

Spin–Phonon and Electron–Phonon Interactions in Multiferroic $\text{GdFe}_3(\text{BO}_3)_4$ and $\text{TbFe}_3(\text{BO}_3)_4$ Evidenced by IR Reflection Spectroscopy

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Abstract We study temperature-dependent polarized reflection spectra of multiferroic $\text{GdFe}_3(\text{BO}_3)_4$ and $\text{TbFe}_3(\text{BO}_3)_4$ single crystals. Signatures of spin–lattice interactions in both compounds and of a formation of the electron–phonon coupled mode in $\text{TbFe}_3(\text{BO}_3)_4$ are discussed.

Keywords Multiferroics · IR-active phonons · Spin–phonon interaction · Coupled electron–phonon mode

1 Introduction

Multiferroic materials are characterized by a considerable interplay between their constituent subsystems (magnetic, charge, lattice, electronic). This offers a possibility to control one subsystem by influencing another, which promises device applications. Rare-earth (RE) iron borates $R\text{Fe}_3(\text{BO}_3)_4$ (RFB), where $R=\text{RE}$ or Y, well recognized as multiferroics, demonstrate remarkable interactions between magnetic, electric, and other degrees of freedom [1–5]. The lattice is involved in such kind of interactions and also exhibits an anomalous behavior [6–8].

Both GdFB and TbFB possess a huntite-type structure described by the trigonal noncentrosymmetric space group (SG) $R\bar{3}2$ at high temperatures [9] and by also trigonal but less symmetric SG $P3_121$ [10] below the temperature T_s of the structural phase

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transition ($T_s = 143$ and 200 K for GdFB and TbFB, respectively). Both compounds order antiferromagnetically at $T_N = 34$ K (GdFB) and 40 K (TbFB). Comprehensive information on Raman-active phonons in RE iron borates is available in the literature [3, 11], while only fragmentary knowledge on the infrared (IR)-active ones exists [12–14].

Both compounds have a similar crystal-lattice structure, but the electronic structure differs principally. Whereas Gd^{3+} does not have any crystal-field (CF) excitations within the energy region of phonons, several CF excitations of the Tb^{3+} ground multiplet fall into this energy interval [15] and can interact with phonon modes. In this work, we present a study of IR reflection spectra of GdFB and TbFB single crystals in wide spectral and temperature ranges and compare the temperature behavior of these spectra.

2 Experiment

The synthesis of RFB single crystals used in the experiment was described in Ref. [16]. Two polished plane-parallel plates of GdFB and TbFB, of good optical quality, green in color, cut parallel to the c -axis were used for measurements. With such crystallographic orientation, it is possible to separate phonons by symmetry, using a linearly polarized light ($E||c$ and $E\perp c$). Reflection spectra were measured with a Bruker IFS 113 Fourier-transform spectrometer in two spectral ranges, which were merged by standard OPUS software. We have used bolometer/Ge-coated mylar and MCT/KBr detector/beamsplitter configurations for the 40 – 700 and 500 – 5000 cm^{-1} spectral ranges, respectively. A helium-flow cryostat with diamond window, specially designed for reflection measurements, equipped with in situ gold evaporator, was used to perform temperature-dependent measurements from 7 to 300 K. Reflection from a gold-coated sample was used as a reference signal to obtain absolute reflectance.

3 Experimental Results and Discussion

Group-theoretical analysis (GTA) predicts three symmetry types of phonons for the $R32$ structure of the RFB compounds. The $P3_121$ structure is less symmetric, but still trigonal, and it maintains the same symmetry representations and polarization activity for phonon modes, while the number of phonons grows considerably as the unit cell triples. Among symmetry types, A_1 modes are Raman active, A_2 modes are IR active, and E modes are active both in Raman and IR, due to the absence of the inversion center. According to GTA, one expects $12A_2(E||c) + 19E(E\perp c)$ modes to be observed in IR spectra of the $R32$ structure and $32A_2 + 59E$ modes—in IR spectra of the $P3_121$ one [3]. BO_3 groups present in the crystal are characterized by the strongest interatomic bonds, which allows to consider them as molecules that keep their vibrational modes; moreover, their frequencies do not change much. Thus, the internal and external (with respect to the BO_3 groups) modes are well separated; the first ones occupy the spectral region above 550 cm^{-1} , whereas the second ones have frequencies lower than 500 cm^{-1} .

