

Spectroscopic properties of Nd³⁺ in orthorhombic δ -BiB₃O₆ crystal

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ABSTRACT

Absorption spectra of the Nd³⁺ ions in an orthorhombic δ -BiB₃O₆ single crystal were measured in the spectral range 11,000–20,500 cm⁻¹. The f–f transition intensities were analyzed in terms of the Judd–Ofelt theory, and the following parameters of the theory were obtained: $\Omega_2 = 6.35 \times 10^{-20}$ cm², $\Omega_4 = 4.86 \times 10^{-20}$ cm², and $\Omega_6 = 11.233 \times 10^{-20}$ cm². The strengths, spontaneous emission probabilities, branching ratios, spectroscopic quality factor and excited state radiative lifetime were calculated for laser transitions from the ⁴F_{3/2} state to ⁴I_J manifold. Spectroscopic properties of Nd³⁺: δ -BiB₃O₆ crystal favor lasing at 1.3 μ m, where this crystal possesses near non-critical phase matching for second harmonic generation.

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1. Introduction

Monoclinic bismuth triborate α -BiB₃O₆ (α -BiBO) is very promising nonlinear crystal (see, e.g. [1] and references therein). The studies of isovalent doping of monoclinic bismuth triborate with rare earths were done in order to obtain new laser materials for diode pumped lasers, but these studies revealed limited extent of doping that is insufficient for laser purposes [2,3]. Later, new polymorph of bismuth triborate, orthorhombic δ -BiB₃O₆ (δ -BiBO) was discovered [4,5]. Despite denser packing of its crystal structure, it was found that much larger concentration of Nd³⁺ ions could be obtained in δ -BiBO [6]. Local environment of neodymium ions in δ -BiBO is rather unique and is characterized by strong asymmetry. On the other hand, nonlinear coefficients of δ -BiBO are found to be rather high [7]. Therefore, investigation of spectroscopic parameters, such as intensity parameters, radiative transition probabilities and branching ratios, is of importance both from academic and practical interest, the latter being due to possibility of using Nd³⁺: δ -BiBO crystal as self-doubling lasing medium.

In the present paper we study the absorption spectra of the Nd³⁺: δ -BiBO single crystal and analyze them using Judd–Ofelt theory.

2. Experimental details

Single crystal of Nd³⁺: δ -BiBO was obtained via Czochralski growth as described in [6]. Concentration of Nd³⁺ ions in the melt

was 5 at.% with respect to Bi³⁺ ions. δ -BiBO crystal belongs to point symmetry class *mm2* and space symmetry group *Pca2*₁. The lattice constants of δ -BiBO crystals are: $a = 18.4557$ Å, $b = 4.451$ Å, and $c = 4.2806$ Å. Crystal structure of δ -BiBO is presented in Fig. 1. Evidently, Nd³⁺ ions substituting bismuth ions will experience the action of rather asymmetric crystal field. For complete characterization of orthorhombic crystals, three components of absorption coefficient must be measured, with the light electric field vector parallel to *a*, *b* and *c* crystallographic axes. Presently we were able to manufacture the Nd³⁺: δ -BiBO sample that allowed the absorption measurements with the light propagation direction along *a* axis for two directions of light electric vector, namely, along *b* and *c* axes. The absorption spectra were measured by the two-beam technique using an automated spectrophotometer, designed on the bases of LOMO MDR-2 monochromator. Measurements were done at room temperature. The spectral resolution was approximately equal to 10 cm⁻¹.

