

## Vibrational spectra and the crystal growth of huntite-like chromium borates $\text{RCr}_3(\text{BO}_3)_4$ , where $\text{R} = \text{La} - \text{Er}$

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In this study, the synthesized huntite-like borates  $\text{RCr}_3(\text{BO}_3)_4$ , where  $\text{R} = \text{La}-\text{Ho}$ , have been characterized by Raman and infrared techniques.

Rare-earth chromium borate crystals  $\text{RCr}_3(\text{BO}_3)_4$ , where  $\text{R} = \text{La} - \text{Ho}$ , were grown by the flux growth method, using  $\text{K}_2\text{MoO}_{10} \cdot \text{B}_2\text{O}_3$  as a solvent, as spontaneous nucleation in the temperature range of 1150-900°C. The infrared absorption spectra of the synthesized compounds were obtained on FSM 12011 FT-IR spectrometer using standard KBr disc technique in the wavenumber region from 4000 to 400  $\text{cm}^{-1}$ . The spectral resolution was about 2  $\text{cm}^{-1}$ . The IR spectra in the region of 550–50  $\text{cm}^{-1}$  were recorded on a Bruker FT-IR spectrometer IFS 125 HR with the resolution of 1  $\text{cm}^{-1}$ . The Raman spectra were obtained on a Vertex 70 Fourier spectrometer, equipped with RAM II FT-Raman module with Ge detector (Bruker) under the excitation of 1064 nm.

Factor group analysis for the compounds, crystallizing in the space groups  $R32$  and  $C2/c$ , which are the polytypes with the very similar structures, has been performed. The differences observed in the spectra have been explained by the differences of symmetry. For borate ions, located in two independent positions of the structure with sp.gr.  $R32 (D_3)$ , in the Raman spectra we can expect seven stretching vibrations: 3  $\nu_1 (2A_1 + E)$ , 4  $\nu_3 (A_1 + 3E)$  and five bending vibrations: 1  $\nu_2 (E)$ , 4  $\nu_4 (A_1 + 3E)$ . In the infrared spectra there should exist five stretching vibrations: 1  $\nu_1 (E)$ , 4  $\nu_3 (A_2 + 3E)$  and seven bending vibrations: 3  $\nu_2 (2A_2 + E)$ , 4  $\nu_4 (A_2 + 3E)$ . For  $\text{BO}_3^{3-}$  unit in two  $C_1$  positions in sp.gr.  $C2/c$  factor group analysis predicts the appearance of 12 Raman – active stretching vibrations:  $2A_g + 2B_g (\nu_1)$ ,  $4A_g + 4B_g (\nu_3)$  and 12 Raman – active bending vibrations:  $2A_g + 2B_g (\nu_2)$ ,  $4A_g + 4B_g (\nu_4)$ , and also 12 infrared – active stretching vibrations:  $2A_u + 2B_u (\nu_1)$ ,  $4A_u + 4B_u (\nu_3)$  and 12 infrared – active bending vibrations:  $2A_u + 2B_u (\nu_2)$ ,  $4A_u + 4B_u (\nu_4)$ .

The external modes include the translational modes of  $\text{R}^{3+}$ ,  $\text{Cr}^{3+}$ , and  $\text{BO}_3^{3-}$  ions, and the  $\text{BO}_3^{3-}$  librations. Group theoretical analysis leads to the following results:  $3A_1 + 11E$  (Raman active) and  $8A_2 + 11E$  (IR active) for  $R32$  sp.gr.; and  $17A_g + 19B_g$  (Raman active) and  $16A_u + 17B_u$  (IR active) for  $C2/c$  sp.gr.

The assignment for the stretching and bending vibrations of  $\text{BO}_3^{3-}$  groups and external modes has been made. The dependence of the realized borate space group from the crystal growth conditions and the type of rare-earth atom was revealed. The main differences are observed in the region of asymmetrical stretching vibrations of  $\text{BO}_3^{3-}$  units. This study shows that  $\text{GdCr}_3(\text{BO}_3)_4$  and  $\text{EuCr}_3(\text{BO}_3)_4$  borates crystallize in sp.gr.  $R32$  irrespective of growth conditions. The borates with the large rare-earth elements  $\text{La} - \text{Nd}$  always form the monoclinic structures, irrespective of crystallization temperature. The borates  $\text{SmCr}_3(\text{BO}_3)_4$ ,  $\text{DyCr}_3(\text{BO}_3)_4$  have been obtained in two modifications.  $\text{TbCr}_3(\text{BO}_3)_4$ ,  $\text{HoCr}_3(\text{BO}_3)_4$  and  $\text{ErCr}_3(\text{BO}_3)_4$  have a monoclinic structure. The formation of chromium borates with the less large cations do not occur.

The solid solution  $\text{GdCr}_3(\text{BO}_3)_4 (R32) - \text{NdCr}_3(\text{BO}_3)_4 (C2/c)$  were investigated by the IR and optical spectroscopy techniques. From the pure Gd compound to composition  $\text{Gd}_{0.3}\text{Nd}_{0.7}$ , the rhombohedral phase crystallizes. At the higher content of Nd, the gradual transition to pure  $C2/c$  sp. gr. takes place.