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FROM STRUCTURE TOPOLOGY TO CHEMICAL COMPOSITION. XV. TITANIUM SILICATES: REVISION OF THE CRYSTAL STRUCTURE AND CHEMICAL FORMULA OF SCHÜLLERITE, $Na_2Ba_2Mg_2Ti_2(Si_2O_7)_2O_2F_2$, FROM THE EIFEL VOLCANIC REGION, GERMANY

Elena SOKOLOVA[§], Frank C. HAWTHORNE, and Yassir A. ABDU

Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

Abstract

The crystal structure of schüllerite, ideally $Na_2Ba_2Mg_2Ti_2(Si_2O_7)_2O_2F_2$, *a* 5.396(1), *b* 7.071(1), *c* 10.226(2) Å, α 99.73(3), β 99.55(3), γ 90.09(3)°, *V* 379.1(2) Å^3, *Z* = 1, from the Eifel volcanic region, Germany, has been refined in the space group $P\overline{1}$ to *R* = 1.33% using 2247 observed ($F_o > 4\sigma F$) reflections collected with a single-crystal Bruker D8 three-circle diffractometer equipped with a rotating-anode generator (Mo*K*α radiation), multilayer optics and an APEX-II detector. The empirical formula for schüllerite was calculated on the basis of 18 (O + F) anions: $(Na_{1.10}Ca_{0.43}Mn_{0.30}Fe^{2+}_{0.17})_{\Sigma 2}(Ba_{1.57}Sr_{0.14}K_{0.14}\square_{0.15})_{\Sigma 2}(Mg_{0.79}Fe^{2+}_{0.71}Na_{0.33}Fe^{3+}_{0.17})_{\Sigma 2}(Ti_{1.67}Fe^{3+}_{0.21}Nb_{0.09}Zr_{0.02}Al_{0.01})_{\Sigma 2}Si_{3.95}O_{15.93}F_{2.07}$, $D_{calc.}$ = 3.879 g/cm^3, *Z* = 1, with $Fe^{3+}/(Fe^{2+}+Fe^{3+})$ ratio determined by Mössbauer spectroscopy. Schüllerite is a Group-IV TS-block mineral: Ti + Mg = 4 *apfu*. The crystal structure of schüllerite is an alternation of TS (Titanium Silicate) and **I** (intermediate) blocks of the ideal composition $[Na_2Mg_2Ti_2(Si_2O_7)_2O_2F_2]^{4-}$ and $[Ba_2]^{4+}$, respectively. The TS block is composed of the central O (octahedral) sheet and two adjacent H (heteropolyhedral) sheets. In the O sheet, there are two brookite-like chains of M^O octahedra of the following ideal compositions: $[Mg_2O_8]^{12-}$ [$M^O(1)$] and $[Na_2O_8]^{14-}$ [$M^O(2)$]; the ideal composition of the O sheet is $[Na_2Mg_2O_2F_2]^0$. The H sheet is composed of the [5]-coordinated Ti-dominant M^H polyhedra and Si_2O_7 groups; the composition of the two H sheets is $[Ti_2(Si_2O_7)_2]^{4-}$. In schüllerite, the TS block has a topology characteristic of Group IV of TS-block minerals: two H sheets connect to the O sheet such that two Si_2O_7 groups link to the Mg-dominant octahedra of the O sheet adjacent along $\mathbf{t_1}$. In the O sheet, occurrence of divalent cations at the $M^O(1)$ site results in the presence of monovalent anions, F^-, at the X^O_A site. The A^P site of the H sheet is occupied mainly by Ba; the A^P site is shifted from the plane of the H sheet, and Ba atoms constitute the **I** block of the composition $[Ba_2]^{4+}$. Schüllerite is the only mineral of Group IV that has (1) a brookite-like $[Mg_2O_8]^{12-}$ chain of octahedra in the O sheet; (2) [5]-coordinated Ti in the H sheet; (3) Ba atoms in the **I** block. The ideal structural formula of schüllerite is of the form $A^P_2M^H_2M^O_4(Si_2O_7)_2(X^O_M)_2(X^O_A)_2$: $Ba_2Ti_2Na_2Mg_2Ti_2(Si_2O_7)_2O_2F_2$, *Z* = 1.

Keywords: schüllerite, crystal-structure refinement, FTIR-spectroscopy, Mössbauer spectroscopy, EMP analysis, chemical formula, Ti-disilicate minerals, TS block, Group IV

Introduction

Schüllerite from the Eifel volcanic region, Germany, was described by Chukanov *et al.* (2011). The crystal structure of schüllerite was solved by Rastsvetaeva *et al.* (2011) in the acentric space group *P*1: *a* 5.4027(1), *b* 7.066(4), *c* 10.2178(1) Å, α 99.816(1), β 99.624(1), γ 90.084(1)°, Z = 1, $D_{calc.}$ = 4.106 g/cm^3. Chukanov *et al.* (2011) reported the following empirical formula based on 18 (O + F): $(Ba_{1.68}Sr_{0.18}K_{0.11}Na_{1.05}Ca_{0.43}Mn_{0.47}Mg_{0.88}Fe^{2+}_{0.44}Fe^{3+}_{1.02}Ti_{1.28}Nb_{0.17}Al_{0.24})Si_{3.98}O_{16.98}F_{1.02}$, and a corresponding simplified formula: $Ba_2Na(Mn,Ca)(Fe^{3+},Mg,Fe^{2+})_2Ti_2(Si_2O_7)_2(O,F)_4$. Chukanov *et al.* (2011) emphasized the close similarity between schüllerite, jinshajiangite, $NaBaFe^{2+}_4Ti_2(Si_2O_7)_2O_2(OH)_2F$ (Sokolova *et al.* 2009), barytolamprophyllite, (BaK)$Na_3Ti_3(Si_2O_7)_2O_2(OH)_2$ (Sokolova & Cámara 2008), and bafertisite, $Ba_2Fe^{2+}_4Ti_2(Si_2O_7)_2O_2(OH)_4$ (Li *et al.* 2011). Note that here and further on, we refer to the most recent structure work. Rastsvetaeva *et al.* (2011) described schüllerite as a new heterophyllosilicate of the "lamprophyllite group", emphasizing its structural similarity to lamprophyllite, (SrNa)$Na_3Ti_3(Si_2O_7)_2O_2(OH)_2$ (Krivovichev *et al.* 2003), barytolamprophyllite, and nabalamprophyllite, (BaNa)$Na_3Ti_3(Si_2O_7)_2O_2(OH)_2$ (Sokolova & Hawthorne 2008). Schüllerite is a TS-block mineral (TS = Titanium Silicate). The TS block consists of the central O (trioctahedral) sheet and two H (heteropolyhedral) sheets containing Si_2O_7 groups. There are four groups of TS-block structures

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[§] *Corresponding author:* Elena_sokolova@umanitoba.ca characterized by a different topology and stereochemistry of the TS block (Sokolova 2006). Each group of structures has a different linkage of H and O sheets in the TS block and a different arrangement of Ti (+ Nb) polyhedra (Sokolova 2006). In the crystal structure of schüllerite, the TS blocks alternate with layers of Ba atoms, which constitute the intermediate (**I**) block. Below, we outline some problems with the current crystal structure of schüllerite and its chemical composition to show that both the crystal structure and chemical composition of this very interesting TS-block mineral need to be re-examined. Following our long-term interest in TS-block minerals, we re-investigated the crystal structure of schüllerite, determined its Fe^{3+}/Fe^{2+} ratio using Mössbauer spectroscopy, and revised its chemical composition. Here we report our results and discuss the crystal chemistry of schüllerite.

