

Manuscript Number: OM-D-18-00600R1

Title: Spectroscopic properties of  $\text{HoFe}_3(\text{BO}_3)_4$ ,  $\text{NdFe}_3(\text{BO}_3)_4$  and  $\text{Ho}_{0.75}\text{Nd}_{0.25}\text{Fe}_3(\text{BO}_3)_4$  single crystals.

Article Type: Original Research

Keywords: holmium and neodymium ferrobates, Judd-Ofelt parameters.

Corresponding Author: Mr. Alexander Leonidovich Sukhachev, Ph.D.

Corresponding Author's Institution: Kirensky Institute of Physics

First Author: Alexander Leonidovich Sukhachev, Ph.D.

Order of Authors: Alexander Leonidovich Sukhachev, Ph.D.; Alexander V Malakhovskii, Ph.D.; Alexander S Aleksandrovsky, Ph.D.; Irina A Gudim, Ph.D.; Vladislav L Temerov, Ph.D.

Abstract: Polarized absorption spectra of ferrobates  $\text{HoFe}_3(\text{BO}_3)_4$ ,  $\text{NdFe}_3(\text{BO}_3)_4$  and  $\text{Ho}_{0.75}\text{Nd}_{0.25}\text{Fe}_3(\text{BO}_3)_4$  were measured at room temperature in spectral range 4000 - 24500  $\text{cm}^{-1}$  (400 - 2500 nm). The studied single crystals were grown from solution-melts. Intensities of the f-f transitions were measured and the Judd-Ofelt parameters  $\Omega_\lambda$  of  $\text{Ho}^{3+}$  and  $\text{Nd}^{3+}$  ions in the studied crystals were calculated. It was revealed that the crystals content not strongly influences the Judd-Ofelt parameters. The  $\Omega_2$  parameter for  $\text{Ho}^{3+}$  ion is the most sensitive to the crystal content. Linear dichroism of the hypersensitive transitions appeared to be the largest one for both rare earth ions.

For every new optical material containing rare-earth (RE) ions it is necessary to study its optical properties, because it is not possible to calculate probabilities of  $f-f$  electronic transitions theoretically. It is also interesting to compare optical properties of the same RE ion in different compounds for understanding the influence of the local environment on the electronic structure of the RE ion and on the allowance of the forbidden  $f-f$  transitions.

In this work the  $\pi$ - and  $\sigma$ -polarized absorption spectra of ferroborates  $\text{HoFe}_3(\text{BO}_3)_4$ ,  $\text{NdFe}_3(\text{BO}_3)_4$  and  $\text{Ho}_{0.75}\text{Nd}_{0.25}\text{Fe}_3(\text{BO}_3)_4$  were measured. On the basis of the obtained spectra intensities of  $f-f$  transitions in the RE ions were defined. Some of the studied  $f-f$  transitions were identified as "hypersensitive" ones. The Judd–Ofelt parameters  $\Omega_\lambda$  of  $\text{Nd}^{3+}$  and  $\text{Ho}^{3+}$  ions in the mentioned crystals were determined. It was revealed that the crystals content not strongly influenced the Judd–Ofelt parameters. The  $\Omega_2$  parameter for  $\text{Ho}^{3+}$  ion is the most sensitive one to the crystal content.

Additionally, the linear dichroism of the  $f-f$  transitions was measured. The linear dichroism of the "hypersensitive" transitions was the largest one. Correlation of the  $f-f$  transitions linear dichroism and the symmetry of the studied crystals was observed.

The authors are thankful to the Editor and Reviewers for useful comments.

1. The comment: “The separation coefficients of Ho<sup>3+</sup> and Nd<sup>3+</sup> ions are not considered in Ho<sub>0.75</sub>Nd<sub>0.25</sub>Fe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> crystal, which will influence the calculation results.”

As we understand, this comment concerns the concentration of rare earth ions Ho<sup>3+</sup> and Nd<sup>3+</sup> in mixed crystal Ho<sub>0.75</sub>Nd<sub>0.25</sub>Fe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>. The composition of this crystal has been given in accordance with calculation of solution-melt. This remark was added to the Revised Manuscript (Experimental details). Unfortunately, we can't carry out additional specification of composition of this crystal with the help of x-ray diffraction in the nearest time, in connection with technical circumstances. However we can contend that the concentrations of Ho<sup>3+</sup> and Nd<sup>3+</sup> ions in the mixed crystal Ho<sub>0.75</sub>Nd<sub>0.25</sub>Fe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> correspond to the declared composition. It follows from the fact that intensities of f-f transitions normalized by concentration of rare-earth ions not strongly differ in mixed and pure crystals (see, for example, oscillator strengths  $f_{IF}$  in Tables 4 and 5, or integrated intensities  $I_{\pi}$ ,  $I_{\sigma}$  in Tables 2 and 3). At the same time, hypersensitive transitions (I for Ho<sup>3+</sup> and D for Nd<sup>3+</sup> ions) should not be taken into account because their intensity is very sensitive to changes of the local environment. These remarks were added in the revised text (Page 6).

For the clarity, we present here the additional calculations. Viz: for each rare-earth ion in each studied crystal the oscillator strengths  $f_{IF}$  of all transitions (except hypersensitive ones) are summed ( $\Sigma f_{IF}$ ):

From Revised Table 4 (for Ho<sup>3+</sup> ions):

HoFe <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub>	$\Sigma f_{IF}$ (with the exception of I transition) = 149.8 * 10 <sup>-7</sup> ,
Ho <sub>0.75</sub> Nd <sub>0.25</sub> Fe <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub>	$\Sigma f_{IF}$ (with the exception of I transition) = 149.3 * 10 <sup>-7</sup> .

From Table 5 (for Nd<sup>3+</sup> ions):

NdFe <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub>	$\Sigma f_{IF}$ (with the exception of D transition) = 251.4 * 10 <sup>-7</sup> ,
Ho <sub>0.75</sub> Nd <sub>0.25</sub> Fe <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub>	$\Sigma f_{IF}$ (with the exception of D transition) = 230.2 * 10 <sup>-7</sup> ,
difference is about 8 %.	

It should be noted that the decreasing of the parameter  $\Omega_4$  with decrease of concentration of Nd<sup>3+</sup> ion mentioned in the article (Table 7, line 1 and 3) is about 40%. Change of the parameter  $\Omega_2$  of Ho<sup>3+</sup> ions (Revised Table 6, line 1 and 2) is connected first of all with the difference of intensities of the hypersensitive transition I in different crystals. When we calculate values of the linear dichroism ( $I_{\sigma} / I_{\pi}$ ) the concentration of a rare-earth ion is automatically canceled.

2. The comment: “The Authors measured the absorption spectra of HoFe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>, NdFe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> and Ho<sub>0.75</sub>Nd<sub>0.25</sub>Fe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> crystal at room temperature in spectral range 400 - 1000 nm. There are 3 absorption bands ion Ho<sup>3+</sup> ion in the 1000 nm to 2500 nm. The Authors didn't consider the influence of these absorption bands at the back of the calculations.”

Accordingly to literature data there are two absorption bands in the denote spectral range from 1000 nm to 2500 nm connected with f-f transitions in Ho<sup>3+</sup> ions: Y (<sup>5</sup>I<sub>8</sub> → <sup>5</sup>I<sub>7</sub>) at 5050 cm<sup>-1</sup> (1980 nm) and A (<sup>5</sup>I<sub>8</sub> → <sup>5</sup>I<sub>6</sub>) at 8550 cm<sup>-1</sup> (1170 nm). After receiving the Reviewer Comments we measured the polarized absorption spectra of the mentioned f-f transitions in HoFe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> and Ho<sub>0.75</sub>Nd<sub>0.25</sub>Fe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> crystals. Obtained spectra were added in article (Figure 5) and used for calculations of Judd-Ofelt parameters (Revised Table 6).

Account of two additional f-f transitions in Ho<sup>3+</sup> ions (Y and A) influenced the obtained Judd-Ofelt parameters very weakly (it is expected if the Judd-Ofelt theory is correct). In particular:

Judd–Ofelt parameters  $\Omega_i$  ( $10^{-20}$  cm<sup>2</sup>) of the Ho<sup>3+</sup> ions (calculation without Y и A transitions):  
in HoFe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>:  $\Omega_2 = 4.952$ ;  $\Omega_4 = 4.566$ ;  $\Omega_6 = 2.303$ ,  
in Ho<sub>0.75</sub>Nd<sub>0.25</sub>Fe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>:  $\Omega_2 = 6.47$ ;  $\Omega_4 = 4.309$ ;  $\Omega_6 = 2.182$ .

After additional measurements. Judd–Ofelt parameters  $\Omega_i$  ( $10^{-20}$  cm<sup>2</sup>) of the Ho<sup>3+</sup> ions (calculation taking into account transitions Y и A):

in HoFe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>:  $\Omega_2 = 4.874$ ;  $\Omega_4 = 4.74$ ;  $\Omega_6 = 2.1$ ,  
in Ho<sub>0.75</sub>Nd<sub>0.25</sub>Fe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>:  $\Omega_2 = 6.557$ ;  $\Omega_4 = 4.106$ ;  $\Omega_6 = 2.49$ .

3. The comment: “Please explain why that values of the total dichroism of Nd<sup>3+</sup> ions in these crystals are similar and independent of the concentration of Nd<sup>3+</sup> ions but linear dichroism of the hypersensitive transitions of Ho<sup>3+</sup> ions is the most sensitive to the crystal content.”

Let us separate this comment into two parts.

Start with the second part: “linear dichroism of the hypersensitive transitions of Ho<sup>3+</sup> ions is the most sensitive to the crystal content”. There is no such conclusion in the article. In the Abstract and in the Summary we present the conclusion that linear dichroism of the hypersensitive transitions is the largest one for both rare earth ions (See Table 2 (transition I) and Table 3 (transition D)). Probably, this is connected with the fact that these transitions are characterized by the large value of the  $\Gamma_2^2$  coefficient relative to other transitions (Tables 4, 5). This means that 1-st and 3-d spherical harmonics  $t$  ( $t = \lambda \pm 1$  [32]) in the expansion of the crystal field take part in the allowance of the mentioned transitions by parity, while only higher harmonics are active in the allowance of the rest of the transitions. (See text, page 6).

