

Optical absorption and Raman spectroscopy of $\text{HoFe}_3(\text{BO}_3)_4$ ferroborate: experimental study with thermodynamic analysis

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ABSTRACT The vibrational and optical properties of $\text{HoFe}_3(\text{BO}_3)_4$ single crystals have been investigated by Raman spectroscopy and optical absorption measurements. The Raman spectrum, recorded at room temperature, reveals well-defined phonon modes associated with lattice vibrations and internal modes of structural units. Intense bands in the range $1200 - 1450 \text{ cm}^{-1}$ are attributed to internal vibrations of BO_3 groups, while features in the $400 - 700 \text{ cm}^{-1}$ region originate from FeO_6 octahedra. The optical absorption spectrum measured in the range $190 - 1100 \text{ nm}$ exhibits weak narrow bands in the visible and near-infrared regions, corresponding to intra-4f transitions of Ho^{3+} ions, and a pronounced absorption edge in the ultraviolet region associated with $\text{O}^{2-} \rightarrow \text{Fe}^{3+}$ charge-transfer transitions. The optical band gap is estimated to be $3.3 - 3.5 \text{ eV}$. A correlation between vibrational and optical properties is established, demonstrating the role of BO_3 groups and FeO_6 octahedra in determining the electronic structure and optical response of the material. The results provide a consistent experimental characterization of $\text{HoFe}_3(\text{BO}_3)_4$ and indicate its potential for optical and magneto-optical applications.

KEYWORDS $\text{HoFe}_3(\text{BO}_3)_4$, rare-earth ferroborates, Raman spectroscopy, optical absorption, optical band gap, charge-transfer transitions, 4f electronic transitions, vibrational properties

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1. Introduction

Rare-earth iron borates with the general formula $\text{RFe}_3(\text{BO}_3)_4$ (R = rare-earth ion) constitute a class of multifunctional materials characterized by a strong interplay between magnetic, optical, and magneto-optical properties. These effects originate from the coupling between the Fe^{3+} 3d subsystem and localized 4f electronic states of rare-earth ions, resulting in complex magnetic ordering, magnetoelectric coupling, and pronounced optical anisotropy [1, 2].

A key structural feature of ferroborates is their non-centrosymmetric trigonal crystal symmetry, which enables coupling between spin, lattice, and electronic subsystems. Depending on temperature, these compounds may undergo structural phase transitions between the space groups P3_121 and R32 , accompanied by modifications in Fe–O–Fe bond geometry and rare-earth coordination environment [3, 4]. These structural changes directly influence magnetic anisotropy, spin–lattice interaction, and the optical response.

Among this family, $\text{HoFe}_3(\text{BO}_3)_4$ is of particular interest due to the coexistence of interacting Fe^{3+} and Ho^{3+} magnetic sublattices, leading to spin-reorientation transitions, strong magnetoelastic coupling, and pronounced magneto-optical effects [2, 5–7], which are of particular interest for optical and magneto-optical applications in rare-earth-based oxide systems [8–11]. Despite extensive studies of magnetic properties, the relationship between lattice dynamics and optical response remains insufficiently clarified, particularly based on direct experimental data.

Raman spectroscopy provides a sensitive probe of lattice vibrations and local symmetry. In ferroborates, Raman-active modes are primarily associated with internal vibrations of BO_3 groups and FeO_6 octahedra, allowing verification of structural integrity and detection of possible distortions [4, 6]. Optical absorption spectroscopy complements this by probing electronic excitations, including intra-4f transitions of Ho^{3+} ions and $\text{O}^{2-} \rightarrow \text{Fe}^{3+}$ charge-transfer processes that determine the fundamental absorption edge [5, 9].

In addition to experimental techniques, thermodynamic stability of complex oxides can be reliably evaluated using first-principles data available in modern materials databases, such as the Materials Project and OQMD [12, 13]. These approaches enable validation of phase stability without performing independent large-scale calculations.

