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Vibrational spectroscopy of GdCr$_3$(BO$_3$)$_4$: quantitative separation of crystalline phases

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Abstract. This work is devoted to the investigation of GdCr$_3$(BO$_3$)$_4$ crystals by the method of infrared spectroscopy. Incongruently melting borate GdCr$_3$(BO$_3$)$_4$ was obtained as a result of spontaneous crystallization. Crystal structures were identified by the method of infrared spectroscopy. Ab initio calculations in the frame of density functional theory enabled us to separate modes belonging to the $R32$ and $C2/c$ phases and to estimate the ratio of these phases in GdCr$_3$(BO$_3$)$_4$ crystals. We have found that the content of the rhombohedral $R32$ (non-centrosymmetric) modification is about 85 %.

1. Introduction

Rare-earth (RE) borates described by the general formula $RM_3(BO_3)_4$ ($R =$ RE or yttrium, $M =$ Al, Ga, Sc, Fe, or Cr) crystallize in a number of space groups (SG) with structure type of the natural mineral huntite [1]. These compounds are of interest due to their optical, magnetic, and magnetoelectric properties [2, 3]. RE aluminum borates possess excellent luminescent, nonlinear optical, thermal, and mechanical properties, are chemically stable and are widely used in self-frequency doubling and self-frequency summing lasers [4-6]. RE iron [7-11], aluminum [12-15] and gallium [16] borates demonstrate attractive magnetoelectric properties. Materials with a large magnetoelectric effect have an application potential as magnetoelectric sensors, magneto-electric and electro-magnetic memory elements, etc. It is important to notice that nonlinear optical and magnetoelectric properties are characteristic only for non-centrosymmetric structures.

RE chromium borates have polytype nature and crystallize in two modifications, namely, the rhombohedral one with the non-centrosymmetric SG $R32$ or the monoclinic one with the centrosymmetric SG $C2/c$. The crystal type depends on the growth conditions. Moreover, a coexistence of differently ordered structural fragments in one single crystal is a characteristic feature of RE chromium borates. [17, 18].

The objective of our present study are to identify the crystal structure of GdCr$_3$(BO$_3$)$_4$ obtained by the method of spontaneous crystallization and to evaluate its potential for practical applications.
2. Crystal structure of huntite-like borates

As was already mentioned in Introduction, RE borates have the structure type of huntite CaMg$_3$(CO$_3$)$_4$. The latter one crystallizes in the SG R32 [19]. Three types of coordination polyhedra are present in this structure, namely, CaO$_6$ trigonal prisms, MgO$_6$ octahedra and two types of CO$_3$ plain triangles [20]. The MgO$_6$ octahedra are connected by common edges forming chains along the c axis. The RO$_6$ trigonal prisms are isolated from each other. In the rare-earth double borates, Ca atoms are replaced by RE elements but instead of Mg atoms one finds M cations (which form a quasi-one-dimensional magnetic system in the case of Fe$^{3+}$ and Cr$^{3+}$ ions) [21]. The CO$_3^{2-}$ groups are replaced by the BO$_3^{3-}$ triangles (figure 1).

Besides the rhombohedral R32 structure there is a monoclinic one with SG C2/c. In each of these two structures it is possible to distinguish two different types of layers, $L_{2n}$ and $L_{2n+1}$, identical for two modifications (figure 2). The first type layer ($L_{2n}$) contains pairs of edge-sharing MO$_6$ octahedra which are further connected into a layer via isolated BO$_3$ triangles. The second one ($L_{2n+1}$) is built by trigonal RO$_6$ prisms and MO$_6$ octahedra connected in columns by vertices and also connected via the BO$_3$ triangles. In the rhombohedral (SG R32) polytype, the $L_{2n+1}$ layers which contain prisms are multiplied around the $L_{2n}$ layers by two-fold axes, whereas in the monoclinic modification (SG C2/c) by centers of symmetry [22, 23].

3. Experimental and computational details

3.1. Sample preparation

The incongruently melting borate GdCr$_3$(BO$_3$)$_4$ was obtained from a molten solution on the basis of K$_2$MoO$_4$ - 3MoO$_3$ as a result of spontaneous crystallization. Experiments were conducted with a ratio of the borate to the solvent in the mixture 1:1. The crucible with the charge was maintained in a furnace until a complete homogenization of the melt for 5 hours at 1100 – 1150 °C. Thereafter, the temperature was lowered to 1000 °C at a rate of 2 °C/h, then at a rate of 1°C/h to 840 °C and to 300 °C at a rate of 10 °C/h. Crystallization of the borate occurred at 1050 - 840°C.

For infrared measurements, a single crystal was grinded into a powder in a pobedite mortar.