Return to the first part of the comment: “Please explain why that values of the total dichroism of Nd<sup>3+</sup> ions in these crystals are similar and independent of the concentration of Nd<sup>3+</sup> ions”.

“Total dichroism”  $\Sigma I_\sigma / \Sigma I_\pi$  – the ratio of the sum of intensities of all studied absorption bands in  $\sigma$  polarization to the sum of intensities of all bands in  $\pi$  polarization. This parameter was calculated for Ho<sup>3+</sup> and Nd<sup>3+</sup> ions in three studied crystals and presented in Tables 2 and 3 (the lowest line).

Calculation of the “total dichroism” is connected with an attempt to find some parameter of f-f transitions which correlates with the symmetry of the local environment of the rare-earth ion. In the process of calculating of the "total dichroism" the hypersensitive transitions were excluded from the summation because they have the largest dichroism. It is experimentally obtained that in crystals with different symmetry at room temperature: HoFe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> (*P3<sub>1</sub>21*) and Ho<sub>0.75</sub>Nd<sub>0.25</sub>Fe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> (*R32*) the “total dichroism” of f-f transitions in Ho<sup>3+</sup> ions is different (1.56 and 1.81, respectively, Revised Table 2). In crystals with identical symmetry at room temperature: Ho<sub>0.75</sub>Nd<sub>0.25</sub>Fe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> (*R32*) and NdFe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> (*R32*) the “total dichroism” of f-f transitions in Nd<sup>3+</sup> ions is practically identical (1.75 and 1.72, respectively, Table 3). Moreover, when we carried out similar calculation of the "total dichroism" of the same set of transitions in Nd<sup>3+</sup> ions in the crystal of Nd<sub>0.5</sub>Gd<sub>0.5</sub>Fe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>, investigated by us earlier, we received value 1.71 (symmetry of this crystal at room temperature is also *R32*). Thus, the experiment has shown that the total dichroism is practically independent of the Nd ion concentration if the symmetry of the crystals is identical.

All corrected and added parts of the revised text and tables were marked by blue color.

Sincerely yours,  
A. Sukhachev.

## \*Highlights (for review)

- Absorption spectra of  $\text{HoFe}_3(\text{BO}_3)_4$ ,  $\text{NdFe}_3(\text{BO}_3)_4$  and  $\text{Ho}_{0.75}\text{Nd}_{0.25}\text{Fe}_3(\text{BO}_3)_4$  crystals.
- Intensities of  $f$ - $f$  transitions in  $\pi$  and  $\sigma$  polarizations.
- Judd–Ofelt parameters of  $\text{Ho}^{3+}$  and  $\text{Nd}^{3+}$  ions in studied crystals.
- Correlation of  $f$ - $f$  transitions linear dichroism with the crystals symmetry.

## Spectroscopic properties of $\text{HoFe}_3(\text{BO}_3)_4$ , $\text{NdFe}_3(\text{BO}_3)_4$ and $\text{Ho}_{0.75}\text{Nd}_{0.25}\text{Fe}_3(\text{BO}_3)_4$ single crystals.

A.L. Sukhachev<sup>1\*</sup>, A.V. Malakhovskii<sup>1</sup>, A.S. Aleksandrovsky<sup>1,2</sup>, I.A. Gudim<sup>1</sup>, V.L. Temerov<sup>1</sup>

<sup>1</sup>Kirensky Institute of Physics, Federal Research Center KSC SB RAS, 660036 Krasnoyarsk, Russian Federation

<sup>2</sup>Institute of Nanotechnology, Spectroscopy and Quantum Chemistry, Siberian Federal University, 660041, Krasnoyarsk, Russian Federation

### Abstract

Polarized absorption spectra of ferrobates  $\text{HoFe}_3(\text{BO}_3)_4$ ,  $\text{NdFe}_3(\text{BO}_3)_4$  and  $\text{Ho}_{0.75}\text{Nd}_{0.25}\text{Fe}_3(\text{BO}_3)_4$  were measured at room temperature in spectral range 4000 – 24500  $\text{cm}^{-1}$  (400 – 2500 nm). The studied single crystals were grown from solution-melts. Intensities of the  $f$ - $f$  transitions were measured and the Judd–Ofelt parameters  $\Omega_\lambda$  of  $\text{Ho}^{3+}$  and  $\text{Nd}^{3+}$  ions in the studied crystals were calculated. It was revealed that the crystals content not strongly influences the Judd–Ofelt parameters. The  $\Omega_2$  parameter for  $\text{Ho}^{3+}$  ion is the most sensitive to the crystal content. Linear dichroism of the hypersensitive transitions appeared to be the largest one for both rare earth ions.

**Keywords:** holmium and neodymium ferrobates, Judd–Ofelt parameters.

\* e-mail: sunya@iph.krasn.ru

## 1. Introduction

Borates  $RM_3(BO_3)_4$  (R–Y or rare earth (RE) element, M–Al, Ga, Cr, Fe, Sc) have huntite-like structure. RE ferrobates  $RFe_3(BO_3)_4$  attract great interest of researchers, because, in a number of cases, such crystals belong to the class of multiferroics [1–3]. Multiferroics are the materials which possess the interrelated magnetic, electric and elastic ordering. Spectroscopic properties of Ho and Nd ions in various compounds were investigated for a long time and extensively (in the network of the Judd–Ofelt theory including) [4–15], however the Judd–Ofelt spectroscopic parameters  $\Omega_\lambda$  of RE ions in  $HoFe_3(BO_3)_4$ ,  $NdFe_3(BO_3)_4$  and  $Ho_{0.75}Nd_{0.25}Fe_3(BO_3)_4$  single crystals were not determined earlier. Fine structure of  $f$ - $f$  transitions was investigated in  $HoFe_3(BO_3)_4$  [16] and in  $NdFe_3(BO_3)_4$  crystals [17] in the visible and near infrared spectral range. Intensities of  $f$ - $f$  transitions strongly depend on the symmetry of compound, on the local environment of the RE ion, in particular. The precise theoretical prediction of  $f$ - $f$  transitions intensities of the RE ion in the specific compound is not possible at the moment. Therefore, the aim of this work was investigation of optical properties of the mentioned ferrobates and search of correlation between obtained results and structure of the crystals.

Structure of the studied crystals belongs to trigonal symmetry class. Trivalent RE ions occupy positions of only one type. They are located at the center of trigonal prisms made up of six crystallographically equivalent oxygen ions. The triangles formed by the oxygen ions in the neighboring basal planes are not superimposed on each other but are twisted by a certain angle. Owing to this distortion, the symmetry  $D_{3h}$  of the ideal prism is reduced to the symmetry  $D_3$  [18]. According to the literature data,  $HoFe_3(BO_3)_4$  crystal, as many of the ferrobates, undergoes the structural phase transition from  $R32$  to  $P3_121$  symmetry. At this transition the local symmetry of RE ion decreases from  $D_3$  to  $C_2$  one. The temperature of the transition depends strongly on the method of crystal growing: it amounts 427 K for the powder samples obtained by the solid-state synthesis [19] and 360 K for the single crystals grown from a solution-melt [20]. At room temperature  $HoFe_3(BO_3)_4$  crystal has  $P3_121$  symmetry. In  $Ho_{0.75}Nd_{0.25}Fe_3(BO_3)_4$  crystal the structural phase transition happens at 200 K [21]. Thus, at room temperature symmetry of this crystal is  $R32$ . Symmetry  $R32$  of  $NdFe_3(BO_3)_4$  crystal does not change with the decrease of temperature till 1.6 K [22].

## 2. Experimental details

Single crystals were grown from a bismuth trimolybdate solution-melts with a nonstoichiometric ratio of the crystal constitutive oxides of (100 -  $n$ ) mass %  $[Bi_2Mo_3O_{12} +$

$p\text{B}_2\text{O}_3 + q(1-x)\text{Ho}_2\text{O}_3 + qx\text{Nd}_2\text{O}_3] + n\%$  mass  $\text{Ho}_{1-x}\text{Nd}_x\text{Fe}_3(\text{BO}_3)_4$  ( $x=0; 0.25; 1$ ) [23]. Values of parameters  $n$ ,  $p$ ,  $q$  and saturation temperature  $T_{\text{sat}}$  see in Table 1. In these solution-melts the trigonal huntite is the high temperature phase and only this phase crystallizes above  $T \approx 900$  °C. The solution-melts with a mass of 100 g were prepared in platinum crucibles. They were kept during 8–10 h at  $T = 1100$  °C with permanent mixing by a reversibly rotating platinum rod for homogenization. When the temperature was lowered to  $T = T_{\text{sat}} - (5-7)$  °C, the rod was lifted over the solution-melt. At the same time the spontaneous crystallization takes place into the thin overcooled layer of the solution-melt which stays on the rod. The rod was again immersed into the solution-melt. Then the temperature was lowered by  $(1-3)$  °C/24 h. The crystallization process was stopped at  $T = 930-945$  °C. **Crystal compositions have been given in accordance with calculation of solution-melts.** Crystals with linear dimensions up to 7 mm were grown. For the optical measurements the samples were prepared as the polished plates about 0.2 mm thick, with the  $C_3$  axis parallel to the plate surface.

The absorption spectra were measured by the two beam technique, using an automated spectrophotometer designed on the basis of the diffraction monochromator MDR-2. In the spectral range 400–500 **and 1000–2500** nm the measurements were carried out on a spectrophotometer SHIMADZU UV-3600. The absorption spectra were obtained with the light propagating normally to the  $C_3$  axis of the crystal for the light electric vector  $\vec{E}$  parallel ( $\pi$  spectrum) and perpendicular ( $\sigma$  spectrum) to the  $C_3$  axis of the crystal. Optical slit width (spectral resolution) was 0.2 nm in the region of 400–600 nm and 0.4 nm in the region of 600–**2500** nm.

