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Spectroscopic properties and energy levels of Yb^{3+} ion in huntite structure

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ABSTRACT

Temperature dependence of Yb^{3+} optical absorption spectrum has been studied in crystals $Yb_xTm_{1-x}Al_3(BO_3)_4$ ($x = 0.1$, 0.2 and 1) in the temperature range 1.7–293 K. The spectra of the crystals appeared to be practically identical for the studied ytterbium concentrations. Raman scattering spectrum of $YbAl_3(BO_3)_4$ crystal has been measured. Group theory analysis of the optical absorption spectra is made, and new energy structure of the ground and excited states of Yb^{3+} ion, based on the experimental data obtained, is presented. Transformation of the local environment of Yb^{3+} ion depending on temperature has been found out. Spectrum of luminescence has been calculated from the absorption spectrum by reciprocity method with the use of the proposed energy structure.

1. Introduction

The growing interest to the huntite-type borates $Y_{1-x}R_xM_3(BO_3)_4$ (R is rare-earth ion, M can be Al, Cr, Ga, Fe, or Sc) is due to their wide potential application as self-frequency doubling lasers (for instance, Refs. [1–4]), microchip lasers [5], nonlinear optical crystals [5–7], and so on. Undoped $YAl_3(BO_3)_4$ crystal demonstrates the largest known nonlinear optical coefficient of the $Y_{1-x}R_xM_3(BO_3)_4$ series of crystals [7]. These crystals have trigonal symmetry with the space group $R32$ (No. 155 of the International Tables for X-Ray Crystallography) [8]. The unit cell contains three formula units ($Z = 3$). Trivalent rare-earth ions usually occupy only one-type positions, what is one of the advantages of the crystal, making the interpretation of spectral information to be more reliable. Fundamental investigations of spectral properties were performed for $Y_{1-x}R_xAl_3(BO_3)_4$ crystals doped by a number of rare-earth ions (see e.g., Refs. [9–18]).

Ytterbium is one of the proper ions for laser applications [3,5,6,19]. Yb^{3+} ion is characterized by the simple energy level structure. It has only two optically accessible bands and, consequently, has no absorption at the doubled wavelength. It has no cross-relaxation process, no fluorescence concentration quenching effect by conventional processes and, small quantum defect between absorption and emission wavelengths [5]. On the other hand, Yb^{3+}, introduced into crystals together with other rare earth ions, offers possibility to excite energy transfer processes, in particular, in combination with Tm^{3+} [20]. The close values of the Y^{3+}, Tm^{3+}, and Yb^{3+} ion radii allow growing high quality crystals with different Yb and Tm concentrations up to stoichiometric compositions.

Yb^{3+} absorption spectra in $Yb{:}YAl_3(BO_3)_4$ crystal at room temperature was studied in a number of works [6,21,22]. Xu et al. [23] presented the room temperature spectrum of $YbAl_3(BO_3)_4$ crystal. Ramirez et al. [24] studied low temperature spectra and energy structure of $Yb{:}YAl_3(BO_3)_4$ crystal with different concentrations of ytterbium.

In this paper we present results of the detailed investigation of Yb^{3+} absorption spectrum as a function of temperature in the concentrated $YbAl_3(BO_3)_4$ and in the mixed $Yb_xTm_{1-x}Al_3(BO_3)_4$ ($x = 0.1$

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and 0.2) crystals. We suggest new energy level diagram, based on the experimental results obtained.

2. Results and discussion

Samples made of the trigonal single crystals $Tm_{1-x}Yb_xAl_3(BO_3)_4$ ($x = 0.1$, 0.2, and 1) were used in the experiments. The crystals have been grown from the solution-melt [25]:

$$86\%\mathrm{mass}[Bi_2Mo_3O_{12} + pLi_2MoO_4 + qB_2O_3]$$
$$+\ 14\%\mathit{massTm}_{1-x}Yb_xAl_3(BO_3)_4$$

For $x = 1$ the coefficient values were $p = 0.5$ and $q = 2$, and for $x = 0.1$, 0.2 they were $p = 0.75$ and $q = 2.5$. Crystallization parameters, the saturation temperature $T_{\mathrm{sat}} \approx 985\,^{\circ}\mathrm{C}$ including, were practically the same in all cases. Single crystals were grown using seeds of about 1 mm in size fixed at the rotating ($\omega = 30$ turn/min) ring crystal-holder at the temperature lowering according to the program with the progressive temp 1–3 °C/day calculated for the crystal growth rate not higher than 1 mm/day. After the growth process has been completed, the holder with crystals was lifted up above the flux and cooled to the room temperature at the switched off furnace power.

When growing crystals $Tm_{1-x}Yb_xAl_3(BO_3)_4$ with $x = 0.1$ and 0.2, the initial solution-melt remaining after synthesis of the crystal with $x = 0$ was used. New portions of the crystal-forming oxides were added in it in quantities corresponding to the mass of the crystal synthesized. Ytterbium oxide was added in the proportions $Yb_2O_3{:}Tm_2O_3 = 1{:}10$ and $Yb_2O_3{:}Tm_2O_3 = 1{:}5$. Dimension of the crystals grown was ∼1 cm^3. The crystal lattice parameters were $a = 9.274(3)$ Å, $c = 7.212(3)$ Å for $YbAl_3(BO_3)_4$. The samples of $YbAl_3(BO_3)_4$ crystal prepared for measurements were 0.168 mm-thick plane-parallel polished platelets oriented parallel and perpendicular to the threefold crystallographic axis. Thickness of $Tm_{1-x}Yb_xAl_3(BO_3)_4$ ($x = 0.1$, 0.2) samples was 0.3 mm.

