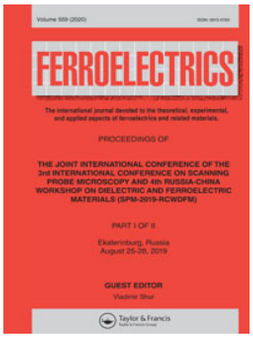

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Structural phase transition in $TbFe_{2.5}Ga_{0.5}(BO_3)_4$ single crystal

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ABSTRACT

The Raman spectra of the $TbFe_{2.5}Ga_{0.5}(BO_3)_4$ single crystal in the temperature range from 8 to 400 K have been observed. The condensation and restoration of the soft modes have been found. The soft modes are associated with the structural phase transition from the $R32$ phase to the $P3_121$ phase. The behavior of the hard modes confirms the structural phase transition close to the tricritical point. The temperature of the structural phase transition $T_1 = 33$ K is established.

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KEYWORDS
Soft modes; low temperatures; phonon–magnon interaction; magnetic ordering; crystal with huntite structure

1. Introduction

The $TbFe_{2.5}Ga_{0.5}(BO_3)_4$ solid solution belongs to the family of borates with huntite structures. The rare-earth ferroborates demonstrate the variety of magnetic, magnetoelectric, magnetodielectric, and structural properties [1–5]. Most of the rare-earth ferroborates could be attributed to multiferroics [6–8]. The coupling interaction between the different order parameters can produce additional functionalities of the multiferroic materials. The magnetic properties of $TbFe_3(BO_3)_4$ crystal have been investigated by neutron diffraction, far-infrared absorption, and reflection spectroscopy [9,10]. The Tb sublattice sets in at exactly the same temperature as that of the Fe sublattice. at $T_N = 40$ K [9]. The substitution of some Fe ions on Ga ions in the $TbFe_3(BO_3)_4$ compound can provide an interesting change of the crystal properties.

Nowadays, the structural and magnetic properties of solid solutions rare-earth huntite structure borates of various compositions are studied by different techniques including the Raman spectroscopy. The structural phase transition accompanied by soft modes condensation and magnetic ordering transition were observed in iron-containing systems. Crystals with close temperatures of the ferroelectric magnetic transitions are of particular interest. Substitution of iron ions for gallium leads to a decrease in the temperature of the structural transition. Thus, it is possible to obtain a crystal with temperatures close to desired.

In the present study, we consider the $TbFe_{2.5}Ga_{0.5}(BO_3)_4$ single crystal. Rare-earth ferroborates are characterized by the internal magnetic field induced by the magnetic ordering below the temperature of the magnetic phase transition. This fact allows

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investigating the feature in the Raman spectra caused by the established magnetic order without external magnetic field. The low-frequency Raman spectroscopy is used as a tool since soft mode frequency tends toward zero as the critical temperature is approached. Two soft modes were also observed earlier in $Nd_xHo_{1-x}Fe_3(BO_3)_4$ solid solutions [11,12]. Their presence was associated with the coexistence of magnetic and structural order parameters. We suppose to observe the anomalies in Raman spectra connected with magnetic ordering and structural changes at low temperatures in the $TbFe_{2.5}Ga_{0.5}(BO_3)_4$.

2. Experimental

Raman scattering spectra of $TbFe_{2.5}Ga_{0.5}(BO_3)_4$ have been studied in the temperature range from 8 to 400 K. Raman spectra were collected in backscattering geometry, using a triple monochromator Jobin Yvon T64000 Raman spectrometer operating in subtractive mode and then detected by a liquid nitrogen-cooled CCD cooled at 140 K. The spectral resolution for the recorded Stokes side Raman spectra was better than 2 cm^{-1} (this resolution was achieved using gratings with 1800 grooves mm^{-1} and 100 μm slits). The resolution of the low-frequency region during soft mode investigation was improved to 1.2 cm^{-1}, which attained a low-frequency limit of 10 cm^{-1} in the present setup. The deformation of the low-frequency spectral edge by an optical slit, which sometimes smears the true features of the low-frequency spectra, was carefully eliminated by rigorous optical alignment. Single-mode argon 514.5 nm of Spectra-Physics Stabilite 2017 Ar^+ laser of 100 mW power (10 mW on the sample) was used as excitation light source.

