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KIRCHHOFFITE, $CsBSi_2O_6$, A NEW MINERAL SPECIES FROM THE DARAI-PIOZ ALKALINE MASSIF, TAJIKISTAN: DESCRIPTION AND CRYSTAL STRUCTURE

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ABSTRACT

Kirchhoffite, $CsBSi_2O_6$, is a new species of silicate mineral from the Darai-Pioz alkaline massif in the upper reaches of the Darai-Pioz River, in the area of the joint Turkestansky, Zeravshansky and Alaisky ridges, Tajikistan. It occurs as equant grains 10 to 80 μm in diameter, associated with quartz, pectolite, baratovite, polylithionite, aegirine, fluorite, leucosphenite, pyrochlore, neptunite and reedmergnerite. Kirchhoffite is colorless, transparent with a white streak, and a vitreous luster; it does not fluoresce under ultraviolet light. No cleavage or parting was observed. The Mohs hardness is 6 to 6½, and it is brittle with a conchoidal fracture. The measured and calculated densities are 3.62(2) and 3.639 g/cm^3, respectively. Kirchhoffite is uniaxial (+) with indices of refraction ω = 1.592(2), ε = 1.600(2). The mineral is tetragonal, space group $I4_1/acd$, *a* 13.019(2), *c* 12.900(3) Å, *V* 2186.3(1) Å^3, Z = 16, *a* : *c* = 1 : 0.9909. The six strongest lines in the X-ray powder diffraction pattern are [*d* in Å(*I*)(*hkl*)] are 3.26(100)(040), 3.48(82)(132), 2.770(67)(332, 233), 2.294(41)(044), 2.109(34)(352, 253), 5.32(32)(121). Chemical analysis by electron and ion microprobes gave SiO_2 40.47, B_2O_3 11.27, K_2O 0.11, Cs_2O 48.16, Rb_2O 0.09, for a sum of 100.10 wt.%. The resulting empirical formula on the basis of six atoms of oxygen is $(Cs_{1.02}K_{0.01})_{\Sigma 1.03}B_{0.96}Si_{2.02}O_6$, ideally $CsBSi_2O_6$. The crystal structure of kirchhoffite was refined to an R_1 index of 3.1% based on 487 observed reflections collected on a four-circle diffractometer with Mo*K*α X-radiation. In the structure, there are two tetrahedrally coordinated sites: *Si* is occupied by silicon, <*Si*–O> = 1.610 Å, *B* is occupied by boron, <*B*–O> = 1.465 Å, and Cs is [12]-coordinated, <Cs–O> = 3.301 Å. Tetrahedra form a $[BSi_2O_6]$ framework, the topology of which is identical to that of tetragonal pollucite, $CsAlSi_2O_6$. The [12]-coordinated Cs atoms occupy the channels along [111] formed by six-membered rings of tetrahedra. Kirchhoffite, $CsBSi_2O_6$, is a B analogue of the tetragonal modification of pollucite.

Keywords: kirchhoffite, new mineral species, silicate, Darai-Pioz massif, Tajikistan, electron and ion microprobe analysis, X-ray powder-diffraction pattern, pollucite-type minerals, crystal structure.

INTRODUCTION

Kirchhoffite occurs in the moraine of the Darai-Pioz glacier in the upper reaches of the Darai-Pioz river, along the Alaisky mountain ridge, Tien-Shan Mountains, northern Tajikistan. The new mineral species and its name were approved by the Commission on New Minerals, Nomenclature and Classification, International Mineralogical Association (IMA 2009–094). The mineral is named *kirchhoffite* after Gustav Robert Kirchhoff (1824–1887), the great German physicist and professor of physics at the universities of Breslau and Berlin in the second half of the 19th century, one of the founders of spectral analysis and codiscoverer (with Robert Bunsen) of cesium and rubidium. The holotype specimen has been deposited in the mineral collection of the Fersman Mineralogical Museum, Moscow, Russia, registration # 3923/1. We describe here this new borosilicate and report its crystal structure.

