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The crystal structure of semenovite[1]

FIORENZO MAZZI, LUCIANO UNGARETTI, ALBERTO DAL NEGRO[2]

C.N.R. Centro di Studio per la Cristallografia strutturale
c/o Istituto di Mineralogia, Via Bassi 4, 27100 Pavia, Italy

OLE V. PETERSEN AND JÖRN G. RÖNSBO

Mineralogisk Museum and Institut for Mineralogi, University of Copenhagen
Öster Voldgade 5-7, DK-1350 Copenhagen, Denmark

Abstract

The crystal structure of semenovite, $(Fe^{2+},Mn,Zn,Ti)RE_2Na_{0-2}(Ca,Na)_8(Si,Be)_{20}(O,OH,F)_{48}$, $Z = 2$, orthorhombic, $a = 13.879(5)$, $b = 13.835(5)$, $c = 9.942(6)$A, space group *Pmnn*, has been determined by Patterson and Fourier methods. The X-ray diffraction data were collected from a twin crystal by a Philips *PW 1100* diffractometer. The refinement was carried out taking into account the average of the chemical analyses made on a number of samples (final conventional R factor = 0.05 for 1366 independent reflections).

The structure consists of tetrahedral layers parallel to (001), superposed at intervals of $c/2$ and connected by cation polyhedra (RE,Na,Ca-antiprisms and Fe,Mn-octahedra).

The {110} twinning, always present and responsible for the tetragonal pseudosymmetry, is explained on structural grounds.

The structure of semenovite is related to the structures of meliphanite, leucophanite, gadolinite, nordite, and hellandite; aminoffite, which has a marked resemblance both in the stoichiometric unit and lattice parameters, shows little similarity with semenovite in regard to the crystal structure.

Introduction

Semenovite, a new mineral from the Ilimaussaq alkaline intrusion (south Greenland), was described by Petersen and Rönsbo (1972), who reported its preliminary chemical and physical properties. The stoichiometric unit $(RE,Ca,Mn,Na)_{12}$ $[Be,Si(F,OH,O)]_8(Si_3O_{10})_4 \cdot H_2O$ was calculated from microchemical analyses, taking also into account the marked analogies with aminoffite, $Ca_{12}(BeOH)_8Si_{12}O_{40}$, tetragonal (Coda *et al.*, 1967). By X-ray diffraction semenovite showed a tetragonal lattice: $a = 13.866$, $c = 9.892$A ($Z = 2$), analogous to that of aminoffite except for $a_{semen} = \sqrt{2}\, a_{aminof}$. However, when examined in oriented thin sections by means of the universal stage, semenovite appeared biaxial with the axial plane parallel to (010) and X parallel to [001] ($\alpha = 1.595$, $\beta = \gamma = 1.614$, $2V = 55°$). The mineral showed an intricate mimetic interpenetration twin after {110}, with composition plane (120).

The crystal structure analysis has been undertaken to clarify the structural relationships with aminoffite, which is so similar in many aspects, and eventually to explain, on structural grounds, the kind of twinning responsible for the apparent tetragonal symmetry conflicting with its optical properties.

Experimental

A first set of X-ray intensities was collected with a Philips *PW 1100* single-crystal automatic diffractometer using graphite-monochromatized Mo$K\alpha$ radiation. The Laue symmetry was $4/mmm$ and the sole systematic absences ($hk0$ with $h + k$ odd) were consistent only with space group $P4/nmm$. Several attempts to solve the crystal structure were unsuccessful. One of these attempts was based on the hypothesis of a twinned crystal structurally related to aminoffite.

Several more fragments were then examined by X-ray diffraction, since the tetragonal symmetry could

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[1] Contribution to the mineralogy of Ilimaussaq No. 51.

[2] Present address: Istituto di Mineralogia, Università di Padova, Italy.

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be a consequence of the mimetic twinning; one of them, measuring 0.11 × 0.21 × 0.38 mm, was considered suitable for collecting a second set of experimental intensities.

The intensities of 6066 reflections in the range 2°–30° 2θ were inspected using θ–2θ scan mode and a scan width of 2°. The scan time was 40 sec for any reflections and 5 sec for each background. Three standard reflections, monitored at three-hour intervals, showed no variation greater than 2.7 percent. No absorption correction was applied. The intensities of the measured equivalent pairs *hkl* and $\bar{h}kl$ were averaged. Processing of the data was carried out as described by Davies and Gatehouse (1973) to yield $|F_{obs}|$ and $\sigma|F_{obs}|$.

The new data set showed *mmm* Laue symmetry and allowed the resolution of the crystal structure. The key was the observation of a constant ratio (2.33) between the intensity of each reflection 0*kl* and that of the corresponding *k*0*l*, when $k + l$ was odd. This evidence suggested that reflections *k*0*l* with $k + l$ odd could be systematically absent, and the observed intensities of such reflections would be those of the corresponding 0*kl* diffractions superposed because of the {110} twin. The crystal was therefore considered a twin composed of two orthorhombic individuals, the ratio of their volumes being 7:3. Apparently the volume of both twin individuals was equal in the first crystal used for data collection.

The relative volumes *x* and 1 − *x* of the two twin individuals were calculated from the ratio of the intensities $I(0kl)/|I(0kl) + I(k0l)|$ for the 19 strongest reflections with $k + l$ odd; the average value for *x* was 0.70. The appropriate structure amplitudes for pairs of *hkl* and *khl* reflections were then obtained by solving the equation system:

$$\begin{cases} 0.7\ F^2(hkl) + 0.3\ F^2(khl) = F^2_{obs}(hkl) \\ 0.3\ F^2(hkl) + 0.7\ F^2(khl) = F^2_{obs}(hkl) \end{cases}$$

The structure factors *F* of 2887 independent reflections were so calculated; these data were used in the crystal structure analysis and refinement.

