



Rapid Communication

Synthesis and crystal structure of new layered BaNaSc(BO₃)₂ and BaNaY(BO₃)₂ orthoboratesYurii V. Seryotkin^{a,b,*}, Vladimir V. Bakakin^c, Aleksandr E. Kokh^a, Nadezhda G. Kononova^a, Tatyana N. Svetlyakova^{a,b}, Konstantin A. Kokh^a, Tatyana N. Drebushchak^{b,d}^a Institute of Geology and Mineralogy RAS, 3, Koptyuga avenue, 630090 Novosibirsk, Russia^b Novosibirsk State University, 2, Pirogova street, 630090 Novosibirsk, Russia^c Institute of Inorganic Chemistry RAS, 3, Lavrentieva avenue, 630090 Novosibirsk, Russia^d Institute of Solid State Chemistry and Mechanochemistry RAS, 18, Kutateladze street, 630128 Novosibirsk, Russia

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ABSTRACT

Crystals of two new layered BaNaSc(BO₃)₂ (**I**) and BaNaY(BO₃)₂ (**II**) orthoborates are grown from the melt-solution by the spontaneous crystallization onto the platinum loop. Single crystal X-ray analysis showed that the compounds are isostructural with the space group $R\bar{3}$, $a=5.23944(12)$ and $5.3338(2)$ Å, and $c=34.5919(11)$ and $35.8303(19)$ Å for **I** and **II**, respectively, $Z=6$. The distinctive feature of the structure is the close-packed composite anion-cation (Ba,Na)(BO₃) layers. The layers are combined into the base building packages of two types: $\{M^{3+}[Ba^{2+}(BO_3)^{3-}]_2\}^+$ and $\{M^{3+}[Na^+(BO_3)^{3-}]_2\}^-$, where M is Sc or Y. Neutral-charge two-package (four-layer) blocks are stacked by the rhombohedral principle into twelve layers of the cubic packing.

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1. Introduction

Rare-earth orthoborates MBO_3 are of interest as scintillators and luminophores with a high light output [1]. These compounds are typically prepared by the melt-solution crystallization because of their sufficiently high melting points (> 1600 °C). This brings up an active search for solvents to prepare crystals at lower temperatures.

The paper [2] reports the growth of orthoborate crystals in M_2O_3 - B_2O_3 - PbO and M_2O_3 - B_2O_3 - PbO - PbF_2 systems, where M is In, Sc, and Lu. The authors managed to lower the crystallization point to 1250 °C but the crystal quality was degraded with a Pb-containing solvent due to the doped radioactive lead isotopes. Bertrand-Chadeyron et al. [3] lowered the formation temperature of $InBO_3$ to 1150 °C using the lithium metaborate $LiBO_2$ as a flux and succeeded in preparing spontaneous thin-plate crystals $30 \times 30 \times 1$ mm³ in size.

A series of experiments on spontaneous crystallization [4] revealed a possibility for the formation of $InBO_3$ crystals in the In_2O_3 - B_2O_3 - BaO - Na_2O system. Bulk crystals weighing as much as 12 g were first obtained over the 950–860 °C range. The

temperature for growing $InBO_3$ was thus lowered to values allowing the use of resistive long-life heating furnaces.

The experimental results permitted to suggest the B_2O_3 - BaO - Na_2O system for growing scandium and yttrium borates. The experiments revealed an interaction between the basic substance and the solvent resulting in two new compounds such as BaNaSc(BO₃)₂ in the Sc_2O_3 - B_2O_3 - BaO - Na_2O system and BaNaY(BO₃)₂ in Y_2O_3 - B_2O_3 - BaO - Na_2O , respectively.

2. Experimental

BaNaM(BO₃)₂ ($M=Sc, Y$) crystals were prepared by the spontaneous crystallization from the initial composition 0.38 BaB₂O₄, 0.38 NaBO₂, and 0.24 MBO₃ at 950–930 °C in the M_2O_3 - B_2O_3 - BaO - Na_2O system. The Na₂CO₃ (99.8%), BaCO₃ (99.0%), H₃BO₃ (99.8%), Sc₂O₃ (99.0%), and Y₂O₃ (99.0%) reagents of high purity grade were used.