REVIEW OF PREVIOUS WORK

Chukanov *et al.* (2011) determined the valence state of Fe in schüllerite by X-ray emission spectroscopy (from the intensity ratio of $FeK\beta_5$ and $FeK\beta_1$): Fe^{3+} = 1.02 *apfu* (atoms per formula unit), Fe^{2+} = 0.44 *apfu*, *i.e.*, $Fe^{3+} > Fe^{2+}$ and $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ = 70% (Table 1). In their refinement of crystal structure of schüllerite, Rastsvetaeva *et al.* (2011) assigned 0.1 Fe^{3+} *apfu* to the H sheet of the TS block (Table 2) and 0.92 Fe^{3+} *apfu* should, therefore, occur in the O sheet for a total Fe^{3+} of 1.02 *apfu*. However Rastsvetaeva *et al.* (2011) assigned only 0.70 Fe^{3+}*apfu* to the *M*(5) and *M*(6) sites of the O sheet, resulting in a $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ ratio of 55%, not 70% as was determined by Chukanov *et al.* (2011) (Table 2). Based on assigned site-populations, the calculated aggregate radii for the assigned cations at these sites are 0.68 [*M*(5)] and 0.74 [*M*(6)] Å. The ionic radii derived from observed mean M–O bond-lengths are 0.79 [*M*(5)] and 0.80 Å [*M*(6)] Å. Comparison of both sets of radii tells us that (1) the *M*(5) site [r_{cat} = 0.79 Å] must be occupied by cations with ionic radii larger than that of Fe^{3+} [r = 0.645 Å, Shannon (1976)]; (2) a larger cation must be assigned to the *M*(6) site [r_{cat} = 0.80 Å] in addition to Fe^{2+}, Mg [r = 0.72 Å], and Fe^{3+}. The observed bond-lengths for the *M*(5,6) sites in the O sheet are too long when compared to typical Fe^{3+}–O and Fe^{3+}–F bond lengths, and hence the amount of Fe^{3+} determined by Chukanov *et al*. (2011) is too high and must be re-measured.

The aggregate ionic radius of the cations at the *M*(3) site derived from observed mean M–O bond lengths, 0.93 Å, tells us that the M(3) polyhedron is too small to accommodate solely the Na [r_{Na} = 1.02 Å] (Table 2) which was assigned to this site; hence the reported order of Na in the O sheet is doubtful.

Rastsvetaeva *et al*. (2011) gave the composition of the two anion sites in the O sheet, O(17) and F, as $(O,F)_2$. They also stated that these two sites are fully occupied by O and F. Our bond-valence calculations for their structure give the sum of the bond valences incident at the *F* and O(17) sites as 0.8 and 1.01 *vu* [(valence unit, bond-valence parameters are from Brown (1981)], indicating that only monovalent anions can occur at the *F* and O(17) sites. As Chukanov *et al.* (2011) reported (1) F = 1 *apfu* (Table 1) and (2) lack of H_2O confirmed by IR spectroscopy, there is major disagreement between the structure-refinement results (*i.e.,* bond-valence values) and the chemical composition. The content of F must be re-measured.

All atoms in the crystal structure of schüllerite are related by a pseudo inversion center, *e.g.*, M(3) and M(4), M(5) and M(6), O(17) and F (Table 2). The structure should be refined in space group $P\overline{1}$.

The study reported here addresses these various ambiguities relating to the structure reported by Rastsvetaeva *et al.* (2011).

EXPERIMENTAL

Sample description

Two grains of schüllerite from the type locality of the Eifel volcanic region, Germany (Chukanov *et al*. 2011) were obtained from an American mineral collector. Both pale brown fragments are complex intergrowths, and the severe interpenetrating character of both fragments was very obvious under a binocular microscope. A pale-yellow crystal of schüllerite, a small thin plate (0.030 × 0.030 × 0.005 mm), was cut from

TABLE 1. CHEMICAL ANALYSIS (wt.%) AND FORMULA UNIT (*apfu*) FOR SCHÜLLERITE

Oxide	(1)	(2)	Formula unit	(1)	(2)
Nb_2O_5	2.45	1.31	Nb	0.17	0.09
ZrO_2	n.d.	0.20	Zr	0.00	0.02
TiO_2	11.17	14.86	Ti	1.28	1.67
SiO_2	26.12	26.40	Si	3.98	3.95
Al_2O_3	1.33	0.05	Al	0.24	0.01
Fe_2O_3	8.89	3.36	Fe^{3+}	1.02	0.38
FeO	3.43	7.06	Fe^{2+}	0.44	0.88
BaO	28.09	26.73	Ba	1.68	1.57
SrO	1.99	1.57	Sr	0.18	0.14
MnO	3.67	2.37	Mn	0.47	0.30
CaO	2.62	2.65	Ca	0.43	0.43
MgO	3.89	3.52	Mg	0.88	0.79
K_2O	0.55	0.73	K	0.11	0.14
Na_2O	3.55	4.97	Na	1.05	1.44
F	2.12	4.37	F	1.02	2.07
O=F	–0.89	–1.84	O	16.98	15.93
Total	98.98	98.31	CATSUM	11.93	11.81

(1) Chukanov *et al.* (2011): EMPA, Fe^{3+}/Fe^{2+} was determined by X-ray emission spectroscopy; (2) This work: EMPA, Fe^{3+}/Fe_{tot} was determined by Mössbauer spectroscopy; n.d. = not detected; the formula unit was calculated on 18 (O + F) *apfu*.

TABLE 2. ASSIGNED SITE-POPULATIONS, AVERAGE BOND-LENGTHS AND CALCULATED AGGREGATE RADII FOR SELECTED CATION SITES, AND ASSIGNED SITE-POPULATIONS AND BOND-VALENCE SUMS FOR SELECTED ANION SITES IN THE CRYSTAL STRUCTURE OF SCHÜLLERITE

	After Rastsvetaeva *et al*. (2011)			
Site	Assigned site-population (*apfu*)	$<\text{M–}\varphi>^*_{\text{obs}}$ (Å)	Calculated aggregate cation radius (Å)	
			$<\text{M–}\varphi>_{\text{obs}}$ – (average anion radius)**	Based on the assigned site-populations**
		Cations		
$^{[5]}M1$	0.7Ti + 0.2Nb + 0.1Fe^{3+}	1.938	0.56	0.53
$^{[5]}M2$	0.6Ti + 0.2Al + 0.2Mg	1.925	0.55	0.53
*M*3	1.0Na	2.299	0.93	1.02
*M*4	0.5Mn + 0.4Ca + 0.1Na	2.295	0.92	0.92
*M*5	0.55Fe^{3+} + 0.45Mg	2.160	0.79	0.68
*M*6	0.6Fe^{2+} + 0.25Mg + 0.15Fe^{3+}	2.169	0.80	0.74
		Anions		
			Bond-valence*** sum (*vu*)	
$^{[3]}$O17	1.0 O		1.01	
$^{[3]}$F	1.0 F		0.80	

* φ = O,F;
**using the ionic radii of Shannon (1976)
***calculated using bond-valence parameters from Brown (1981)

a fragment for the collection of X-ray diffraction data. Three additional grains of schüllerite were selected for microprobe analysis, infra-red, and Mössbauer spectroscopy.