Accurate lattice parameters were calculated by a least-squares method from the θ values of 25 strong *hkl* reflections corresponding to absent *khl* reflections, to avoid any superposition of diffraction due to the twin; the lattice parameters so obtained are: a = 13.879(5), b = 13.835(5), c = 9.942(6)A.

The systematic absences (*h*0*l* with $h + l$ odd and *hk*0 with $h + k$ odd) suggested space groups *Pmnn* or *P2nn*; the crystal structure was straightforwardly solved by Patterson and Fourier methods in the space group *Pmnn*.

Refinement of the structure

Difficulties arose during the refinement from three sources: (1) poor quality of part of the X-ray diffraction data; (2) marked pseudosymmetry in the structure; (3) some uncertainties in the chemical composition.

(1) Many structure amplitudes were rather poor in quality because of their weakness and the further errors introduced by the process for the twin correction of the intensities. Only 1366 reflections (47 percent of the total number) had $F^2 > 3\sigma(F^2)$ and were used in the refinement; furthermore they were unequally distributed between the groups with the same parity of the indices: 1071 reflections had $h + k + l$ even and only 295 had $h + k + l$ odd. The latter reflections were also weaker than the former, as the lattice of semenovite is very nearly body-centered.

(2) The crystal structure of semenovite shows a marked pseudo-repeat $c/2$ from a purely geometrical point of view. The unit cell contains two similar tetrahedral layers made up of seven independent tetrahedra (Fig. 1); due to the symmetry the T(3) and T(5) tetrahedra (tentatively identified as Be in the three-dimensional Fourier map) are superposed at $c/2$ respectively on the T(2) and T(4) tetrahedra (mainly centered by Si). Similarly the M(2), M(4), and M(6) sites are superposed at $c/2$ on the M(1), M(3), and M(5) sites, which show higher electron density in the Fourier map. Therefore the value of *c* is determined by the difference in occupation of a few sites in the unit cell.

(3) The preliminary results of the crystal structure investigation indicated a silicon content far above the value reported by Petersen and Rönsbo (1972), and called for a redetermination of the chemical analysis. New partial analyses were carried out on a Hitachi *XMA-5B* scanning electron microanalyzer at the Institute of Mineralogy, University of Copenhagen. Stoichiometric oxides and silicates plus synthetic rare-earth glasses were used as standards. Except for Y, the analyses were performed at 15 kV and 20 nA; Y was analyzed at 30 kV. Normal ZAF-corrections were carried out using the program EMSKOR (Pedersen *et al.*, 1975).

Five grains were analyzed, unfortunately not in thin sections. Four of these grains showed an identical marked variation for silicon and sodium; the two elements are sympathetically related, Na_2O varying from 13.5 to about 8 percent and SiO_2 from 45.8 to