3. Results and discussion

Absorption spectra of the Nd³⁺: δ -BiBO crystal for $\vec{E}||b$ and $\vec{E}||c$ polarizations are shown in Fig. 2. They consist of narrow bands corresponding to f–f transitions in Nd³⁺ ions. Intensities of the transitions I_{if} are found from these spectra using $I_{if} = \int \frac{K(k)}{C} dk$, where $K(k)$ is the decimal absorption coefficient, k is the wavenumber, C is the molar concentration, i and f denote initial and final states of a transition, and integration is done over the area of corresponding f–f transition. There is no drastic difference between absorption spectra measured for different polarizations (Fig. 2). On the other hand, examining the crystal structure, one can expect that the third component of absorption should not drastically differ from the

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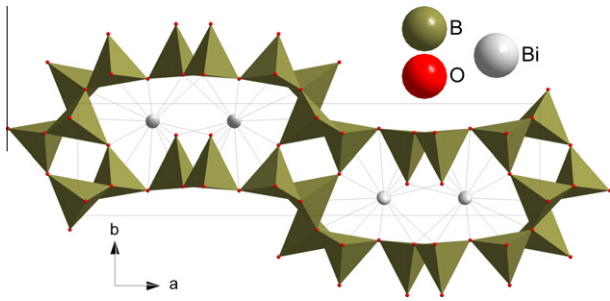


Fig. 1. Crystal structure of δ -BiBO viewed in the direction of c axis. Nd^{3+} ions are expected to substitute for Bi^{3+} ions.

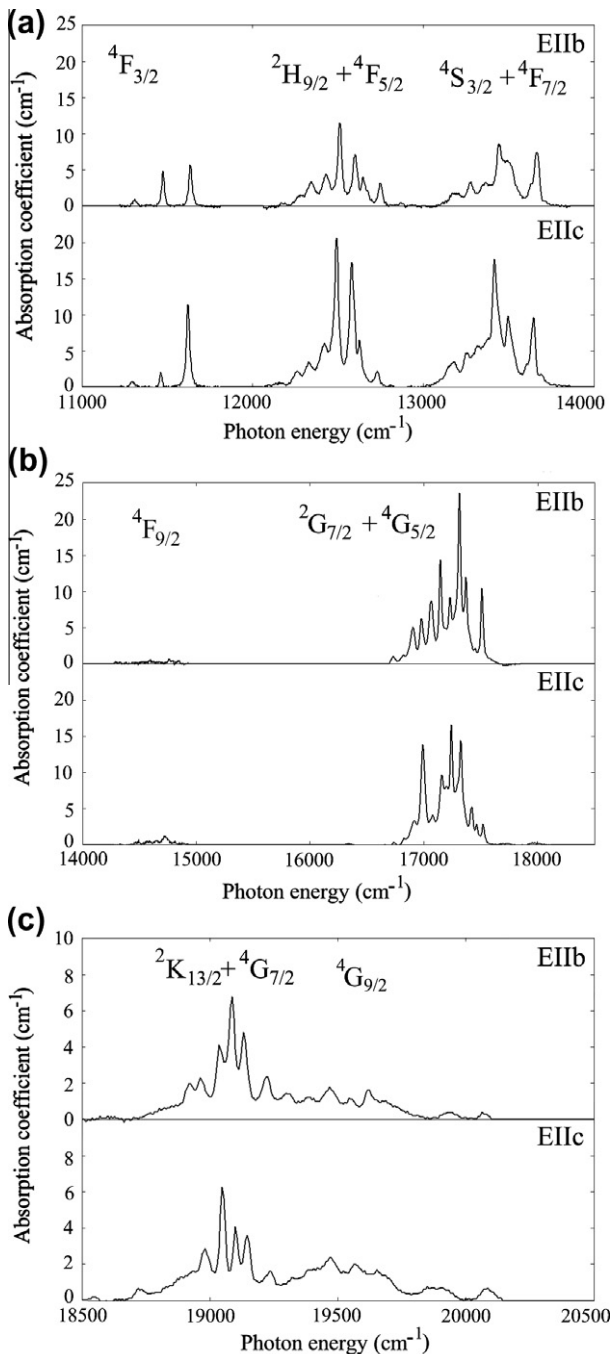


Fig. 2. Polarized absorption spectra of f–f transitions in $\text{Nd}^{3+}:\delta\text{-BiBO}$ single crystal at room temperature.

measured ones, too. Therefore, averaging of the transition intensities in the first approximation can be done in the following way:

$$I_{IF} = \frac{I_b + I_c}{2}. \quad (1)$$

Following Ref. [8], oscillator strengths of transitions $I \rightarrow F$ between initial and final J multiplets are calculated by the formula:

