

STRUCTURE
OF INORGANIC COMPOUNDS

Synthesis and Crystal Structure of New Carbonate
 $\text{NaPb}_2(\text{CO}_3)_2(\text{OH})$

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Abstract—Crystals of a new lead carbonate, $\text{NaPb}_2(\text{CO}_3)_2(\text{OH})$, sp. gr. $P\bar{3}1c$, were prepared by hydrothermal synthesis. The crystal structure was established by the heavy-atom method without knowing the exact chemical formula of the compound. The polar structure of the carbonate and the distortion of the pseudosymmetry described by the supergroup $P\bar{3}1c$ are caused by the acentric arrangement of the oxygen atoms providing the satisfactory coordination of Pb and Na atoms. The bonds between a hydroxyl group and two crystallographically independent Pb atoms are directed along the c -axis and have different lengths. The study of the carbonate by the second harmonic generation method in a temperature range of 20–250°C revealed the nonlinear optical properties comparable with the similar properties of quartz. The comparison of the structure of the new carbonate with a number of carbonates demonstrated that the new compound is structurally similar to ewaldite $\text{BaCa}(\text{CO}_3)_2$, diorthosilicate $\text{NaBa}_3[\text{Si}_2\text{O}_7](\text{OH})$, and $\text{Ba}[\text{AlSiO}_4]_2$ containing a double silicon–oxygen layer.
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INTRODUCTION

Carbonates belong to one of the most important classes of inorganic compounds containing planar $[\text{CO}_3]^{2-}$ anions as the major structural unit. Natural and synthetic Ca, Mg, Fe, Mn, Na, Ba, Zn, and Cu carbonates are the most widespread and well-known compounds of this type [1]. Lead carbonates are rather rare and are found in nature as minerals such as phosgenite $\text{Pb}_2(\text{CO}_3)\text{Cl}_2$, cerussite PbCO_3 , and hydrocerussite $\text{PbCO}_3 \cdot \text{PbO}(\text{H}_2\text{O})_2$. Due to the high electron polarizability of Pb^{2+} ions explained by their specific electronic structure, the constituent oxides of lead carbonates have a dipole structure and possess piezo- and pyroelectric and nonlinear-optical properties. Hence, the preparation and the study of polar compounds in the carbonate systems involving lead are of interest in terms of both crystal chemistry and materials science.

EXPERIMENTAL

Synthesis of Single Crystals and Their Preliminary Diagnostics

Single crystals were synthesized when studying the phase formation in the $\text{Na}_2\text{CO}_3\text{--PbO--B}_2\text{O}_3\text{--H}_2\text{O}$ system. The experiments were carried out in 5 to 6-cm³-large standard fluoroplastic-lined autoclaves at ~70 atm and 270–280°C. The lower temperature limit was dictated by the kinetics of hydrothermal reactions, whereas the upper one was determined by the apparatus used. The experiments were carried out for 18–20 days to bring the reactions to completion. The coefficient of

autoclave filling was chosen so as to maintain a constant pressure. Colorless transparent hexagonal single crystals of sizes up to ~1 mm had a habit ranging from tabular to isometric. The crystals had perfect cleavage along the (001)-plane.

No analogues of the X-ray diffraction powder pattern (a DRON-UM1 diffractometer, Co radiation, 40 kV, 25 mA) were found in the PDF data base, which indicated that we synthesized a new compound. The composition of the crystals was determined by qualitative X-ray spectral analysis on a CAMSCAN 4DV scanning electron microscope equipped with a LINK attachment for the energy-dispersive analysis at the Department of Petrography of the Faculty of Geology of Moscow State University. This investigation confirmed the presence of Na and Pb atoms in the sample. Thus, with due regard for the composition of the initial system, the new compound could be related either to carbonates or borates.