### 3. Results and discussion

Absorption spectra (decimal absorption coefficient) of  $\text{HoFe}_3(\text{BO}_3)_4$ ,  $\text{NdFe}_3(\text{BO}_3)_4$  and  $\text{Ho}_{0.75}\text{Nd}_{0.25}\text{Fe}_3(\text{BO}_3)_4$  single crystals for  $\pi$  and  $\sigma$  polarizations at room temperature in the range from 10000 to 24500  $\text{cm}^{-1}$  are presented in Figs. 1–4. Observed spectra consist of sets of narrow lines connected with the  $f-f$  transitions in  $\text{Ho}^{3+}$  and  $\text{Nd}^{3+}$  ions and of wide bands due to  $d-d$  transitions in  $\text{Fe}^{3+}$  ions. At  $E \sim 11500, 16000$  and  $22750$   $\text{cm}^{-1}$  the transitions  ${}^6A_1 \rightarrow {}^4T_1, {}^4T_2, {}^4A_1$  (in cubic crystal field notation) in  $\text{Fe}^{3+}$  ions are observed (Figs. 1–4), and at  $E > 25000$   $\text{cm}^{-1}$  the edge of the strong absorption occurs [24]. Absorption, caused by  $\text{Fe}^{3+}$  ions, were approximated by Gaussian curves and subtracted from the full spectra. As a result we received absorption spectra only of  $f-f$  transitions in RE ions. **In Fig. 5 the  $f-f$  transitions of  $\text{Ho}^{3+}$  ions in  $\text{HoFe}_3(\text{BO}_3)_4$  and  $\text{Ho}_{0.75}\text{Nd}_{0.25}\text{Fe}_3(\text{BO}_3)_4$  crystals in spectral range 4000–10000  $\text{cm}^{-1}$  are presented.**



Identification of  $f$ - $f$  absorption lines was carried out on the basis of Carnall [25] and Kaminskii [26].

Intensities of  $f$ - $f$  absorption lines in  $\pi$  and  $\sigma$  polarizations ( $I_\pi$  and  $I_\sigma$ ) were determined from the spectra as integrals  $I = \int \frac{k(E)}{C_{RE}} dE$ , where  $C_{RE}$  is the molar concentration of the corresponding RE ion in the crystal in units of mol/l,  $E$  is the energy in  $\text{cm}^{-1}$ . Concentration of RE ions ( $C_{RE}$ ) in the  $\text{HoFe}_3(\text{BO}_3)_4$  and  $\text{NdFe}_3(\text{BO}_3)_4$  crystals was accepted to be identical and equal to 8.34 mol/l. For the  $\text{Ho}_{0.75}\text{Nd}_{0.25}\text{Fe}_3(\text{BO}_3)_4$  crystal the values  $C_{RE}$  were calculated according to the chemical formula of the compound and were equal to  $C_{\text{Ho}} = 6.255$  mol/l and  $C_{\text{Nd}} = 2.085$  mol/l. Experimentally obtained intensities of  $f$ - $f$  transitions in  $\pi$  and  $\sigma$  polarizations ( $I_\pi$  and  $I_\sigma$ ) are presented in Tables 2, 3. The transition intensities were averaged over the polarizations according to the common relation for uniaxial anisotropic crystals:  $I_{IF} = (2I_\sigma + I_\pi)/3$ . Following to the Ref. [27], we calculated oscillator strengths of transitions  $I \rightarrow F$  between  $J$  multiplets by the equation:

$$f_{IF} = 4.318 \cdot 10^{-9} \frac{3n}{(n)^2 + 2} I_{IF}. \quad (1)$$

There are no experimental data about refractive index  $n$  of the studied crystals up to date. Refractive index of ferrobates slightly depends on rare earth ion. Earlier [28] we measured refractive index for  $\text{ErFe}_3(\text{BO}_3)_4$  single crystal:  $n \approx 2$ , and we used this value in the present work. Calculated oscillator strengths  $f_{IF}$  are presented in Tables 4, 5.

The transition strength is defined as:  $s_{IF} = \frac{1}{e^2} \sum_{if} |\bar{D}_{if}|^2$ , where  $i \in I$ ,  $f \in F$  and  $\bar{D}_{if}$  – the matrix element of the electric dipole moment. The transition strength and the oscillator strength are related by the expression [29]:

$$s_{IF} = \frac{3hg_I}{8\pi^2 mck_{IF}} f_{IF}, \quad (2)$$

where  $g_I$  is the degree of degeneracy of the initial state and  $k_{IF}$  is the average wave number of the absorption band. Experimentally obtained  $k_{IF}$  of the studied  $f$ - $f$  transitions are given in Tables 2 and 3.

In the network of the Judd–Ofelt theory, the strength of an  $f$ - $f$  transition in RE ion in the non-centrosymmetrical crystal field is described by the relationship [30-32]:

$$s_{IF} = \sum_{\lambda} \Omega_{\lambda} \Gamma_{\lambda}^2(I, F). \quad (3)$$

Coefficients  $\Gamma_{\lambda}^2(I, F) = \left\langle I \left\| U^{(\lambda)} \right\| F \right\rangle^2$  are calculated theoretically and are considered to be independent of the crystal structure. For the calculations we used coefficients  $\Gamma_{\lambda}^2(I, F)$  from the

works of Carnall [25] for  $\text{Ho}^{3+}$  ion and of Kaminskii [26] for  $\text{Nd}^{3+}$  ion (Tables 4, 5). The index  $\lambda$  for  $f$ - $f$  transitions takes three values: 2, 4, and 6. It is possible to find three parameters  $\Omega_\lambda$  from the experimentally obtained strengths of the viewed transitions in the RE ion and to calculate the strengths of all other possible  $f$ - $f$  transitions. The transitions under consideration are forbidden in the free RE ion in the electric dipole approximation not only by the parity, but some of them are forbidden by the total momentum in accordance with the selection rule  $\Delta J = 0, \pm 1$ . According to the Judd–Ofelt theory [32], when transitions are allowed by the parity selection rule due to the odd components of the crystal field, they can occur at  $\Delta J \leq \lambda$  ( $\lambda = 2, 4$  and  $6$ , as mentioned above). Among all studied transitions (Tables 2, 3) only one transition does not satisfy this condition:  ${}^5I_8 \rightarrow {}^5F_1$  (Band I) in  $\text{Ho}^{3+}$  ions (Table 2). Correspondingly, all parameters  $\Gamma_\lambda^2 = 0$  for this transition [25, 26] (Table 4), and it is possible to assume that intensity of this transition is indistinguishably small and its contribution to the intensity of the band I is insignificant although this transition coincides by energy with transition  ${}^5I_8 \rightarrow {}^5G_6$ .

Equation (3) can be written in the vector form:

$$\vec{s} = A\vec{\Omega}. \quad (4)$$

Here  $\vec{s}$  is the  $q$ -dimensional vector consisting of the measured strengths of the transition groups;  $q$  is the number of the considered groups of transitions;  $\vec{\Omega}$  is the three-dimensional vector of parameters  $\Omega_\lambda$  ( $\lambda = 2, 4, 6$ );  $A$  is the  $3 \times q$ -dimensional matrix of the coefficients  $\Gamma_\lambda^2(I, F)$ . The vector  $\vec{\Omega}$  that minimizes the sum of the squares of the deviations between the measured and theoretical transition strengths is given by the matrix equation [33]

$$\vec{\Omega} = (A^T A)^{-1} A^T \vec{s}, \quad (5)$$

where  $A^T$  is the transposed matrix. Thus we received the set of parameters  $\Omega_\lambda$ .

For calculation of the  $\Omega_\lambda$  parameters we used  $f$ - $f$  bands **Y, A**, B, D, E, F, G, H, I, J in  $\text{Ho}^{3+}$  ions (Table 2, 4) and R, S, A, B, C, D, E, F bands in  $\text{Nd}^{3+}$  ions (Table 3, 5). On the basis of the received parameters  $\Omega_\lambda$ , the strengths of the transitions were calculated from Eq. (3) (Tables 4, 5). Correlation between the experimentally obtained and calculated strengths of the transitions estimates the precision of the results. The relative root mean square error of the theoretical description of the transition strengths is defined by equation:

$$\delta = \left[ \frac{q \sum \Delta s^2}{(q-p) \sum s^2} \right]^{1/2}. \quad (6)$$

Here  $s$  are the measured transition strengths,  $\Delta s$  are the differences between the measured and calculated transition strengths (see Tables 4, 5),  $p$  is the number of the determined parameters, being equal to 3 in our case.

As a result, we determined parameters  $\Omega_\lambda$  for the  $\text{Ho}^{3+}$  and  $\text{Nd}^{3+}$  ions in the studied crystals with accuracy  $\delta$  about 7% and 12% respectively. The received Judd-Ofelt parameters and their comparison with the literature data for other compounds containing the studied RE ions are presented in Tables 6, 7. It should be noted that parameter  $\Omega_4$  of the  $\text{Nd}^{3+}$  ions (see Table 7, lines 1-3) considerably decreases with the decrease of concentration of the ions in the investigated ferroborate crystals. The set of the studied transitions and of their  $\Gamma_\lambda^2(I, F)$  coefficients for the  $\text{Ho}^{3+}$  ion (Table 4) shows that parameter  $\Omega_2$  (Table 6) is almost completely defined by intensity of the I-band.

Transitions I ( $^5I_8 \rightarrow ^5G_6$ ) in  $\text{Ho}^{3+}$  ions and D ( $^4I_{9/2} \rightarrow ^4G_{5/2}$ ) in  $\text{Nd}^{3+}$  ions were referred to the hypersensitive ones in Ref. 32. The hypersensitive transitions are usually characterized by the large intensity which strongly depends on the local environment. The mentioned transitions reveal the hypersensitive properties also in our crystals (Tables 4, 5). These transitions are also characterized by the large value of the  $\Gamma_2^2$  coefficient relative to other transitions (Tables 4, 5). This means that 1-st and 3-d spherical harmonics  $t$  ( $t = \lambda \pm 1$  [32]) in the expansion of the crystal field take part in the allowance of the mentioned transitions by parity, while only higher harmonics are active in the allowance of the rest of the transitions.

