The crystal structure of hingganite-(Yb), $(Y_{0.51}TR_{0.36}Ca_{0.13}) \cdot Fe_{0.065}Be[SiO_4](OH)$

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The authors have made an x-ray diffraction study (automatic diffractometer, 1345 reflections, 2θ-θ method, λ Mo Kα, $\sin\theta/\lambda \leq 1.08$ Å^{-1}) of the new mineral hingganite, $(Y_{0.51}TR_{0.36}Ca_{0.13})Fe_{0.065}Be[SiO_4](OH)$, $a = 9.888(5)$, $b = 7.607(3)$, $c = 4.740(2)$ Å, $\beta = 90.45(4)°$, Fedorov group $P2_1/a$, $Z = 2$, $R_{hkl} = 6.59\%$ (in isotropic approximation). The structural data confirm that hingganite belongs to the gadolinite-datolite group of minerals.

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The mineral hingganite (Yb)$^{1)}$ was discovered in 1981 by A. V. Voloshin and Ya. A. Pakhomov in amazonite pegmatites of the Kola peninsula. It consists of spherical aggregates of fine acicular crystals. The composition of the specimens corresponds to the chemical formula $(Y_{1.02}TR_{0.72}Ca_{0.19}Fe_{0.08}Pb_{0.01}Al_{0.01})_{2.03}Be_{1.95}Si_{2.04}O_8(OH)_{2.03}$, or in idealized form $(Y, TR)_2Be_2O_8(OH)_2$, close to the formula of gadolinite $FeY_2Be_2Si_2O_{10}$, except that in the idealized formula of hingganite there is no Fe and two O atoms are correspondingly replaced by OH groups. The parameters of the monoclinic unit cell of hingganite are as follows: $a = 9.888(5)$ Å, b = 7.607(3) Å, c = 4.740(2) Å, $\beta = 90.45(4)°$ ($d_e = 4.08$ g/cm^3, Z = 2), also similar to the parameters of gadolinite, $a = 9.87$ Å, b = 7.52 Å, c = 4.71 Å, $\beta = 90°33'$.

A mineral of similar composition has been found in granitic pegmatites in Tuva.[1] Its chemical and structural features have not been studied. Somewhat later, a synthetic compound of the same composition, $H_2(Y, TR)_2Be_2 \cdot Si_2O_{10}$, was obtained by the hydrothermal method.[2,3] Ito[2] proposed the following general formula for gadolinites: $H_{2-x}Fe^{2+}_{2-x-y}Fe_y^{3+}Ca_y\,(Y, TR)^{3+}_{4-y}Be_4Si_4O_{20}$, where $0 \leqslant x \leqslant 2, 0 \leqslant y \leqslant 2, 0 \leqslant x+y \leqslant 2$; gadolinite itself, $Fe^{2+}(Y, TR)_2{}^{3+}Be_2Si_2O_{10}$, calciogadolinite $Fe^{3+}Ca(TR, Y)^{3+}Be_2Si_2O_{10}$, and $H_2(Y, TR)_2{}^{3+} \cdot Be_2Si_2O_{10}$ are the end members of this group of compounds.

The similarity between the diffraction patterns, unit-cell parameters, and chemical formulas of minerals and synthetic compounds of the gadolinite–datolite group, on the one hand, and hingganite, on the other, suggested that their crystal structures are similar. Starting from the idealized chemical formula of hingganite $(Y, TR)_2Be_2Si_2 \cdot O_8(OH)_2$, we can regard it either as datolite $Ca_2B_2Si_2O_8(OH)_2$ in which Ca and B are replaced by (Y, TR) and Be, or as gadolinite $Fe(Y, TR)_2Be_2Si_2O_8O_2$ with vacancies instead of Fe^{2+} ions and corresponding replacement of two O^{2-} by by two OH^- groups, especially as Aleksandrova et al.[4] have advanced the hypothesis that there is continuous isomorphism from datolite to gadolinite.