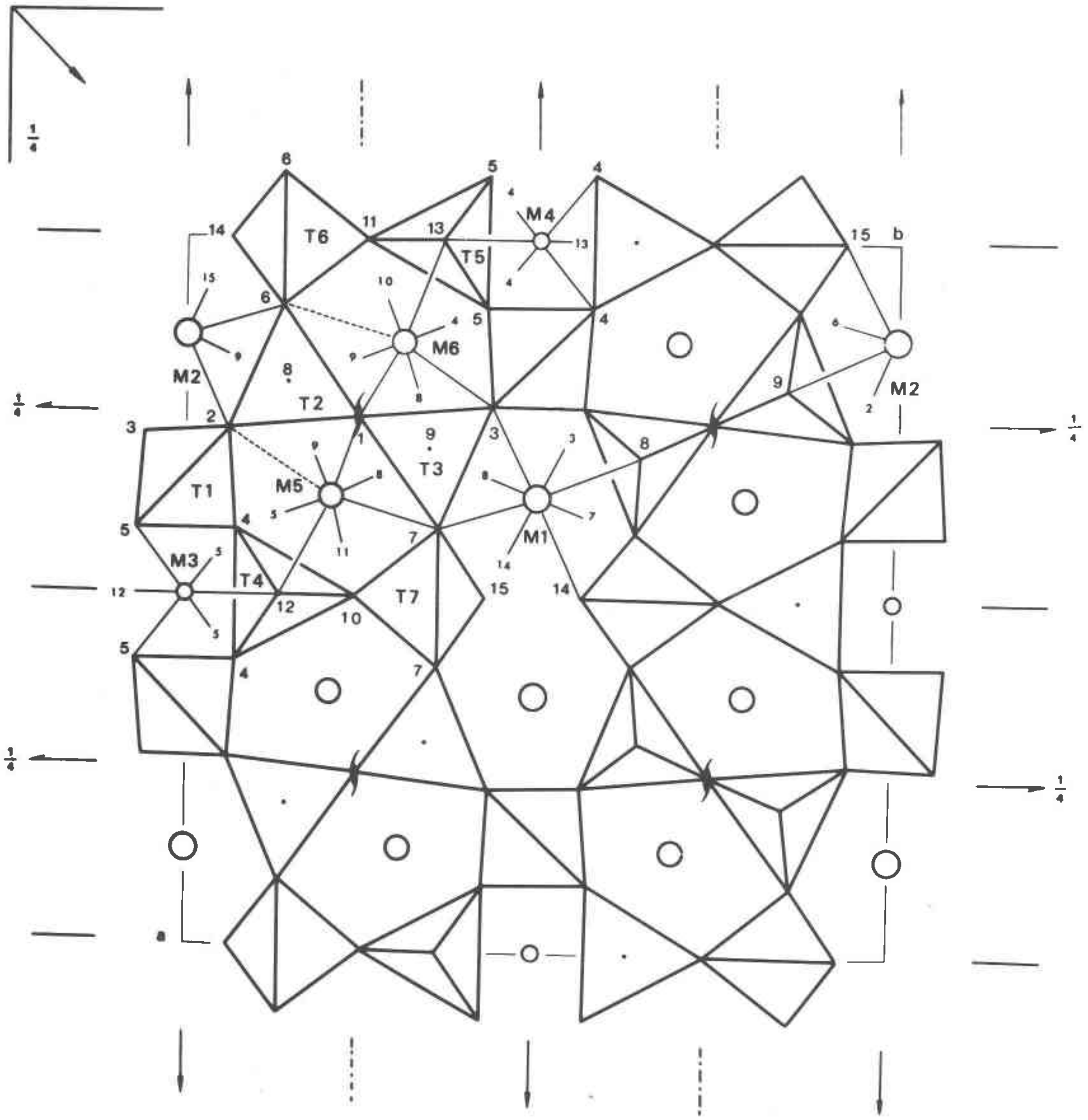

Fig. 1. A slab of the crystal structure of semenovite projected along [001]. Only one of the two tetrahedral layers in the unit cell is drawn. Cations are at nearly $z = 0$ and the tetrahedral layer is roughly at $z = 1/4$. The numbers at the tetrahedral vertices correspond to those of the oxygens listed in Table 3. Interrupted lines followed by a number represent bonds between cations and the corresponding oxygens of an adjacent tetrahedral layer. The largest distances, M(5)–O(2) and M(6)–O(6), are drawn with dashed lines.

42.6 percent (Table 1). The lowest level for both elements always occurred in the outermost part of the crystals. The highest sodium and silicon content was found in the unzoned grain, and the mean value for this grain is reported in Table 1 as analysis 3. For comparison the mean values of all microprobe analyses are reported in Table 1 as analysis 4. The other major elements which were analyzed by the microprobe did not show any appreciable variation.

The structural peculiarities of semenovite and the uncertainties in the chemical composition of the crystal examined by X-rays (particularly the Na, Si and consequently Be contents) forced us to follow different hypotheses during the refinement.

Main questions were the occupancy and the extent of the mutual substitutions among Na, Ca, RE in M(1), M(2), M(5), and M(6) sites. Variations in the substitutions of such atoms produced only small differences in the agreement between F_{obs} and F_{calc}, in the calculated density and in the electrostatic charge balance. The increases of the atomic number and of the formal charge, due to the replacement of lighter

Table 1. Chemical analyses of semenovite

	1	*2*	*3*	*4*	*5*
SiO_2	42.8	42.7	46.3	45.1	46.2
Al_2O_3	0.7	0.1	0.1	0.1	-
RE_2O_3°°°	19.0°°	17.6°	17.8°	18.0°	18.1°
CaO	6.0	7.6	7.3	7.8	8.0
PbO	0.5	-	-	-	-
Na_2O	11.0	8.3	13.3	11.5	11.6
K_2O	0.1	0.1	0.1	0.1	-
FeO	0.8	1.8	2.1	1.9	2.1
Fe_2O_3	2.4	-	-	-	-
MnO	1.8	1.2	1.2	1.1	1.2
ZnO	0.5	0.9	0.1	0.4	0.4
TiO_2	-	0.2	0.2	0.2	0.2
BeO	8.2	= (12.7)	(12.7)	(12.7)	8.3
F	4.5				4.2
H_2O (+)	1.0				1.5
H_2O (-)	0.9				-
O = F	-1.9				-1.8
Total	98.3	93.2	101.2	98.9	100.0

° $RE^{3.46+}$= .46Ce+.29La+.07Y+.14Nd+.04(Gd,Sm,Eu) = 1.

°° $RE^{3.33+}$= .33Ce+.35La+.17Y+.11Nd+.04(Gd,Sm,Eu) = 1.

°°° including CeO_2.

1 by microchemical analyses *(Petersen and Rönsbo, 1972)*

by electron microprobe analyses:

2 outermost parts of the zoned crystals,

3 unzoned crystal,

4 mean values of all analyses;

5 by the crystal structure.

atoms by heavier ones (*e.g.* Na by Ca and Ca by RE), were in fact balanced by the decrease of the occupancy of the sites. In any case, the value of the electron density in M(6) could be justified by the prevalent occupancy of such site by Na and that in M(5) by the presence of Ca plus Na. Therefore any ambiguity was confined to the nature of the atoms in the M(1) and M(2) sites, which could be occupied partially by RE or by RE and the variable amounts of Na in different zones of the crystals.

Another source of difficulties was the possible mutual substitution between Si and Be; some evidence of it was observed for the tetrahedra T(2)–T(3) and T(4)–T(5) which are superposed at *c*/2 in adjacent tetrahedral layers. A preliminary isotropic refinement in fact showed negative B factors for the Be atoms placed in T(3) and T(5), while the temperature factors for the Si atoms in T(2) and T(4) were abnormally high. The evidence suggested a mutual substitution between Si and Be, at least in these tetrahedra, without excluding it in the other tetrahedra, according to the variations in Si content indicated by the chemical analyses.

