New Layer Borate \((\text{Nd}_{0.925}\text{Na}_{0.075})\text{Nd}[\text{B}_9\text{O}_{15}(\text{OH})_2]\text{Cl}_{0.85} \cdot 2.65\text{H}_2\text{O}\) and Its Place in the Structural Systematics

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Received April 13, 2010

STRUCTURE OF INORGANIC COMPOUNDS

Abstract—Crystals of a new aqueous rare-earth borate—(\((\text{Nd}_{0.925}\text{Na}_{0.075})\text{Nd}[\text{B}_9\text{O}_{15}(\text{OH})_2]\text{Cl}_{0.85} \cdot 2.65\text{H}_2\text{O}\), space group \(P2\overline{1}n\)—are obtained under hydrothermal conditions. The crystal structure is determined by the heavy-atom method without preliminary knowledge of the chemical formula. The independent anionic radical is a new corrugated layer related to layer pentaborates. Layers related by centers of inversion form sheets. Nd and Cl atoms are located in the intersheet space and in the large voids of the sheet. One of the positions of both Nd and Cl atoms is isomorphously shared with Na atoms and \(\text{H}_2\text{O}\) molecules, respectively. The new borate is characterized as a polyborate (megaborate) containing the \((4:3[2T + \Delta] + 1[\Delta])_{s\infty} + (5[3T + 2\Delta])_{s\infty}\) complex anionic radical. The topological variants of the completion of the layer by additional triangles and the connection of layers into a framework are considered. The relationship between the new borate and the earlier studied \(\text{LaB}_5\text{O}_8(\text{OH})_2 \cdot 1.5\text{H}_2\text{O}\) framework borate is revealed.

DOI: 10.1134/S1063774510050068

INTRODUCTION

Rare-earth borates are of interest due to their luminescent, nonlinear optical, laser, and ion-conduction properties. These compounds are synthesized by various methods. Aqueous rare-earth borates are poorly studied compounds. They are obtained by hydrothermal synthesis. The following borates are known: \(\text{LiNd}[\text{BO}_3(\text{OH})]\) [1], \(\text{Ln}[\text{BO}_3(\text{OH})_2]\text{Cl}\) (\(\text{Ln} = \text{La, Ce, Pr, Nd}\) [2], \(\text{Ln}[\text{BO}_5(\text{OH})_3]\) (\(\text{Ln} = \text{Sm–Lu}\) [3], \(\text{LnH}[\text{BO}_4(\text{OH})]\) (\(\text{Ln} = \text{Sm, Gd}\) [4], \(\text{NaNd}[\text{BO}_6(\text{OH})_4]\) [5], \(\text{La}[\text{BO}_6(\text{OH})_2]\) \cdot 1.5\text{H}_2\text{O}\) [6], \(\text{La}[\text{BO}_5(\text{OH})_2]\) [7], \(\text{Ln}[\text{BO}_5(\text{OH})_2]\) (\(\text{Ln} = \text{La–Nd}\), \(\text{Ln}[\text{BO}_6(\text{OH})_4]\) \cdot \text{H}_2\text{O}\) (\(\text{Ln} = \text{Pr–Eu}\), and \(\text{Ce}[\text{BO}_6(\text{OH})_2]\text{NO}_3\) \cdot 3\text{H}_2\text{O}\) [8]. Two of these compounds exhibit high optical nonlinearity [2, 3]. Aqueous borates have original anionic radicals (from frameworks to chains) which are of crystal-chemical interest. In this article the results of the hydrothermal synthesis and a crystal-structure determination of the new borate \((\text{Nd}_{0.925}\text{Na}_{0.075})\text{Nd}[\text{B}_9\text{O}_{15}(\text{OH})_2]\text{Cl}_{0.85} \cdot 2.65\text{H}_2\text{O}\) (1) are reported and a crystal chemical analysis of its structure is performed.