We can contend that the concentrations of  $\text{Ho}^{3+}$  and  $\text{Nd}^{3+}$  ions in the mixed crystal  $\text{Ho}_{0.75}\text{Nd}_{0.25}\text{Fe}_3(\text{BO}_3)_4$  correspond to the declared composition. It follows from the fact that intensities of  $f-f$  transitions normalized by concentration of rare-earth ions not strongly differ in mixed and pure crystals (see, for example, oscillator strengths  $f_{IF}$  in Tables 4 and 5, or integrated intensities  $I_\pi, I_\sigma$  in Tables 2 and 3). At the same time, hypersensitive transitions (I for  $\text{Ho}^{3+}$  and D for  $\text{Nd}^{3+}$  ions) should not be taken into account because their intensity is very sensitive to changes of the local environment.

In all studied crystals we observe the difference of  $f-f$  spectra measured in the  $\pi$  and  $\sigma$  polarizations, i.e. linear dichroism. The measure of the dichroism is the ratio of intensities of bands in  $\sigma$  and  $\pi$  polarizations -  $I_\sigma / I_\pi$ . For all studied transitions these values were calculated and presented in Tables 2, 3. It should be noted that the dichroism of the hypersensitive transitions is much larger than dichroism of other measured transitions. In particular, value of the dichroism of the I-band of the  $\text{Ho}^{3+}$  ions (Table 2) in both crystals is about 10, whereas the dichroism of other transitions does not exceed value 3.5. The total dichroism  $\Sigma I_\sigma / \Sigma I_\pi$  (Table 2) of all studied  $f-f$  bands in the  $\text{Ho}^{3+}$  spectra (with the exception of I-band) is 1.56 for the  $\text{HoFe}_3(\text{BO}_3)_4$  crystal and 1.81 for the  $\text{Ho}_{0.75}\text{Nd}_{0.25}\text{Fe}_3(\text{BO}_3)_4$ . Difference of these values can be explained by the difference of parameters of the local environment of the  $\text{Ho}^{3+}$  ions in the studied crystals.

For the  $\text{Nd}^{3+}$  ions (Table 3) the dichroism of hypersensitive transition D:  $I_\sigma / I_\pi \sim 4$  also noticeably exceeds the dichroism of other studied transitions. The total dichroism (Table 3) of all

studied  $f-f$  bands of the  $\text{Nd}^{3+}$  ions (with the exception of D-band) is 1.72 for the  $\text{NdFe}_3(\text{BO}_3)_4$  and 1.75 for the  $\text{Ho}_{0.75}\text{Nd}_{0.25}\text{Fe}_3(\text{BO}_3)_4$  crystals. The total dichroism of the same set of transitions in  $\text{Nd}^{3+}$  ions in the  $\text{Nd}_{0.5}\text{Gd}_{0.5}\text{Fe}_3(\text{BO}_3)_4$  crystal was equal to 1.71 [11]. Values of the total dichroism ( $\Sigma I_\sigma / \Sigma I_\pi$ ) are practically identical for the above mentioned three crystals with identical symmetry  $R32$  at room temperature and it is possible to conclude that parameters of the local environment of  $\text{Nd}^{3+}$  ions in these crystals are similar, in spite of the large difference of the  $\text{Nd}^{3+}$  ions concentrations in these crystals.

#### 4. Summary

Absorption spectra of single crystals  $\text{HoFe}_3(\text{BO}_3)_4$ ,  $\text{NdFe}_3(\text{BO}_3)_4$  and  $\text{Ho}_{0.75}\text{Nd}_{0.25}\text{Fe}_3(\text{BO}_3)_4$  for  $\pi$ - and  $\sigma$ -polarizations were measured at room temperature in spectral range from 4000 to 24500  $\text{cm}^{-1}$  (400 – 2500 nm). The crystals were grown from a solution-melt. The  $d-d$  absorption of the  $\text{Fe}^{3+}$  ions and  $f-f$  transitions of  $\text{Ho}^{3+}$  and  $\text{Nd}^{3+}$  ions in the spectra were separated. The  $f-f$  spectra of the rare earth ions were analyzed in the network of the Judd–Ofelt theory. Intensities of the  $f-f$  transitions were measured and the Judd–Ofelt parameters  $\Omega_2$  of  $\text{Ho}^{3+}$  and  $\text{Nd}^{3+}$  ions in the studied crystals were calculated. It was revealed that the crystals content not strongly influences the Judd–Ofelt parameters. The  $\Omega_2$  parameter for  $\text{Ho}^{3+}$  ion is the most sensitive to the crystal content. Linear dichroism of the hypersensitive transitions is the largest one for both rare earth ions, especially for holmium. The total dichroism of  $f-f$  transitions is independent of the concentration of  $\text{Nd}^{3+}$  ions in the studied crystals which has identical symmetry. For the  $\text{Ho}^{3+}$  containing crystals the total dichroism depends on the crystal symmetry.

#### Acknowledgements

The work was supported by the Russian Foundation for Basic Researches grants 17-52-45091, 17-52-53031 and 16-02-00273.

#### References

- [1] A.K. Zvezdin, S.S. Krotov, A.M. Kadomtseva, G.P. Vorob'ev, Yu.F. Popov, A.P. Pyatakov, L.N. Bezmaternykh, E.N. Popova, Magnetolectric effects in gadolinium iron borate  $\text{GdFe}_3(\text{BO}_3)_4$ , JETP Letters 81 (6) (2005) 272-276.
- [2] A.K. Zvezdin, G.P. Vorob'ev, A.M. Kadomtseva, Yu.F. Popov, A.P. Pyatakov, L.N. Bezmaternykh, A.V. Kuvardin, E.A. Popova, Magnetolectric and magnetoelastic interactions in  $\text{NdFe}_3(\text{BO}_3)_4$  multiferroics, JETP Letters 83 (11) (2006) 509-514.

- [3] A.M. Kadomtseva, Yu.F. Popov, G.P. Vorob'ev, A.P. Pyatakov, S.S. Krotov, K.I. Kamilov, V.Yu. Ivanov, A.A. Mukhin, A.K. Zvezdin, A.M. Kuz'menko, L.N. Bezmaternykh, I.A. Gudim, V.L. Temerov, Magnetolectric and magnetoelastic properties of rare earth iron borates, *Low Temp. Phys.* 36 (6) (2010) 511-521.
- [4] B. Zhou, E.Y.B. Pun, H. Lin, D. Yang, L. Huang, Judd–Ofelt analysis, frequency upconversion, and infrared photoluminescence of Ho<sup>3+</sup>-doped and Ho<sup>3+</sup>/Yb<sup>3+</sup> -codoped lead bismuth gallate oxide glasses, *J. Appl. Phys.* 106 (2009) 103105 (9 pages).
- [5] B.M. Walsh, G.W. Grew, N.P. Barnes, Energy levels and intensity parameters of Ho<sup>3+</sup> ions in Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> and Lu<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>, *J. Phys. Chem. Solids* 67 (2006) 1567–1582.
- [6] N. Rakov, G.S. Maciel, C.B. de Araujo, Y. Messaddeq Energy transfer assisted frequency upconversion in Ho<sup>3+</sup> doped fluorindate glass, *J. Appl. Phys.* 91 (2002) 1272-1276.
- [7] X. Wang, H. Lin, D. Yang, L. Lin, E.Y.B. Pun, Optical transitions and upconversion fluorescence in Ho<sup>3+</sup>/Yb<sup>3+</sup> doped bismuth tellurite glasses, *J. Appl. Phys.* 101 (2007) 113535 (7 pages).
- [8] D. Kasprowicz, M.G. Brik, A. Majchowski, E. Michalski, A. Biadasz, Spectroscopic studies of KGd(WO<sub>4</sub>)<sub>2</sub>: Ho<sup>3+</sup> single crystals, *J. Alloys Compd.* 509 (2011) 1430–1435.
- [9] D.K. Sardar, S.R. Chandrasekharan, K.L. Nash, J.B. Gruber, A. Burger, U.N. Roy, Intensity analysis and crystal-field modeling of Ho<sup>3+</sup> in KPb<sub>2</sub>Cl<sub>5</sub> host, *J. Appl. Phys.* 103 (2008) 093112 (8 pages).
- [10] K.L. Nash, R.C. Dennis, N.J. Ray, J.B. Gruber, D.K. Sardar, Absorption intensities, emission cross sections, and crystal field analysis of selected intermanifold transitions of Ho<sup>3+</sup> in Ho<sup>3+</sup>: Y<sub>2</sub>O<sub>3</sub> nanocrystals, *J. Appl. Phys.* 106 (2009) 063117 (8 pages).
- [11] A.V. Malakhovskii, A.L. Sukhachev, A.A. Leont'ev, I.A. Gudim, A.S. Krylov, A.S. Aleksandrovsky, Spectroscopic properties of Nd<sub>0.5</sub>Gd<sub>0.5</sub>Fe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> single crystal, *J. Alloys Compd.* 529 (2012) 38-43.
- [12] D. Jaque, O. Enguita, U.G. Caldillo, M.O. Ramírez, J. García Solé, C. Zaldo, J. E. Muñoz-Santiuste, A. D. Jiang, Z. D. Luo, Optical characterization and laser gain modeling of a NdAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> (NAB) microchip laser crystal, *J. Appl. Phys.* 90 (2001) 561-569.
- [13] X. Chen, Z. Luo, D Jaque, J J Romero, J García Solé, Y. Huang, A. Jiang, C. Tu, Comparison of optical spectra of Nd<sup>3+</sup> in NdAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> (NAB), Nd: GdAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> (NGAB) and Nd: Gd<sub>0.2</sub>Y<sub>0.8</sub>Al<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> (NGYAB) crystals, *J. Phys.: Condens. Matter* 13 (2001) 1171-1178.
- [14] A. Majchrowski, S. Klosowicz, L.R. Jaroszewicz, M. Swirkowicz, I.V. Kityk, M. Piasecki, M.G. Brik, Judd–Ofelt analysis and optically stimulated two-photon absorption of Yb<sup>3+</sup>-doped NdAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> single crystals, *J. Alloy Compd.* 491 (2010) 26-29.