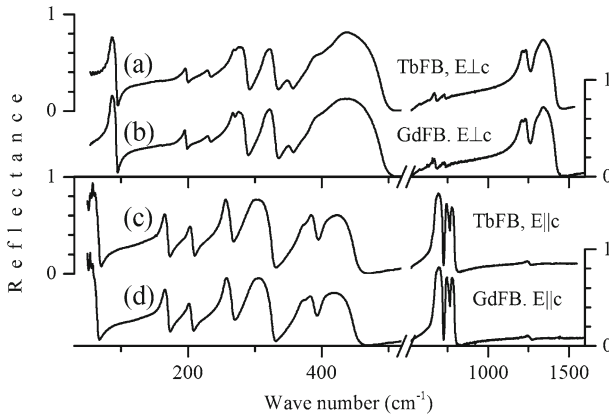


Fig. 1 Reflection spectra of *a, c* TbFB and *b, d* GdFB in *a, b* $E_{\perp c}$ and *c, d* $E_{\parallel c}$ polarizations at 300 K. Notice the different frequency scales below and above the scale break which separates the spectral regions of external and internal vibrations

Figure 1 shows polarized room-temperature reflection spectra of the two compounds. They correspond to the $R32$ phase. For each polarization, the spectra of TbFB and GdFB are very similar because their lattices as well as mass parameters are very close. The reflection spectra obtained were modeled with the aid of the program RefFit [17]. The reflectance was calculated via a dielectric function, which was varied via phonon parameters in the frame of the so-called Drude–Lorentz model [17] to obtain the best agreement with the experimental reflectance.

An example of modeling is shown in Fig. 2a, where a model spectrum is compared with the experimental one for TbFB in the $E_{\perp c}$ polarization. Within the model, LO frequencies can be found as maxima of the loss function $\text{Im}(-1/\epsilon)$. This function is presented in Fig. 2b. Comparison with Raman frequencies [3] demonstrates a good agreement between the loss function maxima and the Raman peaks. The same good agreement was achieved when applying this procedure to the $E_{\perp c}$ polarized reflection spectra of GdFB. Modeling of the reflection spectra in the $E_{\parallel c}$ polarization resulted in sets of TO and LO frequencies of the A_2 IR-active phonon modes for TbFB and GdFB.

The number of phonons registered in the $R32$ phase coincides well with GTA except the absence of one A_2 mode belonging to the ν_1 totally symmetric vibration of the BO_3 groups. This vibration is forbidden in the IR spectra of a free BO_3 molecule and becomes allowed in a crystal due to a lower symmetry of a crystal site. We suppose that its intensity is too small to be registered in the reflection spectra.

A $E_{\perp c}$ polarized reflection spectrum of a TbFB crystal at 7 K is presented in Fig. 2c. The low-symmetry phase possesses much more phonon modes, in accordance with GTA. Changes occurring at the structural phase transition in the region of internal modes are not so big as those in the region of external ones, which emphasizes that the BO_3 groups are the most rigid part of the crystal structure. Analyzing reflection spectra for the two compounds in the $P3_121$ phase in both polarizations, we have found that the total number of phonons is smaller than that predicted by GTA (24 out

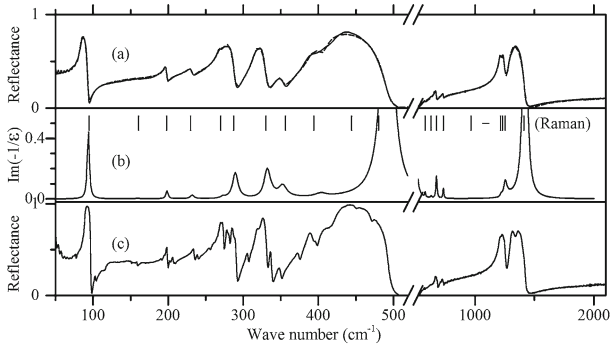


Fig. 2 *a* Reflection spectrum of TbFB at 300 K in $E_{\perp c}$ polarization (solid line) compared with a model fit (dotted line) for the E modes. *b* Loss function calculated within the model fit. Positions of Raman peaks for the E modes [3] are indicated by vertical bars. *c* Reflection spectrum of TbFB at 7 K in $E_{\perp c}$ polarization. A large number of new modes are observed