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Review of the Relevant Literature

Kirchhoffite, ideally $CsBSi_2O_6$, is an anhydrous boron analogue of tetragonal pollucite, (Cs,Na)($AlSi_2O_6$)•H_2O, ideally Cs($AlSi_2O_6$), a member of the analcime group. The crystal structures of the cubic and tetragonal modifications of pollucite were first solved by Náray-Szabó (1938) (Table 1). In cubic pollucite, the structural unit is a framework of [(Si,Al)O_4] tetrahedra. In the lower-symmetry modification, Si–Al order results in tetragonal symmetry of the framework. The interstitial Cs atoms occur in the channels formed by six-membered rings along [111]. In nature, pollucite usually has a cubic symmetry. A detailed discussion of the crystal structure of cubic pollucite was provided by Gatta *et al.* (2009a, 2009b, and references therein). The crystal structure of tetragonal pollucite was described in detail by Frank-Kamenetskaya *et al.* (1995) (Table 1). Crystal-structure refinements of tetragonal and monoclinic modifications of synthetic analogues of pollucite were reported by Yanase *et al.* (1997) and Kamiya *et al.* (2008), respectively (Table 1).

Provenance of the Samples

Kirchhoffite was found in rock samples from the Upper Dara-Pioz alkaline massif, collected in the moraine of the Darai-Pioz glacier, located in Garm district, central Tajikistan. The massif is situated near the watershed on the southern slope of the Alaisky mountain range (N 39°27', E 70°43'). In plan, the Darai-Pioz massif is equant and covers an area of ~16 km^2. The massif has a multiphase structure; the root is granite, and the central part of the massif is composed of aegirine quartz-bearing and quartz-free syenites. A small stock of cancrinite syenite occurs in the southwestern part of the massif. The massif contains a variety of granitic, alkaline granitic and syenitic pegmatites, various hydrothermal rocks (albitites, fenites) and carbonatites. Abundant and varied mineralization involving Cs, Li, B, Zr, REE, Ti, Ba is associated with the rocks of the massif.

In the Dara-Pioz massif, six Cs minerals have been described to date (excluding kirchhoffite): kupletskite-(Cs), telyushenkoite, sokolovaite, zeravshanite, senkevichite and mendeleevite-(Ce). The most complete description of the geology and mineralogy of the massif was given by Dusmatov (1968, 1971). Specific details of the mineralogy and geochemistry of the Darai-Pioz massif have been discussed in numerous publications (Ganzeev *et al.* 1969, Semenov & Dusmatov 1975, Efimov 1983, Belakovskiy 1991, Grew *et al.* 1993, and Reguir *et al.* 1999).

Kirchhoffite was found in a rock composed mainly of granular quartz with subordinate and variable amounts of polylithionite, pectolite, fluorite, sogdianite, stillwellite-(Ce), leucosphenite, turkestanite, reedmergnerite, pyrochlore, microcline, and kapitsaite-(Y). Kirchhoffite occurs in pale brown polymineralic aggregates that reach up to 10 cm across. Those aggregates (which occur in quartz) consist mainly of pectolite, with subordinate quartz, fluorite, sokolovaite, baratovite, aegirine, polylithionite, stillwellite-(Ce), neptunite, pekovite, senkevichite, and mendeleevite-(Ce). Kirchhoffite is generally intergrown with quartz and pectolite (Fig. 1).

Physical Properties

Kirchhoffite occurs as colorless equant grains 10 to 80 μm in diameter. It is transparent with a white streak and vitreous luster, and does not fluoresce under ultraviolet light. It is brittle with a conchoidal fracture, and no cleavage or parting was observed. The Mohs

TABLE 1. COMPARATIVE TABLE FOR KIRCHHOFFITE AND POLLUCITE

	Kirchhoffite	Pollucite	Pollucite sample II-3	Synthetic $CsAlSi_2O_6$	Pollucite sample M3	Synthetic (Cs,Na)$AlSi_2O_6$*
Empirical formula	$(Cs_{1.02}K_{0.01})_{\Sigma 1.03}$ $B_{0.96}Si_{2.02}O_6$	$CsAlSi_2O_6$	$Cs_{0.7\text{-}0.8}Na_{0.1}$ $Al_{0.8}Si_{2.2}O_6$ •(0.3-0.2)H_2O	–	$(Cs_{0.66}Rb_{0.02})_{\Sigma 0.68}$ $Na_{0.12}(Al_{0.90}Si_{2.12})_{\Sigma 3.02}O_6$ •0.25H_2O	$Cs_{0.70}Na_{0.15}$ $Al_{0.89}Si_{2.11}O_6$ •0.29H_2O
System	tetragonal	tetragonal	tetragonal	tetragonal	cubic	monoclinic
Space group	$I4_1/acd$	$I4_1/acd$	$I4_1/acd$	$I4_1/acd$	$Ia\bar{3}d$	$C2/c$
a (Å)	13.019(2)	13.74	13.677(2)	13.6337(4)	13.6927(3)	13.6788(7)
c	12.900(2)	13.74	13.691(2)	13.6986(6)		11.8476(7)
V (Å^3)	2186.5(1)	2593.34	2561.2	2546.27	2567.25	2560.2(2)
Z	16	16	16	16	16	16
D_{calc} (g/cm^3)	3.639	3.2	2.76	–	–	2.940
Reference	this work	(1)	(2)	(3)	(4)	(5)