- [15] K.L. Nash, R.C. Dennis, J.B. Gruber, D.K. Sardar, Intensity analysis and energy-level modeling of Nd<sup>3+</sup> in Nd<sup>3+</sup>: Y<sub>2</sub>O<sub>3</sub> nanocrystals in polymeric hosts, *J. Appl. Phys.* 105 (2009) 033102 (6 pages).
- [16] A.V. Malakhovskii, S.L. Gnatchenko, I.S. Kachur, V.G. Piryatinskaya, I.A. Gudim, Low-temperature absorption spectra and electron structure of HoFe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> single crystal, *Low Temp. Phys.* 43 (5) (2017) 610–616.
- [17] M.N. Popova, E.P. Chukalina, T.N. Stanislavchuk, B.Z. Malkin, A.R. Zakirov, E. Antic-Fidancev, E.A. Popova, L.N. Bezmaternykh, V.L. Temerov, Optical spectra, crystal-field parameters, and magnetic susceptibility of multiferroic NdFe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>, *Phys. Rev. B* 75 (2007) 224435 (12 pages).
- [18] I. Couwenberg, K. Binnemans, H. De Leebeeck, C. Görller-Walrand, Spectroscopic properties of the trivalent terbium ion in the huntite matrix TbAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>, *J. Alloys Compd.* 274 (1998) 157-163.
- [19] Y. Hinatsu, Y. Doi, K. Ito, M. Wakeshima, A. Alemi, Magnetic and calorimetric studies on rare-earth iron borates LnFe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> (Ln=Y, La–Nd, Sm–Ho), *J. Solid State Chem.* 172 (2003) 438-445.
- [20] D.A. Erofeev, E.P. Chukalina, L.N. Bezmaternykh, I.A. Gudim, M.N. Popova, High-resolution spectroscopy of HoFe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> crystal: a study of phase transitions, *Optics and Spectroscopy* 120 (4) (2016) 558-565.
- [21] G.P. Vorob'ev, Yu.F. Popov, A.M. Kadomtseva, E.V. Kuvardin, A.A. Mukhin, V.Yu. Ivanov, L.N. Bezmaternykh, I.A. Gudim, V.L. Temerov, Magnetic, magnetoelastic, magnetoelectric and magnetodielectric properties of ferroborate Ho<sub>0.75</sub>Nd<sub>0.25</sub>Fe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>, book of abstracts of III international multidisciplinary symposium "Media with structural and magnetic ordering" (Multiferroics-3), Rostov-on-Don, Loo, Russia, 2011 (in Russian).
- [22] P. Fischer, V. Pomjakushin, D. Sheptyakov, L. Keller, M. Janoschek, B. Roessli, J. Schefer, G. Petrákovskii, L. Bezmaternikh, V. Temerov, D. Velikanov, Simultaneous antiferromagnetic Fe<sup>3+</sup> and Nd<sup>3+</sup> ordering in NdFe<sub>3</sub>(11BO<sub>3</sub>)<sub>4</sub>, *J. Phys.: Cond. Matter* 18 (2006) 7975-7989.
- [23] I.A. Gudim, E.V. Eremin, V.L. Temerov, Flux growth and spin reorientation in trigonal Nd<sub>1-x</sub>Dy<sub>x</sub>Fe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> single crystals, *Journal of Crystal Growth* 312 (2010) 2427–2430.
- [24] A.V. Malakhovskii, A.L. Sukhachev, A.D. Vasil'ev, A.A. Leont'ev, A.V. Kartashev, V.L. Temerov, I.A. Gudim, Nature of optical properties of GdFe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> and GdFe<sub>2.1</sub>Ga<sub>0.9</sub>(BO<sub>3</sub>)<sub>4</sub> crystals and other 3d<sup>5</sup> antiferromagnets, *Eur. Phys. J. B* 85 (2012) 80 (13 pages).

- [25] W.T. Carnall, P.R. Fields, K. Rajnak, Electronic Energy Levels in the Trivalent Lanthanide Aquo Ions. I. Pr<sup>3+</sup>, Nd<sup>3+</sup>, Pm<sup>3+</sup>, Sm<sup>3+</sup>, Dy<sup>3+</sup>, Ho<sup>3+</sup>, Er<sup>3+</sup>, and Tm<sup>3+</sup>, J. Chem. Phys. 49 (1968) 4424-4442.
- [26] A.A. Kaminskii, Crystalline Lasers: Physical processes and Operating Schemes, CRC Press, New York, London, Tokyo, 1996.
- [27] A.V. Malakhovskii, A.E. Sokolov, V.L. Temerov, L.N. Bezmaternykh, A.L. Sukhachev, V.A. Seregin, S.L. Gnatchenko, I.S. Kachur, V.G. Piryatinskaya, Polarized absorption spectra and spectroscopic parameters of Tm<sup>3+</sup> in the TmAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> single crystal, Phys. Solid State 50 (2008) 1287-1293.
- [28] A.V. Malakhovskii, V.V. Sokolov, A.L. Sukhachev, A.S. Aleksandrovsky, I.A. Gudim, M.S. Molokeev, Spectroscopic properties and structure of the ErFe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> single crystal, Physics of the Solid State 56 (2014) 2056-2063.
- [29] I.I. Sobel'man, Introduction to the Theory of Atomic Spectra, Pergamon Press, Oxford, 1972.
- [30] B.R. Judd, Optical absorption intensities of rare-earth ions, Phys. Rev. 127 (1962) 750-761.
- [31] G.S. Ofelt, Intensities of crystal spectra of rare-earth ions, J. Chem. Phys. 37 (1962) 511-520.
- [32] R.D. Peacock, The intensities of lanthanide  $f \leftrightarrow f$  transitions, Structure and Bonding 22 (1975) 83-122.
- [33] W.F. Krupke, Radiative transition probabilities within the 4f<sup>3</sup> ground configuration of Nd: YAG, IEEE J. Quant. Electron. 7 (4) (1971) 153-159.
- [34] G. Dominiak-Dzik, S. Golab, J. Zawadzka, W. Ryba-Romanowski, T. Lukasiewicz, M. Swirkowicz, Spectroscopic properties of holmium doped LiTaO<sub>3</sub> crystals, J. Phys.: Condens. Matter 10 (1998) 10291-10306.
- [35] M.R. Reddy, S.B. Raju, N. Veeraiiah, Optical absorption and fluorescence spectral studies of Ho<sup>3+</sup> ions in PbO–Al<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub> glass system, J. Phys. Chem. Solids 61 (10) (2000) 1567- 1571.
- [36] M. J. Weber, B. H. Matsinger, V. L. Donlan, G. T. Surratt, Optical transition probabilities for trivalent holmium in LaF<sub>3</sub> and YAlO<sub>3</sub>, J. Chem. Phys. 57 (1) (1972) 562-567.
- [37] D. Jaque, J. Capmany, Z.D. Luo, J. Garcia Sole, Optical bands and energy levels of Nd<sup>3+</sup> ion in the YAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> nonlinear laser crystal, J. Phys.: Condens. Matter 9 (1997) 9715-9729.
- [38] A.A. Kaminskii, L. Li, Analysis of spectral line intensities of TR<sup>3+</sup> ions in disordered crystal systems, Phys. Stat. Sol. (A) 26 (1974) K21-K26.

[39] M.J. Weber, T.E. Varitimos, Optical spectra and intensities of Nd<sup>3+</sup> in YAlO<sub>3</sub>, J. Appl. Phys. 42 (11) (1971) 4996-5005.



## Figure captions

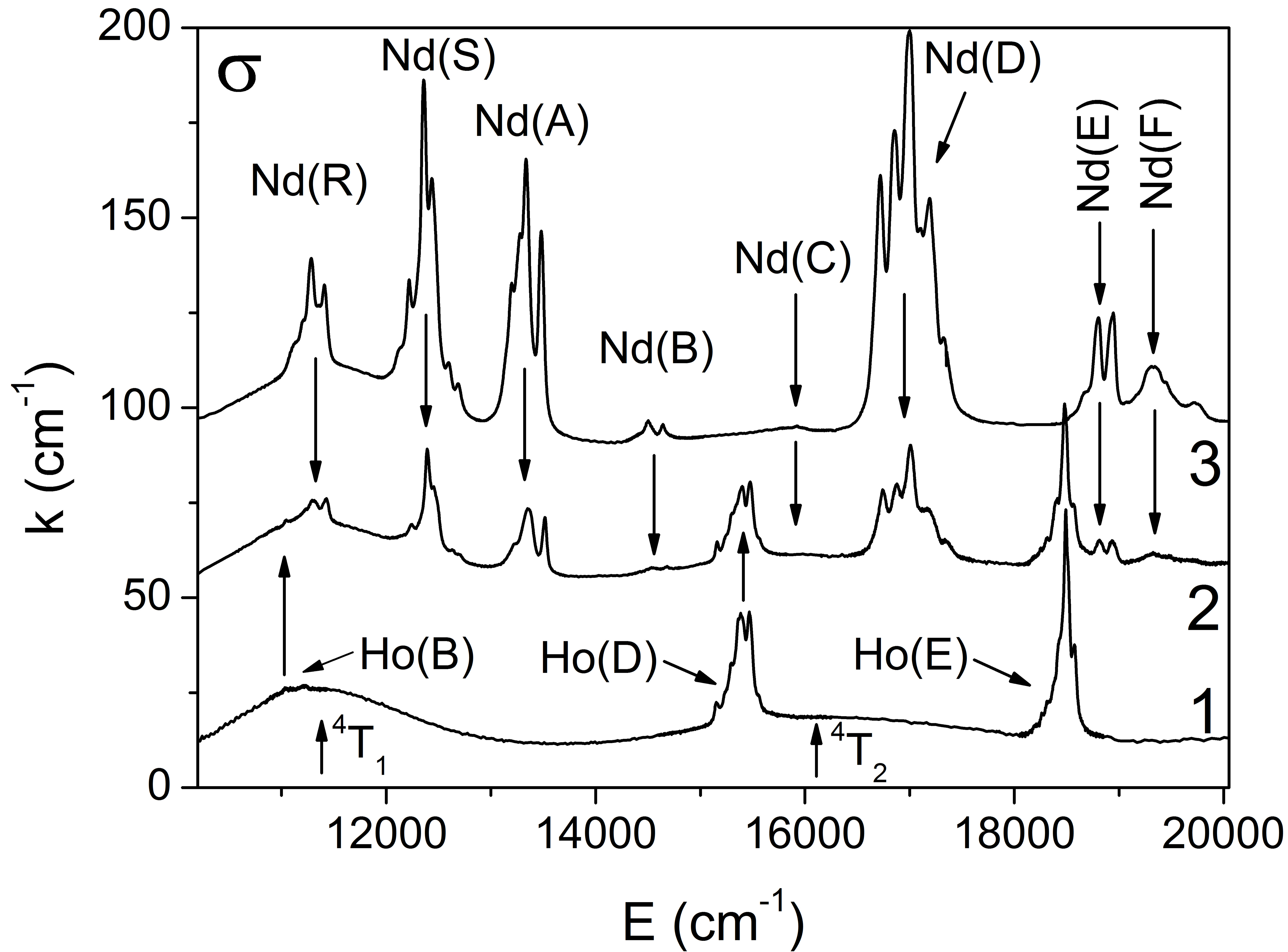
Fig.1. Absorption spectra in  $\sigma$ -polarization of the  $\text{HoFe}_3(\text{BO}_3)_4$  (1),  $\text{Ho}_{0.75}\text{Nd}_{0.25}\text{Fe}_3(\text{BO}_3)_4$  (2) and  $\text{NdFe}_3(\text{BO}_3)_4$  (3) single crystals at room temperature.