The experimental material necessary in order to determine the crystal structure of hingganite – the intensities of 1345 independent nonzero ($I \geq 1.96\sigma I$) reflections – was obtained by the 2θ:θ method with a variable scanning rate of 6–24 degrees/min (λMo Kα, $\sin\theta/\lambda \leq 1.08$ Å^{-1}) in a Syntex P$\bar{1}$ automatic diffractometer with a nonrounded single crystal ($l_{max} = 0.01$ cm). The presence of regular extinctions in reflections of the type h0l (h = 2n) and 0k0 (k = 2n) uniquely determined the Fedorov group as $C_{2h}^5 = P2_1/a$, characteristic of gadolinite. In the determination of the crystal structure, all the calculations were made by means of the specialized E-XTL Syntex computing system. On the basis of the x and y coordinates of the heavy Y and Si atoms, established for the structure of gadolinite,[5] and the z coordinates of the Ca and Si atoms in datolite, also taken from Ref. 5, we constructed the three-dimensional electron density distribution. This revealed five independent O and Be atoms. After least-squares refinement of the model, the discrepancy factor was $R_{hkl} = 7.33\%$. In the subsequently constructed difference electron density synthesis, an additional peak appeared in the (000) position, occupied by Fe atoms. On the basis of x-ray spectral analysis and analysis of the interatomic distances, we find that the (000) position, surrounded by an octahedron of six oxygen atoms at distances of 2.05–2.31 Å, is also occupied by Fe^{2+} ions in hingganite. But whereas in gadolinite the special position 2a is occupied by Fe^{2+} ions completely in conformity with the structural formula of the mineral,

TABLE I. Coordinates of Basis Atoms and Isotropic Temperature Factors

Atom	x/a	y/b	z/c	B_{iso}
Y	0.33301(9)	0.1089(1)	0.9987(2)	0.80(1)
Si	0.0791(3)	0.2763(4)	0.5190(7)	0.33(4)
Be	0.335(1)	0.413(2)	0.448(3)	0.1(2)
Fe	0	0	0	0.9(3)
O_1	0.1950(8)	0.347(1)	0.300(2)	0.5(1)
O_2	0.1485(8)	0.109(1)	0.687(2)	0.6(1)
O_3	0.0332(8)	0.412(1)	0.764(2)	0.5(1)
O_4	0.4499(8)	0.284(1)	0.326(2)	0.5(1)
O_5(OH)	0.3305(8)	0.412(1)	0.786(2)	0.5(1)

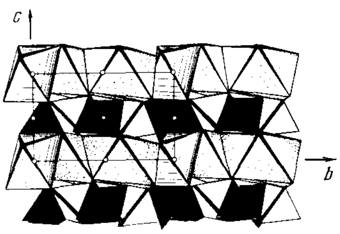

FIG. 1. Alternation of layers of Y-polyhedra and Fe-octahedra with layers of Be-tetrahedra and Si-tetrahedra along c axis in crystal structure of "hingganite."

TABLE II. Interatomic Distances in Ångstroms

Si tetrahedron		Be tetrahedron		Fe octahedron	
Si–O_1	1.641(9)	Be–O_1	1.63(2)	Fe–O_2(2)	2.253(8)
–O_2	1.648(9)	–O_2	1.63(2)	–O_4(2)	2.308(8)
–O_3	1.618(8)	–O_4	1.61(2)	–O_5(2)	2.063(8)
–O_4	1.633(9)	–O_5	1.60(1)		
Average	1.635	Average	1.62	Average	2.208
O_1–O_2	2.62(1) *	O_1–O_2	2.53(1) **	O_2–O_4(2)	2.65(1) ‡
–O_3	2.77(1)	–O_4	2.57(1) **	O_2–O_4(2)	2.72(1) †
–O_4	2.63(1)	–O_5	2.70(1) **	–O_5(2)	2.71(1) ‡
O_2–O_3	2.60(1)	O_2–O_4	2.65(1) ‡	O_4–O_5(2)	2.67(1) ‡
–O_4	2.72(1) †	–O_5	2.71(1) ‡	–O_5'(2)	3.21(1)
O_3–O_4	2.68(1) *	O_4–O_5	2.67(1) ‡	O_2–O_5(2)	2.92(1)
Average	2.67	Average	2.64	Average	2.81

Y polyhedron					
Y–O_1	2.686(8)	O_2–O_5'	2.71(1)	O_1–O_2	2.62(1) *
–O_1'	2.460(8)	–O_5	2.96(1)	–O_5(2)	2.70(1) **
–O_2	2.339(8)	–O_3'	3.82(1)	–O_5'	3.34(1)
–O_3	2.291(8)	O_4–O_5	2.67(1)	–O_4	2.57(1)
–O_3'	2.284(8)	–O_3	2.87(1)	O_2–O_1'	2.53(1)
–O_4	2.344(8)	–O_3'	2.68(1) *	O_3–O_5'	2.94(1)
–O_5	2.519(8)	–O_5'	3.99(1)	O_3'–O_1'	2.92(1)
–O_5'	2.432(8)	O_3–O_1'	2.77(1)	–O_5	3.18(1)
Average	2.419	–O_3'	2.91(1)		
			Average	2.94	

Note. Asterisks denote common edges: * Si tetrahedron and Y polyhedron; † Si tetrahedron and Fe octahedron; ‡ Be tetrahedron and Fe octahedron; ** Be tetrahedron and Y polyhedron.