IR Spectroscopy

The IR spectrum of a liquid sample obtained as a neat thin film between KBr supporting plates was measured on a Specord-75 IR spectrophotometer in the frequency ranges 1800–400 and 3800–3000 cm⁻¹ (Fig. 1). The IR spectrum has stretching vibration bands of the carbonate ion. Thus, the intense band at 1432 cm⁻¹ corresponds to the asymmetric stretching vibration ν_3 , the weak band at 1055 cm⁻¹ belongs to the symmetric stretching vibration ν_1 , and the bands at 847 and

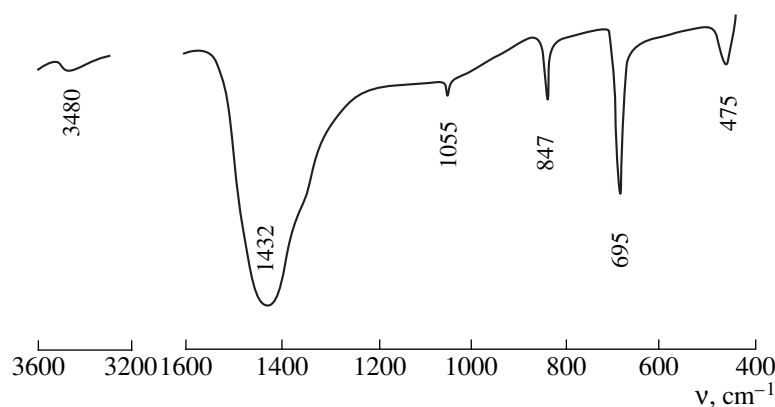


Fig. 1. IR spectrum of $\text{NaPb}_2(\text{CO}_3)_2(\text{OH})$.

695 cm^{-1} are attributed to the out-of-plane and in-plane deformation vibrations ν_2 and ν_4 , respectively. By analogy with the spectrum of cerussite PbCO_3 [2], the band at 475 cm^{-1} was assigned to lattice vibrations. The vibration band of the hydroxyl group is observed at 3480 cm^{-1} . The degeneration of the ν_3 and ν_4 vibrations is indicative of the positional symmetry with a threefold axis for a CO_3 ion. The presence of the stretching vibration ν_1 shows that the symmetry group of a CO_3 ion contains neither the inversion center nor twofold axes perpendicular to the threefold axis. Thus, the carbonate ion has the positional symmetry $C3$. The superposition of the resonance vibrations of all the CO_3 ions in the unit cell does not change the number of the bands in the spectrum. Consequently, the crystal structure may belong to the symmetry class $C3$ or $C3v$.

Table 1. Crystallographic data for $\text{NaPb}_2(\text{CO}_3)_2(\text{OH})$ and details of X-ray diffraction study

Molecular formula	$\text{HC}_2\text{O}_7\text{NaPb}_2$
Sp. gr.	$P31c$
a , Å	5.268(4)
c , Å	13.48(1)
V , Å ³	324.0(7)
ρ_{calc} , g/cm ³	5.877(9)
μ , cm ⁻¹	512.1(1)
Refinement mode	$F(hkl)$
Weighting scheme	$w = 1/[(\sigma(F))^2 + 0.0010F^2]$
Number of parameters in the refinement	21
2θ (deg) and $\sin\theta/\lambda_{\text{max}}$	93.55 and 1.025
Number of reflections with $F > 4\sigma(F)$	851
$R(F)$, R_w	0.0445, 0.0472
S	1.080
Reduction coefficient	0.685(4)

Single-Crystal X-ray Diffraction Analysis

The symmetry of the Laue patterns obtained from a large ($0.6 \times 0.3 \times 0.15\text{ mm}$) transparent tabular single crystal oriented normally to the incident beam showed that the crystal belongs to the diffraction class $\bar{3}1m$. The X-ray data were collected from a small isometric ($0.125 \times 0.125 \times 0.15\text{ mm}$) well-faceted crystal providing the formation of high-quality reflections in the Laue diffraction patterns. The parameters of the triclinic unit cell were determined and refined on a Syntex P1 diffractometer (Table 1). The three-dimensional set of intensities I_{hkl} were collected within the independent region of the reciprocal space in accordance with the diffraction class. The intensities were processed and converted into F_{hkl}^2 using the PROFIT program [3]. All the subsequent calculations were carried out with the use of the CSD program package. The observed systematic absences of the hhl reflections with $l = 2n$ indicated the space group $P31c-C_{3v}^4$. The interatomic vectors of the Patterson function P_{uvw} showed that the heavy Pb atoms occupy special positions on the threefold axes spaced by the distance of $\sim 1/3c$. The refinement of two basis Pb(1) and Pb(2) atoms converged with the satisfactory R factor. The Na atom, the O(1) atom of the hydroxyl group (involved in the coordination environment only about the Pb(1) and Pb(2) atoms), two C atoms, and the O(2) and O(3) atoms forming the triangular coordination environments about the C atoms were localized from the difference electron-density syntheses by the method of successive approximations. The resulting formula $\text{NaPb}_2(\text{CO}_3)_2(\text{OH})$ (I) is electrically neutral. The structure model was refined with allowance for anomalous absorption of the Mo radiation by lead atoms using only isotropic thermal parameters. Attempts at anisotropic refinement failed because of the pronounced pseudosymmetry of the structure in the space group $P\bar{3}1c$, which is seen from the analysis of the atomic

