

# Crystal Chemistry of a Group of Microporous Inorganic Compounds Obtained Hydrothermally

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**Citation:** Belokoneva EL, Stefanovich SY. Crystal Chemistry of a Group of Microporous Inorganic Compounds Obtained Hydrothermally. Struct Chem Crystallogr Commun. 2015, 1:1.

## Abstract

Silicates, phosphates, borates and complex compounds as borosilicates and borophosphates have been synthesized under hydrothermal conditions similar to common in nature, and structurally investigated in the past decade in search of optical nonlinear crystals. Representatives with voids or channels of effective cross sections up to 10 Å are selected and analyzed from the point of view crystal chemistry and possible applications. It is noticed that crystals with framework or layered structures equally accumulate in their voids large ions, or groups of ions, or water molecules from the water solution during the crystallization, and frequently exhibit zeolite properties. Frameworks built on the base of silicate, phosphate or boron tetrahedral demonstrate topological similarity. In a number of crystals the zeolite properties appear in combination with optical non-linearity that is being the bottom of their attraction for integral optics. In non-centro symmetric crystals origin of high optical non-linearity is connected with the highly polarizable electron density of heavy atoms in the voids and channels of the structures. Significant rules are withdrawn from the results of hydrothermal synthesis of crystalline micro porous materials.

**Keywords:** Hydrothermal synthesis; Microporous structures; Silicates; Phosphates; Borates; Optical nonlinearity

**Received:** September 25, 2015, **Accepted:** November 02, 2015, **Published:** November 06, 2015

## Introduction

Structures with tetrahedral anionic groups, predominantly with Si- and Al-, condensed via common vertices into frameworks, have been separated from other structure type's long time ago. Found in the nature, their representatives with special large voids were nominated as zeolites. The most well-known minerals between them are shabazite, cancrinite, fozhazite, analcim, natrolie, harmotome, mordenite, sodalite, ultramarine, and others [1]. Up to now, a huge amount of synthetic zeolites have been synthesized. One of the very first and the most known is "Linde molecular sieve of type A" [1]. Special feature of such structures is sorption of water inside the voids, which may be lost under heating, or substituted by gas molecules of smaller (H<sub>2</sub>, N<sub>2</sub>), or larger size (NH<sub>4</sub>, or C<sub>2</sub>H<sub>5</sub>OH, and so on). Thus, dehydrated crystals may be used as sorbent, or ion exchangers for metals separation, or in catalysis. Substances with guest metal atoms are used as luminescence materials, semiconductors or nonlinear crystals

in optoelectronics. The latter application results from lack of center of symmetry that occurs in many crystals containing large cavities. Smaller ions in these cavities are frequently displaced from central positions thus producing polar structures with compliant nonlinear activity. Combination of zeolite properties with nonlinear optical activity is of interest in engineering of integrated media for optoelectronic devices [2]. The origin of specific properties is directly connected with size of the voids and their interconnections by pass-ways to produce channels going in one, two or three dimensions.

Principles of systematic and processing of zeolites are summarized in database [3]. Synthesis of the zeolites at present is also carried out using different combination of inorganic and organic components [4]. Good example of the type gives a compound which contains isolated Ga-tetrahedra connected by the organic linker forming porous anionic network. In the material obtained

in [4], positively charged ions including alkali-metals and solvent molecules are distributed in a disordered manner in pores, compensating negative charge of the framework. They could be exchanged with different components. Other important and successful example is using layered silicate kanemite  $\text{NaHSi}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$  as a matrix for combination with organic component, namely alkyltrimethyl-ammonium ions [5]. As a result new silicate-organic complex meso porous material was obtained. As far as dimensions of the pores directly determine technical functions of zeolites, crystal structures of them are under intensive investigations on both natural and synthetic representatives. Inorganic compounds with micro porous structures, natural and synthetic, are very numerous, annually increasing in number and often presenting unusual structural features and possessing useful properties. In this paper we do not present comprehensive review of all types of micro porous compounds, but essentially analyze crystal chemistry of some of them recently selected by us among silicates, borosilicates, phosphates, borates obtained in the course in our systematic search for framework nonlinear optical crystals of UV. Their structures with large voids and channels of zeolite character investigated in the last decade (see corresponded references) are compared with the known structure types. Some of them could be used as a matrix for new zeolite materials similar to kanemite mineral. Optical nonlinearity combined with more traditional zeolite properties is of technical importance. In our discussion of structure-properties relations we also focus interest on conditions favorable for hydrothermal synthesis of such the crystals.

## Experimental Part

New zeolite-type crystals have been synthesized in our work hydrothermally, similar to many crystals of different classes with tetrahedral anionic groups. The experiments were carried out in a standard autoclaves (volume 5-6  $\text{cm}^3$ ) lined with Teflon. The duration of the experiments (18-20 days) corresponded to the completion of the reaction. The temperature in crystallization process was 250-280°C and the pressure was 70-80 atm. Final cooling after synthesis to the room temperature lasted for 24 hours. We choose the synthesis conditions taking into account known geological processes, therefore, as a rule, initial mixtures of reagents were multi-component. Compounds were crystallized from initial components, oxides and salts with the variation of composition and weight ratio. Boron oxide, phosphorus anhydride, or silicon oxide exceed was typically used for crystallization of borates, phosphates and silicates correspondingly. Oxides or salts of such metals as Pb, Ba, Sr, RE, Sc, Ga, Fe were employed. The ratio of solid and liquid phase was 1:5. As mineralizers, there were used halogenides or carbonates of alkali ions from lithium to cesium.