$Fe^{2+}(Y, TR)_2Be_2[SiO_4]_2O_2$, in hingganite refinement of the occupancy factor of this position revealed that it is filled only to the extent of 13% by Fe^{2+} cations. These results corresponded to a discrepancy index of R_{hkl} = 6.89%.

Final refinement of the crystal structure of hingganite by the method of least squares in the isotropic approximation was made with the aid of the mixed atomic scattering curve for the Y position. The mixed f curve was maximally close to the composition obtained as a result of x-ray spectral analysis of hingganite, $Y^{3+}_{0.51}Ca^{2+}_{0.13}\cdot Yb_{0.23}Er_{0.09}Dy_{0.04}$. Refinement led to R_{hkl} = 6.59%. The structural model found for hingganite corresponded to the formula $(Y^{3+}_{0.51}TR^{3+}_{0.36}Ca^{2+}_{0.13})\cdot Fe^{2+}_{0.065}Be[SiO_4](OH)$ (d_{calc} = 4.2 g/cm^3, Z = 4). Least-squares refinement of the structure in the anisotropic approximation was not made owing to failure to allow for absorption (μr = 1.9). The final coordinates of the basis atoms, the individual temperature factors, and the interatomic distance are listed in Tables I and II.

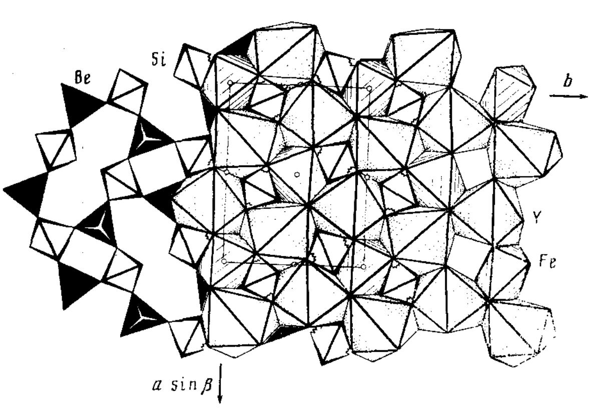

FIG. 2. Showing xy projection of crystal structure of hingganite. Foreground (right-hand side of drawing): sheets of Y, Fe polyhedra; background (left-hand side of drawing): Si, Be sheets with composition $(SiBeO_4(OH))^{3-}_{\infty\infty}$.

The separation of the OH groups in the anionic part of the structural formula was made on the basis of an analysis of the balance of valence forces. The somewhat low value B_{iso} = 0.1 for Be may be due to partial replacement by Si, since, according to x-ray spectral analysis data, there is more silicon (2.04) than beryllium (1.95) in hingganite. Several remarks have been made[4] concerning the possibility of a similar substitution in gadolinites.

The cations Y^{3+}, TR^{3+}, and Ca^{2+}, occupying one crystallographic position in the structure of hingganite, lie in Thomson cubes with cation–anion distances between 2.28 and 2.69 Å, averaging 2.42 Å, corresponding to the analogous distances in other compounds with structures of the gadolinite type.[6] The $Fe^{2+}-O^{2-}$ distances in the octahedra are, as usual, between 2.06 and 2.31 Å (average 2.21 Å). Two types of tetrahedra in the structure, with nearly equal dimensions, are occupied by Si and Be atoms: Si–O = 1.62–1.65 Å (average 1.64 Å), Be–O = 1.60–1.63 Å (average 1.62 Å), the average O–O lengths being 2.67 and 2.64 Å respectively.

As expected, the crystal structure of hingganite proved to be very similar to the structures of the minerals of the gadolinite–datolite group.[1,4–8] Along the c axis two types of layers alternate (Fig. 1). At the levels z = 0 and 1 there are layers of Y-polyhedra (with eight vertices) and Fe-octahedra, linked via common edges, similar to those in gadolinite (Fig. 2). However, whereas in gadolinite the octahedra are entirely occupied by Fe^{2+} cations, in the case of hingganite they are occupied only to the extent of 13%. A direct consequence of the deficiency of Fe^{2+} ions in hingganite in comparison with gadolinite is the replacement of one O atom by an OH group. The layers of the other type, at the level z = 0.5, are networks of Si and Be tetrahedra, linked via common vertices (Fig. 2). Within the networks we can distinguish four-membered and eightmembered rings. If we consider the structure of hingganite from the viewpoint of the classical systematics of silicates, then by analogy with other minerals of the gadolinite–datolite group we must regard it as an island-type orthosilicate. On the other hand, hingganite is a layered beryllosilicate with the anion radical $[BeSiO_4(OH)]_{\infty\infty}^{3-}$.