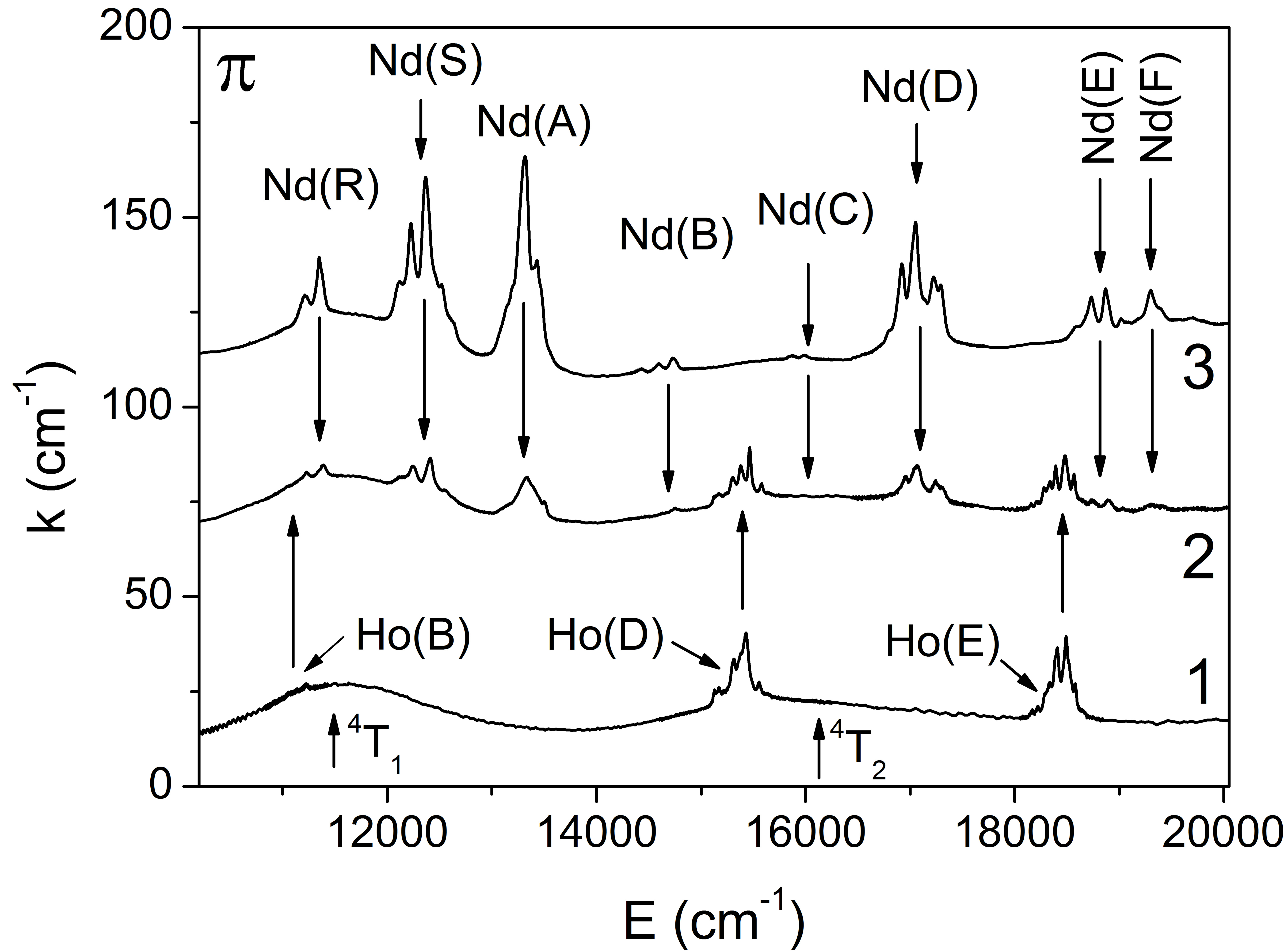
Fig.2. Absorption spectra in  $\pi$ -polarization of the  $\text{HoFe}_3(\text{BO}_3)_4$  (1),  $\text{Ho}_{0.75}\text{Nd}_{0.25}\text{Fe}_3(\text{BO}_3)_4$  (2) and  $\text{NdFe}_3(\text{BO}_3)_4$  (3) single crystals at room temperature.

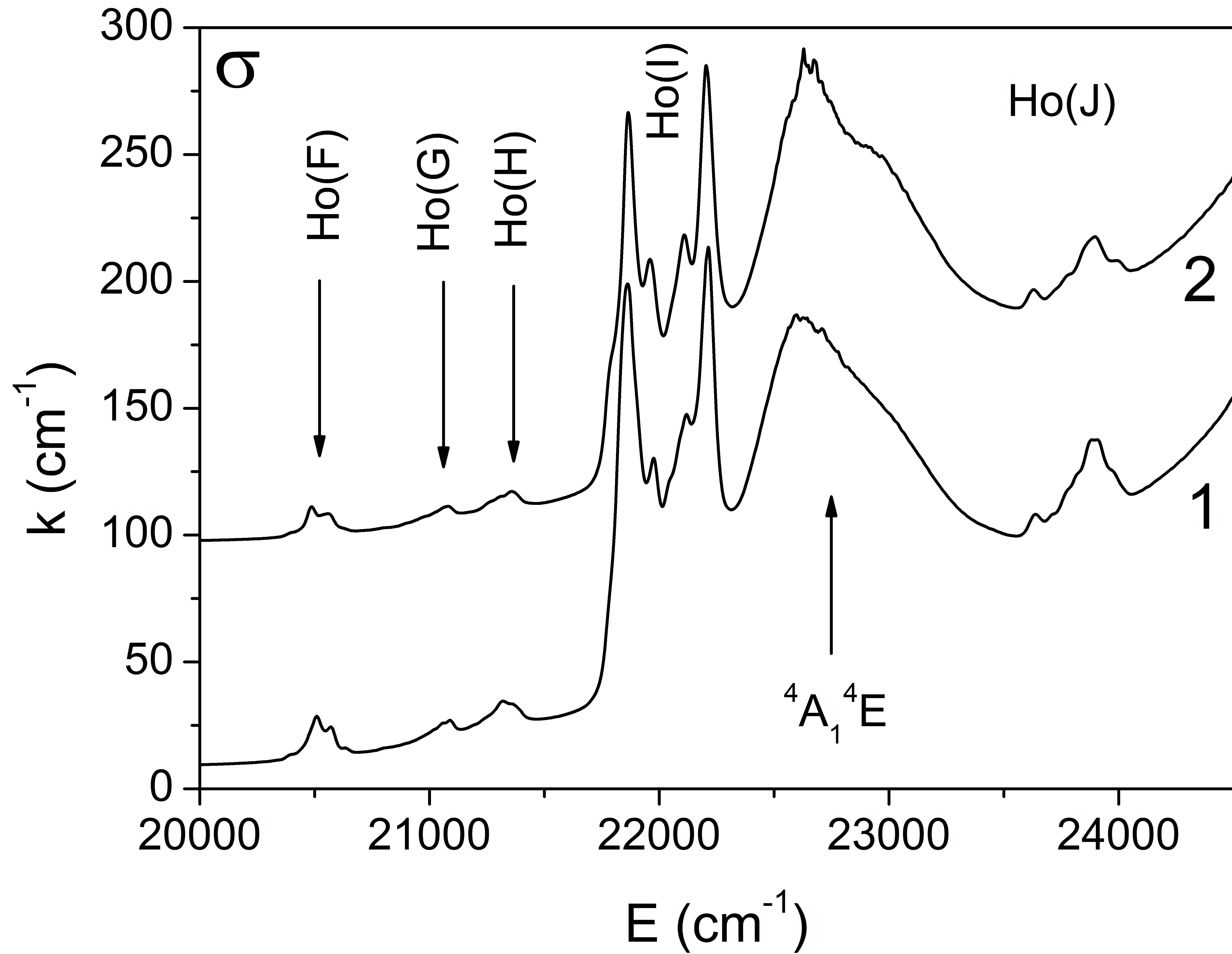
Fig.3. Absorption spectra in  $\sigma$ -polarization of the  $\text{HoFe}_3(\text{BO}_3)_4$  (1) and  $\text{Ho}_{0.75}\text{Nd}_{0.25}\text{Fe}_3(\text{BO}_3)_4$  (2) single crystals at room temperature.

Fig.4. Absorption spectra in  $\pi$ -polarization of the  $\text{HoFe}_3(\text{BO}_3)_4$  (1) and  $\text{Ho}_{0.75}\text{Nd}_{0.25}\text{Fe}_3(\text{BO}_3)_4$  (2) single crystals at room temperature.

Fig.5.  $\sigma$  and  $\pi$  absorption spectra of the  $f$ - $f$  transitions of  $\text{Ho}^{3+}$  ions in  $\text{HoFe}_3(\text{BO}_3)_4$  and  $\text{Ho}_{0.75}\text{Nd}_{0.25}\text{Fe}_3(\text{BO}_3)_4$  crystals.