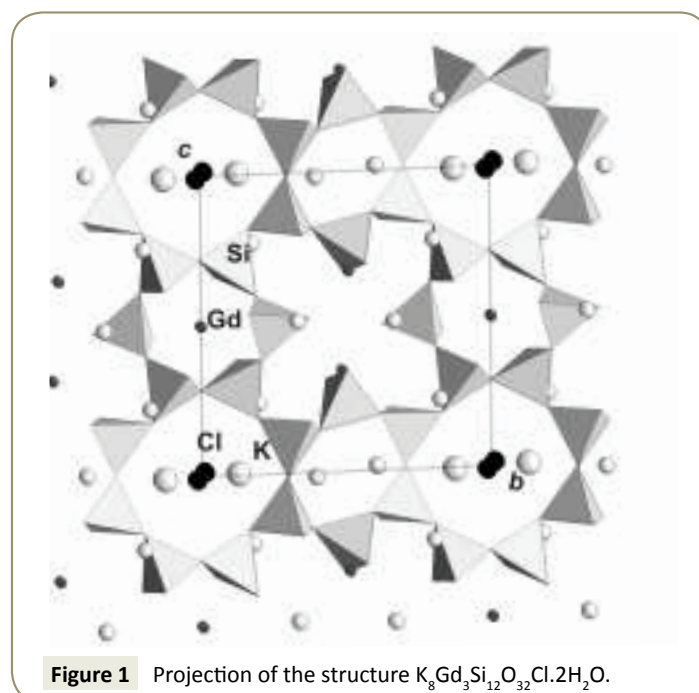
Nonlinear optical properties were examined in Second Harmonic Generation (SHG) measurements using Nd:YAG pulsed laser. The SHG experiments were produced on powdered crystals relative to standard  $\alpha\text{-SiO}_2$  powder with 3-5  $\mu\text{m}$  crystalline grains. Experimental procedure is principally similar to powder technique of Kurtz and Perry [6] except for our preference for using of thin powders as the most accessible and reliable way for comparison of nonlinear

optical activities. Substances with high nonlinearities (classes A and B after Kurtz) on one hand, small nonlinearity (classes C and D, and centrosymmetric E) are usually distinguishable. More definite conclusions on optical nonlinearity often required more coarse powders. Such powders with grain size up to 100  $\mu\text{m}$  sometimes are also available in hydrothermal experiments and may be separated in necessary quantities. The X-ray diffraction data were collected at  $\beta$ -filtered Mo  $K_\alpha$  radiation with diffractometers Syntex P-1 equipped with point detector, or with diffractometer Xcalibur S equipped with a CCD area detector using graphite-monochromated Mo  $K_\alpha$  radiation. Structure solutions and refinements were made with CSD and SHELXS-97, SHELXL-97 suits of programs. The results of the crystal structures determinations are given in details in corresponding publications including synthesis conditions and properties investigations. Drawing of structures used in crystal chemical analysis is fulfilled using ATOMS suit of programs.

## Results and Discussion

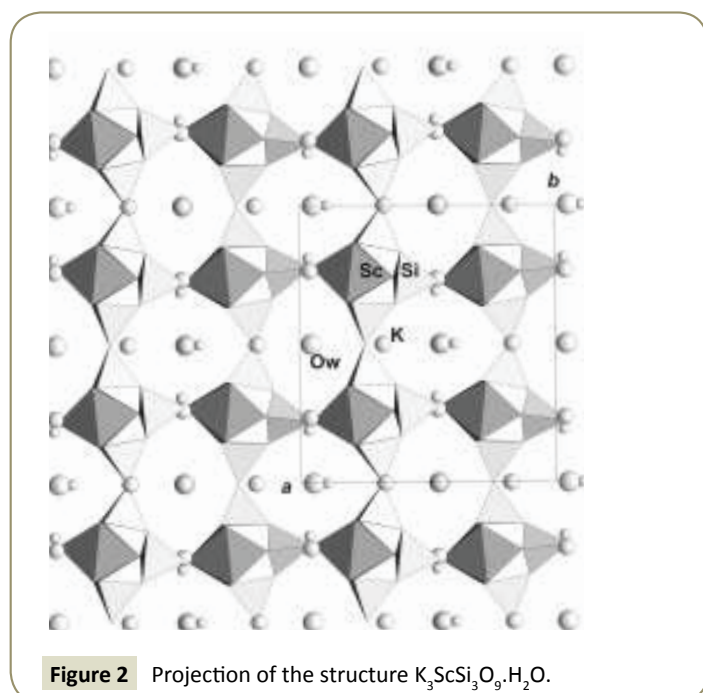
### Silicates and borosilicates

A new member of the family of poroussilicates,  $\text{K}_8\text{Gd}_3\text{Si}_{12}\text{O}_{32}\text{Cl} \cdot 2\text{H}_2\text{O}$  [7], was synthesized and structurally investigated (hereafter **Table 1** gives information on unit cell dimensions, space groups, dimensions of voids and nonlinear optical properties of all compounds under investigation). As far as earlier described compounds  $\text{Na}_3\text{NdSi}_6\text{O}_{15} \cdot 2\text{H}_2\text{O}$  and  $\text{K}_3\text{NdSi}_6\text{O}_{15}$  [8] of the same type are ionic-conductive, we consider  $\text{K}_8\text{Gd}_3\text{Si}_{12}\text{O}_{32}\text{Cl} \cdot 2\text{H}_2\text{O}$  as a promising ion-conductor. In this compound it was found for the first time for the whole family that structural channels (**Figure 1**) are occupied by Cl-ions. Hereafter in the Figures tetrahedra and octahedra are shown; while ions and water molecules are given by circles. Other member of the family investigated recently  $\text{K}_7\text{Eu}_3\text{Si}_{12}\text{O}_{32} \cdot 4\text{H}_2\text{O}$  [9] is to the most degree close to our silicate, but have more water molecules and no Cl ions in the channels.



Large channels surrounded by 8 tetrahedra are preferable for large K-cations, or Cl-ions, or water molecules. Smaller channels formed only by 6 tetrahedra are occupied with RE elements. The cross section of the channels is given in **Table 1**. New microporous silicate  $K_3ScSi_3O_9 \cdot H_2O$  is a member of the family of rare earth silicates (Sc is the smallest-size analogue of RE elements) [10,11]. The channels in the framework are also constructed with eight polyhedral, six tetrahedra and two octahedra. The corresponding cross sections of the channels are slightly oval being close in dimensions (**Table 1**). The channels are populated with K ions and water molecules (**Figure 2**). The smallest ion in the composition, Sc, leads to formation of regular polar framework in contrast to more deformed framework in the case of Ho-silicate. A number of other related frameworks with zeolite properties may be predicted using topology-symmetry principles [10].