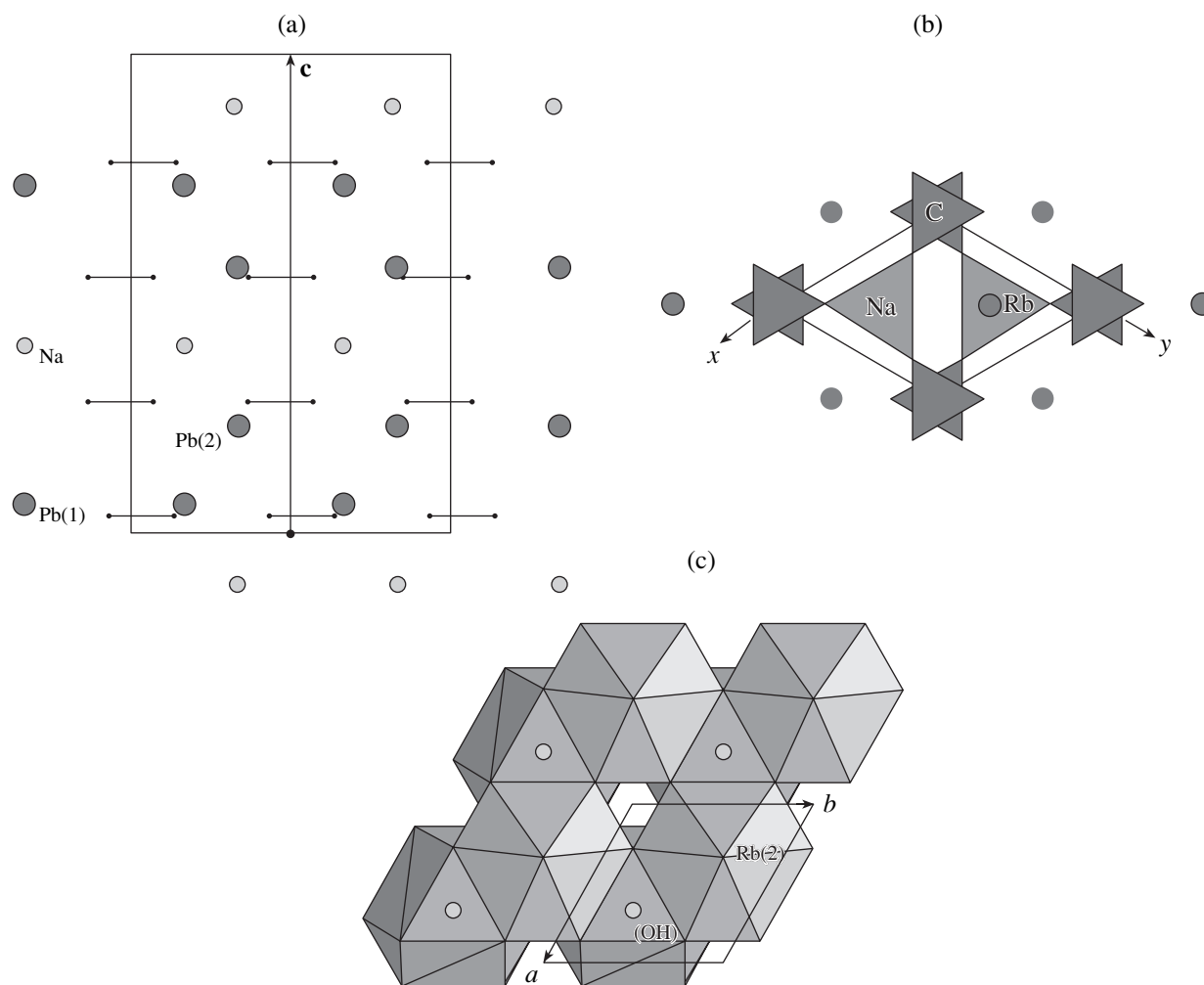


Fig. 2. Crystal structure of $\text{NaPb}_2(\text{CO}_3)_2(\text{OH})$: (a) the side diagonal projection onto the (110) plane (CO_3 -triangles are shown by solid lines and Na and Pb atoms are represented by circles); (b) the projection onto the (001) plane (CO_3 groups are shown by triangles and Na and Pb atoms are represented by prisms and circles, respectively); (c) the projection onto the (001) plane (the Pb(2)-polyhedra are visible; OH groups are represented by circles).