In this work, we present a combined experimental study of $\text{HoFe}_3(\text{BO}_3)_4$ single crystals using Raman spectroscopy and optical absorption measurements, supported by database-driven thermodynamic analysis. The aim is to establish a consistent relationship between lattice dynamics and optical response and to confirm the phase stability of $\text{HoFe}_3(\text{BO}_3)_4$ within the Ho–Fe–B–O system.

2. Materials and experimental-computational methods

2.1. Crystal structure and sample preparation

Holmium ferroborate $\text{HoFe}_3(\text{BO}_3)_4$ belongs to the family of rare-earth iron borates $\text{RFe}_3(\text{BO}_3)_4$ and, in the high-symmetry modification considered in this work, adopts a trigonal crystal structure described by the non-centrosymmetric space group R32 (No. 155). The crystal structure is built from Fe^{3+} ions occupying octahedral FeO_6 coordination sites interconnected by planar BO_3 groups, forming a rigid three-dimensional anionic framework. Ho^{3+} ions reside in trigonal-prismatic oxygen coordination and form cationic sublattices alternating along the crystallographic c axis. Such an arrangement gives rise to pronounced magnetic anisotropy and enables strong spin–lattice and magnetoelastic coupling, which critically influence the optical and magneto-optical properties of the compound.

A schematic representation of the $\text{HoFe}_3(\text{BO}_3)_4$ crystal structure is shown in Fig. 1, illustrating the unit cell and its projection along the c axis. The lattice parameters are $a = b = 9.65 \text{ \AA}$ and $c = 7.63 \text{ \AA}$, corresponding to a unit-cell volume of $615.73 \text{ \AA}^3$ and a calculated density of $4.59 \text{ g}\cdot\text{cm}^{-3}$. These values are consistent with previously reported structural data for R32-type rare-earth ferroborates [3, 4].