Several refinements were carried out according to different assumptions, mainly concerning the population of M(1), M(2), and the tetrahedral sites. The differences in the atomic parameters among the various refinements were within their standard deviation, whereas significant variations were shown by the thermal parameters and the site populations.

The scattering factors used in the refinements were those listed by Cromer and Waber (1974) for neutral atoms. The scattering curve for RE was obtained according to the results of the chemical analysis (Table 1, 4); similarly the scattering curve for the octahedral cations was calculated on the basis of the amount of Fe, Mn, Zn, and Ti given in the same analysis. A highly-modified version of the ORFLS program (Busing *et al.,* 1962) was used to refine atomic and thermal parameters as well as site occupancies. To avoid correlations among parameters the variables were alternatively: (a) the scale factor, (b) either the site occupancies or the thermal factors, (c) either the atomic parameters of a set of atoms or those of the corresponding set pseudosymmetrical for the *c*-repeat. The refinements were stopped when the variations in the parameters were lower than their standard deviations.

Some refinements were based on the crystal chemical analogies with other minerals (gadolinite, leucophanite, meliphanite, hellandite), *i.e.* RE were placed only in the sites M(1) and M(2) and Na,Ca in M(5) and M(6). In other refinements M(1) and M(2) were also allowed to contain Na, in order to account for the results of the chemical analyses; finally the possible Si–Be substitution in all tetrahedra was considered.

It followed from the results of such refinements that the sum of the occupancies of RE in M(1) + M(2), as well as the sum of the occupancies of (Fe,Mn) in M(3) + M(4) approached unity; furthermore, the largest substitutions of Be for Si occurred just in the tetrahedra T(2) and T(4) superposed in the unit cell to T(3) and T(5), mainly occupied by Be. An "idealized crystal structure" was therefore assumed having the following features: M(1) completely filled by RE; M(2) either empty or occupied by variable amounts of Na, according to charge-balance necessity; M(3) completely filled by (Fe,Mn) and M(4) empty; M(5) completely filled by (Ca,Na) and M(6) completely filled by Na; T(1), T(2), T(4), T(6), T(7) centered by Si and T(3), T(5) by Be.

Taking into account the pseudo-repeat $c/2$, the actual crystal structure was interpreted as affected by a partial disorder, *i.e.* as built up by a fraction y of the "idealized structure," matched with a fraction $(1 - y)$ of the same structure translated by $c/2$. This hypothesis was tested by least squares in a simplified way, which involved only the site pairs: M(1)–M(2), M(3)–M(4), M(5)–M(6), T(2)–T(3), and T(4)–T(5). The y value was taken as a variable: the atomic content of M(1) was constrained to be composed by y amount of the atom placed at M(1) in the idealized structure and by $(1 - y)$ amount of the atom placed in M(2); the atomic content in M(2) was treated conversely; all the above-mentioned site pairs were constrained in the same way. Positional and thermal parameters were refined normally.

The refinements so obtained, both with and without Na in M(2), were equally reliable from a crystallographic point of view; the conventional R factors for the observed reflections (0.050 and 0.048 respectively) were comparable, and the calculated densities were just slightly higher (3.17 g/cm^3) or lower (3.12 g/cm^3) than that observed (3.14 g/cm^3).

The results of the refinement with Na in M(2) are reported in this paper, as the most consistent with the chemical results (Table 1).

We think that the "idealized structure" is actually the true crystal structure of semenovite, the partial disorder (y = 0.8) being a consequence of the twin nature of the examined crystal. A further proof of it will be given in the next section by its satisfactory charge balance, together with a more detailed description of the crystal structure.

Observed and calculated structure factors are compared in Table 2.[3] Positional and thermal parameters