coordinates. A singular point on the pseudoaxis $\bar{3}$ (an inversion pseudocenter) is located at a height $z = 0.14$ (and 0.64). Two positions of Pb atoms in the sp. gr. $P31c$ are related by this pseudocenter, which corresponds to one independent Pb atom in the position $4f$ of the supergroup $P\bar{3}1c$. In this supergroup, a Na atom (with the z coordinate rounded to $1/4$) occupies the $2c$ position, a Cl atom is located in the $4e$ position, the O(1) atom (with the z coordinate also rounded to $\sim 1/4$) occupies the $2d$ position, and the O(2) and O(3) atoms merging into one atom are located in the general position $12i$. The refinement of this model within the sp. gr. $P\bar{3}1c$ did not allow us to reduce the R factor below 0.087. The supergroup was rejected because of the violation of two principal structural criteria—(1) the isotropic thermal parameter ($B = 4.42 \text{ \AA}^2$) for the O atom with the coordinates corresponding to the position $12i$

in the supergroup was too high and (2) the Pb–O interatomic distance (1.908 \AA ; the ionic radius of Pb^{2+} is 1.20 \AA) and the too long Na–O interatomic distance (3.04 \AA ; the ionic radius of Na^+ is 0.97 \AA) were too short. The splitting of the position $12i$ of the oxygen atom into two positions, O(2) and O(3), substantially improved the Pb–O (2.62 – 2.74 \AA) and Na–O (2.38 – 2.59 \AA) distances, reduced the difference in the lengths of the bonds between the Pb(1) and Pb(2) atoms and the common O(1) atom of the hydroxyl group, and lowered the symmetry (the loss of the inversion center), which is in agreement with the IR spectral data. At the final stage of the refinement, the correction for absorption, too high despite the small size of the sample, was applied using the DIFABS program [4]. The atomic coordinates and interatomic distances are given in Tables 2 and 3, respectively.

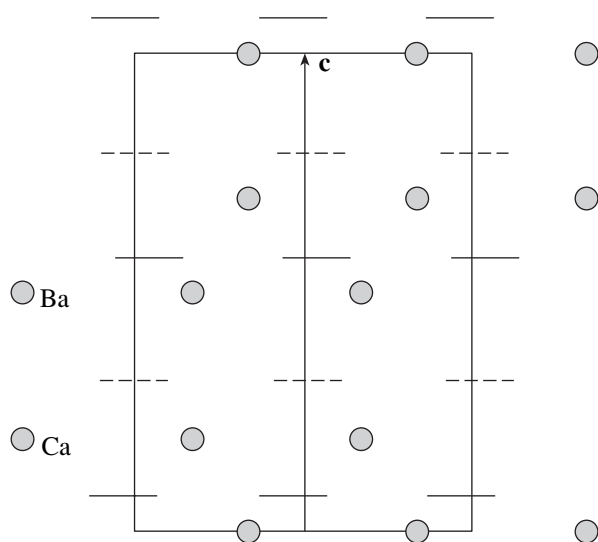


Fig. 3. Crystal structure of ewaldite projected onto the (110) plane; Ca and Ba atoms are represented by circles, CO_3 -triangles are shown by solid lines, and unlocalized CO_3 groups are indicated by dashed lines.

Study by Method of the Second Harmonic Generation

The nonlinear-optical activity of carbonate **I** was examined using powdered samples obtained by grinding. A sample with 100 to 150- μm particles was prepared by isolating the coarse-ground fraction with the use of sieves. A sample of the finely dispersed fraction with 3 to 5- μm grains was obtained by 20-min precipitation of an alcoholic suspension. The temperature dependence of the second harmonic generation (SHG) was obtained on the samples placed into an electric furnace. The test for the second harmonic generation was performed in the reflection mode using a YAG : Nd laser according to the procedure described in our earlier studies [5]. At room temperature, the second-harmonic intensity with respect to that of the reference sample of crystalline quartz with a dispersity of 3 μm were 1.2 and 0.7 for the coarse- and finely-dispersed samples,