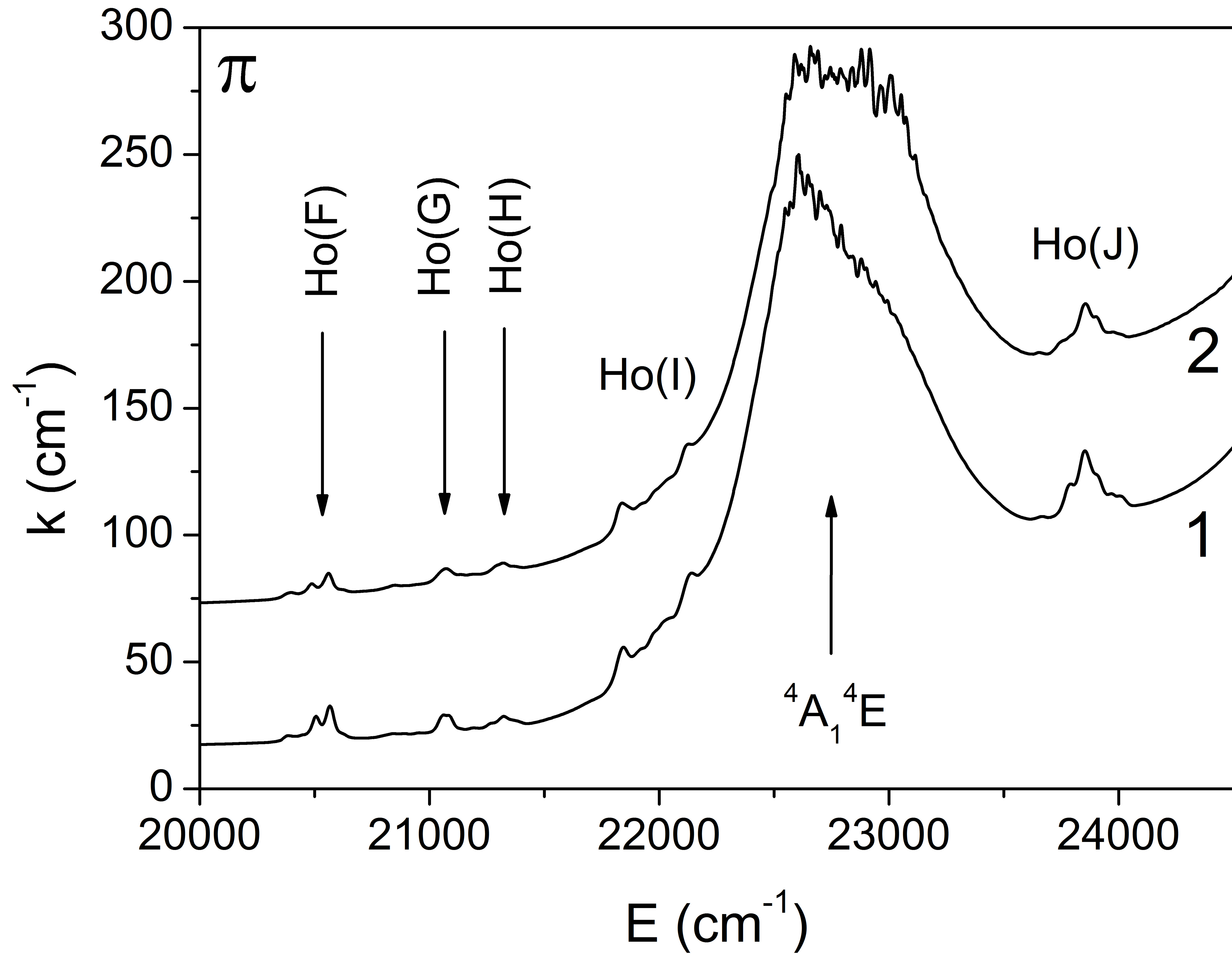
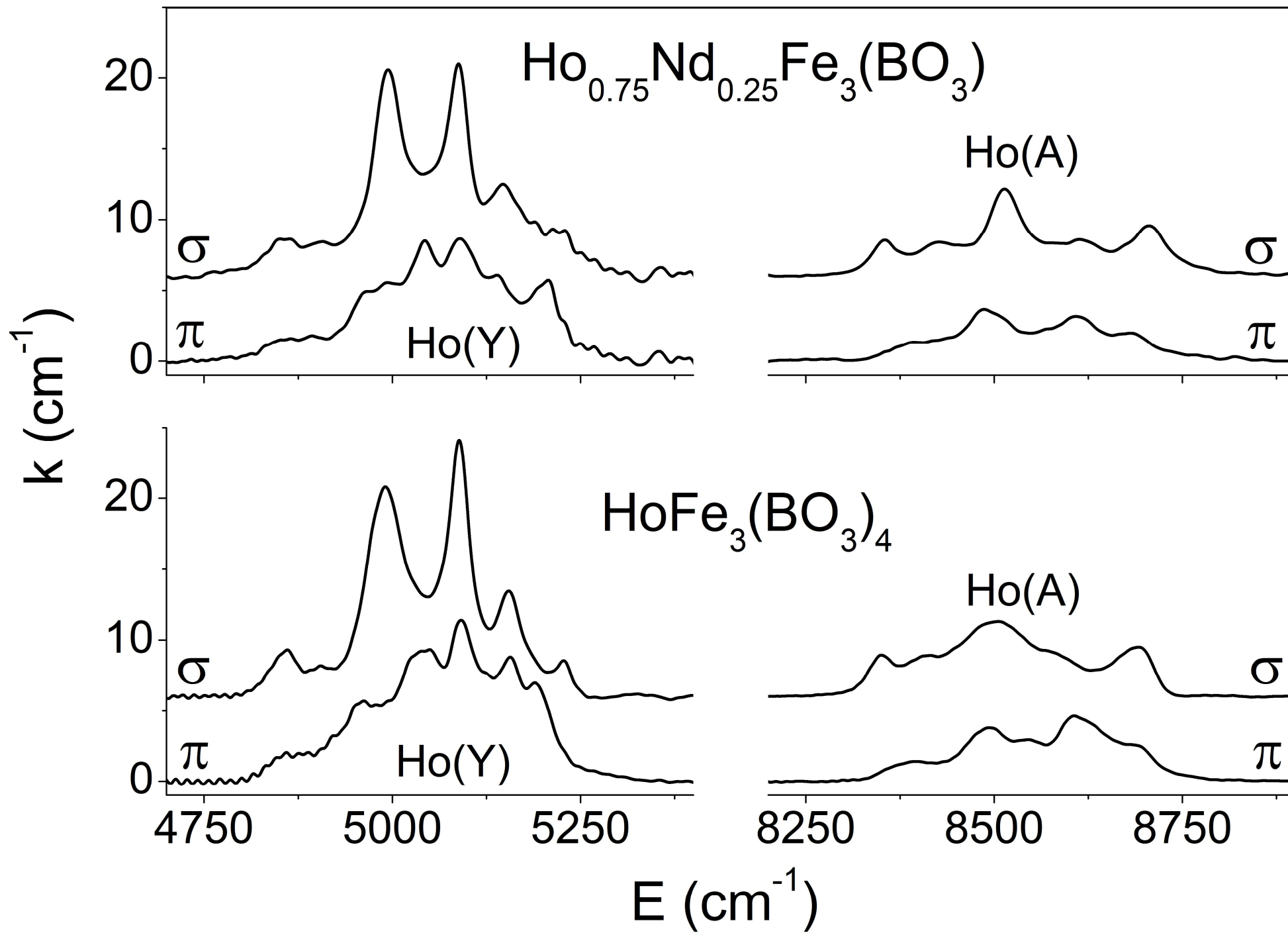


Figure 5



**Table 1**

Crystallization parameters.

Crystal composition	$n$	$p$	$q$	$T_{\text{sat}}$ (°C)
HoFe <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub>	25	3	0.5	960
NdFe <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub>	23.3	3.14	0.54	945
Ho <sub>0.75</sub> Nd <sub>0.25</sub> Fe <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub>	24.5	3	0.6	970

**Table 2**

Parameters of  $f-f$  transitions in  $\text{Ho}^{3+}$  ion in the  $\text{HoFe}_3(\text{BO}_3)_4$  and  $\text{Ho}_{0.75}\text{Nd}_{0.25}\text{Fe}_3(\text{BO}_3)_4$  single crystals at room temperature: average wave numbers  $k_{IF}$ , integrated intensities  $I_\pi$  and  $I_\sigma$ , dichroism  $I_\sigma / I_\pi$ .

Label	$^5I_8 \downarrow$	$k_{IF}$ ( $\text{cm}^{-1}$ )	$\text{HoFe}_3(\text{BO}_3)_4$		$I_\sigma / I_\pi$	$\text{Ho}_{0.75}\text{Nd}_{0.25}\text{Fe}_3(\text{BO}_3)_4$		$I_\sigma / I_\pi$
			$I$ ( $\text{cm}^{-2} \text{mol}^{-1} \text{l}$ )			$I$ ( $\text{cm}^{-2} \text{mol}^{-1} \text{l}$ )		
			$\pi$	$\sigma$		$\pi$	$\sigma$	
Y	$^5I_7$	5050	289.8	310.7	1.07	314	401.4	1.28
A	$^5I_6$	8550	121.5	154	1.27	134.9	189.5	1.41
B	$^5I_5$	11125	48.2	49.4	1.02	46.3	83.1	1.79
D	$^5F_5$	15375	514.5	889.1	1.73	378.3	781.8	2.07
E	$^5S_2 + ^5F_4$	18450	539.8	1052	1.95	535.9	1063.8	1.99
F	$^5F_3$	20500	172.7	234.8	1.36	154.4	223	1.44
G	$^5F_2$	21000	90.7	131.9	1.45	84.9	133	1.57
H	$^3K_8$	21300	62.5	216.7	3.47	63.5	186	2.93
I	$^5G_6 + ^5F_1$	22000	558.1	5423.3	9.72	639.5	6394.7	10
J	$^5G_5$	23850	681.9	904.4	1.33	533.9	1000.2	1.87
		$\Sigma I_\sigma / \Sigma I_\pi$ (without I-band)			1.56			1.81



**Table 3**

Parameters of  $f-f$  transitions in  $\text{Nd}^{3+}$  ion in the  $\text{NdFe}_3(\text{BO}_3)_4$  and  $\text{Ho}_{0.75}\text{Nd}_{0.25}\text{Fe}_3(\text{BO}_3)_4$  single crystals at room temperature: average wave numbers  $k_{IF}$ , integrated intensities  $I_\pi$  and  $I_\sigma$ , dichroism  $I_\sigma / I_\pi$ .

