

Calculation of the Electronic Structure, Lattice Dynamics, and Optical and Magnetic Properties of Europium Tetraborate EuB_4O_7

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Abstract—The electronic band structure, lattice vibration frequencies, and optical and magnetic properties of EuB_4O_7 crystal with α - SrB_4O_7 -type structure are calculated within the density functional method. It is found that this compound is a dielectric with a band gap of the order of 4 eV. It is found that the ground state of this crystal is the state with ferromagnetic ordering of Eu^{2+} spins. Exchange interaction constants are calculated; the ferromagnetic ordering temperature is estimated within the molecular field approximation ($T_c \approx 1$ K). The EuB_4O_7 compound is a magnetic pyroelectric and, hence, can exhibit magnetoelectric properties. The calculated polarization change during ferromagnetic ordering of this crystal is $3973 \mu\text{C}/\text{m}^2$.

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1. INTRODUCTION

Tetraborate compounds with the general chemical formula AB_4O_7 (where A is the divalent element) are promising materials for applications in laser engineering. The distinguishing features of these compounds are a wide transparency window in the UV and optical spectral regions, high nonlinear optical coefficients, and resistance to optical, chemical, and physical exposures. Depending on the composition and growth conditions, various structural modifications can be implemented in tetraborate compounds; physical properties of these modifications can differ significantly. Special attention from researchers is being paid to compounds isomorphic to α -modification of strontium tetraborate with polar rhombic space group, in which large values of the second optical harmonic are observed, which, along with the wide optical transparency window, makes such materials promising for applications in nonlinear optics [1, 2]. Among crystals isomorphic to α -modification of strontium tetraborate, EuB_4O_7 (EBO) is probably the single known compound containing a magnetic ion, which makes it attractive from the viewpoint of the study of nonlinear optical, magneto-optical, and magnetoelectric properties.

However, the literature contains a very small number of works devoted to the study of this compound. In [3, 4], the data on the EuB_4O_7 structure, lattice vibration frequencies active in the IR region, and the results

of measurements of the magnetic susceptibility are presented.

In this paper, we present the results of ab initio calculations of the lattice dynamics, electronic band structure, and magnetic and optical properties of the EBO crystal.

2. CALCULATION METHOD

Calculations were performed using the VASP (“The Vienna Ab initio Simulation Package”) package [5, 6] by the Projector Augmented Wave (PAW) method [7, 8]. The functional of the exchange-correlation interaction of the electron energy took into account the generalized gradient approximation of Perdew—Burke—Ernzerhof (GGA-PBE) [9]. The valence electron configuration for Eu, B, and O ions is $4f^7 5s^2 5p^6 6s^2$, $2s^2 2p^1$, and $2s^2 2p^4$, respectively. The number of plane waves was limited by the energy of 600 eV, the Monkhorst—Pack grid [10] in the optimization of unit cell parameters was chosen as $4 \times 9 \times 9$, and the grid for calculating the electronic band structure was $9 \times 22 \times 23$; in the calculation of magnetic properties for an increased cell of $1 \times 2 \times 2$, the Monkhorst—Pack grid was taken as $4 \times 4 \times 5$. The strong correlations of f -electrons of Eu ions were considered using the GGA+U method in the Dudarev approximation [11]. The parameters and coordinates of atoms were optimized until the residual forces acting on ions became less than $1 \text{ meV}/\text{\AA}$. The calculation was per-

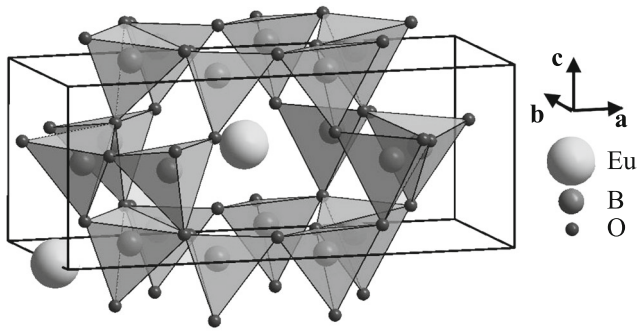


Fig. 1. Crystal structure of europium tetraborate with space group $Pmn2_1$.

formed at several values of the parameter U for the Eu ion ($U = 2-8$ eV).