Table 2. Coordinates of basis atoms and isotropic thermal parameters for the $\text{NaPb}_2(\text{CO}_3)_2(\text{OH})$ structure

Atom	x/a	y/b	z/c	B_j
Na	2/3	1/3	0.8927(11)	1.59(6)
Pb(1)	2/3	1/3	0.5570	0.85(4)
Pb(2)	2/3	1/3	0.2258(1)	0.90(4)
C(1)	0	0	0.035(3)	0.44(6)
C(2)	0	0	0.276(3)	0.32(6)
O(1)	2/3	1/3	0.388(4)	1.47(6)
O(2)	0.151(7)	0.288(8)	0.536(2)	1.20(6)
O(3)	0.276(7)	0.141(7)	0.755(2)	0.83(6)

respectively. The low SHG signal and an insignificant increase in its intensity for the coarse-ground sample indicate that carbonate **I** exhibits rather weak optical nonlinearity and, probably, possesses no phase synchronism with the neodymium laser radiation and its second harmonic. According to Kurts [6], crystals **I** should be related to the nonlinear-optical class *D*.

A rise in the temperature to 220–250°C resulted in no substantial changes in the nonlinear-optical properties. In the temperature range from 250 to 300°C, the intensity of the second-harmonic signal rapidly decreased and finally became zero. Subsequent cooling did not restore the nonlinear-optical activity of the samples, which proves the irreversibility of the structural change occurred. X-ray diffraction analysis and IR spectroscopy data show that, upon thermal treatment, carbonate **I** lost the quadratic optical nonlinearity which can be associated with the removal of the OH group from the sample.

RESULTS AND DISCUSSION

In the structure of new carbonate **I** (Figs. 2a, 2b), the CO_3 -triangle has the symmetry 3, which is consistent with the results of IR spectroscopy. The plane of the CO_3 -triangle is parallel to the *ab*-plane of the unit cell. The C–O distances are slightly different (Table 3) but range within the corresponding values known for a number of minerals. The C–O distances in dawsonite $\text{NaAl}(\text{OH})_2\text{CO}_3$ [7] are 1.25 and 1.308 Å (two distances); in fairchildite $\text{K}_2\text{Ca}(\text{CO}_3)_2$ [8], 1.284 (two distances) and 1.288 Å; in paralstonite $\text{BaCa}(\text{CO}_3)_2$ [9], 1.279, 1.289, and 1.285 Å; and in barytoalcite $\text{BaCa}(\text{CO}_3)_2$ [10], they range from 1.15 to 1.43 Å. The average C–O distance for two triangles in carbonate **I** is identical to that in dolomite $\text{CaMg}(\text{CO}_3)_2$ [11] (C–O = 1.285 Å). The Pb atoms in the minerals phosgenite $\text{Pb}_2(\text{CO}_3)\text{Cl}_2$ [12], cerussite PbCO_3 [13], and hydrocerussite $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ [14] with known structures adopt high coordination numbers (9 or 10). If seven O atoms located at distances up to ~2.7 Å (Table 3) are included into the coordination sphere of Pb atoms, the polyhedra remain open, like those in hydrocerussite; however, the addition of three more O atoms located at distances larger than 3 Å complements the coordination of the Pb(1) and Pb(2) atoms to ten-vertex polyhedra (because of the pseudosymmetry). These polyhedra can be described by hexahedral “boxes” with flat bottoms and caps ended with shared hydroxyl groups closest to the Pb(1) and Pb(2) atoms (Fig. 2c). The distances in these polyhedra around lead atoms in phosgenite (from 2.36 to 3.34 Å), cerussite (from 2.59 and 2.76 Å), and hydrocerussite (from 2.75 to 3.10 Å) are quite consistent with the Pb–O distances in carbonate **I** refined within the acentric space group. The coordination polyhedra around Na atoms are almost regular trigonal prisms.