The low-temperature experiments were carried out using a closed-cycle helium cryostat ARS CS204-X1.SS, controlled by LakeShore 340 temperature controller. The temperature was monitored by a calibrated silicon diode LakeShore DT- 670SD1.4L. Indium foil was used as a thermal interface. Measurements were taken inside the cryostat under pressure of 10^{-6} mBar.

The experiments were carried out in the dynamic regime by varying the sample temperature, and it was identical to the measurement procedure described in our past work [13]. This technique implies that the temperature does not stabilize, but changes continuously during the experiment. Thus, the measurement temperature uncertainty of one spectrum is determined by the measurement time and temperature cooling or heating rate. The rates of temperature variation range were 0.7 K/min. The overall time for taking a single spectrum was within 30 sec. The uncertainty of the measured temperature for a given rate estimated as a difference between adjacent measurements was ±0.17 K per spectra.

The samples under study were optically transparent greenish single crystals with a size of about 3 mm and did not contain any colored defects or inclusions visible under a microscope.

3. Results and discussion

The $TbFe_3(BO_3)_4$ crystal belongs to *R*32 space group in the high-temperature phase. Under cooling, crystal undergoes structural phase transition with symmetry reducing to

Table 1. Wyckoff positions and irreducible representations (Γ-point phonon modes) for $TbFe_3(BO_3)_4$ (Space group: *R*32, No. 155).

Atom Space group: *R*32 (No. 155) Point group: *D*3	Wyckoff position	Γ-point phonon modes
Tb	3a	A_2+E
Fe	9d	A_1+2A_2+3E
O	9e	A_1+2A_2+3E
O	9e	A_1+2A_2+3E
O	18f	$3A_1+3A_2+6E$
B	3b	A_2+E
B	9e	A_1+2A_2+3E

Modes classifications

$\Gamma_{Raman}=7A_1+19E$	$\Gamma_{IR}=12A_2+19E$	$\Gamma_{ac}=A_2+E$	$\Gamma_{Mehanical}=7A_1+13A_2+20E$

Raman tensor

$$A_1=\begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{bmatrix} \quad E(x)=\begin{bmatrix} c & 0 & 0 \\ 0 & -c & d \\ 0 & d & 0 \end{bmatrix} \quad E(y)=\begin{bmatrix} 0 & -c & -d \\ -c & 0 & 0 \\ -d & 0 & 0 \end{bmatrix}$$

$P3_121$. The number of Raman active modes is 26 for the high-temperature phase and 86 for the low-temperature phase. The vibrational modes symmetry analysis of the *R*32 structure of $TbFe_3(BO_3)_4$ is presented in Table 1.

The vibrational modes symmetry analysis of the $P3_121$ structure of $TbFe_3(BO_3)_4$ crystal is presented in Table 2.

The Raman spectra of $TbFe_{2.5}Ga_{0.5}(BO_3)_4$ solid solution should have some differences from the Raman spectra of $TbFe_3(BO_3)_4$, but according to Raman selecting rules we can expect the splitting E symmetry modes and appearance of new modes under the sample cooling in the experimental spectra.

The changes in the full spectrum of the $TbFe_{2.5}Ga_{0.5}(BO_3)_4$ crystal with temperature are demonstrated in Figure 1. There are no significant changes in the spectra above 1100 cm^{-1}. Therefore, we paid more attention to the region of low and medium wavenumbers. The soft modes condensation and restoring at 33 K have been observed and result as a low-frequency intensity map presented in Figure 2. The observed soft modes are very weak and it is hard to see them in one spectrum presented in journal scale. The only one possibility to see this phenomenon in the investigated crystal is to present all the measured data in one picture – Raman signal map. Every horizontal line corresponds to the measured Raman spectrum at the exact temperature, different colors correspond to different signal values. Some anomalies could be seen in the frequency region below 40 cm^{-1} (indicated by green and red arrows). The condensation and restoration of the soft modes at 33 K may be connected with possible magnetic ordering below 40 K.