Fourier-transform infra-red (FTIR) spectroscopy

The FTIR spectrum was collected in transmission mode using a Hyperion 2000 IR microscope equipped with a liquid-nitrogen-cooled MCT detector. The sample was prepared as a thin film using a Diamond Micro Compression Cell. Data over the range 4000–650 cm^{-1} were obtained by averaging 100 scans with a resolution of 4 cm^{-1}. The FTIR spectrum (Fig. 1) shows no evidence for the presence of H_2O and OH, as indicated by the absence of absorption bands in the region 4000–1200 cm^{-1}. This conclusion is in accord with interpretation of the infra-red spectrum by Chukanov *et al.* (2011). The strong peaks at ~ 995, 967, and 860 cm^{-1} are due to Si–O stretching vibrations of the Si_2O_7 groups. The weak peak at ~675 cm^{-1} may be assigned to the stretching vibrations of the Si–O–Si bridges of Si_2O_7 group (Le Cléac'h & Gillet 1990).

Mössbauer spectroscopy

The Mössbauer spectrum of schüllerite was collected with a point source from a few small crystals stuck to a thin-glass slide that was mounted on a Pb disk with ~300 μm aperture. As there was only a very small amount of sample available, it took ~5 months to collect the spectrum shown in Figure 2. Although there is a lot of scatter in the spectrum, the dominance of Fe^{2+} over Fe^{3+} is quite clear. It is fitted with two QSD-sites: Fe^{2+} (solid subspectrum) and Fe^{3+} (dashed subspectrum). The A_{-}/A_{+} parameter (*i.e.*, the intensity ratio of the low-velocity peak to the high-velocity peak) was fixed at 1.67 for both Fe^{2+} and Fe^{3+} (assuming the γ-ray direction is perpendicular to V_{zz}). CS = 1.16 mm/s; QS = 2.00 mm/s for Fe^{2+}, and CS = 0.40 mm/s; QS = 0.47 mm/s for Fe^{3+}. Assuming equal recoilless fractions for Fe^{2+} and Fe^{3+} sites, the Fe^{3+}/(Fe^{2+} + Fe^{3+}) ratio is 0.37(10). If we dispense with fitting specific line-shapes to the spectrum and just compare the aggregate background-corrected counts in the channel ranges –1 to +1.2 (≡ Fe^{2+} + 2Fe^{3+}) and +1.2 to +3.2 mm/s (≡ Fe^{2+}), we get a statistically identical value for the Fe^{3+}/(Fe^{2+} + Fe^{3+}) ratio. The Fe^{3+}/(Fe^{2+} + Fe^{3+}) ratio obtained here is significantly smaller than that of 70% determined by X-ray emission spectroscopy (Chukanov *et al.* 2011), and is in accord with our structural results (see below).

Electron-microprobe analysis

One grain of schüllerite was analyzed with a Cameca SX-100 electron-microprobe operating in wavelength-

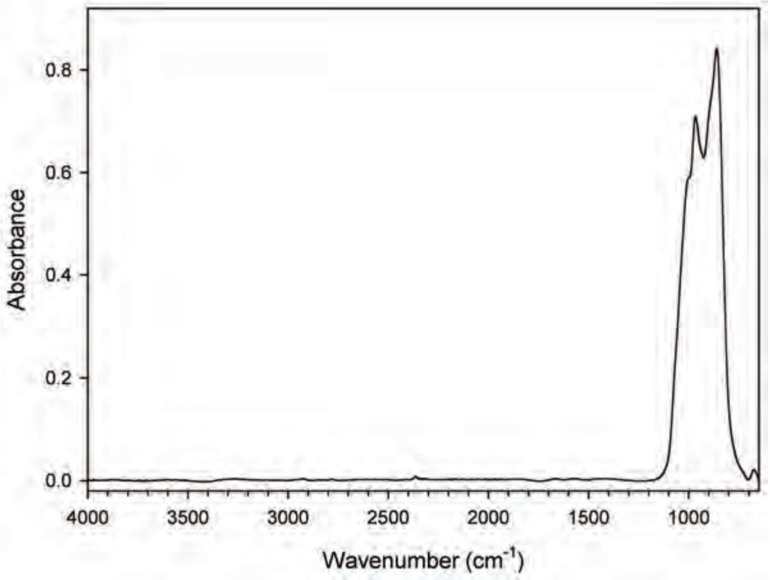

FIG. 1. The FTIR spectrum of schüllerite (thin film).

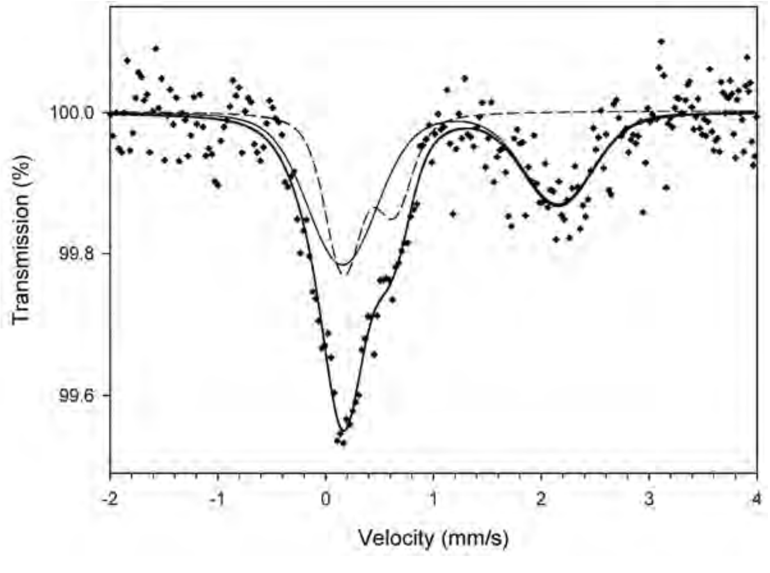

FIG. 2. The Mössbauer spectrum of schüllerite. Solid subspectrum: Fe^{2+}; dashed subspectrum: Fe^{3+}.

