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Study of the line intensity in the optical and magnetooptical spectra in holmium-containing paramagnetic garnets

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ABSTRACT

Studies of line intensity in the optical and magneto-optical spectra in the holmium-containing paramagnetic garnet Ho^{3+}:YAG were carried out within the visible spectrum at $T = 85$ K. Detailed investigation of the magnetic circularly polarized luminescence spectra at 85 and 300 K on $^5S_2 \rightarrow {}^5I_8$ emission transition in Ho^{3+}:YAG was carried out. A quasi-doublet state in the energy spectrum of the Ho^{3+} ions was observed, characterized by a significant magneto-optical activity, which is caused by a large Zeeman splitting of the quasi-doublet. The measurement of the magnetic circular polarized luminescence spectrum carried out within one of the emission lines of the luminescence band $^5S_2 \rightarrow {}^5I_8$ in Ho^{3+}:YAG at 85 K shows significant magneto-optical effects of the intensity change of the emitted light, compared to that measured for the other emission lines in the same luminescent band.

1. Introduction

Crystals of yttrium aluminum $Y_3Al_5O_{12}$ (YAG) and yttrium gallium $Y_3Ga_5O_{12}$ (YGG) garnets doped with the Non-Kramers (with an even number of electrons in the unfilled 4*f*-shell) trivalent rare-earth (RE) Ho^{3+} ions have attracted attention of designers and engineers of lasers for a long time, where the materials are used as laser active mediums to generate coherent stimulated emission in the visible region [1,2]. Furthermore, these RE-compounds can be used in sensors, e.g., scintillators, and in various photonics components [2,3].

YGG and YAG doped with Ho^{3+} ions are also interesting in view of development of the infrared lasers with diode pumping. The garnets doped with Ho^{3+} have become a center of attention for researchers studying *up*-conversion pumping of the laser medium. The *up*-conversion pumping generates stimulated emission in the visible and near ultra-violet regions [3]. At the same time, information about energy spectra, spectroscopic parameters, and wavefunctions of excited states (>10,000 cm^{-1}) of Ho^{3+} ions in garnet crystals is still quite limited. It is connected with that the results of optical and magneto-optical studies of similar RE-compounds mostly have been interpreted qualitatively. It is important to carry out more extensive experimental and theoretical studies of the spectroscopic features of the Stark splitting of energy levels of Ho^{3+} ions in the crystal surroundings of D_2 symmetry in the garnet structure [4,5]. In contrast with above-mentioned, a large number of studies of the ground state (multiplet $^5I_8$) of the YGG and YAG crystals doped by the Ho^{3+} ions have been done [4,6,7].

On the other hand, the study of the polarized emission spectra in the magnetic field *H* can provide reliable observation and symmetry identification of the crystal-field (Stark) levels of the ground and low-energy excited multiplets of the $4f^{(n)}$-configurations of the Non-Kramers Ho^{3+} ions combined in the optical $4f \rightarrow 4f$ transitions [5,8]. Moreover, magnetic circularly polarized luminescence (MCPL) spectra, i.e., circular anisotropy of emission spectra in the external magnetic field *B* caused by the polarization and splitting of the Zeeman components of luminescence lines [9] are characterized by the spectral dependence of the MCPL degree within the luminescence line having a simpler form as compared to the similar magnetic circular dichroism (MCD) dependence for the absorption line [10]. Indeed, the spectral dependence of the MCPL degree represents itself a linear function of the light frequency, and its parameters (angle of slope, intercept on the *y*-axis) are associated

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with different microscopic mechanisms of the magnetooptical activity (MOA) of the $4f^{(n)}$ (or $3d^{(n)}$) ions [5,8–10].

In this connection, it is important to note that the standard luminescence spectroscopy measures the total intensity of emission, $I = (I_+ + I_-)$, as a function of the wavelength λ (or frequency ω). At the same time, applying a static magnetic field, H, parallel (or antiparallel) to the direction of observation, the relative magnitudes of I_+ and I_- can be changed, resulting in a field-dependence of the intensity difference, $\Delta I = (I_+ - I_-)$. From the spectrum of the $\Delta I/I$ ratio, one can obtain unique information regarding the electronic states involved in the magnetooptical transitions and information about the symmetry of the crystal environment of the emitting center. In this situation, the MCPL spectrum in the longitudinal Faraday geometry of the experiment is frequently called "returned magnetic circular dichroism," emphasizing the physical equivalence of both magnetooptical effects. While a lot of experimental work was devoted to the studies of the different phenomena in the RE-compounds (including RE-garnets [11,12]), MCPL studies performed in the diamagnetic garnet hosts doped by RE-ions are quite few. In particular, it relates to the Ho^{3+} ions embedded in the structure of the diamagnetic garnet YAG, since at present little work has been done on the MCPL phenomenon in this RE-compound [10].