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1) For brevity we shall henceforth call it simply "hingganite."

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The crystal structure of Sc_3NiSi_3

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By diffraction from a single crystal, the crystal structure of the compound Sc_3NiSi_3 is established. The silicide Sc_3NiSi_3 is the first representative of a new structural type of intermetallic compounds and crystallizes in the monoclinic system, space group *C2/m*, $a = 0.9801(3)$ nm, $b = 0.3974(2)$ nm, $c = 1.3193(4)$ nm, $\beta = 114.16(3)^\circ$, $N = 28$. The structure was refined by the method of least squares in the anisotropic approximation to $R = 0.049$. The structure of Sc_3NiSi_3 has coordination polyhedra round the silicon atoms in the form of trigonal prisms $[SiSc_4Ni_2]$ and $[SiSc_6]$. The compound Sc_3NiSi_3 forms a series of related structures with the compounds ScCoSi (of the TiNiSi type), $Sc_3Co_2Si_3$ (the type representative), Sc_2CoSi_2 (the type representative), and ScSi (of the CrB type).

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In a study of the phase equilibria in the Sc–Ni–Si system[1] a ternary compound of the approximate composition $Sc_{44}Ni_{12}Si_{44}$ (compound X), with unknown structure, was discovered. It is of interest to study the crystal structure of X, because its composition lies in the cross section between the silicides ScNiSi (of the TiNiSi structural type)[2] and ScSi (or the CrB type),[3] while in the related system Sc–Co–Si in the cross section ScCoSi–ScSi, a number of structures, ScCoSi–$Sc_3Co_2Si_3$–Sc_2CoSi_2–ScSi, have been found and studied.[4] The end members of this series – ScCoSi and ScSi – also belong to the TiNiSi and CrB types, respectively, while $Sc_3Co_2Si_3$ and Sc_2CoSi_2 crystallize in their own characteristic types, the structures of which are closely related to the structures of TiNiSi and CrB (Ref. 4). Starting from the stoichiometric composition, silicide X might be another member of this series of interrelated structures. Our investigation was aimed at studying the crystal structure of this compound, also enabling us to refine its composition.

A prismatic single crystal measuring 0.028 × 0.023 × 0.102 mm was found in an alloy of the composition $Sc_{44}\cdot Ni_{12}Si_{44}$ made in an arc furnace in an atmosphere of argon. We used metals of high purity (not less than 0.999 mass fraction of main component). Our primary investigation revealed that the structure is monoclinic. The lattice periods, obtained by least-squares refinement of the values of 2θ for 20 reflections measured in a Philips PW 1100 automatic single-crystal diffractometer (Mo $K\alpha$ radiation, graphite monochromator), were $a = 0.9801(3)$ nm, $b = 0.3974(2)$ nm, $c = 1.3193(4)$ nm and $\beta = 114.16(3)^\circ$. Three space groups are consistent with the systematic extinctions: C2/m, C2, and Cm. The reflected intensities were measured in the automatic diffractometer by the θ-2θ method, $\sin\theta/\lambda \leq 5.74\ \mathrm{nm}^{-1}$. From 724 measured reflections, 714 with $I \geq 2.0\sigma(I)$ were used in the second stage of the structural investigation. The intensities were corrected for the Lorentz, polarization, and absorption factors (linear absorption coefficient $\mu = 8.66\ \mathrm{mm}^{-1}$). The calculations were made on a UNIVAC 1100 computer with the aid of the SYST program complex.[5]

An analysis and comparison of the data obtained in the first stage of the structural investigation revealed that compound X, like Sc_2CoSi_2, is monoclinic and belongs to the same x-ray class (provided that we change the setting). Two of their lattice periods are approximately equal: $a_X \simeq a_{Sc_2CoSi_2} \simeq 1.0$ nm, $b_X \simeq c_{Sc_2CoSi_2} \simeq 0.4$ nm. These results indicated that the structures are related. Taking as a model the structure of Sc_2CoSi_2, which, as shown in Ref. 4, can be represented by means of chains of trigonal prisms of two types around silicon atoms, $[SiSc_4Co_2]$ and $[SiSc_6]$, and subtracting every alternate layer of pairwise-linked prisms $[SiSc_4Co_2]$ and correspondingly shifting the remaining fragments so as to form common faces, we obtained a structure which satisfied the symmetry of the same space group B2/m as that of Sc_2CoSi_2. The dimensions of the unit cell were very close to those of the nickel compound under test, while the composition is represented by the formula Sc_3CoSi_3 (four formula units per unit cell), close to the composition of X (Fig. 1c-d). Moreover, the model so obtained