Label	$^4I_{9/2} \downarrow$	$k_{IF}$ ( $\text{cm}^{-1}$ )	$\text{NdFe}_3(\text{BO}_3)_4$			$\text{Ho}_{0.75}\text{Nd}_{0.25}\text{Fe}_3(\text{BO}_3)_4$			
			$I$ ( $\text{cm}^{-2} \text{mol}^{-1} \text{l}$ )		$I_\sigma / I_\pi$	$I$ ( $\text{cm}^{-2} \text{mol}^{-1} \text{l}$ )		$I_\sigma / I_\pi$	
			$\pi$	$\sigma$		$\pi$	$\sigma$		
R	$^4F_{3/2}$	11350	282.9	756.4	2.67	167.5	483.6	2.89	
S	$^2H_{9/2} + ^4F_{5/2}$	12400	1216.1	2076.1	1.71	1250.6	2336.6	1.87	
A	$^4S_{3/2} + ^4F_{7/2}$	13350	1557.2	2138.7	1.37	1247.2	1995.4	1.6	
B	$^4F_{9/2}$	14600	104.6	122.1	1.17	68.5	110.3	1.61	
C	$^2H_{11/2}$	16000	17.6	32.8	1.86	12.4	8	0.64	
D	$^2G_{7/2} + ^4G_{5/2}$	17000	1340.1	5567.5	4.15	1280.2	4838.9	3.78	
E	$^2K_{13/2} + ^4G_{7/2}$	18900	383.1	884.9	2.31	405.6	694.3	1.71	
F	$^4G_{9/2}$	19400	364	757.3	2.08	406.2	589.7	1.45	
		$\Sigma I_\sigma / \Sigma I_\pi$ (without D-band)				1.72			1.75

**Table 4**

Coefficients  $\Gamma_{\lambda}^2(I, F)$  [25], oscillator strengths  $f_{IF}$ , experimental and calculated transition strengths  $s_{IF}$  of  $\text{Ho}^{3+}$  ions in the  $\text{HoFe}_3(\text{BO}_3)_4$  and  $\text{Ho}_{0.75}\text{Nd}_{0.25}\text{Fe}_3(\text{BO}_3)_4$  single crystals.

Label	$^5I_8 \downarrow$	$\Gamma_2^2$	$\Gamma_4^2$	$\Gamma_6^2$	$\text{HoFe}_3(\text{BO}_3)_4$			$\text{Ho}_{0.75}\text{Nd}_{0.25}\text{Fe}_3(\text{BO}_3)_4$		
					$f_{IF}$ ( $10^{-7}$ )	$s_{IF}$ ( $10^{-20} \text{ cm}^2$ )		$f_{IF}$ ( $10^{-7}$ )	$s_{IF}$ ( $10^{-20} \text{ cm}^2$ )	
						exp.	calc.		exp.	calc.
Y	$^5I_7$	0.0250	0.1344	1.5216	13.11	4.07	3.954	16.07	4.988	4.505
A	$^5I_6$	0.0084	0.0386	0.6921	6.18	1.133	1.677	7.4	1.356	1.937
B	$^5I_5$	0	0.0100	0.0936	2.12	0.298	0.261	3.06	0.431	0.247
D	$^5F_5$	0	0.4250	0.5687	33	3.364	3.25	27.95	2.849	3.072
E	$^5S_{2+}$	0	0	0.2268	38.05	3.232	3.243	38.33	3.256	3.068
	$^5F_4$	0	0.2392	0.7071						
F	$^5F_3$	0	0	0.3460	9.24	0.707	0.797	8.64	0.661	0.755
G	$^5F_2$	0	0	0.1921	5.1	0.381	0.442	5.05	0.377	0.419
H	$^3K_8$	0.0208	0.0334	0.1578	7.14	0.525	0.619	6.27	0.461	0.623
I	$^5G_{6+}$	1.5201	0.8410	0.1411	164.15	11.694	11.693	193.29	13.769	13.767
	$^5F_1$	0	0	0						
J	$^5G_5$	0	0.5338	0.0002	35.85	2.356	2.438	36.48	2.397	2.3

**Table 5**

Coefficients  $\Gamma_{\lambda}^2(I, F)$  [26], oscillator strengths  $f_{IF}$ , experimental and calculated transition strengths  $s_{IF}$  of  $\text{Nd}^{3+}$  ions in the  $\text{NdFe}_3(\text{BO}_3)_4$  and  $\text{Ho}_{0.75}\text{Nd}_{0.25}\text{Fe}_3(\text{BO}_3)_4$  single crystals.

Label	${}^4I_{9/2} \downarrow$	$\Gamma_2^2$	$\Gamma_4^2$	$\Gamma_6^2$	$\text{NdFe}_3(\text{BO}_3)_4$		$\text{Ho}_{0.75}\text{Nd}_{0.25}\text{Fe}_3(\text{BO}_3)_4$		
					$f_{IF}$ ( $10^{-7}$ )	$s_{IF}$ ( $10^{-20} \text{ cm}^2$ ) exp. calc.	$f_{IF}$ ( $10^{-7}$ )	$s_{IF}$ ( $10^{-20} \text{ cm}^2$ ) exp. calc.	
R	${}^4F_{3/2}$	0	0.2293	0.0548	25.85	2.994 2.385	16.33	1.327	1.743
S	${}^2H_{9/2+}$	0.0092	0.0080	0.1155	77.27	5.745 6.106	85.26	6.339	5.628
	${}^4F_{5/2}$	0.0010	0.2371	0.3972					
A	${}^4S_{3/2+}$	0	0.0027	0.2352	83.98	5.799 5.495	75.39	5.206	5.659
	${}^4F_{7/2}$	0.0010	0.0423	0.4246					
B	${}^4F_{9/2}$	0.0009	0.0092	0.0417	5.02	0.317 0.405	4.16	0.263	0.397
C	${}^2H_{11/2}$	0.0001	0.0027	0.0104	1.2	0.069 0.104	0.41	0.024	0.101
D	${}^2G_{7/2+}$	0.0757	0.1848	0.0314	179.56	9.737 9.687	157.72	8.553	8.522
	${}^4G_{5/2}$	0.8979	0.4093	0.0359					
E	${}^2K_{13/2+}$	0.0069	0.0002	0.0312	30.99	1.512 2.274	25.83	1.26	1.89
	${}^4G_{7/2}$	0.0550	0.1571	0.0553					
F	${}^4G_{9/2}$	0.0046	0.0609	0.0406	27.04	1.285 0.854	22.82	1.085	0.698

**Table 6**Judd–Ofelt parameters  $\Omega_2$  ( $10^{-20}$  cm<sup>2</sup>) of the Ho<sup>3+</sup> ions in different compounds.

Compound	$\Omega_2$	$\Omega_4$	$\Omega_6$
HoFe <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub> [This work]	4.874	4.74	2.1
Ho <sub>0.75</sub> Nd <sub>0.25</sub> Fe <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub> [This work]	6.557	4.106	2.49
Ho: PbO–Bi <sub>2</sub> O <sub>3</sub> –Ga <sub>2</sub> O <sub>3</sub> [4]	6.81	2.31	0.67
Ho: Y <sub>3</sub> Al <sub>5</sub> O <sub>12</sub> [5]	0.101	2.086	1.724
Ho: InF <sub>3</sub> –ZnF <sub>2</sub> –SrF <sub>2</sub> [6]	1.37	2.35	2.22
Ho: Li <sub>2</sub> O–K <sub>2</sub> O–BaO–Bi <sub>2</sub> O <sub>3</sub> –TeO <sub>2</sub> [7]	4.37	1.91	1.45
Ho: KGd(WO <sub>4</sub> ) <sub>2</sub> [8]	10.14	3.09	1.99
Ho: KPb <sub>2</sub> Cl <sub>5</sub> [9]	1.30	1.34	1.06
Ho: Y <sub>2</sub> O <sub>3</sub> [10]	1.55	1.44	1.40
Ho: LiTaO <sub>3</sub> [34]	12.6	6.1	4.3
Ho: PbO–Al <sub>2</sub> O <sub>3</sub> –B <sub>2</sub> O <sub>3</sub> [35]	5.83	17.15	26.5
Ho: LaF <sub>3</sub> [36]	1.16	1.38	0.88
Ho: YAlO <sub>3</sub> [36]	1.82	2.38	1.53

**Table 7**Judd–Ofelt parameters  $\Omega_2$  ( $10^{-20}$  cm<sup>2</sup>) of the Nd<sup>3+</sup> ions in different compounds.

Compound	$\Omega_2$	$\Omega_4$	$\Omega_6$
NdFe <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub> [This work]	4.198	8.55	7.738
Nd <sub>0.5</sub> Gd <sub>0.5</sub> Fe <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub> [11]	4.4	8.04	8.25
Nd <sub>0.25</sub> Ho <sub>0.75</sub> Fe <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub> [This work]	4.742	5.646	8.184
NdAl <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub> [12]	4.01	4.58	7.65
NdAl <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub> [13]	6.07	9.14	14.58
Nd: GdAl <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub> [13]	3.35	3.50	4.64
Nd: Gd <sub>0.2</sub> Y <sub>0.8</sub> Al <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub> [13]	2.71	2.68	5.22
NdAl <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub> : Yb 3% [14]	1.31	2.87	5.77
NdAl <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub> : Yb 6% [14]	0.387	3.65	3.11
Nd: Y <sub>2</sub> O <sub>3</sub> [15]	10.97	5.68	5.37
Nd: Y <sub>3</sub> Al <sub>5</sub> O <sub>12</sub> [33]	0.2	2.7	5
Nd: YAl <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub> [37]	3.09	5.04	3.11
Nd: Y <sub>3</sub> Al <sub>5</sub> O <sub>12</sub> [38]	0.37	2.29	5.97
Nd: YAlO <sub>3</sub> [39]	1.3	4.7	5.7