New synthetic silicate  $KNaTmSi_8O_{19} \cdot 4H_2O$  belongs to the family of mineral structures as rhodseite, delhayelite, shlikovite, umbrianite, and hilleshaymite and other representatives [12]. It has been shown that all members of the family demonstrate similarity in main structural units of octahedra and tetrahedra and some difference derived in the topology-symmetry analysis. All of them possess large voids occupied by cations, anionic groups and water molecules. Cross sections of large channels with K ions and  $H_2O$  (**Figure 3a and 3b**) have close to similar dimensions (**Table 1**). Layered structures are realized as well in the family (shlykovite, mountainite), being close relative to the framework structures [12], and interlayer space concentrates a lot of ions of different radii and increased amount of water. There is a class of borosilicates with both Si and B tetrahedra presenting simultaneously in the structures. Borosilicates are known as minerals and also as synthetic compounds. Two iso-formula compounds are synthesized: new monoclinic modification of boroleucite  $K(BSi_2)_2O_6$  and chiral synthetic  $KBSi_2O_6$  [13] known also as a rare mineral. They have similar framework structures formed by equal tetrahedra occupied by Si and B with the statistical



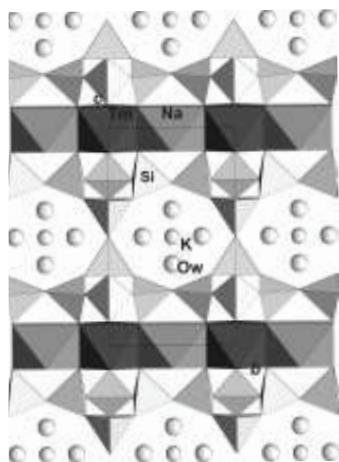
**Figure 2** Projection of the structure  $K_3ScSi_3O_9 \cdot H_2O$ .

isomorphic substitution of 1Si:2B in the former compound, while in the latter tetrahedra are occupied in ordered way by Si or B atoms. The voids with 8 and 7 tetrahedral rings accommodate K atoms. On **Figure 4a and 4b** layered fragments of the frameworks are presented and demonstrate oval voids in  $K(BSi_2)_2O_6$  and more symmetrical voids in  $KBSi_2O_6$  (**Table 1**). Unusual silicate - formally borosilicate - with the isomorphic impurity of B-atoms in one of the Si-tetrahedral positions,  $Pb_{4.8}Na_{1.2}Si_8(Si_{1.2}B_{0.8})O_{25.7}$  has a double layer of new type [14]. The layer has relationship with the layer in the structure of benitoite, as well as layers in the structures of lead silicates barisilite and hyttsoeite (**Figure 5a and 5b**). Similar topological blocks consisting of an octahedron and six tetrahedra are found in all these structures. New double layer is derived from the hyttsoeite layer by the replacement of the octahedron in the block by two tetrahedra what leads to the increase of the silicon fraction. Pb ions are located inside oval voids of the layers with the dimensions  $\sim 5.6 \text{ \AA}$  (interlayer space is  $\sim 3.5 \text{ \AA}$ , **Table 1**) and this structural type and relative minerals are collectors of heavy metals.

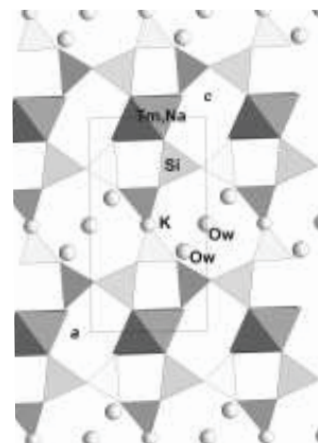
### Phosphates and borophosphates

Class of phosphates in our studies gives new examples of framework structures similar to classical zeolite nepheline,  $NaAlSi_3O_8$ . Nepheline structure was first solved under assumption of a disorder, but synthetic sample gave good confirmation on real unit cell and framework peculiarities. The analogue between classes with the different tetrahedral groups, silicates or phosphates, is demonstrated on similarity of structures of synthetic nepheline and synthetic  $BaFePO_4(OH)$  (**Figure 6a and 6b**) [15]. In nepheline structure, framework is built of Si and Al-tetrahedra; in Ba-phosphate it is built of P-tetrahedra and Fe-half-octahedra on tetrahedral position condensed into the framework. Large oval channels are open along *b*-axes in phosphate and along *c*-axes in nepheline. They are formed by six tetrahedra (or half-octahedra) with the practically similar dimensions (**Table 1**) for both structures and are occupied by large Ba ions in new phosphate and by Na-ions in nepheline. Different framework, similar to nepheline, may exist as example not only by pair Fe-P with different ionic radii and coordination, but a pair with smaller radii Si-Al or Si-Be and equal tetrahedral coordination. Thus topology of nepheline type is very stable and may be realized in different representatives. It is favorable for ion exchange and ion conducting properties. Synthetic analogue of mineral brazilianite with Ga substituted of Al in octahedra,  $NaGa_3(PO_4)_2(OH)_4$  has a framework structure formed by two types of polyhedra: tetrahedra and octahedra. Open channels along *a*-axes (**Table 1**) are occupied by Na ions [16]. Ion exchange is possible in this new microporous phosphate crystal.

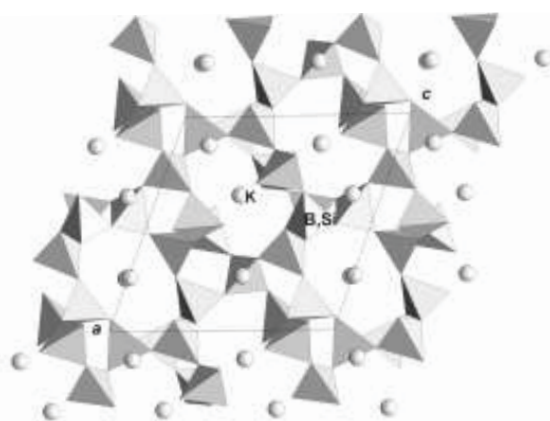
New phosphate-borophosphate  $Fe_{2.5}[BP_2O_7(OH)_2][PO_3(OH)] [PO_3(O_{0.5}OH_{0.5})] \cdot H_2O$  [17] has microporous framework of Fe-octahedra and of several tetrahedra: two isolated P-tetrahedra with the protonated oxygen apices and one borophosphate soro-unit of condensed P- and B-tetrahedra. Large channels which go along *a*-axis with the cross-section of  $\sim 9.5$  long and  $1.5 \text{ \AA}$  wide (**Table 1**) are occupied by water molecules.



