

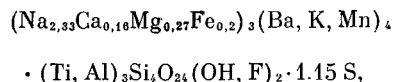
CRYSTAL STRUCTURE OF INNELITE, $\text{Na}_2\text{Ba}_3(\text{Ba}, \text{K}, \text{Mn})(\text{Ca}, \text{Na})\text{Ti}(\text{TiO}_2)_2[\text{Si}_2\text{O}_7]_2(\text{SO}_4)_2$

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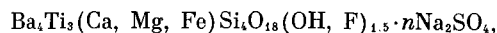
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 Translated from *Kristallografiya*, Vol. 16, No. 1,
 pp. 87-92, January-February, 1971
 Original article submitted August 21, 1970

The crystal structure of the complex acentric titanosilicate, innelite, was completely solved. The unit cell dimensions are: $a = 14.76$, $b = 7.14$, $c = 5.38$ Å, $\alpha = 90^\circ$, $\beta = 95^\circ$, $\gamma = 99^\circ$. The basic structure was determined from the Patterson function by the multiple peak method. The most characteristic feature of the structure is the mica-like packages ("cores" of Ti + Na + M octahedra, "armor" of Ti + Si networks) and the "barite" layers of large Ba polyhedra with SO_4 tetrahedra in the holes in the Ba skeleton.

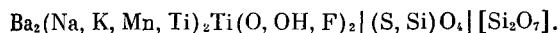
Barium titanosilicate—innelite—was found in 1957 in pegmatites in the Inaglinskii Massif (Southern Yakutsk). A characteristic of the plate-like crystals of the mineral is the polysynthetic Manebach twinning, which is constantly observed. Sometimes the plates of innelite form radiating aggregates. The mineral is biaxial, pleochroic, and optically positive. $N_g = 1.766 \pm 0.001$, $N_m = 1.737 \pm 0.001$, $N_p = 1.726 \pm 0.001$. The density is 3.96. There is a strong piezoeffect.¹ According to chemical analyses (M. E. Kazakova), the formula of innelite is as follows [1]:



or, more schematically,



where $n (=1.15)$ may be variable (cf. lomonosovite or hillebrandite, which also have "supplemental branches" in their formulas). Later, Strunz [2] examined the isotopy of ioshimuraite [3] and innelite, and gave another variant for the formula:



The material for the x-ray structural analysis was samples of innelite from the collections of

S. M. Kravchenko and A. F. Efimov. Among the more than 600 polysynthetic twins, one definite single crystal chip, $0.1 \times 0.12 \times 0.15$ mm, was selected. The triclinic cell has the parameters: $a = 14.76$, $b = 7.14$, $c = 5.38$ Å; $\alpha = 90^\circ$, $\beta = 95^\circ$, $\gamma = 99^\circ$. There is one formula unit in the cell according to [1], or two formula units according to Strunz [2]. The space group is thus P1.

The experimental set of intensities consisted of more than 2000 nonzero reflections from the $hk0-hk4$ and $h0l-h1l$ layers (Weissenberg goniometer, $\text{MoK}\alpha$ radiation, maximum $\sin\theta/\lambda = 1.0$ Å). The intensities were estimated with an intensity strip obtained from the $(2\bar{2}0)$ reflection of the same crystal with a Weissenberg camera (steps of the scale: $2^{1/4}$). An absorption correction was not made because of the arbitrary shape of the crystal. We did not succeed in interpreting single peaks on the three-dimensional Patterson function $P(uvw)$, and so we turned to an algorithm for isolating the main system according to the method of multiple peaks [4]. A somewhat modified method (for the steps of the 4-gons, multiplicity vectors N_3, N_4, N_5 , etc., were used for the construction, up to the points isolated from the first 4-gon N_1N_2 [4]) en-

¹The measurements were made in the Department of Crystal Physics, Moscow State University