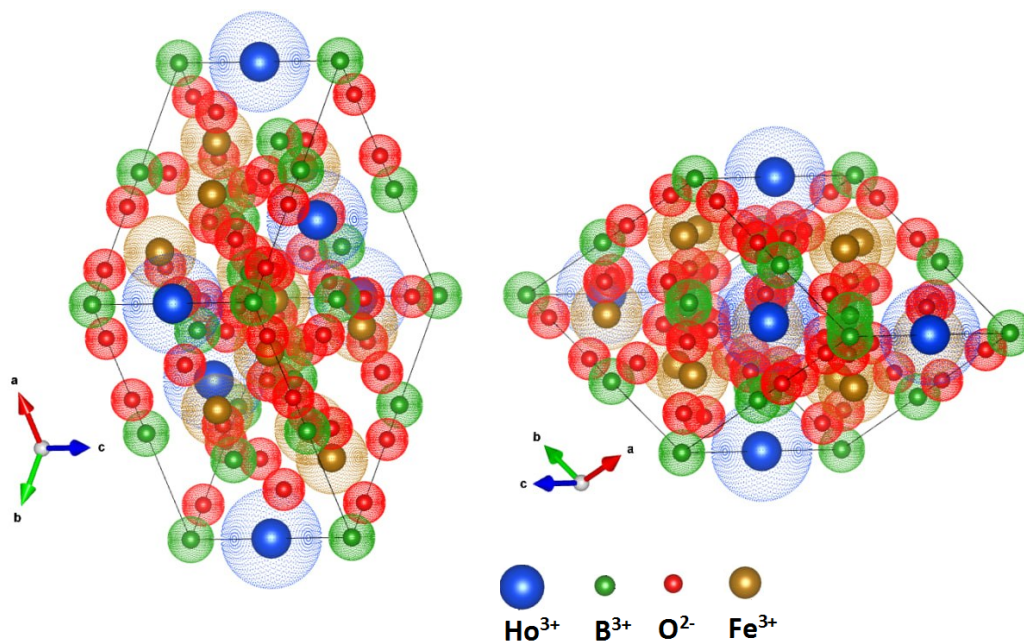


FIG. 1. Crystal structure of $\text{HoFe}_3(\text{BO}_3)_4$

Single crystals of $\text{HoFe}_3(\text{BO}_3)_4$ were grown by the flux method from an oxide melt based on bismuth borate at the Kirensky Institute of Physics, Siberian Branch of the Russian Academy of Sciences. High-purity Ho_2O_3 , Fe_2O_3 , and H_3BO_3 were used as starting materials. The growth process was carried out in platinum crucibles at temperatures of $950 - 1000 \text{ }^\circ\text{C}$, followed by slow cooling to $700 \text{ }^\circ\text{C}$ at a rate of $1 - 2 \text{ }^\circ\text{C}\cdot\text{h}^{-1}$. This procedure yielded homogeneous, optically transparent single crystals with a characteristic dark-pink coloration.

2.2. Raman spectroscopy

Raman spectroscopy was used to investigate lattice dynamics and to verify the structural integrity of $\text{HoFe}_3(\text{BO}_3)_4$ single crystals.

Raman spectra were recorded using a RENISHAW inVia Raman microscope at room temperature in a standard backscattering geometry. Excitation was provided by a solid-state laser with a wavelength of 532 nm . The laser power at the sample surface was kept 50 mW in order to avoid local heating effects and possible modification of phonon line positions or linewidths.

The measurements were performed in the spectral range $100 - 2000 \text{ cm}^{-1}$. The recorded spectra were corrected for background and instrumental response.

The Raman spectra were analyzed with respect to vibrational modes associated with:

- internal vibrations of BO_3 groups,
- stretching and bending modes of FeO_6 octahedra,
- external lattice modes involving Ho^{3+} ions.

Raman spectroscopy provides a sensitive probe of local symmetry and structural order and enables detection of structural distortions or secondary phases that may not be visible in X-ray diffraction data [4, 6].

2.3. Optical and magneto-optical measurements

Optical absorption and magneto-optical measurements were carried out in the wavelength range $190 - 1100 \text{ nm}$ using a double-beam Specord 50 spectrophotometer (Analytik Jena, Germany) operating with polarized light.

Measurements were performed at room temperature and, when required, in the temperature range $80 - 300 \text{ K}$ using a closed-cycle cryostat. Magneto-optical experiments were performed in the Faraday geometry, with magnetic fields up to 10 kOe generated by a Lakeshore EM4 electromagnet. The magnetic field was applied parallel to the optical c axis of the crystal.

For optical studies, thin plate-like samples with thicknesses of $0.2 - 0.5 \text{ mm}$ were prepared. The sample surfaces were carefully polished to optical quality in order to minimize light scattering. The rotation of the polarization plane and magnetic dichroism were measured using modulation techniques with phase-sensitive detection, providing high sensitivity and reproducibility.

All optical spectra were normalized to the optical density of the unmagnetized sample to eliminate surface-related artifacts. Representative as-grown $\text{HoFe}_3(\text{BO}_3)_4$ single crystals are shown in Fig. 2.



FIG. 2. External view of $\text{HoFe}_3(\text{BO}_3)_4$ single crystals grown by the flux method from a bismuth borate-based melt

2.4. Thermodynamic stability analysis

The thermodynamic stability of $\text{HoFe}_3(\text{BO}_3)_4$ was analyzed using formation energies and phase diagram data obtained from open computational materials databases, including the Materials Project and the Open Quantum Materials Database (OQMD) [12, 13].

The stability of the compound was evaluated using the energy above the convex hull (ΔE_{hull}), defined as:

$$\Delta E_{\text{hull}} = E_{\text{compound}} - E_{\text{hull}},$$

where E_{hull} corresponds to the energy of the most stable combination of competing phases at the same overall composition.