dispersive mode with an accelerating voltage of 15 kV, a specimen current of 10 nA, a beam size of 10 μm, and count times on peak and background of 20 and 10 s, respectively. The following standards were used for $K\alpha$ or $L\alpha$ X-ray lines (analyzing crystals are given in brackets): F(LTAP): topaz; Na(TAP): jadeite; K(LPET): orthoclase; Ca(LPET), Si(TAP): diopside; Nb(LPET), Ba(LLiF): $Ba_2NaNb_5O_{15}$; Sr(LPET): $SrTiO_3$; Ti(LLiF): titanite; Hf(LLIF): $HfSiO_4$; Ta(LLiF): $Mn(Ta_{1.7}Nb_{0.3})O_6$; Mn(LLiF): spessartine; Mg(TAP): forsterite; Fe(LLiF):

fayalite; Zr(LPET): zircon, Al(TAP): andalusite. Data were reduced using the φ(ρZ) procedure of Pouchou & Pichoir (1985). The chemical composition of schüllerite is given in Table 1 and is the mean of 10 determinations. The empirical formula for schüllerite was calculated on the basis of 18 (O + F) anions and is given in Table 1; the structural formula is as follows: $(Na_{1.10}Ca_{0.43}Mn_{0.30}Fe^{2+}_{0.17})_{\Sigma 2}(Ba_{1.57}Sr_{0.14}K_{0.14}\square_{0.15})_{\Sigma 2}(Mg_{0.79}Fe^{2+}_{0.71}Na_{0.33}Fe^{3+}_{0.17})_{\Sigma 2}(Ti_{1.67}Fe^{3+}_{0.21}Nb_{0.09}Zr_{0.02}Al_{0.01})_{\Sigma 2}(Si_{3.95}O_{14})O_{1.93}F_{2.07}$, $D_{\mathbf{calc.}} = 3.879$ g/cm^3, $Z = 1$, with the $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ ratio determined by Mössbauer spectroscopy and adjusted (within its standard deviation) in accord with structure-refinement results to 30%.

Crystal structure: data collection and structure refinement

Single-crystal X-ray diffraction data for schüllerite were collected with a Bruker D8 three-circle diffractometer equipped with a rotating-anode generator (Mo*K*α radiation), multilayer optics and an APEX-II detector. The intensities of 22085 reflections with $-7 \leq h \leq 7$, $-9 \leq k \leq 10$, $-14 \leq l \leq 14$ were collected with a frame width of 0.2° and a frame time of 15 s, out to 2θ = 60.45°. The refined unit-cell parameters were obtained from 8111 reflections ($I > 10\sigma I$) and are given in Table 3. We used the CELL_NOW program (Bruker 2007) to establish the twin law described by the twin matrix ($\bar{1}00\ 010\ 00\bar{1}$). An empirical absorption correction (TWINABS, Bruker 2001) was applied. The Bruker SHELXTL Version 5.1 system of programs (Sheldrick 2008) was used for the solution and refinement of the schüllerite structure. For the structure refinement in space group $P\bar{1}$, we used the HKLF 5 dataset; this dataset contains reflections of two types: (1) those that belong only to the primary (first) domain (1142) and (2) those that are overlapping with reflections from the second domain (1105) and have dual indexing. The refinement converged to $R_1 = 1.33\%$ and a GoF of 1.134, with the fraction of the second component being equal to 27.8(1)%. The occupancies of the Ti-dominant M^H site, the $M^O(1,2)$ sites (occupied mainly by Na, Fe^{2+}, Mg, and Mn), and the Ba-dominant A^P site were refined with the scattering curves of Ti, Fe, and Ba, respectively. Scattering factors were taken from the International Tables for X-ray Crystallography (1992).

We also refined the crystal structure of schüllerite in space group $P1$ using the atom coordinates of Rastsvetaeva *et al.* (2011) as a starting model. In the $P1$ structure, all cation sites are related by a pseudo-inversion center (we considered site-scattering values and bond lengths). We did not observe any cation or anion order in the $P1$ structure if compared to the $P\bar{1}$ structure (*cf.* REVIEW OF PREVIOUS WORK). In the $P1$ refinement, the Flack parameter is 0.43(3), indicating that the $P1$ structure has problems. R_1 values for P1 and $P\bar{1}$ refinements are 1.49 and 1.33, respectively. Hence we chose the space group $P\bar{1}$ as the true symmetry of the schüllerite structure. Details of the X-ray data collection and structure refinement in space group $P\bar{1}$ are given in Table 3, final atom parameters in Table 4, selected interatomic distances and angles in Table 5, refined site-scattering values and assigned populations for selected sites in Table 6, and bond-valence values in Table 7. A list of observed and calculated structure factors and a CIF file may be obtained from The Depository of Unpublished Data on the MAC website [document Schüllerite CM_715].

Site-population assignment

There are six cation sites in the crystal structure of schüllerite: the M^H, A^P, and two *Si* sites of the H sheet and two M^O sites of the O sheet; site labeling is in accord with Sokolova (2006). Consider first the Ti-dominant [5]-coordinated M^H site. The bond lengths around the M^H site vary from 1.734 to 1.983 Å (Table 5). We assign cations to this site based on our previous work on TS-block minerals: Ti(+ Nb)-dominant sites are always fully occupied. In schüllerite, cations available

TABLE 3. MISCELLANEOUS REFINEMENT DATA FOR SCHÜLLERITE

a (Å)	5.396(1)
b	7.071(1)
c	10.226(2)
α (°)	99.73(3)
β	99.55(3)
γ	90.09(3)
V (Å^3)	379.1(2)
Refl. ($I_o > 10\sigma I$)	8111
Space group	$P\bar{1}$
Z	1
Absorption coefficient (mm^{-1})	7.53
F(000)	412.80
$D_{calc.}$ (g/cm^3)	3.879
Second component (%)	27.8(1)
Crystal size (mm)	0.030 × 0.030 × 0.005
Radiation/filter	Mo*K*α/graphite
$2\theta_{max}$ (°)	60.45
R(σ) (%)	0.84
Reflections collected	22085
Independent reflections	2247
$F_o > 4\sigma F$	2223
Refinement method	Full-matrix least squares on F^2, fixed weights proportional to $1/\sigma F_o^2$
No. of refined parameters	141
Final $R_{(obs)}$ (%)	
R_1 [$F_o > 4\sigma F$]	1.33
R_1 [all data]	1.35
wR_2	3.84
Highest peak, deepest hole (e Å^{-3})	0.84, –0.49
Goodness of fit on F^2	1.134