The melt-solution was prepared in a platinum crucible of volume 50 cm³ in amounts of 40 g with a preliminary solid-phase synthesis of an initial charge at 800 °C by a patented method [5]. This was due to the complicated preparation of the melt from reagents containing boric acid and carbonates owing to the intense decomposition. The synthesis was performed for 2–3 h to remove CO₂ and H₂O completely. Then the temperature in the furnace was elevated to 1000 °C and the melt was held for 20 h to

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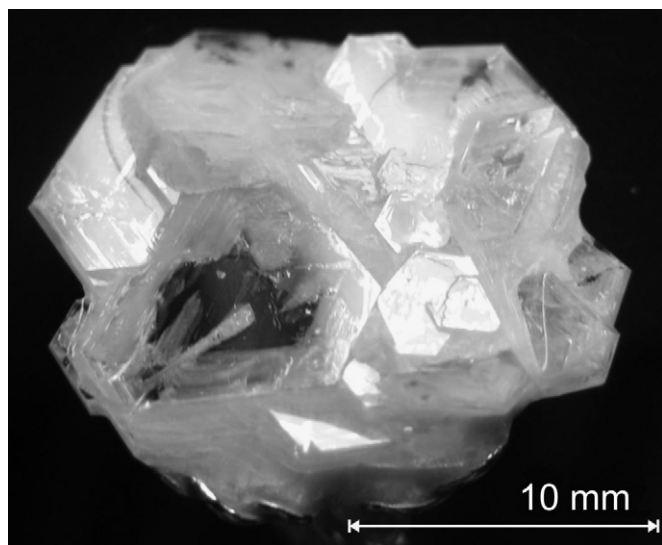


Fig. 1. A photograph of the BaNaSc(BO₃)₂ crystal grown onto the Pt-loop.

homogenize. A platinum wire with a loop was placed in the center of the melt surface and the temperature was lowered with the 10 °C/h rate. After the initial stage of crystallization to be visualized, the melt was cooled with the 1–2 °C/day rate. When spontaneous crystals deposited on the platinum loop have reached the required dimensions, a scab was taken out of the melt and cooled to room temperature. Fig. 1 shows a photograph of the BaNaSc(BO₃)₂ crystal.

3. X-ray crystallographic analysis

The crystals were inspected under a polarizing microscope to check for twinning. Diffraction intensity data were collected with an Oxford Diffraction Gemini R Ultra diffractometer equipped with a CCD, using a graphite monochromator for MoK α -radiation, operated at 50 kV and 40 mA. Experimental details for the data collection and structure determination are given in Table 1. Data reduction, including a background correction and Lorentz and polarization corrections, was performed with the CrysAlis program package. An empirical absorption correction using the multi-scan technique was applied. Metrically hexagonal lattice was observed for both the crystals. In deciding on a space group, R $\bar{3}$ was preferred.

The structures were solved by direct methods with the SHELXS-97 program [6] and refined using the SHELXL-97 program [7] with neutral atom scattering factors. Table 2 contains the coordinates and thermal parameters for the atomic positions. Table 3 lists the interatomic distances in the studied structures. The structural data are deposited as CIFs at the ICSD (CSD-nos. 421411 and 421412).

4. Results and discussion

Compounds BaNaSc(BO₃)₂ (I) and BaNaY(BO₃)₂ (II) belong to a new structure type in the large family of layer orthoborates. Planar anion (BO₃)³⁻ groups of the threefold symmetry are located layer-by-layer. The large Ba²⁺ and Na⁺ cations in the threefold positions are in the vicinity of the borate layers. The cations intermediate in size, Sc³⁺ or Y³⁺, are situated in the interlayer positions of the $\bar{3}$ symmetry and are coordinated octahedrally to the oxygen atoms of six borate groups (Fig. 2).