TABLE 1

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Ba ₁	0	0	0	O ₃	0.918	0.288	0.733
Ba ₂	0.299	0.293	0.0624	O ₇	0.771	0.445	0.952
Ba ₃	0.078 ₄	0.537	0.513	O ₈	0.763	0.742	0.452
Ba ₄	0.302	0.842	0.575	O ₉	0.125	0.212	0.767
Ti ₁	0.488	0.368	0.602	O ₁₀	0.129	0.217	0.295
Ti ₂	0.677	0.916	0.319	O ₁₁	0.130	0.919	0.558
Ti ₃	0.889	0.480	0.976	O ₁₂	0.264	0.150	0.561
Si ₁	0.495	0.652	0.108	O ₁₃	0.234	0.615	0.284
Si ₂	0.500	0.079 ₁	0.098 ₂	O ₁₄	0.238	0.619	0.833
Si ₃	0.877	0.195	0.473	O ₁₅	0.244	0.919	0.072 ₁
Si ₄	0.875	0.760	0.474	O ₁₆	0.917	0.675	0.233
T ₁ (S ₁)	0.204	0.705	0.045	O ₁₇	0.919	0.686	0.741
T ₂ (S ₂)	0.164	0.122	0.528	O ₁₈	0.599	0.407	0.605
M	0.678	0.149	0.784	O ₁₉	0.451	0.172	0.867
Na ₁	0.681	0.423	0.270	O ₂₀	0.453	0.148	0.348
Na ₂	0.677	0.662	0.761	O ₂₁	0.450	0.538	0.333
O ₁	0.452	0.858	0.106	O ₂₂	0.915	0.994	0.495
O ₂	0.610	0.895	0.606	O ₂₃	0.767	0.127	0.444
O ₃	0.919	0.295	0.233	O ₂₄	0.600	0.114	0.127
O ₄	0.447	0.542	0.845	O ₂₅	0.607	0.683	0.108
O ₅	0.095 ₇	0.689	0.045 ₈	O ₂₆	0.752	0.919	0.016 ₇