The results of calculations of the EBO lattice dynamics and magnetic properties appeared poorly sensitive to U . Optical properties, in particular the electromagnetic wave absorbance, are more sensitive to U . At $U = 4$ eV, the calculated and experimental absorption factors are in the best agreement. Therefore, the calculated results presented below correspond to $U = 4$ eV.

3. STRUCTURE

The EBO crystal has a structure with polar space group $Pmn2_1$ [4] and represents a three-dimensional network consisting of boron–oxygen vertex-sharing tetrahedra BO_4 with europium ions in its cavities (Fig. 1).

The unit cell contains two molecular units. The equilibrium lattice parameters and relative atomic coordinates calculated without regard to spin polarization are given in Table 1. For comparison, the experimental values obtained in are also listed [4]. We can see that the calculated data are in good agreement with experimental results.

4. LATTICE DYNAMICS

To obtain the equilibrium EBO structure, the lattice dynamics were calculated. The calculated vibration frequencies at the Brillouin zone center are given in Table 2. For comparison, the experimental frequencies of vibrational modes active in the IR spectrum from [3] are also presented.

The expansion of the vibrational representation in irreducible representations has the form $\Gamma = 19A_1 + 17A_2 + 17B_1 + 19B_2$ (including acoustic modes $A_1 + B_1 + B_2$). Among optical modes, A_1 , B_1 , and B_2 are polar; they are active in Raman and IR spectra. Non-polar A_2 modes are only Raman-active. The set of experimental values of IR-active vibration frequencies in Table 2 is incomplete (frequencies below 400 cm^{-1} were not observed), and frequencies are not classified by irreducible representations (in [3], the study was performed on polycrystalline samples); therefore, it seems impossible to directly compare them with calculated frequencies. We can only note that IR-active vibration frequencies close to experimental values are present among the calculated ones. An exception is a vibration with a frequency of 1450 cm^{-1} observed experimentally and absent in this calculation. Such high vibration frequencies are inherent to borate com-

Table 1. Cell parameters and relative atomic coordinates of the europium tetraborate crystal (space group $Pmn2_1$) experimentally determined in [4] and calculated in the present study (parenthetical)

Cell parameters, Å			Atom	Atomic coordinates		
a	b	c		x/a	y/b	z/c
10.731 (10.805)	4.435 (4.461)	4.240 (4.267)	Eu	0	0.2116	0
				(0)	(0.2116)	(0)
			B1	0.1220	0.6720	0.4630
				(0.1215)	(0.6650)	(0.4955)
			B2	0.2510	0.1780	0.484
				(0.2514)	(0.1677)	(0.4712)
			O1	0	0.7680	0.5810
				(0)	(0.7601)	(0.5805)
			O2	0.1410	0.3580	0.5460
				(0.1418)	(0.3476)	(0.5414)
			O3	0.1350	0.7270	0.1340
				(0.1350)	(0.7199)	(0.1388)

Table 2. Frequencies (cm^{-1}) of EBO crystal lattice vibrations, calculated in this study and experimentally determined in [3]

A_1	A_2	B_1	B_2	Data [3]
1123	1133	1181	1304	1450
1082	1073	1041	1046	1310
1020	1043	993	1036	1222
971	976	957	948	1192
874	914	915	937	1160
791	784	869	876	1100
732	740	781	793	1020
706	713	773	780	970
639	651	651	717	905
621	608	647	611	886
574	535	595	543	812
485	504	505	511	777
431	420	447	444	725
368	337	294	316	705
311	280	211	305	658
289	217	135	275	644
127	116		114	626
68			83	554
				532
				515
				470
				445
				418

pounds whose structures contain boron–oxygen triangles BO_3 [12]. In isostructural SrB_4O_7 and PbB_4O_7 crystals, no vibrations with such high frequencies were detected during theoretical calculations and experimental studies of Raman and IR spectra [13, 14].