TABLE 4. FINAL ATOM COORDINATES AND ANISOTROPIC DISPLACEMENT PARAMETERS (Å^2) FOR SCHÜLLERITE

Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
M^H	0.31624(5)	0.29918(5)	0.70911(3)	0.00608(14)	0.00731(15)	0.00961(14)	0.00162(12)	0.00141(9)	0.00015(12)	0.00764(10)
Si(1)	0.18162(10)	0.41608(8)	0.27263(5)	0.0082(2)	0.0068(3)	0.0108(2)	0.00163(18)	0.00191(17)	0.00025(18)	0.00858(12)
Si(2)	0.17716(10)	0.97192(8)	0.27515(5)	0.0076(2)	0.0070(3)	0.0102(2)	0.00183(18)	0.00153(17)	0.00044(18)	0.00823(12)
A^P	0.27134(2)	0.76552(2)	0.56608(1)	0.00889(6)	0.00793(6)	0.01328(6)	0.00234(5)	0.00245(4)	0.00053(5)	0.00990(4)
M^O(1)	0.25709(9)	0.11913(9)	0.99788(4)	0.0199(2)	0.0129(2)	0.0137(2)	0.0028(2)	0.00105(15)	–0.0020(2)	0.01566(14)
M^O(2)	0.24601(9)	–0.37376(11)	–0.00081(5)	0.0134(2)	0.0175(3)	0.0242(3)	0.0028(3)	–0.00166(17)	0.0004(3)	0.01901(16)
O(1)	0.0475(3)	1.0985(2)	0.65434(16)	0.0086(6)	0.0093(6)	0.0182(7)	0.0028(5)	0.0035(5)	–0.0014(5)	0.0118(3)
O(2)	0.1185(3)	0.9202(4)	0.11411(15)	0.0200(7)	0.0291(10)	0.0112(6)	0.0030(7)	0.0016(5)	0.0038(8)	0.0203(3)
O(3)	–0.0473(3)	0.5214(2)	0.33847(17)	0.0098(6)	0.0100(6)	0.0187(7)	0.0033(5)	0.0037(5)	0.0025(5)	0.0126(3)
O(4)	0.4457(3)	0.8997(2)	0.34327(16)	0.0086(6)	0.0095(6)	0.0158(7)	0.0021(5)	0.0011(5)	0.0020(5)	0.0114(3)
O(5)	0.8030(3)	0.7921(2)	0.67156(15)	0.0138(6)	0.0067(6)	0.0245(7)	0.0047(6)	0.0045(5)	0.0006(6)	0.0146(3)
O(6)	0.4491(3)	0.5233(2)	0.34310(17)	0.0095(6)	0.0093(6)	0.0192(7)	0.0036(5)	0.0024(5)	–0.0014(5)	0.0125(3)
O(7)	0.1379(3)	0.3824(3)	0.11218(16)	0.0253(8)	0.0299(11)	0.0114(6)	0.0011(7)	0.0042(6)	–0.0016(8)	0.0224(4)
X^O_M O	0.3699(3)	0.3312(4)	0.88348(16)	0.0189(7)	0.0301(10)	0.0159(7)	0.0016(8)	0.0061(6)	0.0023(8)	0.0215(3)
X^O_A F	0.3874(3)	0.8679(4)	0.88901(17)	0.0283(8)	0.0445(12)	0.0267(7)	0.0045(9)	0.0063(6)	–0.0070(9)	0.0332(4)

TABLE 5. INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR SCHÜLLERITE

Si(1)–O(7)	1.595(2)	Si(2)–O(2)	1.603(2)
Si(1)–O(6)	1.626(2)	Si(2)–O(4)	1.623(2)
Si(1)–O(3)	1.626(2)	Si(2)–O(1)$_b$	1.627(2)
Si(1)–O(5)$_a$	1.664(2)	Si(2)–O(5)$_c$	1.663(2)
<Si(1)–O>	1.628	<Si(2)–O>	1.629
Si(1)$_a$–O(5)–Si(2)$_c$	142.0(1)		
M^H–X^O_M	1.734(2)	A^P–O(1)	2.733(2)
M^H–O(1)$_d$	1.971(2)	A^P–O(6)$_a$	2.738(2)
M^H–O(4)$_a$	1.974(2)	A^P–O(4)$_c$	2.752(2)
M^H–O(6)$_a$	1.978(2)	A^P–O(3)$_e$	2.754(2)
M^H–O(3)$_e$	1.983(2)	A^P–O(5)	2.887(2)
<M^H–O>	1.928	A^P–O(4)	2.901(2)
		A^P–O(1)$_b$	2.901(2)
		A^P–O(5)$_f$	2.902(2)
		A^P–O(6)	2.909(2)
		A^P–O(3)	2.943(2)
		<A^P–O>	2.842
M^O(1)–(X^O_A)$_g$	2.063(2)	M^O(2)–O(7)$_j$	2.188(2)
M^O(1)–(X^O_A)$_d$	2.118(2)	M^O(2)–(X^O_M)$_k$	2.209(2)
M^O(1)–O(2)$_e$	2.149(2)	M^O(2)–O(7)$_d$	2.354(2)
M^O(1)–O(7)$_h$	2.183(2)	M^O(2)–O(2)$_d$	2.371(2)
M^O(1)–O(2)$_i$	2.192(2)	M^O(2)–(X^O_M)$_l$	2.373(3)
M^O(1)–O(8)	2.194(2)	M^O(2)–(X^O_A)$_a$	2.388(2)
<M^O(1)–φ*>	2.150	<M^O(2)–φ>	2.313

φ = O,F;
Symmetry operators: a: –*x*+1, –*y*+1, –*z*+1; b: –*x*, –*y*+2, –*z*+1;
c: –*x*+1, –*y*+2, –*z*+1; d: *x*, *y*–1, *z*; e: –*x*, –*y*+1, –*z*+1; f: *x*–1, *y*, *z*;
g: –*x*+1, –*y*+1, –*z*+2; h: *x*, *y*, *z*+1; i: *x*, *y*–1, *z*+1; j: –*x*, –*y*, –*z*;
k: –*x*+1, –*y*, –*z*+1; l: *x*, *y*–1, *z*–1.

for the *M*^{H} site are (Ti$_{1.67}$Nb$_{0.09}$Zr$_{0.02}$)$_{\Sigma 1.79}$ *pfu* (Table 1); to fill the site, we add Fe$^{3+}_{0.21}$ *apfu* (ionic radii for $^{[5]}$Ti and $^{[5]}$Fe^{3+} are 0.51 and 0.58 Å, respectively), with a total calculated scattering of 46.82 *epfu* (electrons per formula unit) compared with a refined site-scattering of 45.9(1) *epfu* (Table 6). The cations available to be assigned to the [10]-coordinated A^P site are Ba, Sr, and K (Table 1). The site-scattering value calculated from EMPA for ($Ba_{1.57}Sr_{0.14}K_{0.14}\square_{0.15}$) is 95.90 *epfu*, refined site-scattering is 100.1(2) *epfu*; the A^P site is occupied by cations at 92.5% (Table 6).

Consider next the [6]-coordinated $M^O(1)$ and $M^O(2)$ sites of the O sheet. Available cations are 1.43 Na + 0.88 Fe^{2+} + 0.79 Mg + 0.43 Ca + 0.30 Mn + 0.17 Fe^{3+} (Table 1), with a total scattering of 68.61 *epfu* and an aggregate cation radius of 0.86 Å. There is an 8% difference between refined site-scattering values at the $M^O(1)$ and $M^O(2)$ sites, 34.9(1) and 32.3(1) *epfu*, respectively, with total scattering 67.2 *epfu*, and there is an 8% difference between the mean bond-lengths at the $M^O(1)$ and $M^O(2)$ sites, 2.150 and 2.313 Å, respectively. Corresponding cation radii derived from $\langle M–\phi\rangle_{obs.}$ are 0.80 [$M^O(1)$] and 0.95 Å [$M^O(2)$], respectively, with $\langle r\rangle$ = 0.88 Å (φ = O, F). Hence we must assign the smallest cations Fe^{3+}, r = 0.645 Å, and Mg, r = 0.72 Å, to the $M^O(1)$ site. These cations assigned to the $M^O(1)$