Table 3. Final atomic positional and thermal parameters

Atom	Multip.	Occupancy			x	y	z	$B_{eq.}$	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
		RE	Na	□										
M(1)	4	.80	.14	.06	0.1390(0)	0	0	1.05	12(0)	15(0)	28(0)	0	0	-3(1)
M(2)	4	.20	.56	.24	0.1349(2)	0	0.5	4.22	53(2)	67(2)	87(3)	0	0	13(3)
		Fe,Mn	□											
M(3)	2	.80	.20		0.5	0	0.5	1.59	24(1)	18(1)	38(2)	0	0	1(2)
M(4)	2	.20	.80		0.5	0	0	1.69	39(6)	13(4)	26(8)	0	0	12(9)
		Ca	Na											
M(5)	8	.52	.48		0.1385(1)	0.2907(1)	0.0128(2)	1.26	15(1)	22(1)	23(2)	8(1)	2(1)	1(1)
M(6)	8	.13	.87		0.1431(2)	0.3060(2)	0.5053(3)	1.94	17(1)	38(1)	40(2)	10(1)	4(2)	-13(2)
		Si	Be											
T(1)	8	1.00	-		0.3373(1)	-0.0044(2)	0.2532(2)	1.32	13(1)	18(1)	40(2)	4(2)	-3(1)	0(1)
T(2)	8	.80	.20		0.2045(2)	0.1509(2)	0.2789(2)	0.73	7(1)	11(1)	21(2)	0(1)	-2(1)	-1(1)
T(3)	8	.20	.80		0.2043(5)	0.1547(5)	0.7769(7)	1.80	15(2)	33(3)	44(5)	1(3)	6(3)	6(4)
T(4)	4	.80	.20		0.5	0.1297(3)	0.2364(3)	0.86	14(2)	10(2)	20(3)	0	0	-9(2)
T(5)	4	.20	.80		0.5	0.1388(8)	0.7289(10)	1.98	15(4)	30(5)	64(9)	0	0	41(6)
T(6)	4	1.00	-		0	0.1493(3)	0.2350(3)	1.31	10(1)	20(1)	42(3)	0	0	4(2)
T(7)	4	1.00	-		0	0.1513(3)	0.7466(3)	1.76	20(2)	24(2)	48(3)	0	0	4(2)
O(1)	8				0.2490(5)	0.2473(4)	0.3393(5)	1.49	27(3)	16(2)	30(4)	-3(2)	-9(4)	-8(3)
O(2)	8				0.2668(4)	0.0627(4)	0.3473(5)	1.60	19(2)	21(3)	43(5)	7(2)	0(3)	-2(3)
O(3)	8				0.2703(4)	0.0649(4)	0.8477(5)	1.34	17(2)	12(2)	46(5)	6(2)	3(3)	1(3)
O(4)	8				0.4061(4)	0.0737(4)	0.1713(5)	1.46	14(2)	23(3)	40(5)	-1(2)	-5(3)	3(3)
O(5)	8				0.4065(4)	0.0742(4)	0.6567(5)	1.43	14(2)	16(2)	51(5)	-1(2)	4(3)	3(3)
O(6)	8				0.0940(4)	0.1379(5)	0.3375(5)	1.64	9(2)	40(3)	30(4)	1(2)	-5(3)	1(3)
O(7)	8				0.0963(4)	0.1395(5)	0.8393(5)	1.83	9(2)	38(3)	48(5)	3(3)	-2(3)	15(4)
O(8)	8				0.2023(4)	0.1449(4)	0.1172(5)	1.23	19(2)	19(2)	21(4)	-1(2)	2(3)	2(3)
O(9)	8				0.2066(4)	0.1547(4)	0.6208(5)	1.42	20(2)	21(3)	28(5)	-2(2)	0(3)	-1(3)
O(10)	4				0.5	0.2397(6)	0.1699(8)	1.52	17(4)	18(4)	47(8)	0	0	-11(5)
O(11)	4				0.5	0.2450(6)	0.6648(8)	1.65	27(4)	20(4)	34(7)	0	0	-1(4)
O(12)	4				0.5	0.1328(6)	0.3934(7)	1.65	24(4)	31(5)	18(6)	0	0	3(5)
O(13)	4				0.5	0.1361(7)	0.8857(8)	1.92	25(4)	30(4)	39(7)	0	0	-3(5)
O(14)	4				0	0.0619(6)	0.1234(8)	1.55	14(3)	24(4)	44(7)	0	0	-9(5)
O(15)	4				0	0.0756(6)	0.6209(9)	2.33	26(4)	21(4)	85(11)	0	0	-18(6)

The anisotropical thermal parameters (× 10^4) are of the form: $exp\ -(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})$.

Estimated standard deviations are in parentheses.

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[3] To receive a copy of this table, order Document AM-78-090 from the Business Office, Mineralogical Society of America, 1909 K Street, N.W., Washington, D.C. 20006. Please remit $1.00 in advance for the microfiche.

Table 4. Interatomic distances (A) and angles (°)