TABLE 2

Ba ₁ polyhedron	Ba ₄ - O ₂₀ * = 2.73	Na ₂ - O ₂₅ * = 2.25
Ba ₁ - O ₃ * = 2.91	Ba ₄ - O ₂₁ = 3.03	Na ₂ - O ₂₆ * = 2.34
Ba ₁ - O ₅ * = 2.81	Ti ₇ polyhedron	Si ₁ tetrahedron
Ba ₁ - O ₆ * = 2.87	(5-coordinate)	Si ₁ - O ₁ = 1.68
Ba ₁ - O ₉ * = 2.61	Ti ₁ - O ₄ = 2.00	Si ₁ - O ₄ * = 1.66
Ba ₁ - O ₁₀ = 2.66	Ti ₁ - O ₁₉ = 2.07	Si ₁ - O ₂₁ = 1.60
Ba ₁ - O ₁₁ * = 3.17	Ti ₁ - O ₂₀ = 2.06	Si ₁ - O ₂₅ = 1.63
Ba ₁ - O ₁₆ * = 2.80	Ti ₁ - O ₂₁ = 1.99	Si ₁ - O _{av} = 1.64 ₅
Ba ₁ - O ₁₇ * = 3.00	Ti ₁ - O ₁₈ = 1.62	Si ₂ tetrahedron
Ba ₁ - O ₂₂ * = 3.00	Ti ₂ octahedron	Si ₂ - O ₁ * = 1.63
Ba ₁ - O ₂₃ * = 3.04	Ti ₂ - O ₂ = 1.90	Si ₂ - O ₁₉ * = 1.58
Ba ₂ polyhedron	Ti ₂ - O ₈ = 2.00	Si ₂ - O ₄ * = 1.57
Ba ₂ - O ₄ * = 2.92	Ti ₂ - O ₂₃ * = 1.93	Si ₂ - O ₂₀ = 1.67
Ba ₂ - O ₆ * = 2.88	Ti ₂ - O ₂₄ * = 2.09	Si ₂ - O ₂₄ = 1.58
Ba ₂ - O ₁₀ = 2.88	Ti ₂ - O ₂₅ = 2.09	Si ₂ - O _{av} = 1.61 ₅
Ba ₂ - O ₁₂ = 2.93	Ti ₂ - O ₂₆ = 2.04	Si ₃ tetrahedron
Ba ₂ - O ₁₂ * = 2.86	Ti ₃ polyhedron	Si ₃ - O ₃ = 1.60
Ba ₂ - O ₁₃ = 2.91	(5-coordinate)	Si ₃ - O ₆ = 1.58
Ba ₂ - O ₁₄ * = 2.87	Ti ₃ - O ₃ * = 1.98	Si ₃ - O ₆ * = 1.62
Ba ₂ - O ₁₅ * = 2.67	Ti ₃ - O ₅ = 2.01	Si ₃ - O ₂₂ * = 1.62
Ba ₂ - O ₁₆ * = 2.71	Ti ₃ - O ₁₆ * = 1.94	Si ₃ - O ₂₃ * = 1.62
Ba ₂ - O ₂₀ = 2.96	Ti ₃ - O ₁₇ = 1.97	Si ₃ - O _{av} = 1.60 ₅
Ba ₂ - O ₂₁ = 2.91	Ti ₃ - O ₇ = 1.71	Si ₄ tetrahedron
Ba ₃ polyhedron	Na ₁ octahedron	Si ₄ - O ₈ = 1.63
Ba ₃ - O ₃ * = 2.98	Na ₁ - O ₇ * = 2.25	Si ₄ - O ₁₆ = 1.64
Ba ₃ - O ₅ = 2.75	Na ₁ - O ₈ = 2.56	Si ₄ - O ₁₇ = 1.65
Ba ₃ - O ₆ * = 3.04	Na ₁ - O ₁₈ = 2.25	Si ₄ - O ₂₂ = 1.68
Ba ₃ - O ₆ * = 3.05	Na ₁ - O ₂₃ = 2.55	Si ₄ - O _{av} = 1.65
Ba ₃ - O ₉ = 2.84	Na ₁ - O ₂₄ = 2.39	T ₁ (S ₁) tetrahedron
Ba ₃ - O ₁₀ = 2.80	Na ₁ - O ₂₅ = 2.42	Ti(S ₁) - O ₅ = 1.58
Ba ₃ - O ₁₁ = 2.71	M octahedron	Ti(S ₁) - O ₁₃ = 1.50
Ba ₃ - O ₁₃ = 2.69	M - O ₃ * = 2.32	Ti(S ₁) - O ₁₄ * = 1.46
Ba ₃ - O ₁₄ = 2.78	M - O ₇ = 2.46	Ti(S ₁) - O ₁₅ = 1.55
Ba ₃ - O ₁₆ * = 3.00	M - O ₁₈ = 2.48	Ti - O _{av} = 1.52
Ba ₃ - O ₁₇ * = 3.07	M - O ₂₃ = 2.36	T ₂ (S ₂) tetrahedron
Ba ₄ polyhedron	M - O ₂₄ * = 2.26	T ₂ (S ₂) - O ₉ = 1.57
Ba ₄ - O ₁ = 2.95	M - O ₂₅ * = 2.41	T ₂ (S ₂) - O ₁₀ = 1.52
Ba ₄ - O ₁ * = 3.04	Na ₂ octahedron	T ₂ (S ₂) - O ₁₁ * = 1.47
Ba ₄ - O ₄ = 2.97	Na ₂ - O ₂ = 2.30	T ₂ (S ₂) - O ₁₂ = 1.46
Ba ₄ - O ₁₂ * = 2.81	Na ₂ - O ₇ = 2.40	T ₂ - O = 1.50
Ba ₄ - O ₁₃ = 2.67	Na ₂ - O ₈ = 2.33	
Ba ₄ - O ₁₄ = 2.71	Na ₂ - O ₁₈ = 2.28	
Ba ₄ - O ₁₅ = 3.17		
Ba ₄ - O ₁₉ * = 2.98		