Table 1
Basic crystallographic and experimental data for studied compounds.

| Chemical content | BaNaSc(BO ₃) ₂ | BaNaY(BO ₃) ₂ |
|---|--|--|
| <i>a</i> (Å) | 5.23944(12) | 5.3338(2) |
| <i>c</i> (Å) | 34.5919(11) | 35.8303(19) |
| <i>V</i> (Å ³) | 822.38(4) | 882.78(7) |
| Space_group | R $\bar{3}$ | R $\bar{3}$ |
| <i>Z</i> | 6 | 6 |
| Crystal size (mm ³) | 0.41 × 0.23 × 0.04 | 0.16 × 0.14 × 0.08 |
| <i>d</i> (g/cm ³) | 3.912 | 4.140 |
| Instrument | Oxford diffraction gemini R Ultra | |
| Radiation | MoK α =0.71069 Å | |
| Scan type | ω | |
| 2 θ range (°) | 7.06–90.96 | 6.82–74.16 |
| <i>h</i> _{min} , <i>h</i> _{max} ; <i>k</i> _{min} , <i>k</i> _{max} ; <i>l</i> _{min} , <i>l</i> _{max} | –10, 10; –10, 10; –69, 69 | –8, 8; –8, 9; –60, 59 |
| <i>F</i> (000) | 876 | 984 |
| μ (MoK α) (mm ⁻¹) | 8.415 | 16.498 |
| Number of <i>I</i> _{hkl} measured | 18,976 | 11,389 |
| Number of unique <i>F</i> _{hkl} ² | 1557 | 1008 |
| <i>R</i> _{int} | 0.0393 | 0.0381 |
| Number of observed reflections [<i>I</i> > 2 σ (<i>I</i>)] | 1508 | 999 |
| Number of variables | 36 | 36 |
| <i>R</i> factors for observed reflections [<i>I</i> > 2 σ (<i>I</i>)] | <i>R</i> ₁ =0.0204, <i>wR</i> ₂ =0.0499 | <i>R</i> ₁ =0.0325, <i>wR</i> ₂ =0.0803 |
| <i>R</i> factors for all data | <i>R</i> ₁ =0.0217, <i>wR</i> ₂ =0.0504 | <i>R</i> ₁ =0.0329, <i>wR</i> ₂ =0.0805 |
| Residual electron density (e/Å ³) | 3.176, –1.592 | 2.862, –2.136 |

Table 2

Atomic coordinates, equivalent isotropic displacement parameters $U_{eq}=1/3 \sum_i (\Sigma_j U_{ij} a_i^* a_j^* a_i a_j)$ (Å²) and occupancies.

| | | | BaNaSc(BO ₃) ₂ | BaNaY(BO ₃) ₂ |
|-----|-------------|------------------------|---------------------------------------|--------------------------------------|
| M1* | 3 <i>a</i> | <i>x</i> | 0 | 0 |
| | | <i>y</i> | 0 | 0 |
| | | <i>z</i> | 0 | 0 |
| | | <i>U</i> _{eq} | 0.00712(7) | 0.00852(15) |
| M2* | 3 <i>b</i> | <i>x</i> | 0.3333 | 0.3333 |
| | | <i>y</i> | 0.6667 | 0.6667 |
| | | <i>z</i> | 0.1667 | 0.1667 |
| | | <i>U</i> _{eq} | 0.00758(7) | 0.00748(15) |
| Ba | 6 <i>c</i> | <i>x</i> | 0 | 0 |
| | | <i>y</i> | 0 | 0 |
| | | <i>z</i> | 0.103197(4) | 0.101928(10) |
| | | <i>U</i> _{eq} | 0.00916(4) | 0.01048(12) |
| Na | 6 <i>c</i> | <i>x</i> | 0.3333 | 0.3333 |
| | | <i>y</i> | 0.6667 | 0.6667 |
| | | <i>z</i> | 0.04628(7) | 0.05259(18) |
| | | <i>U</i> _{eq} | 0.0306(4) | 0.0365(12) |
| B1 | 6 <i>c</i> | <i>x</i> | 0.6667 | 0.6667 |
| | | <i>y</i> | 0.3333 | 0.3333 |
| | | <i>z</i> | 0.03739(7) | 0.0399(2) |
| | | <i>U</i> _{eq} | 0.0078(3) | 0.0154(12) |
| B2 | 6 <i>c</i> | <i>x</i> | 0.6667 | 0.6667 |
| | | <i>y</i> | 0.3333 | 0.3333 |
| | | <i>z</i> | 0.13060(7) | 0.1271(2) |
| | | <i>U</i> _{eq} | 0.0080(3) | 0.0137(11) |
| O1 | 18 <i>f</i> | <i>x</i> | 0.3652(2) | 0.3728(8) |
| | | <i>y</i> | 0.2175(3) | 0.1986(15) |
| | | <i>z</i> | 0.03732(3) | 0.03957(10) |
| | | <i>U</i> _{eq} | 0.01494(16) | 0.0505(17) |
| O2 | 18 <i>f</i> | <i>x</i> | 0.9687(2) | 0.9627(6) |
| | | <i>y</i> | 0.4841(2) | 0.4812(6) |
| | | <i>z</i> | 0.12992(4) | 0.12720(10) |
| | | <i>U</i> _{eq} | 0.01514(17) | 0.0170(5) |