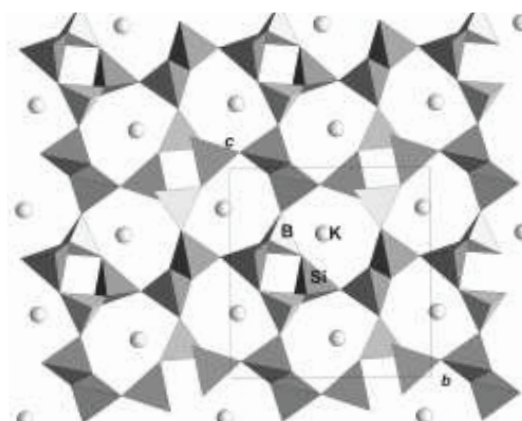
3(a)



3(b)

**Figure 3** Crystal structure of  $\text{KNaTmSi}_8\text{O}_{19}\cdot 4\text{H}_2\text{O}$  in two projections, *bc* (a) and *ac* (b).

4(a)



4(b)

**Figure 4** Fragments of the frameworks in  $\text{K}(\text{BSi}_2)\text{O}_6$  (a) and  $\text{KBSi}_2\text{O}_6$  (b).

## Borates

Borates are known as indispensable in many applications: nonlinear optical, luminescence, magnetic. Their ion exchanging or ions conducting properties are also very interesting. In class of borates we managed to reveal one of the most intriguing structures, namely, noncentrosymmetric hilgardites: their name being after rare mineral hilgardite,  $\text{Ca}_2\text{B}_5\text{O}_9\text{Cl}\cdot\text{H}_2\text{O}$ . All representatives of the family have different compositions and frameworks of different symmetry, but nevertheless they are close to each other. The framework is composed of B-tetrahedra and B-triangles combined in blocks, chains, than into equal layers joint into frameworks by different symmetrical combinations, what was analyzed in [18]. Polar-structure of natural hilgardite, sp. group  $Aa$ , has never been obtained as synthetic phase but only as its polar topologically new modification [19].

Centrosymmetric variants are represented with  $\text{Pb}_2\text{B}_5\text{O}_9(\text{OH})\cdot\text{H}_2\text{O}$  [18] and  $\text{Na}_{0.5}\text{Ba}_2\text{B}_5\text{O}_9\text{FCl}_{0.5}$  [20]. Most promising for application are orthorhombic polar modifications, known for many compositions:  $\text{Ca}_2\text{B}_5\text{O}_9\text{Br}$  [21],  $\text{Eu}_2\text{B}_5\text{O}_9\text{Br}$  [22],  $\text{Pb}_2\text{B}_5\text{O}_9\text{Br}$  [23],  $\text{Na}_{0.5}\text{Pb}_2\text{B}_5\text{O}_9(\text{OH})_{1.5}\cdot 0.5\text{H}_2\text{O}$ , (**Figure 7**) [24],  $\text{Na}_{0.5}\text{Pb}_2\text{B}_5\text{O}_9\text{Cl}(\text{OH})_{0.5}$  [25],  $\text{Ba}_2\text{B}_5\text{O}_9\text{Cl}\cdot 0.5\text{H}_2\text{O}$  [26],  $\text{Ba}_2\text{B}_5\text{O}_9\text{Cl}$  [27],  $\text{Pb}_2\text{B}_5\text{O}_9\text{Cl}$  [28],  $\text{Pb}_2\text{B}_5\text{O}_9\text{I}$  [29]. Chemical formulas and structure investigations demonstrate that in the similar framework open channels may be filled with different cations, anions, hydroxyl groups and water molecules. Nonlinear optical properties were established in polar crystals. The largest SHG response among borates was found in  $\text{Pb}_2\text{B}_5\text{O}_9\text{I}$ : 13.5 times that of KDP and  $\sim 3$  time that of  $\text{Pb}_2\text{B}_5\text{O}_9\text{Br}$  according to [29]. Relative to  $\alpha\text{-SiO}_2$ , nonlinear optical activity of different hilgardite representatives varies from maximal in  $\text{Pb}_2\text{B}_5\text{O}_9\text{I}$  and  $\text{Pb}_2\text{B}_5\text{O}_9\text{Br}$  to middle in  $\text{Na}_{0.5}\text{Pb}_2\text{B}_5\text{O}_9\text{Cl}(\text{OH})_{0.5}$  and  $\text{Na}_{0.5}\text{Pb}_2\text{B}_5\text{O}_9(\text{OH})_{1.5}\cdot 0.5\text{H}_2\text{O}$ , and to lower in  $\text{Ba}_2\text{B}_5\text{O}_9\text{Cl}\cdot 0.5\text{H}_2\text{O}$



**Figure 5** Projection of the structures  $\text{Pb}_{4.8}\text{Na}_{1.2}\text{Si}_8(\text{Si}_{1.2}\text{B}_{0.8})\text{O}_{25}$  onto  $ac$  plane (a), one double layer in  $ab$ -projection (b).