According to database data, $\text{HoFe}_3(\text{BO}_3)_4$ is characterized by a small positive value of ΔE_{hull} ($\sim 0.016 \text{ eV/atom}$), which lies within the typical uncertainty of density functional theory calculations and indicates thermodynamic stability or near-stability of the compound.

The phase stability analysis includes competing phases in the Ho–Fe–B–O system as reported in the databases. These data are used for qualitative interpretation of phase equilibria and for consistency analysis with experimentally observed synthesis conditions.

It should be emphasized that no independent first-principles calculations were performed in this work; all thermodynamic data were obtained from validated database sources.

3. Results and discussion

3.1. Raman spectroscopy

The vibrational properties of $\text{HoFe}_3(\text{BO}_3)_4$ were investigated by Raman spectroscopy at room temperature (Fig. 3). The recorded spectrum covers a wide frequency range and reflects both lattice dynamics and internal vibrations of structural units. The observed distribution of Raman modes is consistent with previously reported spectra of rare-earth ferroborates [4, 6].

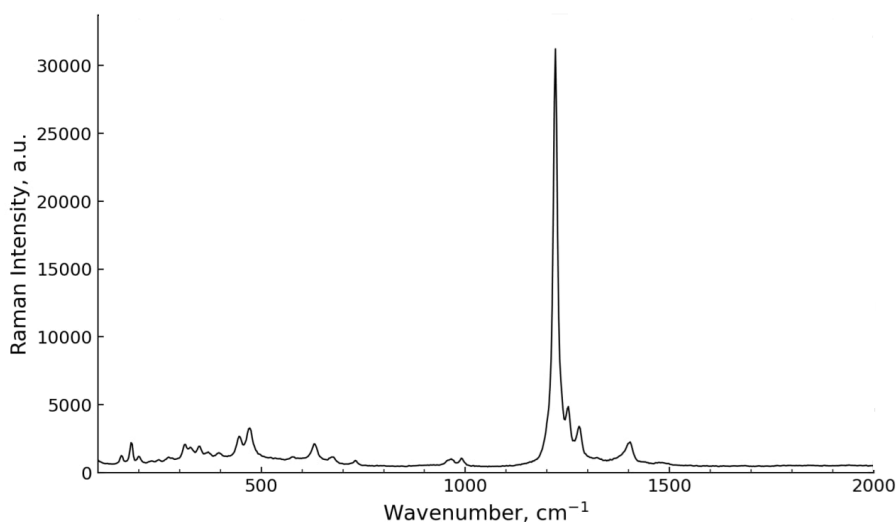


FIG. 3. Raman spectrum of $\text{HoFe}_3(\text{BO}_3)_4$ single crystal measured at room temperature ($\lambda = 532$ nm, backscattering geometry)

In the low-frequency region ($< 300 \text{ cm}^{-1}$), weak bands are observed, which can be attributed to lattice vibrations involving translational motions of heavy Ho^{3+} ions and acoustic modes of the crystal lattice. The intermediate spectral range ($400 - 700 \text{ cm}^{-1}$) is characterized by several bands of moderate intensity associated with vibrations of FeO_6 octahedra. These include both stretching and bending modes of Fe–O bonds and are typical for iron–oxygen coordinated systems.

The most prominent features are located in the high-frequency region between 1200 and 1450 cm^{-1} , where intense peaks are observed. These bands originate from internal vibrations of planar BO_3^{3-} groups. The modes in the range $1200 - 1250 \text{ cm}^{-1}$ are attributed to symmetric B–O stretching vibrations within BO_3 groups, while those in the $1280 - 1400 \text{ cm}^{-1}$ region are associated with asymmetric B–O stretching vibrations. An intense band located around $1410 - 1420 \text{ cm}^{-1}$ is characteristic of BO_3 units and reflects the rigidity of B–O bonds. At frequencies above 1500 cm^{-1} , weak features can be detected, which are attributed to overtone and combination modes. The absence of additional bands associated with impurity phases suggests that the investigated sample is spectroscopically homogeneous.