Table 3.
Interatomic distances (Å).

| BaNaSc(BO ₃) ₂ | | BaNaY(BO ₃) ₂ | |
|---------------------------------------|------------|--------------------------------------|------------|
| B1–O1 (3 ×) | 1.3799(10) | B1–O1 (3 η) | 1.359(4) |
| B2–O2 (3 ×) | 1.3708(10) | B2–O2 (3 η) | 1.368(3) |
| Sc1–O1 (6 ×) | 2.1087(10) | Y1–O1 (6 η) | 2.231(4) |
| Sc2–O2 (6 ×) | 2.0863(10) | Y2–O2 (6 η) | 2.221(3) |
| Ba–O2 (3 ×) | 2.7805(11) | Ba–O2 (3 η) | 2.821(3) |
| Ba–O2 (3 ×) | 2.7828(11) | Ba–O2 (3 η) | 2.823(3) |
| Ba–O1 (3 ×) | 2.8235(11) | Ba–O1 (3 η) | 2.822(4) |
| Mean | 2.796 | Mean | 2.822 |
| Na–O1 (3 ×) | 2.4610(13) | Na–O1 (3 η) | 2.650(8) |
| Na–O1 (3 ×) | 2.8231(13) | Na–O1 (3 η) | 2.777(8) |
| Mean | 2.642 | Mean | 2.714 |
| Na–O2 (3 ×) | 3.333(3) | Na–O2 (3 η) | 3.174(6) |
| [Na–B1] | 2.894(3) | [Na–B1] | 3.313(10) |
| [Na–B1 (3 ×)] | 3.0406(4) | [Na–B1 (3 η)] | 3.1130(15) |

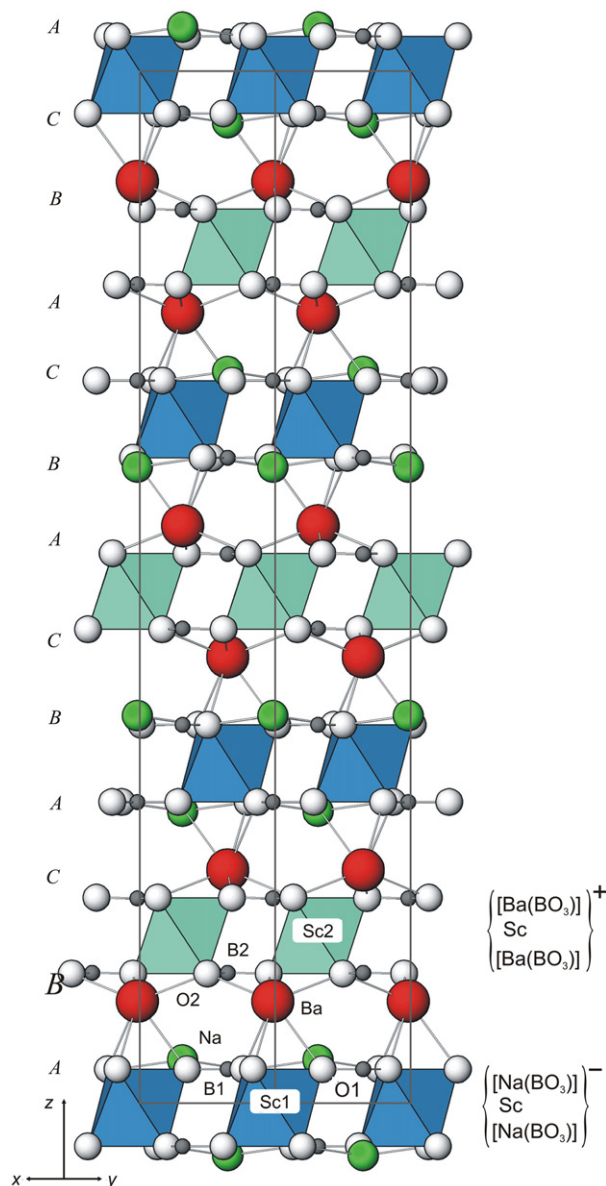


Fig. 2. The projection of the BaNaSc(BO₃)₂ structure on the (110) plane. The alternation of two-layer [Sc[Ba(BO₃)₂]⁺ and [Sc[Na(BO₃)₂]⁻ packages is shown in terms of the closest cubic packing of the A(BO₃) layers, (ABC)₄.