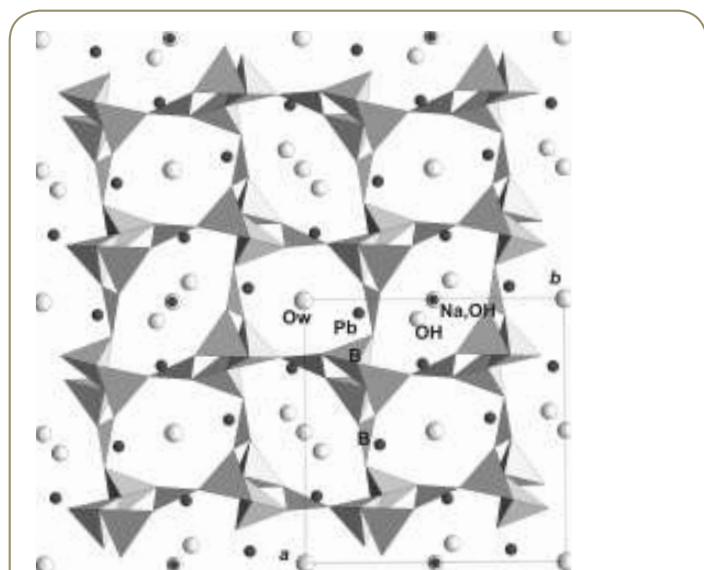
6(a)

6(b)

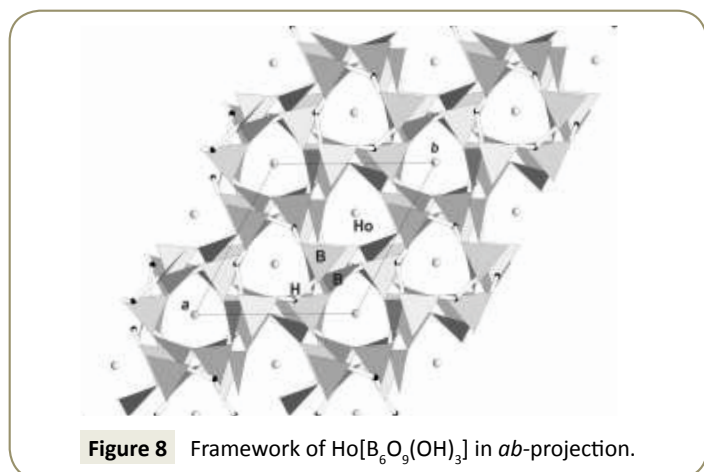
**Figure 6** Frameworks of  $\text{BaFePO}_4(\text{OH})$  in  $ac$ -projection (a); of synthetic nepheline  $\text{NaAlSi}_4$  in the same view in  $ab$  projection (b).

**(Table 1).** It was shown [23] that the optical nonlinearity regularly increases in series of hilgardites upon the substitution of the cations  $\text{Ca} \rightarrow \text{Sr} \rightarrow \text{Ba} \rightarrow \text{Pb}$  and the anions  $\text{Cl} \rightarrow \text{Br}$ . This suggests that the role played by the extra-framework atoms in the voids, as well as electron density on their bonds, is the most important in the formation of nonlinearity in compounds with the similar boron-oxygen framework. Large cavities going along  $c$ -axis are real open channel. Its cross section has dimension  $\sim 5.5 \text{ \AA}$  for all modification of microporous structures. Complicate compositions for different representatives display possibility for absorption of ions from the solution and principally to the ion exchange for this structure type often combined with the optical nonlinearity. Trigonal polar borates (**Figure 8**) with common formula  $\text{REE}[\text{B}_6\text{O}_9(\text{OH})_3]$ ,  $\text{REE}=\text{Sm} - \text{Lu}$ , are synthesized, structurally investigated and analyzed from crystal chemistry point of view in [30]. These compounds demonstrate structural relation to

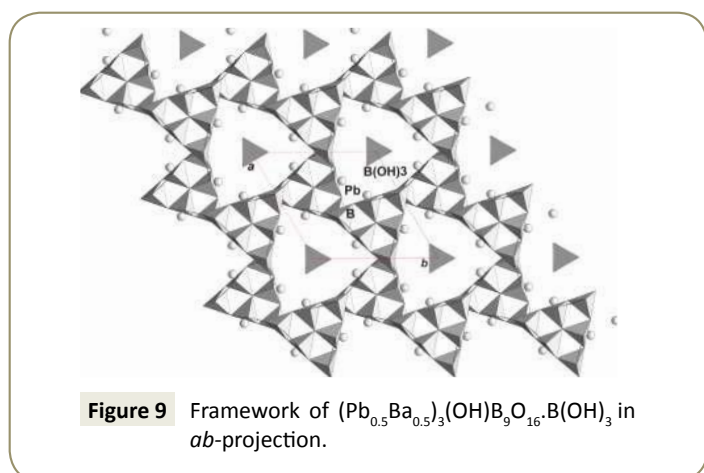
cubic (natural or synthetic) boracites. Many non-cubic boracites are also very close to Li-boracite  $\text{Li}_4[\text{B}_7\text{O}_{12}]\text{Cl}$  known to possess Li-ion conductivity [31]. The framework of this type of borates is constructed from six member rings of triangles and tetrahedra, however it has common features with that of berillonite and nepheline minerals which are built only from  $\text{BO}_4$ -tetrahedra. Compared to Li-boracite, RE metals occupy Cl positions - central in the open channels (**Table 1**). Electric conductivity found in some representatives of  $\text{REE}[\text{B}_6\text{O}_9(\text{OH})_3]$  family exceeds  $10^{-6} \text{ S/cm}$ . and may be explained by proton diffusion (H-position corresponds not to OH-group but to  $\text{H}^+$  as cation). Except that, crystals demonstrate nonlinear optical properties (**Table 1**). New borates  $\text{Pb}_3(\text{OH})\text{B}_9\text{O}_{16}\cdot\text{B}(\text{OH})_3$ ,  $(\text{Pb}_{0.5}\text{Ba}_{0.5})_3(\text{OH})\text{B}_9\text{O}_{16}\cdot\text{B}(\text{OH})_3$  and  $\text{Ba}_3\text{Na}(\text{OH})\text{B}_9\text{O}_{16}\cdot\text{B}(\text{OH})_4$  [32] have framework of borate non-group built of six polar tetrahedra added by three polar triangles. Large open channels along  $c$ -axis have cross-section of  $\sim 8.75 \text{ \AA}$ .