A more detailed analysis of the spectrum allows the identification of distinct Raman peaks, summarized in Table 1. An intense band at $\sim 1415 \text{ cm}^{-1}$ corresponds to asymmetric B–O stretching vibrations of BO_3 groups. Additional bands in the range $1200 - 1350 \text{ cm}^{-1}$ are also associated with internal vibrations of borate units. Lower-frequency peaks originate from FeO_6 octahedral vibrations and lattice modes involving heavy Ho^{3+} ions. Peak positions were determined from local maxima of the spectra without performing detailed peak deconvolution.

3.2. Optical absorption spectrum

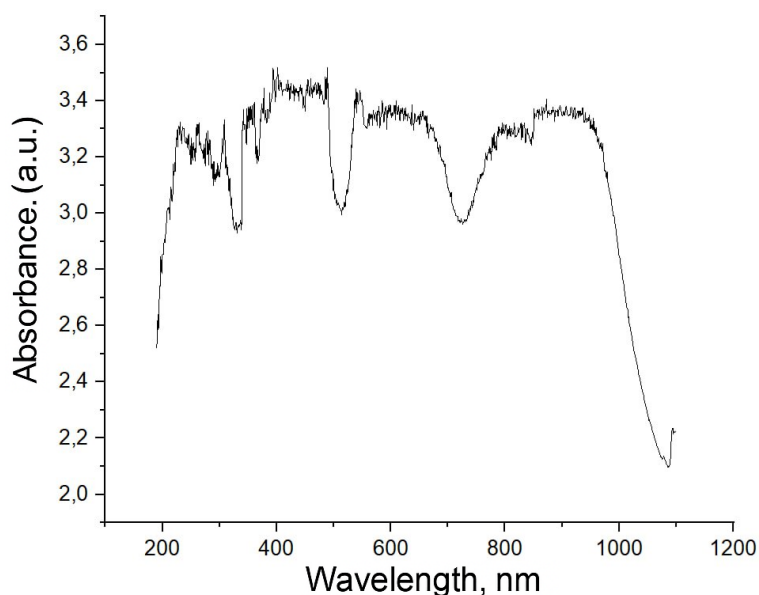
The optical absorption spectrum of $\text{HoFe}_3(\text{BO}_3)_4$ single crystals measured at room temperature in the range $190 - 1100 \text{ nm}$ is shown in Fig. 4. The spectral profile results from the superposition of localized electronic transitions and a broad fundamental absorption edge. These features are consistent with earlier optical studies of $\text{HoFe}_3(\text{BO}_3)_4$ and related compounds [5, 9].

In the visible and near-infrared regions (approximately $350 - 900 \text{ nm}$), the absorption remains relatively low, with several weak and narrow bands superimposed on the background. These features are attributed to intra-4f transitions of Ho^{3+} ions from the ground multiplet 5I_8 to excited states such as 5G_6 , 5F_5 , 5F_4 , 5S_2 , and 5F_3 . Although these transitions are parity-forbidden for free ions, they become weakly allowed in the crystal due to crystal-field-induced mixing.

A pronounced increase in absorption is observed in the ultraviolet region (approximately $250 - 350 \text{ nm}$), which is associated with charge-transfer transitions from O^{2-} ligands to Fe^{3+} ions within FeO_6 octahedra. These transitions define the fundamental absorption edge of the material. The optical band gap was estimated from the onset of strong absorption

TABLE 1. Experimental Raman peaks of $\text{HoFe}_3(\text{BO}_3)_4$

Raman shift (cm^{-1})	Relative intensity	Assignment
~ 1415	medium–strong	asymmetric B–O stretching vibrations
~ 1335	medium	asymmetric B–O stretching vibrations
~ 1255	very strong	symmetric B–O stretching vibrations
~ 1005	medium	mixed B–O vibrations
~ 820	weak–medium	lattice / Fe–O bending
~ 680	medium	FeO_6 vibrations
~ 520	medium	Fe–O stretching
~ 300	weak	lattice modes
$\sim 120 - 200$	weak	external modes (Ho-related)