The metrics of the axes in the structures of carbonate **I** and ewaldite $\text{BaCa}(\text{CO}_3)_2$ ($a = 5.284$ Å, $c = 12.78$ Å,

sp. gr. $P6_3mc$ [15]) are virtually identical. The replacement of Ba^{2+} by Na^+ leads to a necessary increase in the number of large cations in the formula of carbonate **I**. One of the CO_3 -triangles in the ewaldite structure has not been localized as yet [15]. Comparing the side diagonal projections of these structures (Figs. 2a, 3), we see that the positions of Ba and Ca atoms in ewaldite are identical to the positions of Na and Pb(1) atoms in carbonate **I**. By analogy, it can be assumed that a CO_3 group not revealed in the ewaldite structure should be located between the Ca- and Ba-layers (dashed lines in Fig. 3) at the height z identical to the height observed for an additional Pb(2) cation in structure **I**.

The mineral paralstonite of the aragonite group with the formula $BaCa(CO_3)_2$ identical to that of ewaldite belongs to the trigonal system (sp. gr. $P321$) [9]. The c -parameter of paralstonite (6.148 Å) is half as large as that of carbonate **I**, whereas the $a(b)$ parameter (8.692 Å) is close to the length of the unit-cell diagonal of carbonate **I**. The close $a(b)$ parameters were also found in phosgenite and hydrocerussite. The cationic motifs in ewaldite and carbonate **I** are complicated by an additional layer built into it and increasing in the c -parameter. The unit cell of the minimum volume (sp. gr. $P312$) is observed in lead- and oxygen-deficient borate $Pb_{0.75}[BO_{2.25}]$ studied recently. The $a(b)$ parameters of the latter (~ 5 Å) are close to those of aragonite, fairchildite, dolomite, and cerussite, whereas its c parameter is equal to that of ewaldite. This borate was found to be structurally close to carbonates, and, first of all, to aragonite.

In the search for compounds structurally close to carbonate **I**, we revealed, quite surprisingly, diorthosilicate $NaBa_3[Si_2O_7](OH)$ [16] (**II**), whose unit-cell parameters ($a = 5.79$ Å, $c = 14.74$ Å, sp. gr. $P6_3/mmc$) are very close to those of **I** (despite the differences between these compounds). The coordination polyhedron around Ba(2) in **II** is identical to Pb-polyhedra in **I** (within the symmetry of the position). This polyhedron was described as the combination of a hexagonal pyramid and a half of the Archimedean cuboctahedron, whose triangular base is formed by a triangular face of the tetrahedron of a linear diortho group. In **II**, Ba(2)-polyhedra are linked in pairs via the shared vertices of

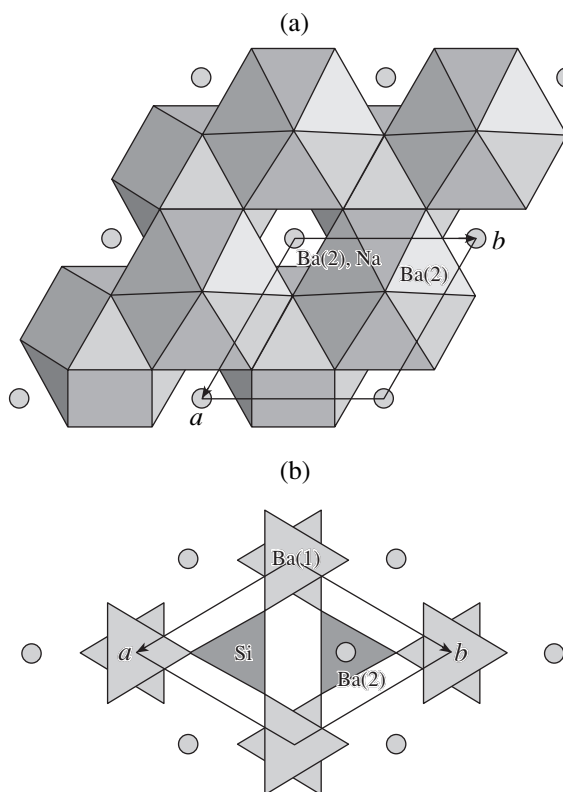


Fig. 4. Crystal structure of $NaBa_3[Si_2O_7](OH)$ (a) projected onto the (001) plane (Ba(2)-polyhedra are seen; Ba(1) and Na atoms are represented by overlapping circles); and (b) projected onto the (001) plane (Ba(1)-prisms and the Si diortho groups are seen; Ba(2) atoms are represented by circles).