TABLE 6. REFINED SITE-SCATTERING VALUES AND ASSIGNED SITE-POPULATIONS FOR SCHÜLLERITE

Site	Refined site-scattering (*epfu*)	Assigned site-population (*apfu*)	Calculated site-scattering (*epfu*)	$\langle X–\varphi\rangle^*_{calc.}$ (Å)	$\langle X–\varphi\rangle_{obs}$ (Å)
$^{[5]}M^H$	45.9(1)	1.67 Ti + 0.21 Fe^{3+} + 0.09 Nb + 0.02 Zr + 0.01 Al	46.82	1.901	1.928
$^{[10]}A^P$	100.1(2)	1.57 Ba + 0.14 Sr + 0.14 K + 0.15 □	95.90	2.890	2.842
$^{[6]}M^O(1)$	34.9(1)	0.79 Mg + 0.71 Fe^{2+} + 0.33 Na + 0.17 Fe^{3+}	35.99	2.143	2.150
$^{[6]}M^O(2)$	32.3(1)	1.10 Na + 0.43 Ca + 0.30 Mn + 0.17 Fe^{2+}	32.62	2.333	2.313
		Bond-valence sum (*vu*)**			
$^{[4]}X^O_M$	2.08	2.00 O			
$^{[3]}X^O_A$	0.76	2.00 F			

* ionic radii from Shannon (1976); X = cation; φ = O,F;

** bond-valence parameters are from Brown (1981).

TABLE 7. BOND-VALENCE VALUES* FOR SCHÜLLERITE

Atom	Si(1)	Si(2)	M^H	A^P	$M^O(1)$	$M^O(2)$	Σ
O(1)		0.99	0.64	0.25 0.17			2.05
O(2)		1.05			0.32 0.29	0.22	1.88
O(3)	0.99		0.62	0.24 0.15			2.00
O(4)		1.00	0.63	0.24 0.17			2.04
O(5)	0.90	0.90		0.18 0.17			2.17
O(6)	0.99		0.63	0.25 0.17			2.04
O(7)	1.07				0.29	0.33 0.23	1.92
X^O_M			1.25		0.29	0.32 0.22	2.08
X^O_A					0.31 0.28	0.17	0.76
Total	3.95	4.01	3.77	1.99	1.78	1.49	
Aggregate charge	4.00	4.00	3.94	1.78	1.92	1.45	

* bond-valence parameters (*vu*) are from Brown (1981); for X^O_A, bond-valence values were calculated using cation-F parameters.

site, (0.79 Mg + 0.17 Fe^{3+}) (= 0.96) *apfu*, give 13.9 *epfu* with a radius of 0.678 Å per 0.96 *apfu*. We have to assign additional 2.00 – 0.96 = 1.04 cations *pfu* to the $M^O(1)$ site to add 34.9 – 13.9 = 21 *epfu* to the scattering at the $M^O(1)$ site (Table 6). We must assign an aggregate cation with a scattering power of ~20 e and a cation radius of ~0.88 Å. We are unable to assign a combination of divalent cations Fe^{2+}, Ca, and Mn, as their aggregate scattering power will be much higher than 20 e. Hence we must assign some Na (*r* = 1.02 Å) and add the smallest divalent cation available (Fe^{2+}, *r* = 0.78 Å) to achieve an aggregate radius of ~0.88 Å. Assignment of 0.71 Fe^{2+} + 0.33 Na (= 1.04) *apfu* gives a scattering of 22.09 *epfu* and a cation radius of 0.89 Å per 1.04 *apfu*. Hence we assign 0.79 Mg + 0.71 Fe^{2+} + 0.33 Na + 0.17 Fe^{3+} to the $M^O(1)$ site and the rest of the available cations, 1.10 Na + 0.43 Ca + 0.30 Mn + 0.17 Fe^{2+}, to the $M^O(2)$ site. There is close agreement between refined and calculated site-scattering and observed and calculated mean bond-lengths at both sites (Table 6).

DESCRIPTION OF THE STRUCTURE

For the description of the cation and anion sites in schüllerite, we use the terminology of Sokolova (2006). The general structural formula for schüllerite is $A^P_2M^H_2M^O_4(Si_2O_7)_2X_4$, where M^O are cations of the O sheet, M^H are [5]-coordinated cations of the H sheet, A^P are cations at the peripheral (*P*) sites, X_4 = X^O_4, where X^O_4 are anions at the common vertices of M^O octahedra and two M^H and two A^P polyhedra; X^O_4 = $(X^O_M)_2 + (X^O_M)_2$.

Cation sites

The O sheet. There are two cation sites octahedrally coordinated by O and F atoms at the X^O_A site (Fig. 3*a*). The $M^O(1)$ site is coordinated by four O atoms and two F atoms (the X^O_A site), with $<M^O(1)–\varphi>$ = 2.150 Å. The composition of the $M^O(1)$ site is $Mg_{0.79}Fe^{2+}_{0.71}Na_{0.33}Fe^{3+}_{0.17}$ *apfu*. Divalent cations Mg and Fe^{2+} sum to 1.50 *apfu* > 50%, Mg > Fe^{2+}, and in accord with the IMA rules, we write simplified and ideal compositions of the $M^O(1)$ site as $(Mg,Fe^{2+})_2$ and Mg_2 *apfu*. The $M^O(2)$ site is coordinated by five O atoms and one F atom (the X^O_A site), with $<M^O(2)–\varphi>$ = 2.313 Å. The composition of the $M^O(2)$ site is $Na_{1.10}Ca_{0.43}Mn_{0.30}Fe^{2+}_{0.17}$ *apfu*, where Na is the dominant cation: Na *apfu* > 50%. We write simplified and ideal compositions of the $M^O(2)$ site as [$(Na,M^{2+})_2$ where M^{2+} = Ca,Mn] and Na_2 *apfu*, respectively. The mean observed bond-lengths at the $M^O(1)$ and $M^O(2)$ sites, 2.150 and 2.313 Å, are in good agreement with bond lengths calculated by summing the constituent ionic radii: 2.143 and 2.333 Å (Table 6). For the O sheet, the cation total at the two sites is $(Mg_{0.79}Fe^{2+}_{0.71}Na_{0.33}Fe^{3+}_{0.17})$ $(Na_{1.10}Ca_{0.43}Mn_{0.30}Fe^{2+}_{0.17})$, with a simplified composition of $(Mg,Fe^{2+})_2(Na,M^{2+})$ where M^{2+} = Ca, Mn and an ideal composition of Mg_2Na_2 *apfu*.

The H sheet. The M^H site is occupied primarily by Ti (Table 6) and is coordinated by five O atoms. The M^H–O distances vary from 1.734 to 1.983 with $<M^H–O>$ = 1.928 Å. There are two tetrahedrally coordinated sites occupied by Si, with a grand <Si–O> distance of 1.629 Å. For the two H sheets, the total of the two M^H cations is $(Ti_{1.67}Fe^{3+}_{0.21}Nb_{0.09}Zr_{0.02}Al_{0.01})_{\Sigma 2}$, with simplified and ideal composition Ti_2 *apfu*. Si_2O_7 groups are considered as complex oxyanions.

The peripheral A^P site. The [10]-coordinated A^P site is occupied mainly by Ba with minor Sr and K, with $<A^P–O>$ = 2.842 Å (Tables 5, 6). Chemical composition of the A^P site is $(Ba_{1.57}Sr_{0.14}K_{0.14}\square_{0.15})$ *pfu*; its simplified and ideal compositions are $(Ba,Sr,K)_2$ and Ba_2 *apfu*, respectively.