**Figure 7** Framework of  $\text{Na}_{0.5}\text{Pb}_2\text{B}_5\text{O}_9(\text{OH})_{1.5}\cdot 0.5\text{H}_2\text{O}$  in *ab*-projection.



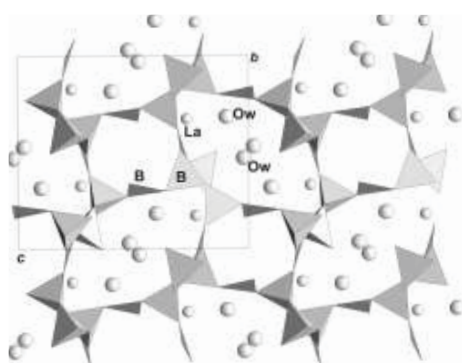
**Figure 8** Framework of  $\text{Ho}[\text{B}_6\text{O}_9(\text{OH})_3]$  in *ab*-projection.



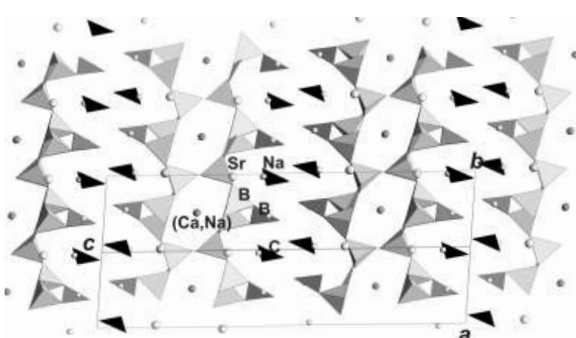
**Figure 9** Framework of  $(\text{Pb}_{0.5}\text{Ba}_{0.5})_3(\text{OH})\text{B}_9\text{O}_{16}\cdot \text{B}(\text{OH})_3$  in *ab*-projection.

Two variants of channels occupations are found with  $\text{B}(\text{OH})_3$  triangles (full sassoline molecule) (**Figure 9**) and with  $\text{B}(\text{OH})_4$ -tetrahedra on the same position at the center. Large cations as Pb, Ba are closer to the walls of the open channels along *c*-axis as in hilgardite and may isomorphically substitute each other

and that demonstrates ions exchange properties. Local polar environments are aligned in the structure and polar material is observed. Concern structure-properties relation, it was concluded [32] that the same rules are valid for nona-borates family as for hilgardite family in the rows with the different ions. The observed maximal signal relative to  $\alpha\text{-SiO}_2$  (**Table 1**) is for Pb-nonaborate with the most polarized large Pb ion; it is somewhat weaker for borate with Ba and Na atoms and polar distorted B-tetrahedral groups, incorporated into channels of the framework; and it is the weakest for borate with isomorphic substitution of Pb, Ba. Even in the last case, the nonlinear optical activity of the borate with the filled framework is compared well with the nonlinear activity of the BBO -  $\beta\text{-BaB}_2\text{O}_4$  borate. This indicates once again that borates with filled frameworks are more promising materials for attaining a maximum optical nonlinearity as compared to borates with isolated polyanion groups. Unusual dodecaborate ring is found in structures of  $\text{Pb}_6[\text{B}_{12}\text{O}_{24}]\cdot \text{H}_2\text{O}$  and  $\text{Pb}_6(\text{Li}_{0.65}\text{Na}_{0.19})[\text{B}_{12}\text{O}_{24}]_{0.84}\cdot 0.168\text{H}_2\text{O}$  obtained in our hydrothermal synthetic experiments [33]. Open channels here with cross-section  $\sim 3.9 \text{ \AA}$  are centered on complex ring and populated with Li(Na), I-ions and water molecules taken from the solution during crystallization. Dodecaborate structures have similarity with beryl and cordierite minerals [33]. The last mineral contains  $\text{CO}_2$ -impurity in the voids of open channels; it is known as sorbent and filter for motor-cars. New borate  $\text{LaB}_5\text{O}_8(\text{OH})_2\cdot 1.5\text{H}_2\text{O}$  [34] has a framework with large oval channels (**Table 1**) occupied by water molecules; La-cations are also inside the channels in the holes of corrugated layers (**Figure 10**). Other smaller voids are empty. Layers of different topology and symmetry are very typical anionic radicals for borates. New synthetic polar borates  $\text{REE}[\text{B}_4\text{O}_6(\text{OH})_2]\text{Cl}$ , REE=La-Nd [35] have layered structure with the rare earth and chlorine ions in the interlayer space, and it is good nonlinear optical crystal (**Table 1**). The example of structure with the layer relative to hilgardite is rare carbonatoborate  $\text{Sr}(\text{Na}_{0.4}\text{Sr}_{0.1})\text{Na}_2[\text{B}_5\text{O}_8(\text{OH})_2](\text{CO}_3)_{1-x}$  [36], **Figure 10**. The interlayer space is filled by ions, water molecules or  $\text{CO}_3$ -triangles which most real hinder condensation of layers into framework. Similar compound was found also for Ca-representative. Other new layer in new borate  $\text{LaB}_5\text{O}_8(\text{OH})_2$  [37] is strongly corrugated and curved, and in the holes of its walls are La ions. New examples of borates with structures possessing large voids inside the complex layers and interlayer space are megaborates  $(\text{Nd}_{0.925}\text{Na}_{0.075})\text{Nd}[\text{B}_9\text{O}_{15}(\text{OH})_2]\text{Cl}_{0.85}\cdot 2.65\text{H}_2\text{O}$  [38] and  $\text{Sm}[\text{B}_{13}\text{O}_{22}(\text{OH})_3](\text{OH})\cdot 3\text{H}_2\text{O}$  [39] (**Figure 12**). Double layer of Nd-borate has similar topology with the framework fragment of  $\text{LaB}_5\text{O}_8(\text{OH})_2\cdot 1.5\text{H}_2\text{O}$  with the two types of voids: larger and smaller (**Table 1**). The former is occupied by Na, Cl ions and water molecules, the latter is also empty. Cations, anions and  $(\text{OH})$ -groups are in the inter layer space (**Figure 12**). Sm-borate has also double layer derived from Nd-layer (**Figure 12**). It contains extension in a form of triborate circle with the additional triangle. Because of that configuration of voids is changed: S-form voids are occupied by Sm ions whereas larger contain water molecules. Wide inter layer space accommodates  $(\text{OH})$ -groups and Sm ions in the holes of corrugated layers with the similar cross section as in Nd-borate.