* The asterisks denote translationally identical atoms.

abled us to fix seven points in the first step. These were present in all copies of the main system obtained from various 4-gons. Subsequent addition of the remaining points [checked with P(uvw)] led to 13 points of the main system, corresponding to almost all of the medium-weight atoms in the structure (19 from 12) and four Ba atoms. The coordinates of these atoms were used in the first electron density syntheses. The disagreement index was 0.30 (seven atoms) or 0.26 (12 atoms). Several cycles of electron density syntheses - both full $\rho(xyz)$ and $\Delta\rho(xyz)$ - permitted us to locate all the remaining atoms in the structure and to differentiate between the cations. The total number - 42 independent atoms - corresponds better to the formula variant of Strunz [2] than to the formula given in [1]. The final R factor [from $\rho(xyz)$ syntheses] was 0.19.

Refinement of positional parameters and introduction of an overall isotropic temperature factor, $B = -0.1 \text{ \AA}$, lowered R to 0.14. Consideration of the isomorphic interactions of the Ba,K(Mn) atoms (Ba₄ in the table), which occupy one crystallographic position, and Ca,Mg,Fe,Na (atom M in the tables), also statistically distributed in another single position, led to $R_{hk\ell} = 0.124$. Further refinement of the fractional multiplicity of each atom (refinement by the method of least squares) and introduction of individual temperature factors did not change $R_{hk\ell}$ significantly (0.119).

The final coordinates of the basis atoms (123 parameters, $R_{hk\ell} = 0.119$) are given in Table 1. The interatomic distances calculated with these values are given in Table 2.

The large Ba cations occupy four nonequivalent positions: two of them (Ba₂ and Ba₃) have 11-coor-

dinate polyhedra with $\text{Ba}_2\text{-O} = 2.67\text{--}2.96 \text{ \AA}$, $\text{Ba}_3\text{-O} = 2.71\text{--}3.07 \text{ \AA}$; the third, Ba_4 , is in a 10-coordinate polyhedron with $\text{Ba}_4\text{-O} = 2.61\text{--}3.17 \text{ \AA}$. According to the chemical formula, the fourth position is occupied by Ba and K(Mn) atoms. The polyhedron about the "mixed" cation is also a 10-coordinate one with $(\text{Ba}, \text{K})\text{-O} = 2.67\text{--}3.17 \text{ \AA}$.²

Of the three titanium atoms (with a small amount of Al), one (Ti_2) is located in a normal octahedron with $\text{Ti}_2\text{-O} = 1.90\text{--}2.09 \text{ \AA}$. The other two are surrounded by only five oxygen atoms at the vertices of a tetragonal pyramid. Recent structure determinations [6-8] have fairly conclusively demonstrated the unusual coordination number of five for Ti and the possibility of the titanyl bond, $\text{Ti}=\text{O}$, in titanosilicates. Inside the tetragonal pyramid (a hemioctahedron), the Ti is displaced from the square plane towards the opposite vertex. Four of the Ti-O distances (to neighbors in the base of the pyramid) are "normal" ($\text{Ti}_1\text{-O} = 1.99\text{--}2.07 \text{ \AA}$, $\text{Ti}_3\text{-O} = 1.94\text{--}2.01 \text{ \AA}$), while the fifth - to the vertex - is greatly shortened: $\text{Ti}_1\text{-O} = 1.62 \text{ \AA}$, $\text{Ti}_3\text{-O} = 1.71 \text{ \AA}$.³