We write the ideal cation part of the structure as the sum of Mg_2Na_2 (O sheet) + Ti_2 (H sheet) + Ba_2 (A^P_2, **I** block) = $Na_2Ba_2Mg_2Ti_2$ *apfu*, with a charge of 18^+.

Anion considerations

There are nine anion sites in the crystal structure of schüllerite and Table 7 lists the bond-valence sums for all anions. Seven anions, O(1–7), with bond-valence sums 1.88–2.17 *vu*, belong to Si_2O_7 groups and are O atoms, giving $(Si_2O_7)_2$ *pfu*. The X^O_M anion receives bond valence from one M^H (ideally Ti) atom in the H sheet and one $M^O(1)$ atom (ideally Mg) and two $M^O(2)$ atoms (ideally Na) in the O sheet, with a bond-valence sum of 2.08 *vu*, it is an O atom, giving O_2 *apfu*. The X^O_A anion receives bond valence from two $M^O(1)$ atoms and one $M^O(2)$ atom in the O sheet (Fig. 3b). Table 7 gives an incident bond-valence of 0.76 *vu* for the X^O_A anion (Table 7), indicating a monovalent anion at the X^O_A site. We assign F to this site, which gives F_2 *apfu*. Chemical analysis gives $F_{2.07}$ *pfu* and we are left with $F_{0.07}$ *pfu* to distribute over O(2) and O(7) anion sites with bond-valence sums 1.88 and 1.92 *vu*, respectively, *i.e.*, less than 2.0 *vu* (Table 7).

We write the anion part of the structure as the sum of $(Si_2O_7)_2$ + O_2 $(X^O_M)_2$ + F_2 $(X^O_A)_2$ = $(Si_2O_7)_2O_2F_2$ *pfu*, with a charge of 18^-. The total number of anions is 18 (O+F) *apfu*. We write the ideal formula of schüllerite as the sum of the cation and anion parts: $Na_2Ba_2Mg_2Ti_2(Si_2O_7)_2O_2F_2$, *Z* = 1. Sokolova (2006) wrote the formulae for the TS-block minerals per $(Si_2O_7)_2$ and, for consistency, we write the formula of schüllerite in the same way.

Structure topology

The TS block is the main structural unit in the crystal structure of schüllerite (Fig. 3a–c). There are two chains of edge-sharing octahedra within the O sheet: the Mg-dominant $M^O(1)$ octahedra form a brookite-

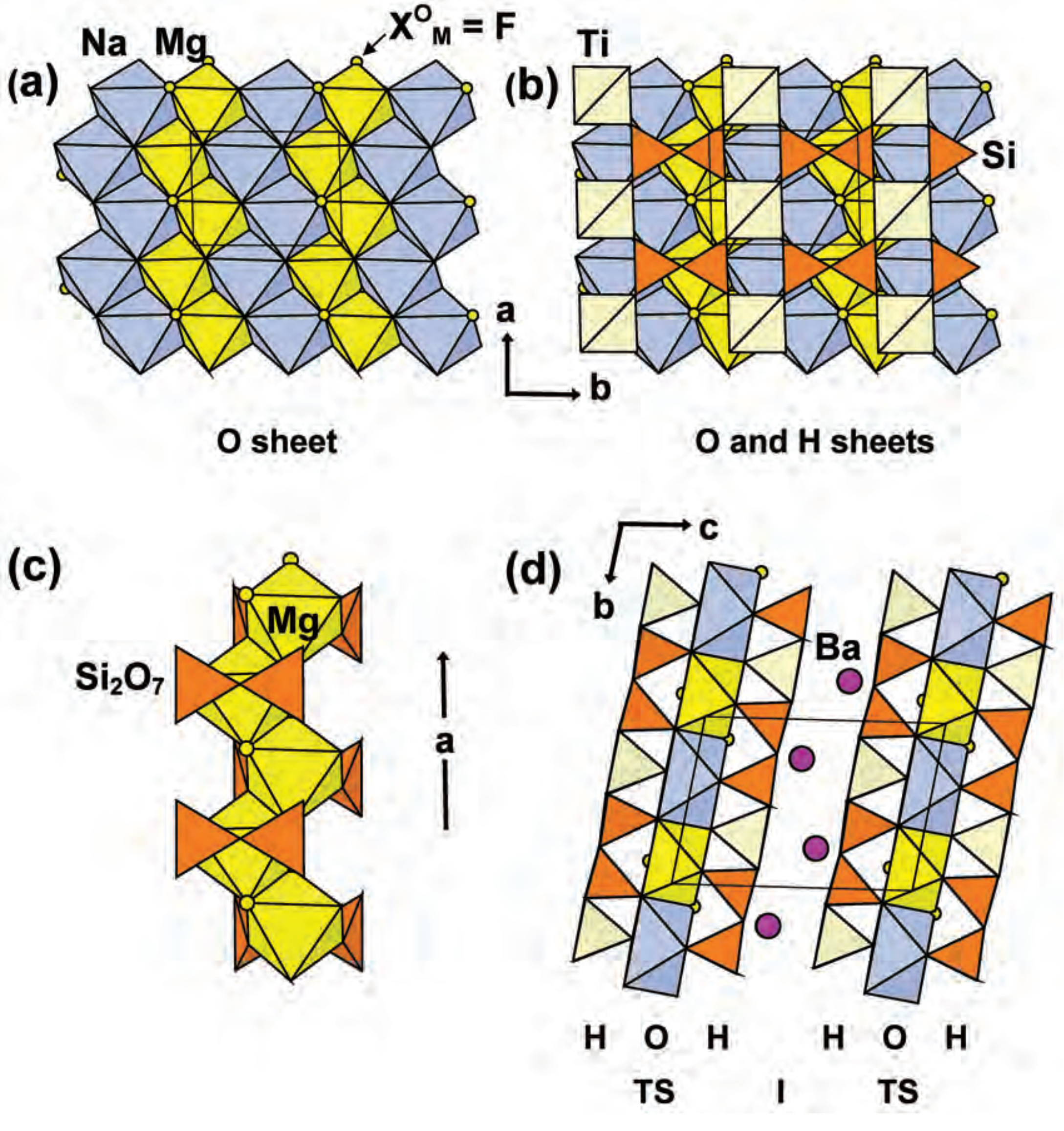

FIG. 3. The crystal structure of schüllerite: (a) the sheet of octahedra (O); (b) linkage of the heteropolyhedral (H) sheet and O sheet; (c) linkage of Si_2O_7 groups and Mg-dominant octahedra in the O sheet; (d) general view of the crystal structure. Ti octahedra are pale yellow, SiO_4 tetrahedra are orange, Na-dominant and Mg-dominant octahedra are blue and yellow, F atoms at the X^O_M sites are shown as yellow spheres; thin black lines show the unit cell.

like $[Mg_2O_8]^{12-}$ chain, and the Na-dominant $M^O(2)$ octahedra form a $[Na_2O_8]^{14-}$ chain of the same topology (Fig. 3a). In the H sheet, Ti-dominant [5]-coordinated M^H polyhedra link to Si_2O_7 groups (Fig. 3b). The H and O sheets link *via* anions at common vertices of $M^O(1,2)$ octahedra in the O sheet and M^H and Si tetrahedra in the H sheet. Linkage of two H and O sheets is such that the two Si_2O_7 groups of two H sheets link to two next-nearest-neighbor $M^O(1)$ octahedra in a brookite-like chain (Fig. 3c). This is the linkage 3 characteristic for TS block in Group-IV TS-block minerals (Sokolova 2006). The crystal structure of schüllerite is an alternation of TS and **I** blocks (Fig. 3d). In the **I** block, the [10]-coordinated Ba atoms at the A^P site form a layer parallel to (001). The general topology of the schüllerite structure is in accord with Rastsvetaeva *et al.* (2011).