5. BAND STRUCTURE

For the compound under study, the band structure was calculated with and without consideration of spin polarization. Figure 2 shows the results of calculations of the dispersion dependences of electronic state energies with consideration of spin polarization for all symmetric directions of the Brillouin zone of space group $Pmn2_1$. The electron density of states is also shown. In Fig. 2, we can see that the europium tetraborate band gap is on the order of 4 eV. The determined band gap is consistent with the experimentally observed luminescence phenomenon in europium

tetraborate [4], which is attributed to the electronic transition $4f^7 \rightarrow 4f^65d^1$ and emits light with wavelength $\lambda = 370$ nm (which corresponds to the energy $E = 3.35$ eV).

The partial electron densities of states are shown in Fig. 3. In view of small values, the density of states for s - and p -electrons of the Eu ion is omitted. We can see that narrow peaks in the density of states near the Fermi level for the “spin-up” configuration in the valence band and at the upper boundary of the conduction band in the “spin-down” configuration correspond to f -electrons of europium.

As seen in Figs. 2 and 3, the narrow band of europium f -electron states in the valence band is spaced from states of other valence electrons by a large energy gap on the order of 3.5 eV. Similar features of the band structure were previously observed in other studies in calculating the band structure of compounds containing Eu^{2+} [15, 16].

In the calculation without regard to spin polarization, the peak of f -electrons in the electron density of states shifts to the bottom of the conduction band, and the band gap becomes on the order of 1 eV, and the energy gap between states of f -electrons and states of other electrons in the valence band increases to 6 eV.

6. OPTICAL PROPERTIES

For europium tetraborate, the frequency dependence of the dielectric function [17] was calculated. The frequency dependence of the absorbance α was calculated by the formula

$$\alpha(\omega) = \frac{2\omega}{c} \sqrt{\frac{|\epsilon(\omega)| - \epsilon'(\omega)}{2}}, \quad (1)$$

where $\epsilon(\omega)$ is the complex permittivity and $\epsilon'(\omega)$ is the real part of the permittivity. The dependence of the absorbance on the wavelength is shown in Fig. 4. We can see that the absorbance has two maxima at wavelengths of 240 and 280 nm. Experimental data on EBO optical properties were not found in the literature. However, it should be noted that the experimental study of the absorbance of the SrB_4O_7 isostructural crystal doped with 5% of Eu^{2+} [18] showed light absorption peaks at wavelengths of ~ 248 and ~ 300 nm.

According to the experimental data on light transmission in the undoped SrB_4O_7 crystal [19] in the wavelength range from 130 to 300 nm, such absorption peaks were not detected, and it can be concluded that the appearance of absorption peaks in the case of doped SrB_4O_7 is caused by europium ions. As noted above, the calculated optical properties appear sensitive to the parameter U . For example, at $U = 2$ eV, the absorption peak maxima shift to the long-wave region

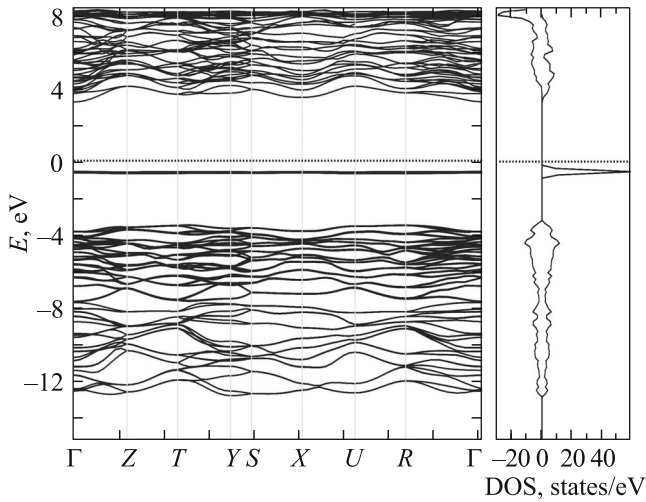


Fig. 2. Electronic band structure and density of states (DOS) of europium tetraborate, calculated with consideration of spin polarization.