In the present study, we carry out a detailed investigation of optical (mainly, luminescent) and magnetooptical (MCPL) spectra of Ho^{3+} in YAG garnets. A group-theoretical analysis with the use of the modern MOA theory elements [9–11,13,14] in discussion of the Ho^{3+}:YAG magneto-optical spectra strengthens interpretation of both the energy and symmetry assignments for the Stark levels of the $^5I_8$ and $^5S_2$ multiplets earlier given by Gruber et al. [15,16]. This approach to the interpretation of the experimental data is supported by the complete crystal-field (CF) calculations for all the multiplet manifolds of Ho^{3+} in YAG using 433 experimental data points up to 45,000 cm^{-1}. The CF calculations used a parameterized Hamiltonian expressed, as (see also [17,18]):

$$\widehat{H}_{CF} = \sum_{k,q} B_q^k C_q^{(k)} \qquad (1)$$

for the $4f^{10}$ – electronic shell of the RE-ion Ho^{3+} located in one of the non-equivalent positions (c-sites) in the YAG lattice. In D_2 symmetry, nine real CF parameters B_q^k are allowed. All calculations of the RE-ion Ho^{3+} energy spectrum include J–J "mixing" of the wave-functions. In the following studies, the directions and notations of axes in a local coordinate system corresponding to one of the crystallographically non-equivalent positions of the Ho^{3+} ion in the YAG structure were chosen such that the parameterization z-axis is parallel to the [0 0 1] cubic crystal axis and perpendicular to the xy-plane of the local coordinate system.

2. Samples and measurements

Single crystals of the Ho-containing paramagnetic garnet Ho^{3+}:YAG ($Ho_{0.2}Y_{2.8}Al_5O_{12}$) were grown by B. V. Mill (Moscow State University) using the Czochralski method and kindly provided through one of the authors (U. V. V.) for the present optical and magnetooptical studies. All samples were oriented radiographically and cut in the crystallographic plane [1 1 0], after their surfaces were polished by diamond pastes with slowly diminishing grain size (up to ~1 μm).

Both the optical and magnetooptical spectra were taken using a conduction Dewar filled with liquid nitrogen. To clarify the structure observed in the photoluminescence (PL), as well as the luminescence excitation spectrum (LES) at $T = 300$ K, we used a high resolution Steady State and Lifetime Fluorescence Spectrometer (FSL920, "Edinburgh Instruments Ltd", UK). At the same time, to study the structure observed in the PL and MCPL spectra at the low temperatures, we used a high resolution diffraction monochromator (MDR model 23, LOMO, Russia). These instruments have a spectral resolution generally better than 0.05 nm over the wavelength range investigated.

Ultraviolet (UV) light between from 240 nm to 400 nm was used to excite the "green" luminescence of the Ho-containing garnets when measuring the PL and MCPL spectra in the vicinity of the emission transition $^5S_2 \rightarrow {}^5I_8$. The circularity degree, P, of the partially polarized emitted (MCPL) light is given by the ratio [8–10]: $P = \frac{I_+ - I_-}{I_+ + I_-}$, where $I_\pm$ are the intensities of the clockwise- and counter-clockwise polarized components of the emitted light. Values for P were measured by a high-sensitivity technique of light polarization modulation [5,8,13].

3. Optical and magnetooptical spectra of Ho^{3+}:YAG

It is well-known that a common practice in the traditional optical spectroscopy of the rare-earth compounds is reconstruction of the electronic structure of the $4f^{(n)}$ and $4f^{(n-1)}5d$ configurations of the trivalent lanthanide ions on the basis of data obtained from optical absorption and luminescence spectra. Usually these two techniques apply together, because the luminescence spectra are suitable for detecting CF levels of the ground and low-energy excited multiplets of the RE-ion, whereas in the absorption spectra one can study the Stark levels of ground and excited multiplets of the same ion which are observed at higher energies.

Previously, Gruber et al. constructed the energy scheme of individual crystal-field (Stark) levels of the ground state multiplet $^5I_8$ and 49 excited multiplets $4f^{(10)}(^{2S+1}L_J)$ of the trivalent holmium ion [19] in the garnet structure, based on the studies of optical absorption spectra in a wide spectral region [15] and site-selective polarized fluorescence [16] at low temperatures in Ho^{3+}:YAG. This large number of the experimentally characterized energy levels (419 of the 486 theoretical Stark levels for these 50 multiplets) provided a suitable basis for detailed CF analysis of the $4f^{(10)}(Ho^{3+})$ electronic structure in Ho^{3+}:YAG. The authors of [15,20] supposed that the results of their research should predict and provide a satisfactory basis for future calculations and modeling studies of interesting optical properties in Ho^{3+}:YAG.

It should be noted, that historically researchers usually have used previously published crystal-field parameters (typically Nd^{3+} and Er^{3+}) as anchor points for new CF-calculations. This results in final parameter sets that are broadly similar to those previously published. However there is no guarantee that this process will result in the best-fit CF parameters. For this reason, two of us (G.W.B and J.B.G) performed a complete CF analysis of Ho^{3+}:YAG using a Monte-Carlo method [8] applied to 433 experimental points up to 45,000 cm^{-1}. In this analysis, we re-interpreted the original energy levels from Refs. [15,20] to yield a more complete and accurate CF data set of Ho^{3+} in YAG structure. The results of the abovementioned numerical CF calculations of Ho^{3+}:YAG are given in part in Table 1. From this table, we see that the Stark sublevels of the excited $^5S_2$ multiplet are located a range from 18,455 to 18,545 cm^{-1} with close lying $^5F_4$ sublevels that occupy spectral range from 18,588 to 18,757 cm^{-1}. In addition, there is considerable J–J "mixing" between states of these two multiplets (see Table 2).

The LES measured on the garnet Ho^{3+}:YAG using high-resolution fluorescence spectrometer FSL920 (see inset in Fig. 1) showed that the most preferable wavelength range for effective excitation of PL in Ho^{3+}:YAG is located in the range of 350–450 nm (Fig. 1). It should be noted that the LES method is very useful to determine the eigen frequencies of the spin-allowed $4f \rightarrow 5d$ (or $5g$) ED transitions in the RE-compounds observed in ultraviolet (UV)