RELATED MINERALS

Schüllerite is a Group-IV TS-block mineral. Sokolova (2006) defined content of Ti for the Group IV as follows: Ti = 4 *apfu*. Here we write Ti (+ Mg + Mn) = 4 *apfu*, taking into account the presence of Mg (in schüllerite) and Mn (in soboloveite) (Table 8). Thus, in Group IV, Ti (+ Mg + Mn) = 4 *apfu*, and the TS block (the main structural unit) has the topology characterized by linkage 3: two H sheets connect to the O sheet such that two Si_2O_7 groups link to the Ti octahedra of the O sheet adjacent along $\mathbf{t_1}$ (Sokolova 2006). There are five other minerals in this Group: murmanite, lomonosovite, quadruphite, sobolevite, and polyphite, and they are listed in Table 8. However, the composition of the $M^O(1)$ site in the O sheet of the TS block of schüllerite is different from that in all other five minerals: in schüllerite, the $M^O(1)$ site is occupied mainly by Mg and Fe^{2+}, giving ideally Mg_2 *pfu*; in murmanite, lomonosovite, quadruphite, and polyphite, the $M^O(1)$ site is occupied mainly by Ti, giving ideally Ti_2 *pfu*; in sobolevite, the $M^O(1)$ site is occupied mainly by Ti and Mn^{2+}, giving ideally (TiMn) *pfu* (Table 8). Occurrence of divalent cations at the $M^O(1)$ site in the O sheet results in the presence of monovalent anions, such as F^-, at the X^O_A site in schüllerite and sobolevite (Table 8). Schüllerite is the only mineral of Group IV that has [5]-coordinated Ti in the H sheet and Ba atoms in the **I** block.

SUMMARY

The space group, chemical composition and both cation and anion order in the structure of schüllerite have been revised.

(1) Schüllerite, ideally $Na_2Ba_2Mg_2Ti_2(Si_2O_7)_2O_2F_2$, $Z = 1$, is a Group-IV TS-block mineral: Ti + Mg = 4 *apfu*. The crystal structure of schüllerite [*a* 5.396(1), *b* 7.071(1), *c* 10.226(2) Å, α 99.73(3), β 99.55(3), γ 90.09(3)°, space group $P\bar{1}$, $Z = 1$] is an alternation of TS and **I** blocks of composition $[Na_2Mg_2Ti_2(Si_2O_7)_2O_2F_2]$ and $[Ba_2]$, respectively.

(2) In schüllerite, the TS block exhibits a topology characteristic of Group IV. In the O sheet of the TS block of schüllerite, there are two brookite-like chains of octahedra of the following compositions: $[Mg_2O_8]^{12-}$ and $[Na_2O_8]^{14-}$. In the TS block, two H sheets connect to the O sheet such that two Si_2O_7 groups link to the Mg-dominant $[M^O(1)]$ octahedra of the O sheet adjacent along $\mathbf{t_1}$. In the O sheet, occurrence of divalent cations at the $M^O(1)$ site results in presence of monovalent anions, such as F^-, at the X^O_A site. The A^P site of the H sheet is occupied mainly by Ba; the A^P site is shifted from the plane of the H sheet and Ba atoms constitute the **I** block.

(3) Schüllerite is the only mineral of Group IV that has (1) a brookite-like $[Mg_2O_8]^{12-}$ chain of octahedra in the O sheet; (2) [5]-coordinated Ti in the H sheet; and (3) Ba atoms in the **I** block.

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TABLE 8. IDEAL STRUCTURAL FORMULAE* AND UNIT-CELL PARAMETERS FOR GROUP-IV Ti-DISILICATE MINERALS WITH THE TS BLOCK

	Ideal structural formula														
	TS block						I block								
Mineral	$2A^P$	$2M^H$	$2M^O(1)$	$2M^O(2)$	$(Si_2O_7)_2\ X^O_4$	X^P_4		*a* (Å)	*b* (Å)	*c* (Å)	α(°)	β(°)	γ(°)	Sp.gr.	*Z*	Ref.
murmanite	Na_2	Ti_2	Ti_2	Na_2	$(Si_2O_7)_2\ O_4$	$(H_2O)_4$	absent	5.3875	7.0579	12.1764	93.511	107.943	90.093	$P\bar{1}$	1	(1)
schüllerite		$^{[5]}Ti_2$	Mg_2	Na_2	$(Si_2O_7)_2\ O_2F_2$		Ba_2**	5.396	7.071	10.226	99.73	99.55	90.09	$P\bar{1}$	1	(2)
lomonosovite	Na_2	Ti_2	Ti_2	Na_2	$(Si_2O_7)_2\ O_4$		$Na_6(PO_4)_2$	5.4170	7.1190	14.4869	99.957	96.711	90.360	$P\bar{1}$	1	(1)
quadruphite	Na_2	Ti_2	Ti_2	Na_2	$(Si_2O_7)_2\ O_4$		$Na_8Ca_2(PO_4)_4F_2$	5.4206	7.0846	20.3641	86.89	94.42	89.94	*P*1	1	(3)
sobolevite	Na_2	Ti_2	(TiMn)	Na_2	$(Si_2O_7)_2\ O_2(OF)$		$Na_9Ca_2Mn(PO_4)_4F_2$	7.0755	5.4106	40.623		93.156		*Pc*	2	(4)
polyphite	Na_2	Ti_2	Ti_2	Na_2	$(Si_2O_7)_2\ O_4$		$Na_{14}Ca_4Mn(PO_4)_6F_4$	5.3933	7.0553	26.451	95.216	93.490	90.101	$P\bar{1}$	1	(4)

* The ideal structural formulae are presented as the sum of the titanium-silicate (TS) block, $A^P_2M^H_2M^O_4(Si_2O_7)_2X^O_4X^P_4$, and the intermediate (**I**) block, in accord with Sokolova (2006); A^P = cations at the peripheral (*P*) sites; M^H = cations of the H sheet; M^O = cations of the O sheet; X^O_4 = anions shared between O and H sheets and not bonded to Si atoms; X^P_4 = apical anions of the M^H and A^P cations (where X^P anions are ligands of P^{5+} cations they are considered as part of the **I** block); coordination numbers are given for non-octahedral sites in the TS block;

Ba atoms occur at the A^P site which is shifted from the plane of the H sheet; hence we consider Ba_2 as the **I block.

References (the most recent reference on the structure): (1) Cámara *et al.* (2008); (2) this work; (3) Sokolova & Hawthorne (2001); (4) Sokolova *et al.* (2005).

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