(290 and 356 nm). At $U = 6$ eV, the peak maxima shift to the short-wave region (200 and 232 nm).

7. MAGNETIC PROPERTIES

The divalent europium ion is magnetic with spin $s = 7/2$.

To determine the magnetic ground state and exchange interaction parameters in europium tetraborate, the total crystal energies were calculated taking into account spin polarization for various magnetic ordered structures. The exchange interaction constants were estimated within the classical Heisenberg model,

$$H = -\frac{1}{2} \sum_{i,j} J_{ij} \hat{S}_i \hat{S}_j, \quad (2)$$

where J_{ij} are constants of the exchange interaction between sites i and j , \hat{S}_i and \hat{S}_j are the spin operators at sites i and j , respectively.

To determine the magnetic ground state and exchange interaction magnitudes, a cell increased by a factor of 4 with doubled parameters b and c containing eight europium ions was used. The system of Eu^{2+} magnetic ions was divided into eight sublattices, and the interactions within four coordination spheres were taken into account, as shown in Fig. 5.

Figure 6 schematically shows the magnetic structures considered in this study in the quadruple cell described above. For each such magnetic structure, the total crystal energy was calculated. Table 3 lists the expressions for magnetic configuration energies in terms of exchange constants of Hamiltonian (2) and the quantities $\Delta E_i = E_{\text{AF}_i} - E_{\text{F}}$, where E_{F} is the total

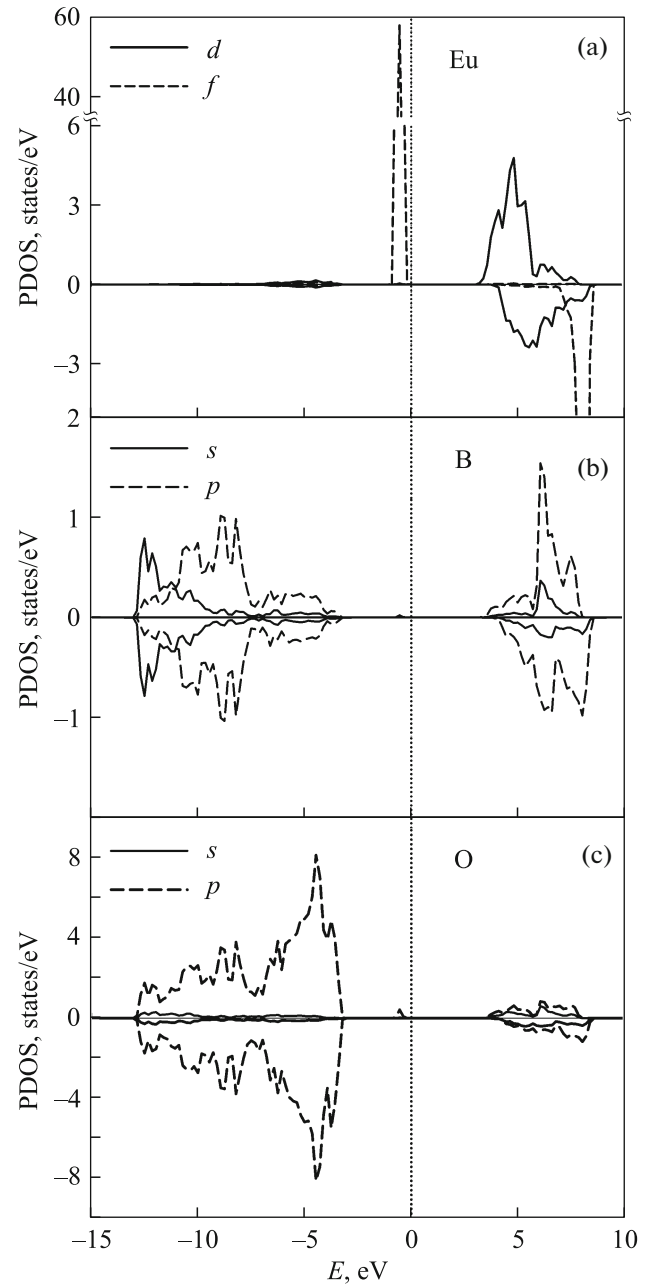


Fig. 3. Partial electron densities of states (PDOS) of (a) Eu, (b) B, and (c) O ions.