* *b* = 19.3468(7) Å, β = 125.260(1)°. References: (1) Náray-Szabó (1938), (2) Frank-Kamenetskaya *et al.* (1995), (3) Yanase *et al.* (1997), (4) Gatta *et al.* (2009a), (5) Kamiya *et al.* (2008).

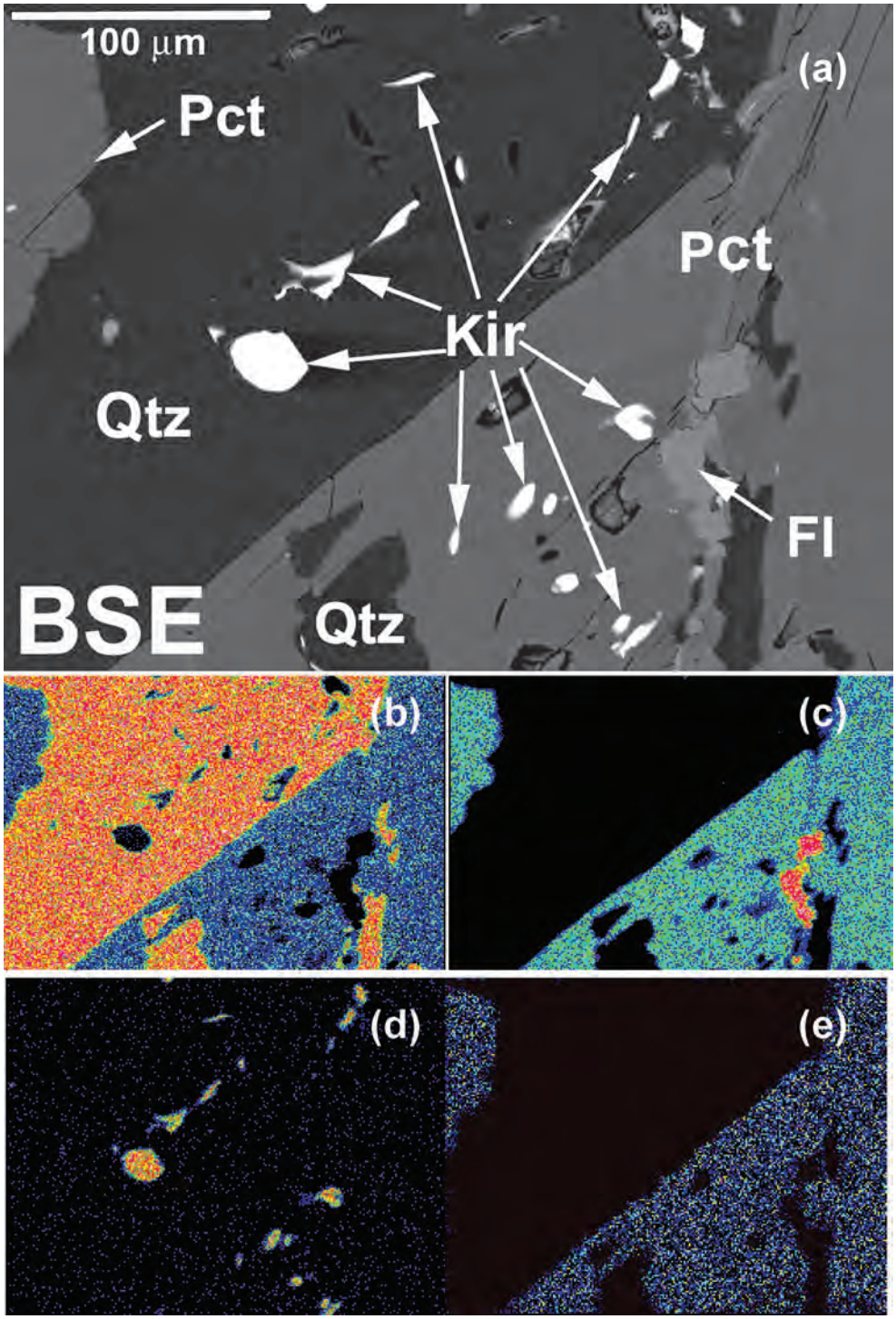

FIG. 1. Segregations of kirchhoffite (Kir) in quartz (Qtz) and pectolite (Pct), with subordinate fluorite (Fl): (a) a BSE (backscattered-electron) image, (b)–(e) characteristic X-ray maps for the following elements: (b) Si$K\alpha$, (c) Ca$K\alpha$, (d) Cs$L\alpha$, (e) Na$K\alpha$.

hardness is between 6 and 6½. The density, measured with Clerici solution, is 3.62(2) g/cm^3, in agreement with the calculated value of 3.639 g/cm^3. Kirchhoffite is uniaxial (+) with indices of refraction (λ = 590 nm) ω = 1.592 (2), ε = 1.600 (2).

Chemical Composition

Crystals were analyzed with a JCXA–50A electron microprobe operating in energy-dispersion mode with an accelerating voltage of 20 kV, a specimen current of 2 nA, and a beam diameter of 2 μm. The following standards were used: microcline USNM143966 (Si, K) and $CsHo(PO_3)_4$(Cs). The data were reduced and corrected by the PAP method of Pouchou & Pichoir (1985). The amount of H, B and Rb was measured with a Cameca SIMS 4f ion microprobe. The O^{2-} ions with an energy of 14.5 kV were used as a primary beam, with a spot size of 10–20 μm. The absolute concentration of each element was calculated from the ratio of the ion current for that element