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

Wavelength-dependent values of refractive indices for the central wavelengths of every absorption band were calculated via Sellmeier law with the coefficients taken from [7]. The transition strength is defined as: $s_{IF} = \frac{1}{e^2} \sum_{if} |\bar{D}_{if}|^2$, where $i \in I, f \in F$. The transition strength and the oscillator strength are related by the expression [9]

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

where g_i is the degree of degeneracy of the initial state, m the mass of electron, and k_{IF} is the average wave number of the absorption band. Experimentally found strengths of the f–f transitions are given in Table 1. Strengths of the transitions in $\text{Nd}^{3+}:\delta\text{-BiBO}$ are compared with those in other laser matrices in Table 2. On the average, they are of order of two times larger than, for instance, in neodymium-doped huntites of the same doping level, where neodymium ions occupy D_3 sites.

In the framework of the Judd–Ofelt theory, the strength of an f–f transition in an ion in the non-centrosymmetrical crystal field is described by the relationship [13–15]

$$s_{IF} = \sum_{\lambda} \Omega_{\lambda} \Gamma_{\lambda}^2(I, F). \quad (4)$$

Coefficients $\Gamma_{\lambda}^2(I, F) = \langle I || U^{(\lambda)} || F \rangle^2$ are calculated theoretically [16] and are considered to be independent of crystal structure. The index λ for the f–f transitions has three values, namely, 2, 4, and 6. Therefore, it is sufficient to find experimentally the strengths of any three transitions in order to determine three parameters Ω_{λ} and to calculate the strengths of all the other transitions. The transitions under consideration in a free Nd^{3+} ion are forbidden 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 [15], when transitions are allowed by the parity selection rule due to the odd components of the crystal field, they can occur at $\Delta J \leq \lambda$. Therefore, within this approximation, all considered f–f transitions in the Nd^{3+} ion are allowed.

Eq. (3) can be written in the vector form:

$$s = A\Omega. \quad (5)$$

Here s is a q -dimensional vector consisting of the measured strengths of the transition groups; q the number of the considered groups of transitions; Ω the three-dimensional vector of parameters Ω_{λ} ; A is the $3 \times q$ -dimensional matrix of coefficients $\Gamma_{\lambda}^2(I, F)$. The vector Ω that minimizes the sum of the squares of the deviations between the measured and theoretical transition strengths is given by the matrix equation [12].

$$\Omega = (A^T A)^{-1} A^T s, \quad (6)$$

where A^T is the transposed matrix. We used five the most intensive groups of transitions: R, S, A, D, (E + F), defined in Table 2, and obtained parameters Ω_{λ} shown in Table 3. Judd–Ofelt parameters of some neodymium containing crystals are also given in Table 3. The relative root mean square error of the theoretical description of the transition strengths is defined by equation

Table 1

Parameters of f–f transitions in Nd³⁺ ion in the Nd³⁺:δ-BiBO single crystal at room temperature: average wave numbers k_{IF} , integrated intensities I_{IF} , oscillator strengths f_{IF} , transition strengths s_{IF} .

Transition $^4I_{9/2} \downarrow$	k_{IF} (cm ⁻¹)	I_{IF} (cm ⁻² mol ⁻¹ l)		f_{IF} (10 ⁻⁷)	s_{IF} (10 ⁻²⁰ cm ²)	
		σ	π		Measured	Calculated
$^4F_{3/2}$	11,451	316	416	15.6	1.26	1.529
$^2H_{9/2} + ^4F_{5/2}$	12,472	1658	2733	93.53	6.935	6.925
$^4S_{3/2} + ^4F_{7/2}$	13,587	1950	3315	112.0	7.635	7.768
$^4F_{9/2}$	14,641	113	184	6.325	0.399	0.522
$^2G_{7/2} + ^4G_{5/2}$	17,456	4466	4090	181.5	9.758	9.819
$^4G_{7/2} + ^4G_{9/2} + ^2K_{13/2}$	19,334	2061	2575	76.9	3.684	2.775
$^4D_{3/2} + ^4D_{5/2} + ^2I_{11/2} + ^4D_{7/2}$	28,236	2597	1036	75.64	2.463	2.645