crystal energy on ferromagnetic ordering and E_{AF_i} is the total crystal energy on particular i -type antiferromagnetic ordering. We can see that ferromagnetic ordering is most energetically favorable in europium tetraborate.

The calculated exchange constants were $J_1 = -1.4 \times 10^{-5}$ eV, $J_2 = 3.9 \times 10^{-5}$ eV, $J_3 = 5.3 \times 10^{-5}$ eV, and $J_4 = 0.7 \times 10^{-5}$ eV.

The ferromagnetic transition temperature was estimated in the molecular field approximation in

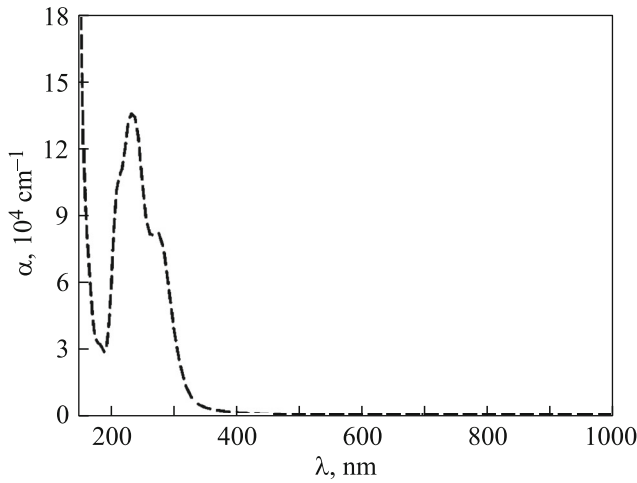


Fig. 4. Calculated dependence of the average absorbance on the wavelength.

which the expression for average sublattice spins are written as

$$\langle S_1 \rangle = B_{S_1} (2J_1 S_4 + 2J_2 S_2 + 4J_3 S_3 + 2J_4 (S_5 + S_6 + S_7 + S_8)), \quad (3)$$

$$\langle S_5 \rangle = B_{S_5} (2J_2 S_8 + 2J_2 S_6 + 4J_3 S_7 + 2J_4 (S_1 + S_2 + S_3 + S_4)), \quad (4)$$

where B_{S_i} is the Brillouin function. Expressions for $\langle S_2 \rangle$, $\langle S_3 \rangle$, $\langle S_4 \rangle$ are derived from the expression for $\langle S_2 \rangle$ by substituting the indices (1 \rightarrow 2, 4 \rightarrow 3, 2 \rightarrow 1, 3 \rightarrow 4), (1 \rightarrow 3, 4 \rightarrow 2, 2 \rightarrow 4, 3 \rightarrow 1), and (1 \rightarrow 4, 4 \rightarrow 1, 2 \rightarrow 3, 3 \rightarrow 2), respectively. For $\langle S_6 \rangle$, $\langle S_7 \rangle$, $\langle S_8 \rangle$, indices should be replaced in the expression for $\langle S_5 \rangle$: (5 \rightarrow 6, 8 \rightarrow 7, 6 \rightarrow 5, 7 \rightarrow 8), (5 \rightarrow 7, 8 \rightarrow 6, 6 \rightarrow 8, 7 \rightarrow 5), and (5 \rightarrow 8, 8 \rightarrow 5, 6 \rightarrow 7, 7 \rightarrow 6), respectively.