	Distances	Angles
T(1) tetrahedron		
T (1)-O (3)ii	1.603(5)	
T (1)-O (5)ii	1.630(5)	
T (1)-O (2)	1.642(6)	
T (1)-O (4)	1.656(6)	
average	1.633	
O (2)-O (4)	2.612(7)	104.8(3)
O (2)-O (3)ii	2.621(7)	107.8(3)
O (4)-O (5)ii	2.667(7)	108.5(3)
O (4)-O (3)ii	2.695(7)	111.6(3)
O (3)-O (5)	2.682(7)	112.1(3)
O (2)-O (5)ii	2.711(7)	111.9(3)
average	2.665	
T(4) tetrahedron		
T (4)-O(12)	1.562(8)	
2×T (4)-O (4)	1.648(6)	
T (4)-O(10)	1.655(9)	
average	1.629	
O (4)-O (4)v	2.607(10)	104.5(4)
2×O (4)-O(10)	2.640(9)	105.9(3)
O(10)-O(12)	2.670(11)	111.9(5)
2×O (4)-O(12)	2.691(8)	113.9(3)
average	2.657	
T(7) tetrahedron		
2×T (7)-O (7)	1.631(5)	
T (7)-O(15)	1.631(9)	
T (7)-O(10)iii	1.691(8)	
average	1.646	
O(15)-O(10)iii	2.602(12)	103.1(5)
O (7)-O (7)vi	2.672(10)	110.0(4)
2×O (7)-O(15)	2.698(9)	111.6(3)
2×O (7)-O(10)iii	2.723(8)	110.1(3)
average	2.686	
M(1) polyhedron		
2×M (1)-O(14)	2.442(5)	
2×M (1)-O (8)	2.479(5)	
2×M (1)-O (3)i	2.534(5)	
2×M (1)-O (7)i	2.575(6)	
average	2.508	
M(2) polyhedron		
2×M (2)-O(15)	2.458(6)	
2×M (2)-O (2)	2.531(6)	
2×M (2)-O (6)	2.563(6)	
2×M (2)-O (9)	2.649(5)	
average	2.550	
T(2) tetrahedron		
T (2)-O (1)	1.588(6)	
T (2)-O (8)	1.610(5)	
T (2)-O (2)	1.642(6)	
T (2)-O (6)	1.651(5)	
average	1.624	
O (1)-O (2)	2.568(8)	105.3(3)
O (2)-O (6)	2.615(7)	105.2(3)
O (1)-O (6)	2.631(8)	108.6(3)
O (6)-O (8)	2.658(7)	109.2(3)
O (1)-O (8)	2.703(7)	115.4(3)
O (2)-O (8)	2.706(7)	112.7(3)
average	2.647	
T(5) tetrahedron		
T (5)-O(13)	1.559(12)	
T (5)-O(11)	1.601(12)	
2×T (5)-O (5)	1.731(10)	
average	1.656	
O (5)-O (5)v	2.595(10)	97.1(7)
2×O (5)-O(11)	2.697(9)	108.0(4)
2×O(11)-O(13)	2.663(11)	114.8(8)
O (5)-O(13)	2.757(9)	113.7(4)
average	2.679	
M(3) octahedron		
2×M (3)-O(12)	2.121(8)	
4×M (3)-O (5)	2.273(5)	
average	2.222	
2×O (5)-O (5)v	2.595(10)	69.6(3)
4×O (5)-O(12)	3.031(8)	87.2(2)
4×O (5)-O(12)ii	3.184(9)	92.8(2)
2×O (5)-O (5)ii	3.731(11)	110.4(3)
average	3.126	
M(5) polyhedron		
M (5)-O (1)iv	2.385(6)	
M (5)-O (5)iv	2.434(5)	
M (5)-O (8)	2.436(5)	
M (5)-O(11)iv	2.495(5)	
M (5)-O(12)iv	2.495(5)	
M (5)-O (9)iv	2.518(6)	
M (5)-O (7)	2.775(7)	
M (5)-O (2)iv	2.924(6)	
average	2.558 (2.505) °	
T(3) tetrahedron		
T (3)-O (9)	1.552(8)	
T (3)-O (1)iii	1.627(9)	
T (3)-O (7)	1.636(8)	
T (3)-O (3)	1.697(8)	
average	1.628	
O (3)-O (1)iii	2.614(8)	103.7(5)
O (3)-O (7)	2.628(7)	104.1(5)
O (9)-O (1)iii	2.634(7)	111.9(5)
O (7)-O (1)iii	2.658(8)	109.1(5)
O (7)-O (9)	2.666(7)	113.5(5)
O (3)-O (9)	2.723(7)	113.8(5)
average	2.654	
T(6) tetrahedron		
T (6)-O(11)iv	1.620(9)	
T (6)-O(14)	1.641(8)	
2×T (6)-O (6)	1.663(5)	
average	1.647	
O (6)-O (6)vi	2.609(10)	103.3(4)
2×O (6)-O(11)iv	2.697(9)	110.5(3)
O(14)-O(11)iv	2.702(11)	111.9(4)
2×O (6)-O(14)	2.709(8)	110.2(3)
average	2.687	
M(4) octahedron		
2×M (4)-O(13)i	2.200(9)	
4×M (4)-O (4)	2.375(5)	
average	2.317	
2×O (4)-O (4)v	2.607(10)	66.6(2)
4×O (4)-O(13)ii	3.232(10)	89.8(2)
4×O (4)-O(13)i	3.242(9)	90.2(2)
2×O (4)-O (4)vii	3.970(10)	113.4(2)
average	3.254	
M(6) polyhedron		
M (6)-O (1)	2.355(6)	
M (6)-O (4)iii	2.441(6)	
M (6)-O(13)iv	2.450(5)	
M (6)-O (8)iii	2.511(6)	
M (6)-O (9)	2.544(6)	
M (6)-O(10)iii	2.649(6)	
M (6)-O (3)iv	2.663(6)	
M (6)-O (6)	2.942(6)	
average	2.569 (2.516) °	

° average after exclusion of the last distance.

Equivalent positions referred to Table 3:

i	x	y	$z-1$
ii	x	$-y$	$1-z$
iii	$\frac{1}{2}-x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$
iv	$\frac{1}{2}-x$	$\frac{1}{2}-y$	$z-\frac{1}{2}$
v	$1-x$	y	z
vi	$-x$	y	z
vii	x	$-y$	$-z$

are given in Table 3. Bond distances and angles are listed in Table 4.

Description of the structure

Figure 1 is a [001] projection of the crystal structure of semenovite. The SiO_4 and BeO_4 tetrahedra are linked in layers parallel to (001). Two out of seven crystallographically-independent tetrahedra, T(3) and T(5), are occupied by Be. Only T(1) tetrahedron shares all vertices with other tetrahedra, whereas the remaining ones have one unshared oxygen.

Two geometrically-similar layers are superposed in the unit cell at distance $c/2$ (Table 3), the main difference being given by the nature of the atoms at the centers of two superposed tetrahedra: Si in T(2) and T(4) and Be in T(3) and T(5).

Three kinds of tetrahedral rings are formed within the layers: 4-fold, 5-fold, and 8-fold rings; the ratio of their frequencies in the unit cell is 2:8:2. The average sharing coefficient between vertices of tetrahedra is 1.8 (Zoltai, 1960) or 3.2 (Coda, 1969).

Cations lie between the tetrahedral layers; pairs of cavities available for cations occur at distances $c/2$ because of the pseudo-repeat. Either two M(1) sites or two M(2) sites lie in the cavity between 8-fold tetrahedral rings; M(1) is filled by RE, whereas M(2) is apparently occupied by variable Na amounts. The occupancy of M(2) can probably range from zero to one, as evidenced by the variable Na content detected by the chemical analyses. M(3) and M(4) are between the centers of couples of 4-fold tetrahedral rings; M(3) is filled by octahedral atoms like Fe,Mn,Zn,Ti, and the analogous M(4) is empty. M(5) and M(6) lie between the centers of 5-fold rings of tetrahedra; M(5) is occupied by (Ca,Na), and M(6) is apparently filled only by Na.