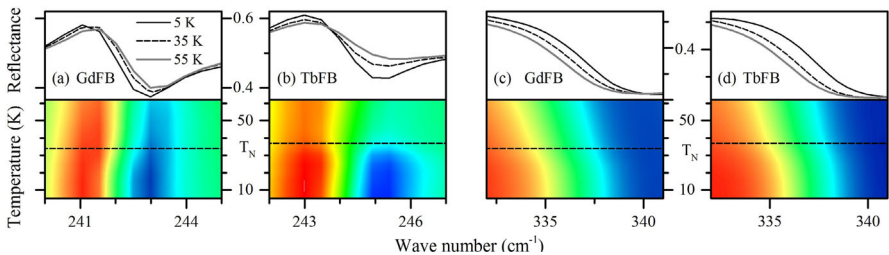


Fig. 3 Examples of the A_2 modes with peculiarities in their behavior at T_N . *a, b* The phonon mode at 241 cm^{-1} . *c, d* High-frequency wing of the phonon mode at 330 cm^{-1} . *a, c* GdFB and *b, d* TbFB. Upper parts of each panel demonstrate reflection spectra at several temperatures, and the lower parts present the reflected intensity maps in the frequency–temperature coordinates (Color figure online)

of 32 A_2 -modes and 36 out of 59 E -modes were observed), which can be explained by small shifts for some of the new modes from already existing ones and small intensities for some others. The already mentioned ν_1 vibration gives $1A_2 + 4E$ modes in the $P3_121$ phase, and none of them were observed.

Figure 3 shows the reflection spectra of both compounds in two spectral regions, in which evident changes of phonon modes occur at temperatures lower than T_N , where an internal magnetic field B_{eff} appears due to a magnetic order in the crystal. Such a behavior clearly demonstrates that the spin–phonon interaction is appreciable in both compounds. Several mechanisms could be responsible for such a phenomenon. One of them already experimentally proved for $\text{EuFe}_3(\text{BO}_3)_4$ [8] is due to subtle atomic displacements caused by B_{eff} (magnetostriction). Also a dynamical mechanism may contribute. In this case, superexchange paths are modulated by lattice vibrations, which, in its turn, affects the phonon frequencies [18].

A markedly different temperature behavior in the spectra of GdFB and TbFB is observed in the region of a single E mode near 195 cm^{-1} (Fig. 4). In GdFB, this mode experiences only a small shift and narrowing in the temperature range 135–5 K, while in TbFB the spectral changes are drastic. At temperatures lower than 120 K,

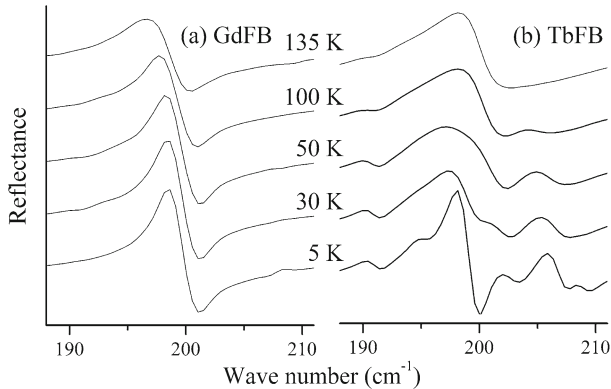


Fig. 4 The $E_{\perp c}$ polarized reflection spectra in the region of a single E mode near 197 cm^{-1} for *a* GdFB and *b* TbFB at several temperatures. Interaction with CF excitations of Tb^{3+} is evident

this mode starts to broaden and a new weak feature appears at 205 cm^{-1} , growing in intensity at cooling down. At temperatures lower than T_N , both modes experience an additional splitting. We attribute such a behavior to an interaction between the E mode and the crystal-field excitation of the same symmetry, connected with the CF level of Tb^{3+} at 200 cm^{-1} (at $T=100\text{ K}$) [15]. The electron–phonon interaction leads to the formation of electron–phonon coupled modes (see, e.g., Ref. [19]). The quasi-electronic excitation borrows the intensity from the vibrational mode and starts to be observable in the IR reflection. The splitting at $T < T_N$ can be connected with the splitting of the $\Gamma_3(E)$ CF level.

4 Conclusion

A study of polarized infrared reflection spectra of $\text{TbFe}_3(\text{BO}_3)_4$ and $\text{GdFe}_3(\text{BO}_3)_4$ single crystals is presented. The temperature-dependent (7–300 K) spectra confirm a structural phase transition $R32 \rightarrow P3_121$ at 200 and 143 K, respectively. Spectral signatures of the spin–lattice interaction are observed at temperatures lower than the Néel temperature, 34 K (TbFB) and 40 K (GdFB). Small but noticeable changes in phonon parameters of several vibrational modes take place below T_N . One of the E vibrational modes is close in energy to the $\Gamma_3(E)$ crystal-field level of Tb^{3+} in TbFB. The electron–phonon interaction leads to the formation of coupled electron–phonon modes that manifest themselves by a mutual energy renormalization, the appearance of new branches in the excitation spectrum, and a splitting of both the quasi-electronic and quasi-phonon branches below T_N .

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