Table 2

Measured strengths (10⁻²⁰ cm²) of f–f transitions in crystals: Nd_{0.5}Gd_{0.5}Fe₃(BO₃)₄ (NGFB), NdAl₃(BO₃)₄ (NAB), Nd:GdAl₃(BO₃)₄ (NGAB) and Nd:Gd_{0.2}Y_{0.8}Al₃(BO₃)₄ (NGYAB).

Symbol	Transition $^4I_{9/2} \downarrow$	NGFB 50% [10]	NAB 100% [11] (C ₂)	NGAB 2.95% [11] (D ₃)	NGYAB 4% [11] (D ₃)	YAG 0.76% [12]	Nd:δ-BiBO this work
R	$^4F_{3/2}$	1.95	3.27	0.99	0.85	0.71	1.26
S	$^2H_{9/2} + ^4F_{5/2}$	6.01	10.53	3.22	3.46	3.5	6.935
A	$^4S_{3/2} + ^4F_{7/2}$	5.9	9.35	3.24	3.43	3.3	7.635
B	$^4F_{9/2}$	0.35	0.91	–	0.19	0.27	0.399
C	$^2H_{11/2}$	0.37	0.38	–	–	0.074	–
D	$^2G_{7/2} + ^4G_{5/2}$	9.56	12.30	5.64	4.56	2.17	9.758
E + F	$^4G_{7/2} + ^4G_{9/2} + ^2K_{13/2}$	3.87	4.45	1.69	1.85	1.27	3.684

$$\delta = \left[\frac{q \sum \Delta s^2}{(q-p) \sum s^2} \right]^{1/2} \quad (7)$$

Here s is the measured transition strengths, Δs the difference between the measured and calculated transition strengths, p is the number of the determined parameters, which is equal to three in our case. With the help of (7) and Table 1 we obtain $\delta = 8.4\%$ for Nd:δ-BiB₃O₆. Comparison with other crystals analyzed with Judd–Ofelt method shows that, despite absence of measured $\vec{E}||a$ spectrum, the deviation of experimental and calculated values for Nd:δ-BiB₃O₆ is better or of the same order like in other cases (for example [12]).

Using Eq. (4) and known Ω_λ parameters, the strengths of the laser transitions from the $^4F_{3/2}$ state are determined (Table 4). Coefficients I_λ^2 were taken from Ref. [23]. Probability of a spontaneous dipole transition between degenerate levels in a condensed matter is given by the relationship [21]

$$A_{IF} = \frac{64\pi^4 e^2 k_{IF}^3 n(k_{IF})}{3hg_i} S_{IF} \quad (8)$$

Here g_i the degree of degeneracy of the initial level, k_{IF} the average values of transition wavenumbers, and $n(k_{IF})$ is the refractive index at the transition frequency (calculated according to data from [7]). Values of k_{IF} for transitions between excited states used in (8) were obtained from separate luminescence experiment done with powder sample of Nd:δ-BiB₃O₆ at room temperature using excitation

Table 3

Intensity parameters Ω_λ (10⁻²⁰ cm²), spectroscopic quality factors $X = \Omega_4/\Omega_6$ and lifetimes τ of the $^4F_{3/2}$ state in different crystals.