The coordination polyhedra around M(1) or M(2) are nearly square antiprisms, that around M(3) is a slightly distorted octahedron, and those around M(5) and M(6) are very distorted antiprisms; without considering the largest M–O distance the polyhedra around M(5) and M(6) may be seen as octahedra with a centered face, *i.e.* a common coordination for Ca and Na.

The general formula unit of semenovite, which accounts for both the structural and chemical results, can be written as follows:

$$(\mathrm{Fe}^{2+},\mathrm{Mn},\mathrm{Zn},\mathrm{Ti})\mathrm{RE}_2\mathrm{Na}_{0-2}(\mathrm{Na},\mathrm{Ca})_8[(\mathrm{Si},\mathrm{Be})_{20}(\mathrm{O},\mathrm{OH},\mathrm{F})_{48}];\ Z = 2$$

Table 5 gives the electrostatic charge balance after Ferguson (1974) for the "idealized structure" with and without Na in M(2); the presence of Na in this site mainly affects the bond strength on the hydroxyl O(15), which therefore should be partly replaced by oxygen.

Table 5. Electrostatic valence balance

Oxygens	Bonded cations	Σ bond strengths		
		1	*2*	*3*
1	T(2),T(3),M(5),M(6)	1.92	1.92	1.94
2	T(1),T(2),M(2),M(5)°	2.04	2.07	1.98
3	T(1),T(3),M(1),M(6)	2.11	2.07	2.07
4	T(1),T(4),M(4),M(6)	2.11	2.12	2.12
5	T(1),T(5),M(3),M(5)	2.06	2.05	2.06
6	T(2),T(6),M(2),M(6)°	2.03	2.06	1.97
7	T(3),T(7),M(1),M(5)	2.16	2.14	2.16
8	T(2),M(1),M(5),M(6)	1.66	1.83	1.85
9 (F,OH)	T(3),M(2),M(5),M(6)	1.16	0.98	0.91
10	T(4),T(7),M(6),M(6)	2.16	2.23	2.23
11	T(5),T(6),M(5),M(5)	2.07	2.00	2.03
12	T(4),M(3),M(5),M(5)	1.65	1.86	1.89
13 (OH,F)	T(5),M(4),M(6),M(6)	1.04	0.82	0.82
14	T(6),M(1),M(1)	1.76	1.90	1.90
15 (OH,O)	T(7),M(2),M(2)	1.34	1.20	1.01

° The large distances: M(5)-O(2) and M(6)-O(6) were not considered in the calculation.

1 Actual crystal structure: the occupancies of the cationic sites are in Table 3.

Idealized crystal structures *(2,3)*:
T(1),T(2),T(4),T(6) and T(7) = Si; T(3),T(5) = Be
M(1) = $\mathrm{RE}^{3.5+}$; M(3) = $(\mathrm{Fe},\mathrm{Mn})^{2+}$; M(4) = □ ;
M(6) = Na, and respectively:

2 M(2) = 0.7 Na; M(5) = $(0.65\mathrm{Ca},0.35\mathrm{Na})^{1.65+}$

3 M(2) = □ ; M(5) = $(0.75\mathrm{Ca},0.25\mathrm{Na})^{1.75+}$

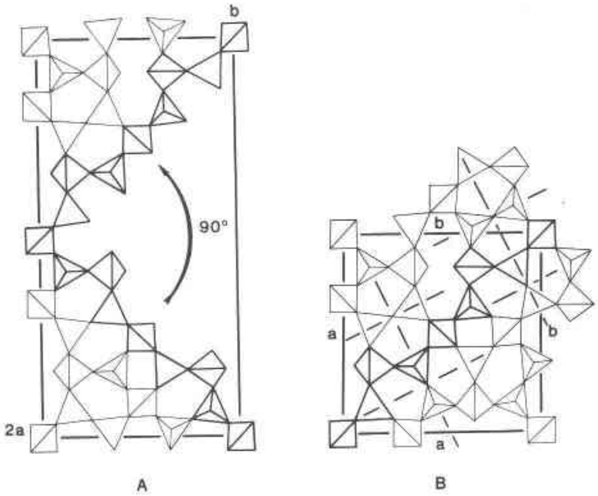

Fig. 2. A: partial [001] projection of the untwinned structure showing two tetrahedral chains, drawn with stronger lines, nearly symmetrical for a $\bar{4}$ axis. B: [001] projection of the twinned structure obtained by $\bar{4}$ rotation of the lower part of the Fig. 2, A; local pseudo-mirror planes, drawn with dashed lines, occur at both sides of the boundary tetrahedral chain and are parallel to (120) and (2$\bar{1}$0).