Under structural second-order phase transitions or first-order transitions close to the tricritical point, the frequency of one or several normal modes of a crystal lattice tends to zero or greatly decreases. The lowest frequency mode with anomalous decreasing is usually named as "soft mode." The concept and the theory of soft mode is a result of a large number of theoretical and experimental studies. It is out of place to present here the history of this field. We can just refer to some work as a good starting point to study the phenomena [14,15]. An excellent review of soft mode spectroscopy in the

Table 2. Wyckoff positions and irreducible representations (Γ-point phonon modes) for $TbFe_3(BO_3)_4$ (Space group: $P3_121$, No. 152).

Atom Space group: $P3_121$ (No. 152) Point group: $D3$	Wyckoff position	Γ-point phonon modes
Tb	3a	A_1+2A_2+3E
Fe	6c	$3A_1+3A_2+6E$
Fe	3a	A_1+2A_2+3E
O	6c	$3A_1+3A_2+6E$
O	6c	$3A_1+3A_2+6E$
O	6c	$3A_1+3A_2+6E$
O	6c	$3A_1+3A_2+6E$
O	6c	$3A_1+3A_2+6E$
O	3b	A_1+2A_2+3E
O	3b	A_1+2A_2+3E
B	3b	A_1+2A_2+3E
B	6c	$3A_1+3A_2+6E$
B	3b	A_1+2A_2+3E
Modes classifications		
$\Gamma_{Raman}=27A_1+59E$	$\Gamma_{IR}=32A_2+59E$	$\Gamma_{ac}=A_2+E$ $\Gamma_{Mehanical}=27A_1+33A_2+60E$
Raman tensor		

$$A_1=\begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{bmatrix} \quad E(x)=\begin{bmatrix} c & 0 & 0 \\ 0 & -c & d \\ 0 & d & 0 \end{bmatrix} \quad E(y)=\begin{bmatrix} 0 & -c & -d \\ -c & 0 & 0 \\ -d & 0 & 0 \end{bmatrix}$$

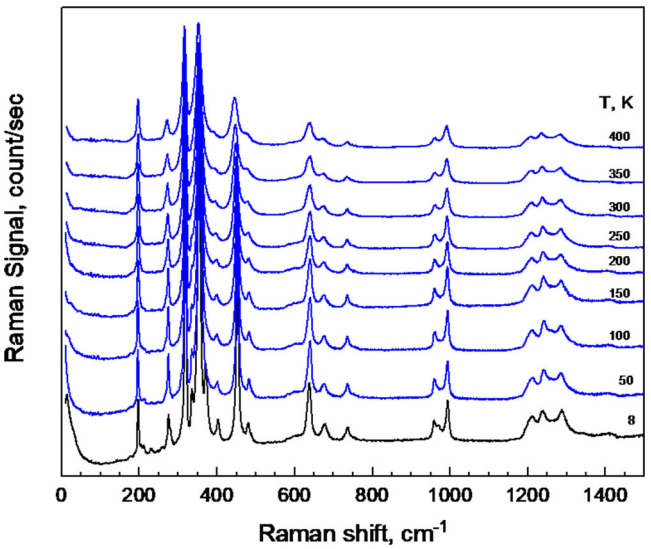

Figure 1. The temperature transformation of the full Raman spectra.

early stage was given by Scott [16]. In opposition to "soft mode," other modes are named "hard modes" (in some works "rigid").

However, we see some anomalies in the behavior of the hard modes below 50 K. New modes at 370 and 970 cm^{-1} appear close to 40 K (Figure 1). The splitting hard mode peaks are attributed to the structural phase transition. The appearance of new modes corresponds to the selection rules. In Figure 3, one can see the dependence of the ratio of the integrated intensities of two hard modes on the temperature. The slope of the curve of this dependence sharply changes near 33 K. This behavior is