FIG. 4. Optical absorption spectrum of $\text{HoFe}_3(\text{BO}_3)_4$ single crystal measured at room temperature in the range 190 – 1100 nm ($E \parallel c$)

using linear extrapolation of the absorption edge and is found to be in the range 3.3 – 3.5 eV, corresponding to wavelengths of approximately 354 – 378 nm. The extension of absorption toward shorter wavelengths (down to ~ 250 nm) is attributed to higher-energy charge-transfer states and possible excitonic contributions. At wavelengths above 900 nm, the absorption decreases significantly, indicating high transparency in the near-infrared region.

TABLE 2. Optical absorption features of $\text{HoFe}_3(\text{BO}_3)_4$

Wavelength (nm)	Energy (eV)	Assignment
350 – 900	1.4 – 3.5	Ho^{3+} intra-4f transitions
250 – 350	3.5 – 5.0	$\text{O}^{2-} \rightarrow \text{Fe}^{3+}$ charge transfer
354 – 378	3.3 – 3.5	optical band gap

3.3. Correlation between vibrational and optical properties

The combined analysis of Raman and optical absorption data provides insight into the relationship between lattice dynamics and electronic structure in $\text{HoFe}_3(\text{BO}_3)_4$. The Raman spectrum is dominated by high-frequency modes associated with internal vibrations of BO_3 groups, particularly in the $1200 - 1450 \text{ cm}^{-1}$ region, indicating the structural rigidity of borate units. At lower frequencies ($400 - 700 \text{ cm}^{-1}$), the observed modes originate from FeO_6 octahedra, reflecting the dynamics of the Fe–O framework. These structural units play an important role in determining the optical properties. The optical absorption edge in the ultraviolet region is governed by $\text{O}^{2-} \rightarrow \text{Fe}^{3+}$ charge-transfer transitions within FeO_6 octahedra, while the weak absorption bands in the visible and near-infrared regions arise from localized intra-4f transitions of Ho^{3+} ions. The coexistence of rigid BO_3 groups and FeO_6 octahedra results in a wide band gap ($\sim 3.3 - 3.5 \text{ eV}$) and low absorption in the visible range. This combination of structural stability and optical transparency is characteristic of rare-earth ferroborates and is favorable for magneto-optical applications.

4. Conclusion

In this work, the structural and optical properties of $\text{HoFe}_3(\text{BO}_3)_4$ single crystals have been investigated using Raman spectroscopy and optical absorption measurements, complemented by thermodynamic analysis based on materials databases.

The Raman spectra reveal well-defined phonon modes corresponding to BO_3 groups and FeO_6 octahedra, confirming the structural integrity of the crystal and the absence of secondary phases. The optical absorption spectrum demonstrates a wide transparency window in the visible region and a fundamental absorption edge in the ultraviolet region associated with charge-transfer transitions. The estimated optical band gap ($\sim 3.3 - 3.5 \text{ eV}$) and the presence of localized 4f transitions indicate the coexistence of localized and band-like electronic states. The consistency between vibrational and optical characteristics highlights the dominant role of BO_3 and FeO_6 structural units in determining the physical properties of the compound. Thermodynamic analysis based on database data confirms that $\text{HoFe}_3(\text{BO}_3)_4$ is located near the convex hull, indicating its stability within the Ho–Fe–B–O system.

The obtained results provide an experimentally supported description of the lattice dynamics and optical behavior of $\text{HoFe}_3(\text{BO}_3)_4$ and indicate its potential applicability in optical and magneto-optical devices consistent with previous studies on rare-earth iron oxides and garnets [14–20].

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Conflict of interest: the authors declare no conflict of interest.