The semenovite twin

The (110) twinning, always present in semenovite crystals, can be explained on structural grounds as follows (Fig. 2): starting from any T(1) two tetrahedral chains develop continuously along [110] and [$\bar{1}$10], nearly symmetrical in respect to a $\bar{4}$ axis on

Table 6. Comparison of the crystal-chemical properties of RE-bearing minerals related to semenovite

	Gadolinite	*Nordite*	*Hellandite*	*Semenovite*
Frequency ratios, $m : n : p$ of the rings (4-,5- and 8-fold respectively) in the tetrahedral layers.	2 : 0 : 2	2 : 4 : 2	2 : 8 : 2	2 : 8 : 2
Tetrahedral atoms.°	4Si;4Be	12Si;2(Zn,Mg)	8Si;8B;4□	14Si;6Be
Anions (O,OH,F).°°	20 O	34 O	40O;8(OH)	40O;8(F,OH,O)
Interlayer cations:				
m between 4-fold rings	2Fe^{2+}	2Na	2(Al,Fe^{3+})	(Fe,Mn);□
n between 5-fold rings	-	4Na	7(Ca,RE);□	4Na;4(Ca,Na)
$2p$ between 8-fold rings	4RE	2RE;2(Ca,Sr)	3.5RE;0.5□	2RE;2(□,Na)
Repeat perpendicular to the tetrahedral layers.(A)	4.84	5.16	4.72	9.94

° *total tetrahedral atoms: (7m + 9n + 17p)/6*
°° *total anions: (16m + 21n + 44p)/6*

which the T(1) atoms lie. This tetragonal pseudosymmetry can account for twinning on (110).

The explanation of why (120) is the composition plane, as observed in thin section, is less evident; one can see that all the atoms of each asymmetric unit except M(3) and M(4) are actually so grouped as to show $mm2$ pseudosymmetry; the pseudo mirror planes are parallel to the twin composition planes and the pseudo 2-fold axis is parallel to c as the $\bar{4}$ twin axis. In Figure 1 one of such planes runs roughly through T(5)–M(6)–O(1)–M(5)–T(4) and the other through M(2)–T(2)–O(1)–T(3)–M(1); the oxygen O(1) is on the pseudo 2-fold axis. However, apart from the c direction, such pseudosymmetry does not extend continuously through the entire structure, contrary to what happens for the previously-mentioned chains of tetrahedra; perhaps this explains why $\bar{4}$ is the twin axis and (120) is the composition plane.

Comparison with related crystal structures

The stoichiometric unit of aminoffite, Ca$_{12}$(Si$_{12}$Be$_8$)(O,OH)$_{48}$, has a marked resemblance to that of semenovite: the total number of cations is the same and the tetrahedral layer has an equal number of atoms. The crystal structure is different, however: in aminoffite the tetrahedral layers comprise rings of 4 and 6 tetrahedra. The similar unit-cell parameters ($a_{\mathrm{sem}} \simeq b_{\mathrm{sem}} \simeq \sqrt{2}\, a_{\mathrm{aminof}}$; $c_{\mathrm{sem}} = c_{\mathrm{aminof}}$) follow from the presence of chains of 6 tetrahedra both along the edges a and b in semenovite and along the [110] diagonal in aminoffite; also the c edges are analogous because both structures are made up of pairs of tetrahedral sheets separated by large cations.

Some structural similarities can be seen with the minerals of the melilite group and related leucophanite (Cannillo *et al.*, 1967) and meliphanite (Dal Negro *et al.*, 1967); however, all these minerals present tetrahedral layers formed only by 5-fold rings, corresponding to the Ca and Na sites of semenovite.

Some resemblance with the crystal structure of gadolinite (Pavlov and Belov, 1960) is given by the presence in this mineral of tetrahedral layers with 4-fold and 8-fold rings, as well as of RE atoms and octahedral cations (Fe^{2+}) coordinated as in semenovite.

Nordite (Bakakin *et al.*, 1970) shows in the tetrahedral layers the same kind of rings as semenovite, even if their relative frequencies in the unit cell are different; moreover all tetrahedra are centered by Si, except one out of seven formed around (Zn,Mg). The coordination around cations is similar to that in semenovite, however. Hellandite (Mellini and Merlino, 1977) is also to some extent comparable with semenovite, even if Be is replaced by B; actually hellandite is a chain silicate, but the filling of a vacant tetrahedral site would transform it into a sheet silicate, whose tetrahedral layers have the same kind and number of rings as in semenovite, although linked in a different way. The coordinations of RE, Ca, and Fe atoms are similar in both minerals.

Note that in the above-mentioned minerals containing rare earths (gadolinite, nordite and hellandite), the repeat perpendicular to the tetrahedral sheets is comparable with the pseudo-repeat $c/2$ of semenovite: only one tetrahedral layer is contained in the unit cell of these minerals. The doubling of the c parameter is probably how in semenovite the sum of the positive charges of the inter-layer cations is balanced with that of the negative charges from the tetrahedral layers. Table 6 shows the different ways these minerals attain this goal.

In gadolinite, where the Si/Be ratio is 1, the charges are balanced by the complete filling of both the octahedral Fe sites and those occupied by RE. In the remaining minerals the sum of the negative charges from the tetrahedral layers is lowered because, at the centers of the tetrahedra, ions with higher formal charges (Si^{4+}, B^{3+}) prevail over ions like Be^{2+} and $(Zn,Mg)^{2+}$. In nordite the deficiency of negative charges is balanced by the lower charges of the inter-layer cations: *i.e.* Na^+ replaces Fe^{2+} in octahedral sites and $(Sr,Ca)^{2+}$ fill half sites occupied in the other minerals by RE. In hellandite the balance is chiefly attained with ordered empty sites in the tetrahedral layers, transforming a sheet silicate into a chain silicate; some disordered vacancies are also present in the positions of the inter-layer cations. Conversely in semenovite the ordering of the vacancies concerns the sites of the inter-layer cations: the doubling of the *c* parameter is mainly a consequence of such ordering.

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