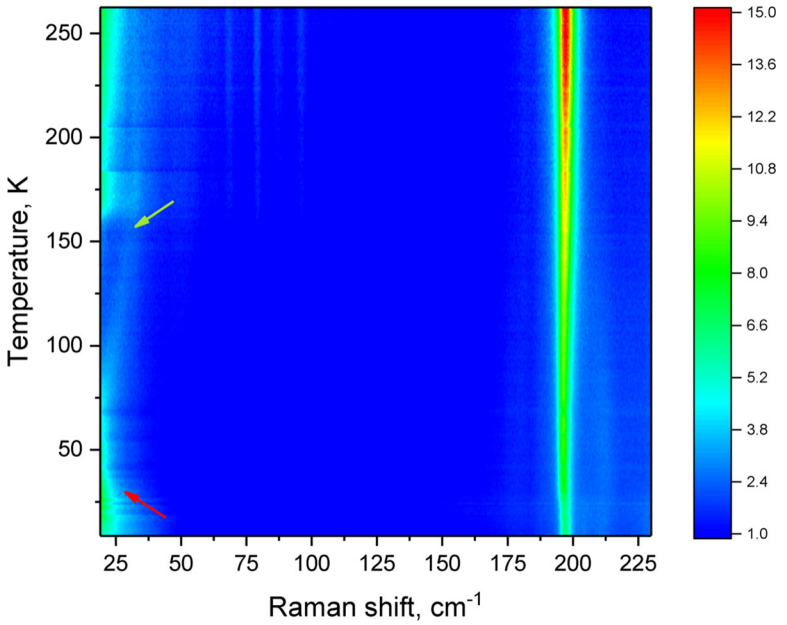

Figure 2. The Raman signal maps in the low-wavenumber part of the spectra. Green arrow condensing soft mode, red arrow – restoring soft mode.

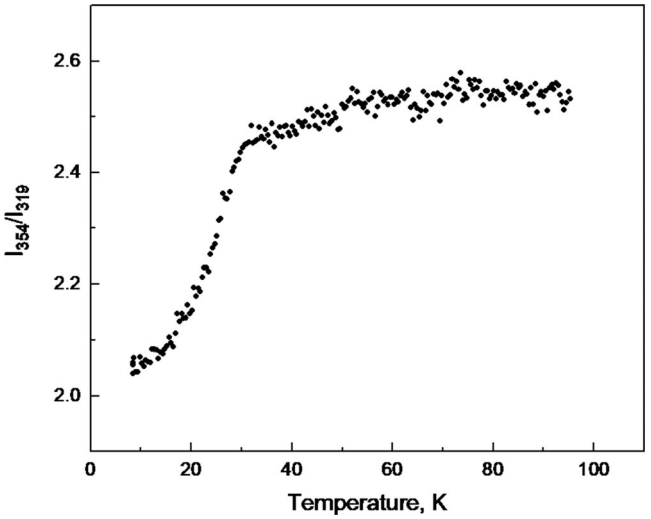

Figure 3. The relation of the integral intensities of the hard modes.

characteristic of a structural phase transition. It is the fine manifestation of fluctuations of the structural order parameter at low temperature.

It is important to note that ion substitution in huntite structure solid solutions did not significantly change the Néel temperature [4,5,11,12]. We assume that the substitution of a part of iron ions for gallium ions will shift the Néel temperature $T_N = 40$ K [9] within 10-15 K. Then, the temperatures of the structural and magnetic transition in

the crystal will be very close. This fact can affect the magnetic properties of the crystal, which have not yet been studied.

4. Conclusion

The crystal $TbFe_{2.5}Ga_{0.5}(BO_3)_4$ undergoes a structural phase transition from the $R32$ phase to the $P3_121$ phase at $T_1 = 33$ K, and the transition is accompanied by soft modes restoration and condensation. The temperature of the structural phase transition is close to the likeliest magnetic ordering temperature. The changes in the spectra are observed in the low-wavenumber region (up to 300 cm^{-1}) and middle part of the spectra (up to 1100 cm^{-1}): the modes related to structural ordering arise. We suggest that the proximity of the structural and magnetic transitions in this crystal can cause a strong interaction of the structural and magnetic order parameters. Studies of the magnetic properties of $TbFe_{2.5}Ga_{0.5}(BO_3)_4$ crystal should be carried out.

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