To estimate the phase transition temperature, the Brillouin functions in the system of equations described above for average sublattice magnetizations were expanded in a series, and a determinant equation was constructed. The solution largest in magnitude to this equation, which was taken as the ferromagnetic transition temperature, was $T_c \approx 1$ K. Such a low transition temperature is caused by both small exchange constants obtained in this calculation and the competition between them.

In [3], the inverse magnetic susceptibilities of europium tetraborate were measured in the temperature range from 2 to 24 K. Magnetic ordering was not detected in this temperature range in [3], and it was concluded that this compound is a paramagnet; therewith, the temperature dependence of the inverse susceptibility is not presented. In [3], the experimentally measured magnetic moment for the europium ion is

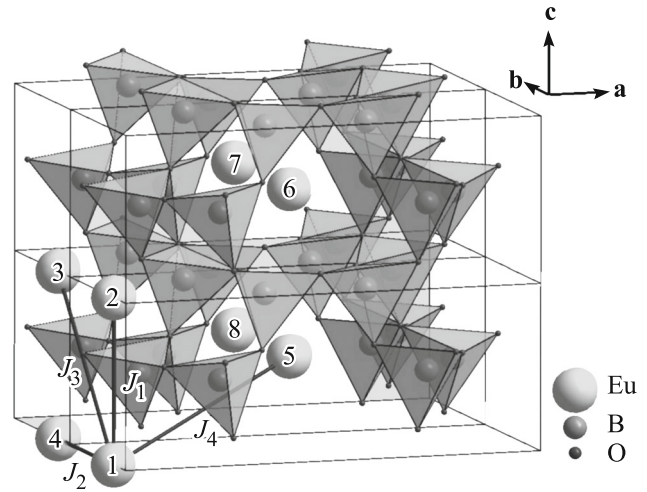


Fig. 5. Increased europium tetraborate cell $1 \times 2 \times 2$ with notations of magnetic ions and exchange constants.

presented, $\mu_{Eu}^{exp} = 8.02 \mu_B$, which is in good agreement with the value calculated in this study ($\mu_{Eu}^{calc} = 6.94 \mu_B$).

As noted above, the europium tetraborate crystal is a pyroelectric and has the structure with polar space group $Pmn2_1$, with electric polarization directed along the z axis. Since EBO contains a magnetic Eu^{2+} ion, the magnetoelectric effect can be expected in this compound. The study of magnetoelectric properties in magnetic pyroelectrics is of interest, since rather strong magnetoelectric effects can be expected in these compounds (see, e.g., [20]). To estimate the polarization change in the europium tetraborate crystal on magnetic ordering, a set of equilibrium coordinates obtained during structure relaxation neglecting without regard to spin polarization and a set of equilibrium coordinates obtained during structure relaxation with consideration of ferromagnetic ordering were used (the unit cell parameters in both calculations corresponded to equilibrium cell parameters with consideration of spin polarization). The found ion displacements are given in Table 4. The polarization change

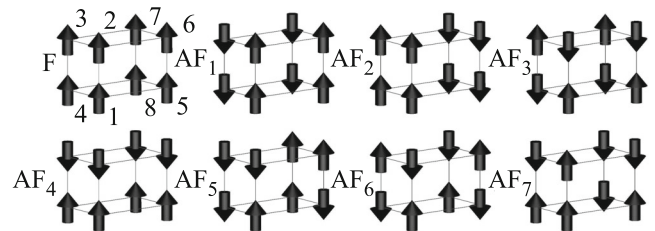


Fig. 6. Schematic representation of considered EBO magnetic configurations.

