixtures of $3d$ ions in the component oxides.

Fig. 4. The temperature dependence of the integrated EPR line intensity for: (a) the centre M_1 ; (b) and the centre M_2 . The solid lines are the best fits to the Curie law.

In the LGT crystal structure there are two types of sites with D_3 symmetry (designated as a and b), two sites with C_3 symmetry (c , d), two sites with C_2 symmetry (e , f), and one site with C_1 symmetry (g) [7]. La ion is located in e site, Ga in a , d , and f sites, Ta in a and f sites, and O ions in d and g sites [8]. Trivalent erbium ions could easily enter substitutionally into La^{3+} site, because its ionic radius (1.14 Å) is slightly smaller than the host ion radius (1.30 Å). The other trivalent ion sites in the crystallographic structure are unsuitable for Er^{3+} due to a large mismatch of ionic radiuses. The La atoms are coordinated to eight O atoms, at distances 2.40–2.87 Å, forming a distorted cubic antiprism.

Trivalent erbium has eleven $4f$ electrons, and the ground state of the free ion is $^4I_{15/2}$. In an electric cubic crystalline field, the 16-fold degeneracy of the ground state splits into three Γ_8 quartets, a Γ_6 doublet and a Γ_7 doublet [9]. A lower symmetry structure can be regarded as a cubic crystal modified by an extra axial electric field. Thus three Γ_8 quartets are split further into six doublets, while Γ_6 and Γ_7 remain unchanged. In general, the EPR spectra of Er^{3+} could be fitted to the following spin Hamiltonian:

$$H = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I} \quad (1)$$

with $S = 1/2$ and $I = 7/2$ which is the spin of the ^{167}Er nucleus, μ_B is the Bohr magneton and $\mathbf{g}$ is the g tensor. The first term is the interaction of the electron spin with the external magnetic field, the second term describes the hyperfine interaction of the electron spin with ^{167}Er nuclei (the isotope abundance 22.9%) and $\mathbf{A}$ is the corresponding tensor. Eight equally intense satellite lines due to the hyperfine interaction are expected, but their intensity will be rather weak (3% of the main line) and the spectrum could not be observed for all orientations. Despite these drawbacks the presence of hyperfine structure lines is usually the direct evidence of the erbium ions presence in the sample. The hyperfine term in Eq. (1) has been used only qualitatively to identify the EPR lines. The hyperfine lines were not observed for the most intense line I, but its large linewidth might be responsible for obscuring the hyperfine lines. For the second intense line IV only the two extreme hyperfine lines on the low field side of the main component could be identified and from their separation the value of the hyperfine constant $A = 9.5$ mT was estimated. No hyperfine lines have been observed for lines II and III.

Disregarding the hyperfine term, the spin Hamiltonian (1) with a g tensor exhibiting monoclinic symmetry has been used to calculate the principal g values for the two observed complexes. For the main M_1 complex $g_1 = 1.449$, $g_2 = 11.534$, and $g_3 = 4.24$. The 1-axis of the complex lies along the crystallographic c -axis, the 2-axis along the crystallographic a -axis and the 3-axis lies in the crystallographic ab -plane, making an angle of $\alpha = 60^\circ$ with the a -axis. For the M_2 complex the following values were calculated: $g_1 = 1.982$, $g_2 = 4.169$, $g_3 = 4.25$. The theoretically predicted isotropic g value for the Γ_6 state is 6.772, while it is 5.975 for the Γ_7 doublet. If the low symmetry modifying field is small enough in comparison with the cubic interactions, an average g factor $g_{av} = (g_1 + g_2 + g_3)/3$, obtained from experiment could be compared with the theoretical predictions made for the cubic type of local symmetry [10, 11]. For the M_1 centre $g_{av} = 5.74$, while for M_2 centre $g_{av} = 3.47$. This suggests that the parent cubic ground state may have Γ_7 representation for monoclinic M_1 centre, while hinting on non-erbium origin of M_2 centre.

In conclusion we have shown that the europium doped LGT single crystal has no dielectric anomalies in the 90–440 K temperature range and the most intense EPR spectrum is produced by Er^{3+} ions entering substitutionally into La^{3+} site.

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