The structures of the compounds studied fall in the category of those built of close-packed composite anion–cation AO₃ layers, where A is the large cation [8]. The AO₃ layers are usually stacked by the closest packing principle being linked through the intermediate M cations in the octahedral vacancies. Typical compounds are the cubic and numerous hexagonal perovskites, e.g., Ba^{[A]Tl^[M]O₃.}

In the minimal four-node rhomb of the unit cell (see Fig. 3), of eight triangular meshes of the AO₃ net, only two meshes are totally anionic, whereas six of those have the cationic A vertex each. When the nets are mutually stacked, the M cations rest on those meshes only with one cation for the net.

The basis for the AO₃ net of the structures considered is the triangular borate (BO₃)³⁻ anion occupying one of two O₃ meshes. In each [A(BO₃)] layer, one O₃ mesh alone remains vacant for the M cation (Fig. 3), and the binding M^[6] cation uses the totality of O₃-mesh resource of the two layers. This results in the two-layer package {[A(BO₃)]–M–[A(BO₃)]} with either BO₃ groups or the faces of the M octahedra as the O₃ meshes. No M cations are located in the interpackage space, the packages are held together owing to the bonds to the high-coordinated Ba²⁺ cations, which are slightly displaced from their layer.

So, the two-layer {M[A(BO₃)₂} package is the base building block for this class of the structures. The Ba₂Mg(BO₃)₂ borate [9] may be thought of as a prototype with the structure of the natural carbonate eitelite, Na₂Mg(CO₃)₂ [10]. In the latter, neutrally charged {Mg[Ba(BO₃)₂} packages possess the six-layer stacking in the rhombohedral cell. In the structures studied, the [A(BO₃)] layers of two compositions form the two-layer packages of two types: {M³⁺[Ba²⁺(BO₃)³⁻]₂}⁺ and {M³⁺[Na⁺(BO₃)³⁻]₂}⁻. Neutrally charged two-package (four-layer) blocks are stacked by the rhombohedral principle into 12 layers of the cubic packing (Fig. 2) with the doubled c-period as compared to the prototype.

All the cations are located on the threefold axes in the sequence . . . M1–Ba–B2–B1–Na–M2–Na–B1–B2–Ba–M1 When repelling from B³⁺ of the adjacent layer, the Ba²⁺ cation is displaced from its layer plane to the face of the M1 octahedron. As a result, of 12 nodes of the original (ideal) cubeoctahedron, only six layer O atoms and three those of the neighboring layer remain in its coordination sphere (Table 3). Similar to Ba²⁺, Na⁺ is slightly displaced from the layer plane.

A comparison of structures I and II shows the a and c parameters to be enlarged of 1.8% and 3.6%, respectively, in II. Replacing the Sc cation (r_i=0.75 Å) with Y (r_i=0.90 Å) in M positions increases the {Y[A(BO₃)₂} package thickness by ≈ 0.3 Å. The increase in the a-parameter is due to the ≈ 0.1 Å enlargement of the shared horizontal edges of the MO₆ octahedron and Ba polyhedron with virtually unchanged B–O distances (Table 3). The height of interpackage space decreases by 0.1 Å in this case. The packages draw together to compensate the enlargement of horizontal sizes of polyhedra, and thus to hold the reasonable Ba–O bond lengths.

In structure I, Na⁺ is displaced from the layer by 0.31 Å. Such a displacement, however, fails to provide its bonding to the oxygen atoms of the adjacent layer (Fig. 4a) and the cation has a unilateral ditrigonal coordination (3+3). Differentiating among the distances is associated with a turn of BO₃ triangles by 7.61° relative to the symmetrical position. This may be suggested to be due to that the three shortened Na–O bonds are more favorable than six elongated of those, as evidenced by virtually symmetrical arrangement (0.06° turn) of the BO₃ groups in the Ba layer with equal Ba–O bonds.