the pyramid occupied by OH groups with shortened Ba–OH distances (Fig. 4a) (as in the structure of carbonate **I**). In carbonate **I**, Na-prisms are observed instead of diortho $[Si_2O_7]$ groups in **II** (which link Ba(2)-polyhedra into columns), with the Na atoms in the prisms occupying the central position of the bridging O atom of a diortho group in **II**. The columns of the second type in **II** along the c -axis consist of Na-octahedra and Ba(1)-trigonal prisms (Fig. 4b). In carbonate **I**, these columns are replaced by CO_3 -triangles (Fig. 2b)

Table 3. Principal interatomic distances (Å) in the $NaPb_2(CO_3)_2(OH)$ structure

Pb(1)-polyhedron		Pb(2)-polyhedron		Na-polyhedron	
Pb(1)–O(1)	2.28(5)	Pb(2)–O(1)	2.18(5)	Na–O(3)	$2.38(4) \times 3$
Pb(1)–O(2)	$2.62(4) \times 3$	Pb(2)–O(3)	$2.72(4) \times 2$	Na–O(2)	$2.59(4) \times 3$
Pb(1)–O(3)	$2.70(4) \times 3$	Pb(2)–O(3)	$2.74(4) \times 3$		
Pb(1)–O(3)	$3.44(5) \times 3$	Pb(2)–O(2)	$3.09(5) \times 3$		
C(1)-triangle		C(2)-triangle			
C(1)–O(2)	$1.31(4) \times 3$	C(2)–O(3)	$1.26(4) \times 3$		
O(2)–O(2)	$2.28(5) \times 3$	O(3)–O(3)	$2.18(5) \times 3$		

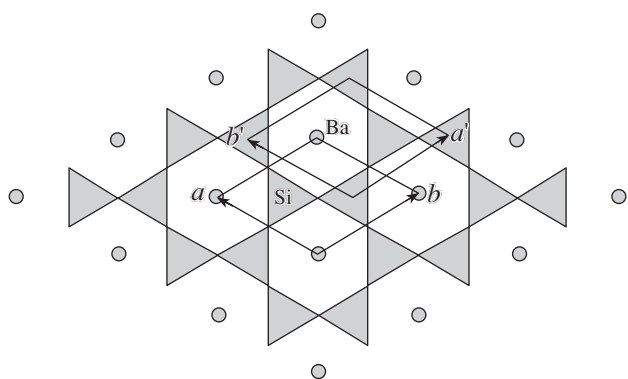


Fig. 5. Crystal structure of $\text{Ba}[\text{AlSiO}_4]_2$ projected onto the (001) plane; Si-tetrahedra are seen; Ba atoms are shown by circles. The a' and b' axes are shown to facilitate the comparison of the structures.

(the shared bases of the octahedra and prisms in **II**). In carbonate **I**, all the distances between the triangles along the c -axis are equivalent (Fig. 2a), whereas the corresponding distances in **II** have different values due to the differences in the heights at which the Na-octahedron and the Ba(1)-prism are located. Similar to the shared bases of the octahedra and prisms in **II** (Fig. 4b), the pairs of CO_3 -triangles in the structure of **I** (Fig. 4b) are rotated with respect to one another by 60° . The $\text{NaBa}_3[\text{Si}_2\text{O}_7](\text{OH})$ silicate is structurally similar to the $\text{NaPb}_2(\text{CO}_3)_2(\text{OH})$ carbonate because the ratio of the ionic radii of the pair Pb^{2+} and C^{4+} is similar to the ratio of the pair Ba^{2+} and Si^{4+} . The fragments of these structures shown in Figs. 2b and 4b are rather similar within the framework of the above-considered topology (Na-prism–Si-tetrahedron, CO_3 -triangle–Ba(1)-prism, and Pb–Ba(1)) and can be approximated by an idealized silicon–oxygen double layer built by the simplest mica $[\text{Si}_4\text{O}_{10}]$ layers linked by shared apical vertices. Such a layer was found in the $\text{Ba}[\text{Al}_2\text{Si}_2\text{O}_8]$ structure [17] (Fig. 5). These layers are translated and, thus, the c -parameter in the latter structure (7.79 \AA) is half as large as that in the structures under consideration. In this layer, the diortho groups can be replaced either by trigonal prisms (of Ba or Na) or other anionic tetrahedral or triangular (CO_3) groups, with the latter replacing the triangular bases of the SiO_4 -tetrahedra. This fact opens new possibilities for crystallochemical analysis and the prediction of new structures. It should be noted that N.V. Belov was the first to analyze the structural

analogy between diorthosilicates and minerals with triangular anions [18].

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