The two cations Na_1 and Na_2 and the M atom have octahedral surroundings: $\text{Na}_1\text{-O} = 2.25\text{--}2.56 \text{ \AA}$, $\text{Na}_2\text{-O} = 2.25\text{--}2.40 \text{ \AA}$ (average $\text{Na-O} = 2.36 \text{ \AA}$), $\text{M-O} = 2.26\text{--}2.48 \text{ \AA}$ (average $\text{M-O} = 2.36 \text{ \AA}$). The four Si atoms are located in normal tetrahedra. The Si-O distances lie within established limits: $\text{Si}_1\text{-O} = 1.60\text{--}1.68 \text{ \AA}$, $\text{Si}_2\text{-O} = 1.58\text{--}1.67 \text{ \AA}$, $\text{Si}_3\text{-O} = 1.58\text{--}1.62 \text{ \AA}$, and $\text{Si}_4\text{-O} = 1.63\text{--}1.68 \text{ \AA}$ (average $\text{Si-O} = 1.62_8 \text{ \AA}$). The tetrahedra are joined pairwise to form diorthogroups inscribed in a trigonal prism, which frequently happens in Ca silicates. More compact tetrahedra are characteristic for

the remaining two tetrahedral atoms.⁴ The distances are $\text{T}_1(\text{S}_1)\text{-O} = 1.47\text{--}1.58 \text{ \AA}$ and $\text{T}_2(\text{S}_2)\text{-O} = 1.46\text{--}1.57 \text{ \AA}$ (average $1.51 \text{ \AA}$), and agree with those known for the SO_4 group.

The structural motif appears most clearly in the xy projection (Fig. 1). In the central mica (chlorite) package, which is infinite in two directions, the "cores" (Fig. 2a) consist of Ti + Na + M octahedra joined to each other along their edges to form a continuous wall (this is completely analogous to the structures of lamprofillite [8], astrofillite [9], murmanite-lomonosovite [10]). In the walls, infinite columns of M + Ti octahedra can be seen along the c axis. They alternate with pure Na columns. The centers are clothed on both sides in "anionic" armor: titanium-silicon-oxygen planar networks with discrete $[\text{Si}_2\text{O}_7]$ diorthogroups and TiO_5 hemioctahedra (Fig. 2b). Similar networks have been found previously in astrofillite [9], bafertisite [11], and in silicates of the murmanite group [10] (the only difference being that the Ti playing the "anionic" role in these structures has the usual octahedral coordination); and also in lamprofillite [8] and fresnoite [6] (in these two minerals

²As has been repeatedly noted earlier for the large cations K, Rb, and Cs (e.g., [5]) and recently for Ba in fresnoite [6], the ligands around Ba form two spheres: one with a radius close to the sum of the ionic radii of barium and oxygen ($\sim 2.61\text{--}2.90 \text{ \AA}$), and a second removed to $r \sim 3.0\text{--}3.17 \text{ \AA}$.

³The average Ti-O distance is $1.634 \text{ \AA}$ [6]; $1.67 \text{ \AA}$ [7].

⁴Primarily S atoms. Two points support this proposal: the peak heights on the $\rho(\text{xyz})$ and $\Delta\rho(\text{xyz})$ syntheses, and the smaller cation-anion distances in the tetrahedra. However, until the chemical analyses are repeated, we will call them T(S) cations.

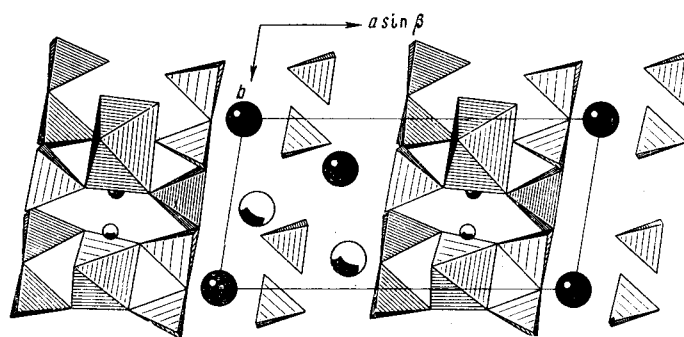


Fig. 1. Innelite. Projection of the structure in polyhedral form onto the xy plane. The packets with (Ti + Na + M) cores, armored on both sides with (Ti + Si) network armor, can be seen. The Ba atoms are located in the interpacket spaces (the light spheres are on the levels $z \sim 1/2$ and $\sim 5/9$, the dark spheres are on the levels ~ 0 and $\sim 1/16$). The SO_4 tetrahedra are also in these spaces. The small circles are Na atoms (in the centers), which are located at various heights.