In II, the Na–O distances in the layer increased on an average and a difference between them reduced (Fig. 4b) with decreasing the turn angle of BO₃ to 2.74°. The change in average Na–O

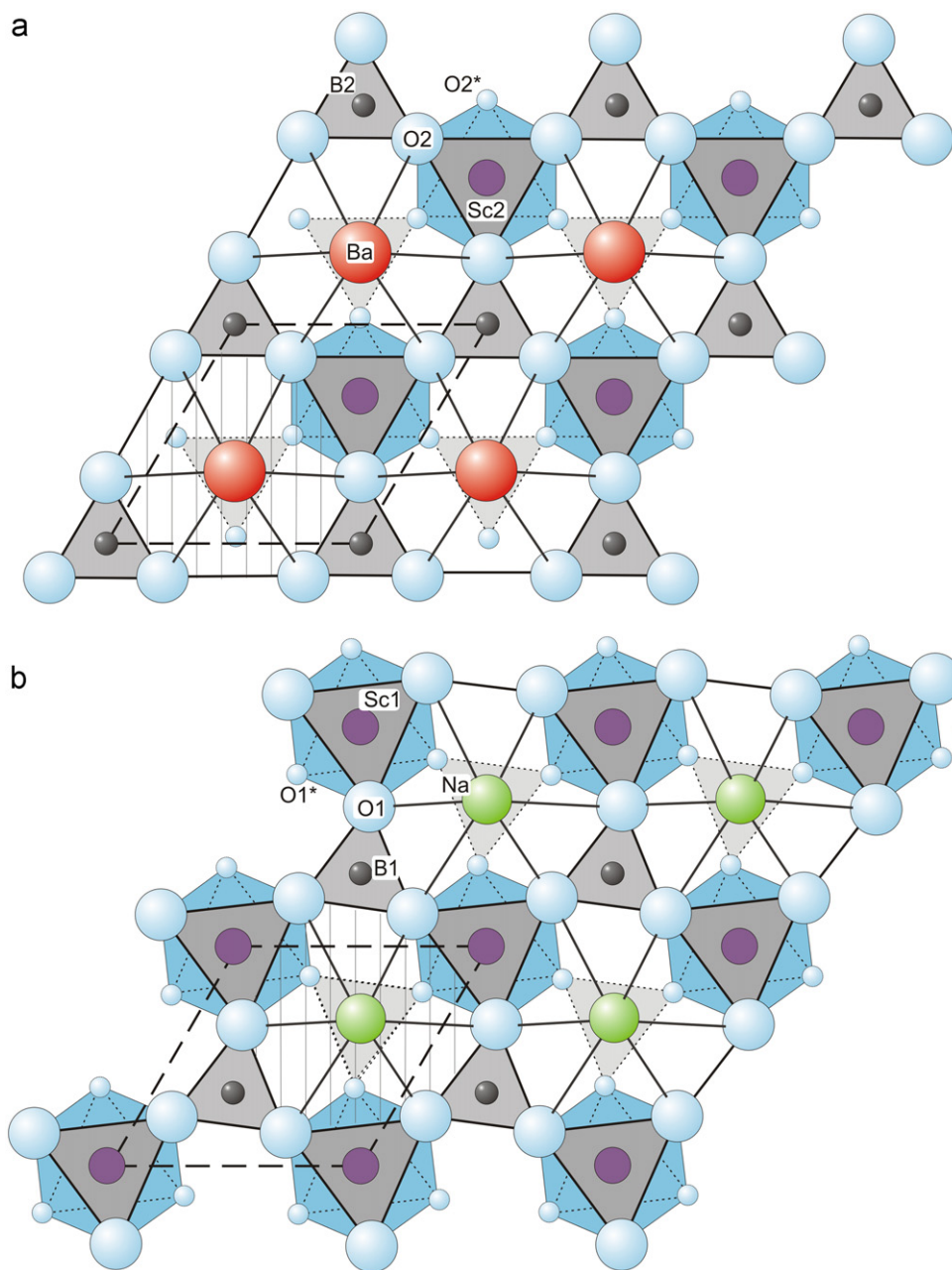


Fig. 3. Two-layer $\{\text{Sc}[\text{Ba}(\text{BO}_3)_2]\}^+$ (a) and $\{\text{Sc}[\text{Na}(\text{BO}_3)_2]\}^-$ (b) packages in the projection along the c -axis. Sections of the Ba- and Na cubeoctahedra are shaded.