Table 3. Expressions for magnetic configuration energies in terms of exchange constants and quantities ΔE_i

Magnetic structure (see Fig. 6)	ΔE_i , meV	Expressions for energies based on Hamiltonian (2)
F	0	$8J_1 + 8J_2 + 16J_3 + 32J_4$
AF ₁	1.80	$8J_1 - 8J_2 - 16J_3$
AF ₂	0.51	$8J_1 + 8J_2 + 16J_3 - 32J_4$
AF ₃	0.94	$-8J_1 - 8J_2 + 16J_3$
AF ₄	1.34	$-8J_1 + 8J_2 + 16J_3$
AF ₅	1.26	$-4J_4$
AF ₆	0.97	$-8J_1 - 8J_2 + 16J_3$
AF ₇	1.13	$-4J_4$

resulting from the magnetoelectric effect was calculated by the formula

$$\Delta P_i = \frac{1}{V} \sum_{j=1}^N Z_j^i u_j^i, \quad (5)$$

where the index $i = x, y, z$; V is the cell volume; N is the number of atoms in the cell; Z_j^i is the nominal charge of the ion with index j ; u_j^i is the displacement of the ion with number i . On ferromagnetic ordering parallel to the crystal z axis, the EBO structure symmetry does not change, and the z axis is a polar axis. Indeed, the polarization change only along z axis appeared non-zero; polar ion displacements occur exactly in this direction. The obtained value $\Delta P_z = 3973 \mu\text{C}/\text{m}^2$ is a rather high magnetoelectric effect magnitude. For comparison, the results of [20] can be noted, where the magnetoelectric effect in pyroelectric Ni_3TeO_6 was experimentally and theoretically studied.

The magnetic field-induced polarization $\Delta P \approx 3000 \mu\text{C}/\text{m}^2$ determined in [20] is called the highest value among those obtained for magnetic pyroelectrics.

8. CONCLUSIONS

The main results of the study are as follows.

The frequencies of EBO lattice vibrations at the Brillouin zone center were calculated. The frequencies obtained are in good agreement with available experimental data. The electronic band structure was calculated, the dispersion curves and electron density of states were constructed. The obtained band gap was ~ 4 eV. The dependence of the absorbance on the wavelength was calculated,

which contains two maxima at wavelengths of 240 and 280 nm. These data are in agreement with the experimental results on the absorbance of the SrB_4O_7 isostructural crystal doped with 5% of Eu^{2+} , which exhibits light absorption peaks at wavelengths of ~ 240 and ~ 300 nm. In this case, according to the experimental data on light transmission in the undoped SrB_4O_7 crystal, such absorption peaks were not detected in the wavelength range from 130 to 300 nm, and it can be concluded that the appearance of absorption peak is caused by europium ions in the case of doped SrB_4O_7 . The calculation of the magnetic properties of the EBO crystal showed that the state with ferromagnetic ordering of Eu^{2+} spins is a ground state. The calculated exchange constants were $J_1 = -1.4 \times 10^{-5}$ eV, $J_2 = 3.9 \times 10^{-5}$ eV, $J_3 = 5.3 \times 10^{-5}$ eV, and $J_4 = 0.7 \times 10^{-5}$ eV.

Within the molecular field approximation, the ferromagnetic transition temperature was estimated as $T_c \approx 1$ K. Such a low transition temperature is caused by both low exchange constants obtained in this calculation and the competition between them. The europium tetraborate crystal under study is a magnetic pyroelectric, hence, it can exhibit magnetoelectric

Table 4. Change in relative ion coordinates on ferromagnetic ordering, nominal ion charges (expression in electron charges), and polarization change

Atom	Wyckoff position	Charge, e	Change in relative atomic coordinates			Polarization change, $\mu\text{C}/\text{m}^2$		
			$\Delta x/a$	$\Delta y/b$	$\Delta z/c$	ΔP_x	ΔP_y	ΔP_z
Eu	$2a$	+2	0	0.00993	0.00380	0	0	3973
B1	$4b$	+3	-0.00024	0.00064	-0.00079			
B2	$4b$	+3	-0.00016	0.00016	-0.00013			
O1	$2a$	-2	0	-0.00100	0.00245			
O2	$4b$	-2	0.00006	-0.00049	-0.00051			
O3	$4b$	-2	-0.00040	0.00065	-0.00113			
O4	$4b$	-2	0.00050	0.00079	-0.00057			

properties. The electric polarization change on ferromagnetic ordering was estimated as $\Delta P_z = 3973 \mu\text{C}/\text{m}^2$.

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