Polarized absorption spectra of the crystals have been studied in the region of transition $^2F_{7/2}$–$^2F_{5/2}$ of Yb^{3+} ion at temperatures 1.7–293 K. Three light polarizations were used: α—light wave vector $\vec{k}$ is parallel to C_3 axis of the crystal and electric vector $\vec{E}$ of light is perpendicular to C_3 axis; $\pi - \vec{k} \perp C_3$, $\vec{E} || C_3$; $\sigma - \vec{k} \perp C_3$, $\vec{E} \perp C_3$. The light was polarized by Glan prism. Precise positions of polarization parallel to the main crystal axes were found according to minimum transparency of the sample in crossed polarizers. The measurements were carried out on home made automatic spectrometer, based on diffraction monochromator MDR-23 with grating diffraction 1200 and 600 lines/mm and dispersion 1.3 and 2.6 nm/mm, respectively. Corresponding optical slit-widths were 1 and 1.9 cm^{-1}. Accuracy of the temperature measurement was ∼0.1–0.2 K in the range of 1.7–100 K. Temperature 1.7 K was obtained by pumping out the vapor of liquid helium.

At room temperature the absorption spectra of Yb^{3+} ion in all studied crystals, measured in absorption cross-section (σ_{abs}) of Yb^{3+} ion, totally coincide. At lower temperatures some absorption lines in the purely ytterbium crystal become too strong to be measured (see Fig. 1). However, the rest parts of the spectra of the studied crystals are practically identical. This is rather natural, since ion radii of Tm^{3+} and Yb^{3+} are close to each other. At the same time, absorption spectra of Yb^{3+} ion in our crystals noticeably differ from those in crystals $Yb^{3+}{:}YAl_3(BO_3)_4$ [21] and $Yb_xGd_{1-x}Al_3(BO_3)_4$ [26]. In our crystals, very high natural dichroism takes place (Figs. 1 and 2), while in $Yb^{3+}{:}YAl_3(BO_3)_4$ [21] it is small. All these means, that, in spite of the generally the same structure of the considered crystals, parameters of the local environment of Yb^{3+} ions are different. The α and σ absorption spectra of our crystals are identical, what testifies to the electric-dipole character of the transition. Absorption spectra for σ and π-polarizations at $T = 1.7$ and 100 K of the crystal $YbAl_3(BO_3)_4$ are presented in Figs. 1 and 2, respectively. The total nomenclature of the observed absorption lines is presented in Table 1.

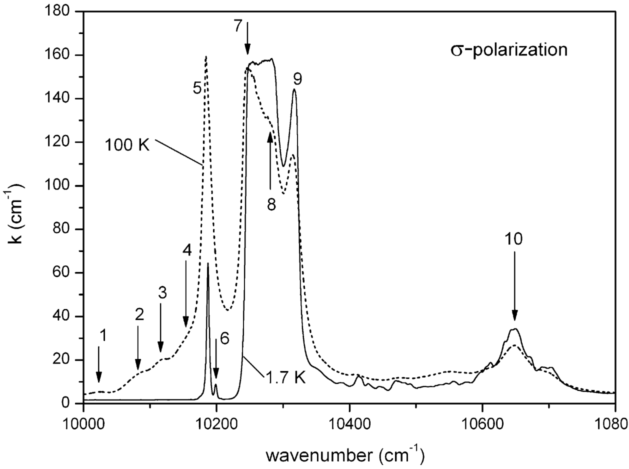

Fig. 1. The σ-polarized absorption spectra of $YbAl_3(BO_3)_4$ crystal.

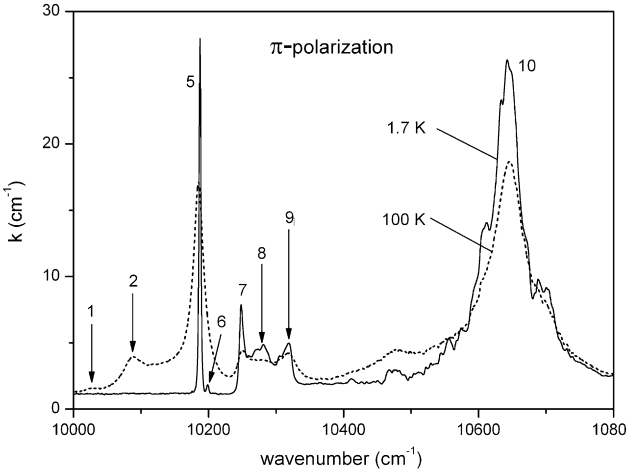

Fig. 2. The π-polarized absorption spectra of $YbAl_3(BO_3)_4$ crystal.

Ytterbium ions, like the other RE ions in the huntite structure, are surrounded by six crystallographically equivalent oxygen ions, forming trigonal prism [27], and the local symmetry, by analogy with the same crystal with Tb, Pr and Nd [12,16,28], is supposed to be D_3 at room temperature. The group D_3 is a subgroup of the cubic O group. In non-centrosymmetric D_3 and O groups *f–f* transitions are parity allowed. In [29,30] we have shown, that at low temperatures the symmetry of the similar crystal containing thulium

Table 1
Energies of absorption lines (cm^{-1}) in π and σ polarizations, observed in the spectra of $^2F_{7/2}$–$^2F_{5/2}$ transition in $YbAl_3(BO_3)_4$ crystal

Number	π	σ
1	10,025	10,020
2	10,087	10,081
3	–	10,117
4	–	10,150
5	10,187	10,187
6	10,198	10,198
7	10,248	10,248
8	10,280	10,280
9	10,318	10,317
10	10,645	10,648