EXPERIMENTAL

Single crystals I were obtained in the course of investigating phase formation in the \(\text{Nd}_2\text{O}_3–\text{NaCl–B}_2\text{O}_3–\text{H}_2\text{O}\) system. The experiments were carried out in standard autoclaves 5–6 cm³ in volume protected with a fluoroplastic covering. The synthesis was performed at \(t = 270–280^\circ\text{C}\) and \(p = \sim 70\) atm. The lower temperature was determined by the kinetics of the hydrothermal reactions, and the upper temperature was limited by the potentialities of the apparatus. The duration of the experiments (18–20 days) was determined by the reaction completion. The filling factor of an autoclave was chosen so that the pressure remained constant. The mass ratio of oxides \(\text{Nd}_2\text{O}_3 : \text{B}_2\text{O}_3\) was 1 : 1. The synthesis was performed in a 20 wt % solution of the NaCl mineralizer.

The crystals that were obtained were rose-lilac in color with a nacreous play. They had perfect cleavage and crystallized in the shape of thin micalike square or rectangular plates which were, on average, \(0.5 \times 0.5 \times 0.05\) mm in size. The plates formed divergent aggregates up to spherulites. The morphology of the crystals suggested that they fall in the lower class of symmetry with the orthogonal coordinate system.

The absence of analogues of an X-ray powder diffraction pattern of compound I in the PDF Database indicated that this compound was new. The X-ray diffraction pattern was characteristic of textured specimens, which indicated that the crystal has a layer structure. Similar phases were obtained under the same conditions in the systems containing La and Ce. A test for second harmonic generation using a pulsed YAG : Nd laser operating in the reflecting mode [9] indicated that the crystals are centrosymmetric.

The first attempt to determine the parameters on a Syntex P–1 diffractometer (\(\lambda\text{MoK}_{\alpha}, \beta\) filter) revealed a set of three coplanar vectors, each of which were \(6.4\) Å long and intersected at an angle of \(60^\circ\), as
is characteristic of pentaborate layers. One of the 6.4 Å-long parameters was taken as the monoclinity axis. Two other parameters chosen were 10.7 Å (the long diagonal of the pseudohexagonal cell) and 11.58 Å (in a plane perpendicular to the set of three vectors) long and formed an angle of 92.5°. A set of experimental data obtained on this diffractometer did not allow us to determine the structural model and gave grounds to assume that the cleavage of crystals and the following imperfect intergrowth of the individuals result in twins.

The final reliable determination and refinement of the parameters of I, as well as the collection of the experimental data for structure solution, was performed on an Xcalibur S diffractometer equipped with a CCD detector for a small rectangular plate (Table 1), which was visually distinguished due to its satisfactory quality. The monoclinic symmetry and the monoclinicity angle β ~ 92.5° (mineralogical setting) were confirmed, two parameters coincided with those found above, and the third parameter was doubled. The data set was collected in the complete sphere of the reciprocal space. The data were processed with the CrysAlis program. The indexing showed that almost all the reflections fit the parameters chosen and the specimen is a single crystal. The reflections were averaged in the corresponding diffraction class; the Friedel pairs were also averaged. The extinction of the \( h0l \) reflections with \( h + l = 2n + 1 \) and the presence of \( 0k0 \) reflections with any \( k \) unambiguously determined space group \( P12/n1 \) (a nonstandard setting of \( P12/c1 = C_{2v}^{4} \)). A search for the model was performed using the CSD program package. Two Nd atoms were located in general positions with the PATS program. The position of the Cl atom at the twofold axis and the positions of 20 O and 9 B atoms were found step by step from difference syntheses.

An analysis of sharing the oxygen vertices in the boron–oxygen radical showed that, in accordance with the electrostatic balance, 15 O atoms that form bridges between B-polyhedra (BO\(_3\) triangles and/or BO\(_4\) tetrahedra) are oxygen atoms, whereas two terminal vertices in the B-polyhedra are oxygen atoms of OH groups. Three O atoms that enter the coordination of a Nd atom only belong to water molecules \( \text{Ow} \). With consideration for this identification of the O atoms, the formula of the new borate I could be represented as

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\text{Nd}_{0.925}\text{Na}_{0.075}\text{Nd}[\text{B}_{9}\text{O}_{15}(\text{OH})_{2}]\text{Cl}_{0.85} \cdot 2.65\text{H}_{2}\text{O}
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