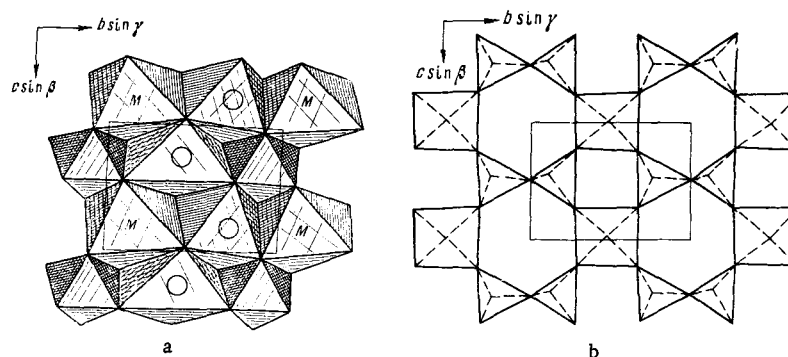


Fig. 2. Innelite. Projection of the mica packet onto the yz plane. a) Core of the packet made of $Ti + Na + M$ octahedra (the Na atoms are circles in the center of the octahedra); b) titanium-silicon-oxygen armor surrounding the cores.

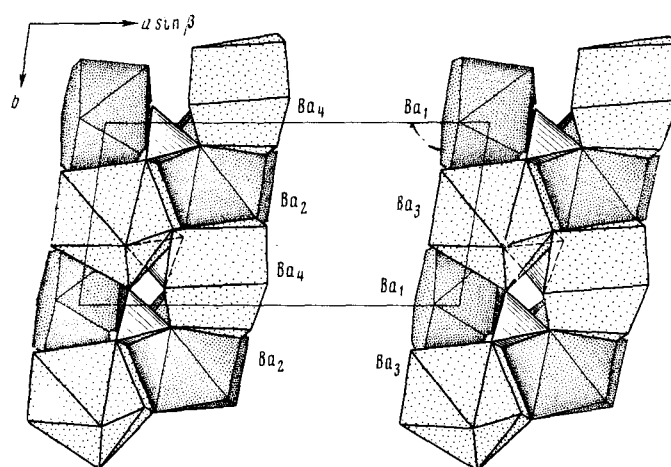


Fig. 3. Innelite. Barite layer. Double wall of Ba polyhedra with SO_4 tetrahedra.

five-coordination is characteristic for titanium in the network). Thus, in innelite, we have still another example of a titanosilicate⁵ where the "diagonal analog" (according to Fersman-Mendeleev) of Al — i.e., the Ti atom — simultaneously plays a double role: cationic (in the octahedron in the center of the packet) and anionic (hemioctahedron in the network armor). In the latter role the network-forming Ti resembles its valence analog in the periodic table, Zr [12, 13], which also tends to form a common skeleton with the primary skeleton construction element, Si.

The mica-like three-layer packets in innelite are separated by the large Ba polyhedra (Fig. 3). These are joined together to make a two-story wall, with the $[SO_4]$ tetrahedra on the mezzanines. As far as resemblance goes, this layer recalls the structure of barite, $BaSO_4$. Thus, with the known conventions, the structure of innelite can be re-

garded as mica and barite packets alternating along the a axis. This corresponds well with the perfect cleavability of innelite along (100).

We thank S. M. Kravchenko and A. F. Efimov for giving us the innelite samples and for their interest in the work.

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⁵In the a priori model of innelite, proposed in [14] in analogy with lomonosovite, only the centers of the packets and the stacking of the packets with respect to the crystallographic axes were guessed at.

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