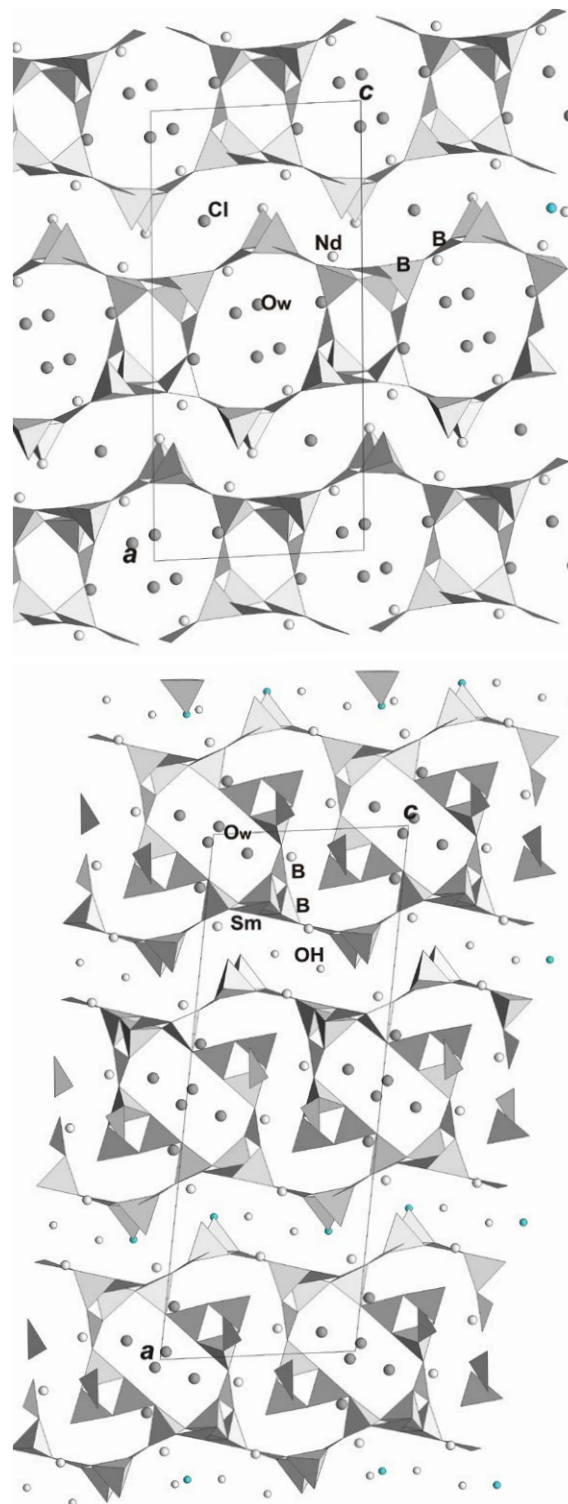
**Figure 10** Framework of  $\text{LaB}_5\text{O}_8(\text{OH})_2 \cdot 1.5\text{H}_2\text{O}$  (b) in bc-projection.



**Figure 11** Carbonato-borate-Sr( $\text{Na}_{0.4}\text{Sr}_{0.1}$ ) $\text{Na}_2[\text{B}_5\text{O}_8(\text{OH})_2](\text{CO}_3)_{1-x}$  in diagonal projection.

## Conclusions

New silicates, borosilicates, phosphates, borophosphates and borates with microporous structures are synthesized in hydrothermal conditions. Significant rules are withdrawn from the results of hydrothermal synthesis of crystalline microporous materials. For borates, excess of boron anhydride in ratio  $\text{REE}/\text{B}_2\text{O}_3$  leads to complexity and higher degree of anionic radical condensation of borate anionic units from the layer to the framework; higher mineralizer's concentration up to 20% favors participation of alkali metals or halogen-ions in the structures. As example, presence of NaBr gives sodium containing hilgardites; presence of ions Cl and Br gives  $\text{Na}_{0.5}\text{Pb}_2\text{B}_5\text{O}_9\text{Cl}(\text{OH})_{0.5}$ ,  $\text{Ba}_2\text{B}_5\text{O}_9\text{Cl} \cdot 0.5\text{H}_2\text{O}$  and  $\text{Pb}_2\text{B}_5\text{O}_9\text{Br}$  etc. Despite Ba and Pb ions are chemically very different, similar nonaborates with both large cations were obtained in our experiments. Phosphate systems demonstrate important role of presence of  $\text{B}_2\text{O}_3$  up to 10% as buffer, and that allows to correct pH of the solution and to slow down crystallization process what assist growth of crystals with a structures with large voids. That was realized for Ga-brazilianite and Ba, Fe phosphate with the structure similar to nepheline. Participation of  $\text{B}_2\text{O}_3$  as mineralizer was also detected for the silicate systems with REE ions as a key to forming high condensed silicate anionic radicals. Phosphates and silicates frequently produce structures with large voids mainly at high temperatures of synthesis, nevertheless presence of  $\text{B}_2\text{O}_3$  make possible crystallization of such structures at lower temperatures. There is no principal difference between tetrahedral frameworks of



**Figure 12** Megaborates structures of  $(\text{Nd}_{0.925}\text{Na}_{0.075})\text{Nd}[\text{B}_9\text{O}_{15}(\text{OH})_2]\text{Cl}_{0.85} \cdot 2.65 \text{H}_2\text{O}$  (a) and  $\text{Sm}_3[\text{B}_{13}\text{O}_{22}(\text{OH})_3](\text{OH}) \cdot 3\text{H}_2\text{O}$  (b) in equal view.

**Table 1** Unit cells parameters, space groups, pores cross section and non-linear optical activities of the new micro porous compounds.