3.2. Measurements by the methods of infrared spectroscopy

Absorption spectra of the powder sample of GdCr$_3$(BO$_3$)$_4$ in the far-infrared (FIR) region 50–550 cm$^{-1}$ were registered with the help of a Bruker IFS 125HR Fourier spectrometer (the spectral resolution was up to 2 cm$^{-1}$), using polyethylene disc technique. The infrared absorption spectra in the middle IR region (MIR) 550-1600 cm$^{-1}$ were registered on the same spectrometer with an attenuated total reflection (ATR) module. The powder sample was pressed to a diamond crystal of the ATR module. The spectral resolution was 2 cm$^{-1}$. We applied methods of vibrational spectroscopy combined with the group-theoretical analysis [24] in order to understand the peculiarities of the structure of the GdCr$_3$(BO$_3$)$_4$ borate.
3.3. *Ab initio* calculations

*Ab initio* calculations of phonon frequencies and intensities of the infrared-active modes in GdCr$_3$(BO$_3$)$_4$ were performed for both R32 and C2/c structures in a frame of the density functional theory (DFT) with hybrid functional B3LYP. The calculations were carried out within MO LCAO approach implemented in CRYSTAL14 code. Non-relativistic pseudopotential was used to describe the inner shells of the rare-earth ion. Details of the calculations can be found in Ref. [25].

4. Results of IR measurements and DFT calculations

Figure 3 shows the IR spectrum in the region 50-1600 cm$^{-1}$. It is typical for RE chromium borates with the SG R32. The majority of the observed modes find their counterparts in the calculated energy spectrum for this phase of GdCr$_3$(BO$_3$)$_4$. It is not possible to extract oscillator strengths from the measured spectra of powder samples. But we have to note that, in general, large calculated oscillator strengths correspond to strong lines in the measured spectrum, whereas for low ones one finds either weak lines or no line at all (see Table 1). Thus, the calculated data for the R32 phase are in good agreement with the experimental ones, which, in turn, confirms the assumption of predominantly rhombohedral structure of gadolinium chromium borate.

However, several features point to the presence of a monoclinic phase fragment. For internal vibrations of BO$_3^-$ groups, they are (i) a shoulder at 747 cm$^{-1}$ in the region of the symmetric bending vibrations, (ii) a splitting of the band at 980 cm$^{-1}$ in the region of the symmetric stretching vibrations, and (iii) shoulders at 1278 and 1372 cm$^{-1}$ in the region of asymmetric stretching vibrations (Figure 3, Table 1). In the FIR region, translational vibrations of the Gd$^{3+}$ and Cr$^{3+}$ ions, as well as translational and librational motions of the BO$_3^-$ groups are observed. Signatures of monoclinic inclusions in this spectral region are (i) a weak band at 73 cm$^{-1}$ of the Gd$^{3+}$ vibrations, (ii) bands at 126, 148, and 275 cm$^{-1}$, (iii) a weak shoulder at 248 cm$^{-1}$ due to the BO$_3^-$ vibrations, and (iv) a splitting of the band at 434 cm$^{-1}$ in the region of Cr$^{3+}$ vibrations. (Figures 3 and 4, Table 1).

![Figure 3](image-url)  
*Figure 3.* Infrared spectrum of GdCr$_3$(BO$_3$)$_4$. At the upper part of the figure, results of the *ab initio* calculations for the R32 (red bars) and C2/c (blue bars) phases are presented.
Table 1. Comparison between calculated and experimentally observed vibrational modes of GdCr₃(BO₃)₄ in the R32 phase. The assignments of particular modes are also given in accordance with the calculated eigenvectors. Experimental extra peaks ascribed to the monoclinic C2/c phase are in bold (their symmetry is indicated in parentheses). The corresponding calculated frequencies are plotted in Figures 3 and 4.