to that for $^{30}Si^+$ using calibration constants. Table 2 gives the chemical composition for five samples (each of which is the mean of ten determinations). The formula unit is based on six O atoms per formula unit (*pfu*). The empirical formula for kirchhoffite on the basis of six O atoms is $(Cs_{1.02}K_{0.01})_{\Sigma 1.03}B_{0.96}Si_{2.02}O_6$, ideally $CsBSi_2O_6$.

X-Ray Powder Diffraction

The powder-diffraction pattern of kirchhoffite (Table 3) was recorded with Mn-filtered Fe*K*α X-ray radiation and a Debye–Scherrer camera 114.6 mm in diameter. Quartz was used as an internal standard. The unit-cell parameters were refined by least squares, giving the following values: *a* 13.011(2), *b* 13.011(2), *c* 12.900(2) Å, *V* 2186.3(1) Å^3.

TABLE 2. CHEMICAL COMPOSITION* AND UNIT FORMULA OF KIRCHHOFFITE

Sample	1	2	3	4	5	Ave.
SiO_2 wt.%	40.97	39.65	40.35	40.76	40.64	40.47
B_2O_3**	11.27	11.27	11.27	11.27	11.27	11.27
K_2O	0.01	0.12	0.06	0.21	0.17	0.11
Cs_2O	47.88	48.63	48.40	47.41	48.48	48.16
Rb_2O**	0.09	0.09	0.09	0.09	0.09	0.09
Total	100.22	99.76	100.17	99.74	100.65	100.10
Si *apfu*	2.03	2.00	2.01	2.02	2.02	2.02
B	0.96	0.98	0.97	0.96	0.97	0.97
K	0.00	0.01	0.00	0.01	0.01	0.01
Cs	1.01	1.05	1.03	1.00	1.03	1.02
Rb	0.00	0.00	0.00	0.00	0.00	0.00

* Chemical composition determined by EMPA, analyst A.A. Agakhanov;
** determined by SIMS; S.G. Simakin, analyst.
The formula unit is calculated on the basis of six atoms of oxygen.