Compound	Ω_2	Ω_4	Ω_6	$X = \Omega_4/\Omega_6$	τ (μs)
δ-BiB ₃ O ₆ :Nd	6.898	3.921	11.495	0.341	517
Nd _{0.5} Gd _{0.5} Fe ₃ (BO ₃) ₄ [10]	4.4	8.04	8.25	0.97	496
NdAl ₃ (BO ₃) ₄ [18]	4.01	4.58	7.65	0.6	188
NdAl ₃ (BO ₃) ₄ [11]	6.07	9.14	14.58	0.627	98
Nd:YAl ₃ (BO ₃) ₄ [17]	3.09	5.04	3.11	1.62	302
Nd:GdAl ₃ (BO ₃) ₄ [11]	3.35	3.50	4.64	0.754	285
Nd:Gd _{0.2} Y _{0.8} Al ₃ (BO ₃) ₄ [11]	2.71	2.68	5.22	0.51	294
Nd:Y ₃ Al ₅ O ₁₂ [19]	0.37	2.29	5.97	0.384	261
Nd:Y ₃ Al ₅ O ₁₂ [12]	0.2	2.7	5	0.54	259
Nd:YAlO ₃ [20]	1.3	4.7	5.7	0.82	157

Table 4

Parameters of laser transitions from the $^4F_{3/2}$ state in the 5 at.% Nd:δ-BiB₃O₆ single crystal at room temperature: average wave numbers k_{IF} , parameters I_λ^2 in Eq. (4), calculated transition strengths s_{IF} , transition probabilities A , branching ratios β and life time τ .

Final level	k_{IF} (cm ⁻¹)	I_2^2	I_4^2	I_6^2	s_{IF} (10 ⁻²⁰ cm ²)	A (s ⁻¹)	β (%)	τ (μs)
$^4I_{15/2}$	5282	0	0	0.028	0.322	12.269	0.63	517
$^4I_{13/2}$	7353	0	0	0.212	2.437	250.601	13.0	
$^4I_{11/2}$	9381	0	0.142	0.407	5.235	1118	57.8	
$^4I_{9/2}$	11,136	0	0.230	0.056	1.546	552.137	28.6	

at 800 nm. The possibility of generating of stimulated emission for a specific emission channel depends on the multiplet luminescence branching ratio

$$\beta_{IF} = A_{IF} / \sum_F A_{IF} = A_{IF} \tau_I, \quad (9)$$

where τ_I is the excited state life time. The calculated values of the transition strengths, the spontaneous emission probabilities, the branching ratios and the state $^4F_{3/2}$ lifetime are presented in Table 4. From this table it is seen, that coefficients I_2^2 for radiative transitions from the $^4F_{3/2}$ state are equal to zero, and, consequently, probabilities of these transitions depend only on Ω_4 and Ω_6 . Therefore, the spectroscopic quality factor $X = \Omega_4/\Omega_6$ was introduced for characterization of the considered transitions [22,23]. Values of this factor and life times of the $^4F_{3/2}$ state in the studied crystal and in some other compounds are given in Table 3. The analytical dependencies of the branching ratios on the factor X are given in Refs. [22,23]. Value of X for Nd:δ-BiB₃O₆ equals to 0.341, what means that branching ratio for $^4F_{3/2} \rightarrow ^4I_{13/2}$ lasing transition (1.3 μm) in this crystal is closer to its maximal allowed value than in most of the other crystals cited in Table 4, except for slightly more favorable Nd:YAG. In addition, the radiative life time of the $^4F_{3/2}$ state in the studied crystal is larger than in most of aluminoborates and aluminogarnets (Table 3).

4. Summary

The polarized absorption spectra of Nd³⁺:δ-BiB₃O₆ single crystal were measured in the spectral range 11,000–20,500 cm⁻¹. The f–f transitions intensities were analyzed in terms of the Judd–Ofelt

theory, and the following parameters of the theory were obtained: $\Omega_2 = 6.898 \times 10^{-20} \text{ cm}^2$, $\Omega_4 = 3.921 \times 10^{-20} \text{ cm}^2$, and $\Omega_6 = 11.465 \times 10^{-20} \text{ cm}^2$. The strengths, spontaneous emission probabilities, branching ratios, spectroscopic quality factor and excited state lifetime were calculated for laser transitions from the $^4F_{3/2}$ state to 4I_j manifold. Spectroscopic properties of $\text{Nd}^{3+}:\delta\text{-BiB}_3\text{O}_6$ crystal favor lasing at $1.3 \mu\text{m}$, where this crystal possesses near non-critical phase matching.

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