| Assignments | Ab initio calculations | Experiment |
|-------------|------------------------|------------|
|             | Wavenumbers, cm⁻¹ | Oscillator strength | Wavenumbers, cm⁻¹ |
| $A_1$       |                        |             |                      |
| $\nu_4$     | 216                    |              | 76 2,97              |
| $\nu_2$     | 342                    | 0,11        | 126 w ($B_a$) 79 m   |
| $\nu_1$     | 495                    | 0,001       | 148 w ($B_a$)        |
| $\nu_3$     | 660                    | 0,72        | 265 s                |
| $\nu_4$     | 975                    |              | 275 w ($A_a$)        |
| $\nu_2$     | 1004                   |              | 290 sh               |
| $\nu_3$     | 1209                   |              | 1278 sh ($B_a$) 1296 sh |
| $T (Gd^{3+})$ | 76 2,97                |              | 73 sh ($B_a$)        |
| $T (R^{3+})$ | 205 0,11               | 126 w ($B_a$)| 198 w                |
| $T (BO_3^{3-})$ | 225 0,001              | 148 w ($B_a$)| 400 s                |
| $T (Cr^{3+})$ | 261 0,72               | 265 s       | 424 sh               |
| $T (BO_3^{3-})$ | 289 0,17               | 275 w ($A_a$)| 653 sh               |
| $T (Cr^{3+})$ | 334 0,78               |              | 707 sh               |
| $\nu_4$     | 391 0,32               |              | 778 sh               |
| $\nu_2$     | 419 0,91               |              | 729 sh               |
| $\nu_3$     | 657 0,004              |              | 1278 sh ($B_a$) 1296 sh |
| $\nu_3$     | 690 0,73               | 202 w sh    | 1278 sh ($B_a$) 1296 sh |
| $\nu_3$     | 760 0,12               | 265 s       | 424 sh               |
| $\nu_3$     | 1302 0,02              |              | 424 sh               |
| $L (BO_3^{3-})$ | 95 2,08                | 99 s        | 440 s (Bu)           |
| $L (BO_3^{3-})$ | 205 0,005              | 202 w sh    | 440 s (Bu)           |
| $L (BO_3^{3-})$ | 224 0,0016             | 223 w       |                      |
| $L (BO_3^{3-})$ | 261 0,044              | 248 sh (Bu) 262 sh |
| $T (BO_3^{3-})$ | 300 0,36               | 294 s       |                      |
| $T (Cr^{3+})$ | 317 0,05               | 306 w       |                      |
| $T (BO_3^{3-})$ | 351 0,15               | 347 s       |                      |
| $T (Cr^{3+})$ | 375 0,015              | 376 m       |                      |
| $T (BO_3^{3-})$ | 420 0,33               | 434 s       |                      |
| $T (Cr^{3+})$ | 454 1,80               | 453 m       |                      |
| $\nu_4$     | 470 0,0007             | 480 s       |                      |
| $\nu_4$     | 605 0,011              | 601 w       |                      |
| $\nu_4$     | 650 0,0038             | 622 w       |                      |
| $\nu_4$     | 687 0,053              | 680 s       |                      |
| $\nu_2$     | 752 0,017              | 739 s       |                      |
| $\nu_2$     | 986 0,005              | 980 w       |                      |
| $\nu_2$     | 1187 0,78              | 1187 s      |                      |
| $\nu_3$     | 1210 0,001             | 990 w (Bu)  1372 sh (Au) |
| $\nu_3$     | 1318 0,30              | 1314 s      |                      |

sh – shoulder, w – weak, s – strong, m – medium
Figure 4. FIR part of the spectrum of GdCr$_3$(BO$_3$)$_4$.

5. Estimate of the relative quantity of the monoclinic phase in the sample

Figure 5. Long-wavelength part of the absorption spectrum of GdCr$_3$(BO$_3$)$_4$ (dashed grey line). Decomposition into two Gaussian peaks is shown by thin lines.
Figure 5 shows the experimental IR spectrum at long wavelengths where the translational vibrations of Gd$^{3+}$ are observed. The band at 79 cm$^{-1}$ has a shoulder 73 cm$^{-1}$, which is associated with a small admixture of the monoclinic phase. We have fitted the experimental spectrum by two Gaussians and found that the intensity of the strongest band constitutes 82.3%. According to calculations, the oscillator strength of the considered vibration in the monoclinic phase is 1.5 times greater than in the rhombohedral one. Taking into account this value, we could estimate that the content of the rhombohedral phase in the sample was about 87.5%.

6. Conclusions

Good quality single crystals of gadolinium chromium borate with the structure of the mineral huntite were obtained by spontaneous crystallization from the flux. IR spectroscopy delivered experimental data on the IR-active phonons. The data were compared with the results of ab initio DFT calculations. This comparison shows that the crystal has a polytype structure, containing mainly the rhombohedral phase $R32$ and a small part of the monoclinic phase $C2/c$. The ab initio calculations allowed us to distinguish between vibrations belonging to the one and the other structural phases. From the relative intensities of the two low-frequency bands corresponding to translational motions of Gd in the $R32$ and $C2/c$ phases and taking into account the calculated oscillator strengths, we were able to evaluate the content of monoclinic phase in the predominantly rhombohedral single crystal of GdCr$_3$(BO$_3$)$_4$, which was around 15%. Thus, we have shown that the gadolinium chromium borate crystallizes, mainly, in the noncentrosymmetric phase $R32$. This indicates a potential of owning magnetoelectric properties, by analogy with noncentrosymmetric iron, aluminium and gallium RE borates. Currently, the work is underway to obtain large single-phase crystals of GdCr$_3$(BO$_3$)$_4$ for investigation of the magnetoelectric effect.

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