distances is due not only to the increase in the unit cell metrics but also to the larger (to 0.46 Å) displacement of Na^+ from the layer plane. Three oxygen atoms of the neighboring layer approached to the Na cation for a distance of 3.17 Å owing to this displacement and the decrease in the interlayer space. The three atoms may be conventionally involved in the coordination environment of the cation with taking into account six unilateral elongated Na–O bonds.

The thermal O1 ellipsoid increased six times along the Na–O bond in structure **II** as compared to **I** (Fig. 4c,d). This may suggest the oscillation of the BO_3 groups around the symmetry axis, as proved by the shortened B–O1 bond length in **II** (Table 3). Thus, of six nearly equal Na–O bonds the three bonds become shorter, while three remaining longer, and the coordination by the oxygen layer atoms approximates to that in **I**, i.e. 3+3.

As indicated above, in the structures studied all the cations occupy special positions and the symmetry of the structure is specified by the distribution of the oxygen atoms in general positions. The symmetry may be improved to $R\bar{3}m$ with the arrangement of the oxygen atoms in m -planes and with no turn of the BO_3 groups. In the Ba layer, the turn angles are 0.06° and 0.03° in structures **I** and **II**, respectively, (Fig. 3b), whereas in the Na layer, those are substantially larger, 7.61° and 2.74° in **I** and **II**, respectively, (Fig. 3a). At ambient conditions, it is clearly preferable for the Na^+ cation to have three Na–O bonds being shortened to the sum of their effective ionic radii and three bonds noticeably elongated than to have six bonds intermediate in the length. It may be suggested that at high temperature (nearly the crystallization point) this difference is aligned and the symmetry improves to $R\bar{3}m$.

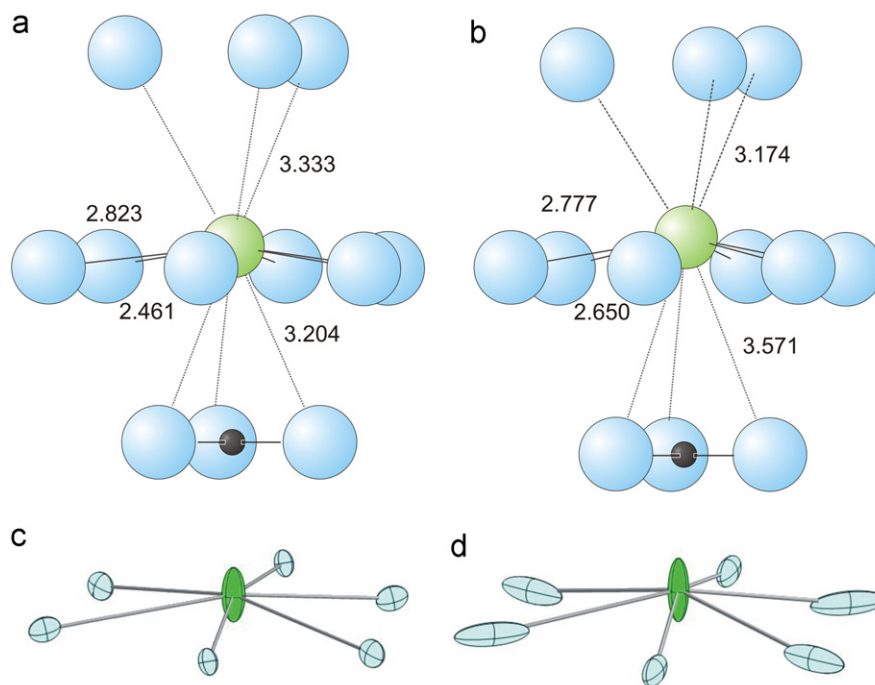


Fig. 4. The neighboring environment of the Na cations. Differentiating among the distances in the NaO_{12} cubeoctahedra in structures **I** (a) and **II** (b). Thermal ellipsoids of the Na cations and the layer oxygen atoms in structures **I** (c) and **II** (d).

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