Crystal Structure

Data collection and structure refinement

Single-crystal X-ray data for kirchhoffite were collected with a Bruker AXS SMART APEX diffractometer with a CCD detector (Mo*K*α radiation). A total of 12700 reflections was measured out to 60° 2θ using 60 s per 0.2° frame. As there were hardly any observed reflections at high angles, we used a cut-off of 50° 2θ for structure refinement: $-15 \le h,k,l \le 15$. Unit-cell dimensions were determined by least-squares refinement of 6400 reflections with $I > 10\sigma I$, and are given in Table 4, together with other miscellaneous information on data collection and structure refinement. An absorption correction was done using the program SADABS (Sheldrick 2008). All calculations were done with the Bruker SHELXTL version 5.1 system of programs (Sheldrick 2008). The diffraction data indicate a tetragonal symmetry, and systematic absences in the single-crystal X-ray-diffraction data are consistent with the space group $I4_1/acd$. We observed only eight weak reflections ($1.05 \le F_o^2 \le 6.41$) that violate this symmetry. The crystal structure was refined in space group $I4_1/acd$ (origin choice 2) using atom coordinates for tetragonal pollucite of Náray-Szabó (1938), recorded by ICSD #15965. Scattering curves for neutral atoms were taken from the International Tables for Crystallography (Wilson 1992). The site occupancies for the *B*, *Si* and

TABLE 3. X-RAY POWDER-DIFFRACTION PATTERN FOR KIRCHHOFFITE*

I_{meas}	d_{meas} Å	I_{calc}	d_{calc} Å	*h*	*k*	*l*	I_{meas}	d_{meas} Å	I_{calc}	d_{calc} Å	*h*	*k*	*l*
32	5.32	24	5.307	1	2	1	13	1.453	11	1.454	4	8	0
2	4.54	2	4.580	0	2	2	2	1.444	5	1.446	0	4	8
82	3.48	79	3.469	1	3	2	9	1.399	6	1.403	1	9	2
100	3.26	100	3.253	0	4	0			6	1.398	1	7	6
2	3.08	2	3.077	0	0	4	6	1.336	8	1.337	3	7	6
5	2.921	4	2.909	2	4	0	3	1.326	7	1.327	4	8	4
67	2.770	18	2.771	3	3	2	3	1.290	7	1.289	7	7	2
		59	2.765	2	3	3	7	1.283	6	1.284	2	7	7
13h	2.544	4	2.545	1	4	3	14	1.239	10	1.240	1	10	3
21	2.373	19	2.374	1	5	2	4	1.230	5	1.232	1	3	10
41	2.294	35	2.294	0	4	4	2	1.211	2	1.213	1	7	8
34	2.109	12	2.110	3	5	2	6	1.196	4	1.197	3	10	3
		17	2.107	2	5	3	6	1.158	7	1.159	5	10	1
3	2.059	2	2.057	0	6	2	7	1.152	7	1.151	1	5	10
14	1.913	10	1.917	1	6	3			4	1.146	0	8	8
10	1.873	7	1.874	4	4	4	11	1.122	9	1.123	5	10	3
3	1.801	3	1.804	4	6	0			8	1.122	7	7	6
3	1.789	2	1.792	0	4	6	4	1.116	6	1.117	3	5	10
22	1.768	20	1.769	3	6	3	1	1.089	2	1.090	5	9	6
11	1.652	19	1.651	2	7	3	5	1.082	5	1.084	8	8	4
21	1.641	17	1.643	2	3	7			6	1.081	4	8	8
11	1.627	10	1.628	0	8	0	11	1.061	9	1.061	2	11	5
3	1.550	5	1.551	3	6	5	4	1.028	9	1.029	4	12	0
8	1.464	4	1.469	2	7	5	3	1.005	7	1.006	2	9	9
		6	1.466	2	5	7							

* A.A. Agakhanov, analyst.

Cs sites were refined with the scattering parameters of B, Si and Cs, and converged to 0.5, 1.0 and 0.487(4), respectively, confirming that the three cation sites are fully occupied. The refinement converged to an R_1 index of 3.1%. Final atom coordinates and anisotropic-displacement parameters are listed in Table 5, selected interatomic distances and framework angles are given in Table 6, and bond-valence values are given in Table 7. Observed and calculated structure-factors and a CIF file may be obtained from The Depository of Unpublished Data on the MAC website [document Kirchhoffite CM50_523].