Compound	$a,$ $b,$ $c$ (Å)	$\alpha,$ $\beta,$ $\gamma$ (°)	Space group	Pores cross section (Å)	$Q = I_{2\omega} / I_{2\omega SiO_2}$
<b>Silicates and borosilicates</b>					
$K_8Gd_3Si_{12}O_{32}Cl \cdot 2H_2O$	6.9060 11.3570 11.6080	88.033 88.508 79.377	$P-1$	7.0 and 4.6	
$K_3ScSi_3O_9 \cdot H_2O$	13.8797 12.7441 5.7276		$Pm2_1n$	7.3 and 6.4	0.7
$KNaTmSi_8O_{19} \cdot 4H_2O$	6.5315 6.9935 11.9430	90.383	$P2/m$	7.0 and 5.3-3.7	
$K(BSi_2O_6)$	10.9320 17.9111 11.0672	110.284	$P2_1/a$	5.6-2.9	
$KBSi_2O_6$	4.7126 9.9693 10.4432		$P2_12_12_1$	5.0	1.0
$Pb_{4.8}Na_{1.2}Si_8(Si_{1.2}B_{0.8})O_{25}$	9.5752 42.565		$R-3c$	5.5; 3.5	
<b>Phosphates and borophosphates</b>					
$BaFePO_4(OH)$	9.711 8.991 4.912		$P2_12_12_1$	6.6-2.45	1.2
$NaGa_3(PO_4)_2(OH)_4$	11.506 7.270 10.320	97.64	$P2_1/n$	4.4	
$Fe_{2.5}[BP_2O_7(OH)_2][PO_3(OH)][PO_3(O_{0.5}OH_{0.5})] \cdot H_2O$	7.3281 9.5762 18.6162	101.205	$P2_1/n$	9.5-1.5	
<b>Borates</b>					
$Pb_2[B_5O_9](OH) \cdot H_2O$	11.320 11.440 6.631	91.03	$P2_1/n$	5.5	
$Pb_2[B_5O_9]Br$	11.434 11.491 6.538		$Pnn2$	5.5	80
$Na_{0.5}Pb_2[B_5O_9](OH)_{0.5} \cdot Cl$	11.510 11.470 6.653		$Pnn2$	5.5	40
$Na_{0.5}Pb_2[B_5O_9](OH)_{1.5} \cdot 0.5H_2O$	11.426 11.328 6.574		$Pnn2$	5.5	40
$Ba_2[B_5O_9]Cl \cdot 0.5H_2O$	11.714 11.552 6.694		$Pnn2$	5.5	14
$La[B_4O_6(OH)_2]Cl$ , REE=La-Nd	6.553 11.256 9.798	105.28	$Cc$	2.7	30
$LnH_3[B_6O_{12}]$ , Ln = Sm-Lu	8.385 20.71		$R3c$	3.75	3
$Pb_3[B_9O_{16}](OH) \cdot B(OH)_3$	10.07 8.530		$P31c$	9.5	20
$Ba_3Na[B_9O_{16}](OH) \cdot B(OH)_4$	10.253 10.286 8.769	90.17 89.80 120.02	$P1$	9.5	14
$Pb_6[B_{12}O_{24}] \cdot H_2O$	11.432 17.385		$R-3c$	3.9	



$\text{Pb}_6(\text{Li}_{0.65}\text{Na}_{0.19})[\text{B}_{12}\text{O}_{24}]_{0.84}\cdot 0.168\text{H}_2\text{O}$	11.4721 17.2285		<i>R-3c</i>	3.9	
$\text{LaB}_5\text{O}_8(\text{OH})_2\cdot 1.5\text{H}_2\text{O}$	6.447 10.580 12.590	89.92	<i>P 2<sub>1</sub>/n</i>	10.0-4.7 and 4.7	
$\text{La}[\text{B}_4\text{O}_6(\text{OH})_2]\text{Cl}$	6.553 11.256 9.798	105.28	<i>Cc</i>	2.7	30
$\text{Sr}(\text{Na}_{0.4}\text{Sr}_{0.1})\text{Na}_2[\text{B}_5\text{O}_8(\text{OH})_2](\text{CO}_3)_{3/1-x}$	11.322 27.182 6.565	94.66	<i>Bb</i>	8.7-5.8 and 5.8-4	2
$\text{LaB}_5\text{O}_8(\text{OH})_2$	6.538 10.367 10.47	101.58	<i>P 2<sub>1</sub>/n</i>	5 and 6.5- 3.0	
$(\text{Nd}_{0.925}\text{Na}_{0.075})\text{Nd}[\text{B}_9\text{O}_{15}(\text{OH})_2]\text{Cl}_{0.85}\cdot 2.65\text{H}_2\text{O}$	10.6987 6.4051 23.1544	92.547	<i>P2/n</i>	7.7-6.6 and 4.0-2.8	
$\text{Sm}_3[\text{B}_{13}\text{O}_{22}(\text{OH})_3](\text{OH})\cdot 3\text{H}_2\text{O}$	10.7152 6.4188 29.9386	98.168	<i>P2/c</i>	7.7-4.5 and 4.5-11.3	

compounds which formally belong to different classes: silicates, phosphates or borates. Potentially, all of them may include ion-conducting, ion-exchanging and optical non-linear crystals. Combination of these properties in one and the same material may be of technical importance. To meet the requirement in microporous structures, dimensions of pores characterized by cross sections from  $\sim 4$  to  $10 \text{ \AA}$ , specifies the crystal chemistry prerequisite. A number of crystal structures possess large voids or interlayer spaces where cations, anions, hydroxyl groups and water molecules are located. From the point of view of ion-exchanging and optical nonlinear properties there is no principal difference between crystals with frameworks or layers. All of

them demonstrate zeolite character and possess voids or cavities occupied by different components taken from the solution during crystallization, and all of them may be principally considered as "breathing" and controlling their optical non-linearity. Borates with filled frameworks are much more promising materials for attaining a maximum optical nonlinearity as compared to borates with isolated polyanion groups.

## Acknowledgments

This study was supported by the RFBR Grant No. 14-03-00480a.

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