Description of the structure

In the crystal structure of kirchhoffite, there are three cation sites (Table 5) coordinated by O atoms: the [12]-coordinated *Cs* site is occupied by Cs, with <Cs–O> = 3.301 Å; the [4]-coordinated *B* and *Si* sites are occupied by B and Si, with <B–O> = 1.465 and <Si–O> = 1.610 Å, respectively (Table 6). Three anion sites, O(1–3), are occupied by O atoms, with bond-valence sums at anions from 2.06 to 2.19 *vu* (*valence units*) (Table 7). In the structure of kirchhoffite, the main structural unit is a framework of SiO_4 and BO_4 tetrahedra (Fig. 2a) identical to that in tetragonal pollucite (Náray-Szabó 1938, Frank-Kamenetskaya *et al.* 1995). In the framework, there are two secondary building units: four-membered rings of Si tetrahedra and six-membered rings of four Si tetrahedra and two B tetrahedra (Figs. 2a, b). Convoluted eight-membered rings of Si and B tetrahedra provide a system of irregular channels within the framework (Figs. 2a, b). The interstitial Cs atoms occur in the channel formed by six-membered rings along [111] (Fig. 2c).

TABLE 4. DATA COLLECTION AND STRUCTURE-REFINEMENT DETAILS FOR KIRCHHOFFITE

Unit-cell parameters *a*, *c* (Å)	13.019(2), 12.899(3)
Unit-cell volume *V* (Å^3)	2186.5(1)
Space group	$I4_1/acd$
Z	16
Absorption coefficient (mm^{-1})	7.32
F(000)	2197.9
$D_{calc.}$ (g/cm^3)	3.639
Crystal size (mm)	0.025 × 0.040 × 0.060
Radiation/filter	Mo*Kα*/graphite
Upper 2θ (°) for refinement	50.00
R(int) (%)	1.69
Reflections collected	12700
Independent reflections, $F_o > 4\sigma\|F\|$	489, 487
Refinement method	Full-matrix least squares on F^2, fixed weights proportional to $1/\sigma F_o^2$
Final $R_{(obs)}$ (%)	
R_1 [$F_o > 4\sigma\|F\|$]	3.07
R (all data)	3.12
wR_2 (all data)	5.77
Goodness of fit on F^2	1.330

SUMMARY

(1) In kirchhoffite, by analogy with pollucite, we conclude that Si–B order over the tetrahedrally coordinated sites results in the tetragonal symmetry of the framework and the overall structure.

(2) The radius of [4]-coordinated B^{3+} [r = 0.11 Å, Shannon (1976)] is smaller than that of [4]-coordinated Al^{3+} (r = 0.39 Å), and this difference results in smaller unit-cell parameters and volume in kirchhoffite compared to pollucite (Table 1).

(3) In the framework of tetrahedra, it is the smaller size of [4]-coordinated B^{3+} relative to [4]-coordinated Al^{3+} and Si^{4+} (r = 0.26 Å) that causes an ordered B–Si arrangement and a tetragonal symmetry rather than a disordered (Si,B) arrangement expected with cubic symmetry.

ACKNOWLEDGEMENTS

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TABLE 5. FINAL COORDINATES AND ANISOTROPIC DISPLACEMENT PARAMETERS (Å^2) OF ATOMS IN KIRCHHOFFITE

ATOM	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Cs	0.12323(3)	0.37323(3)	0.125	0.0201(3)	0.0201(3)	0.0176(3)	-0.00231(17)	0.00231(17)	-0.0009(2)	0.0193(2)
Si	0.09119(12)	0.11581(12)	0.33656(12)	0.0096(9)	0.0073(9)	0.0094(8)	-0.0012(6)	0.0002(6)	0.0005(6)	0.0088(6)
B	0.3362(5)	0.5862(5)	0.125	0.010(3)	0.010(3)	0.004(4)	-0.003(3)	0.003(3)	-0.005(4)	0.0080(18)
O(1)	0.1296(3)	0.1468(3)	0.0363(3)	0.020(2)	0.015(2)	0.015(2)	0.0034(17)	-0.0009(18)	0.0016(18)	0.0164(11)
O(2)	0.1382(3)	0.2191(3)	0.3900(3)	0.023(2)	0.010(2)	0.021(2)	-0.0054(18)	-0.002(2)	-0.0008(17)	0.0181(11)
O(3)	0.2740(3)	0.1018(3)	0.1448(3)	0.011(2)	0.021(2)	0.013(2)	0.0029(18)	-0.0017(17)	-0.0045(17)	0.0151(11)

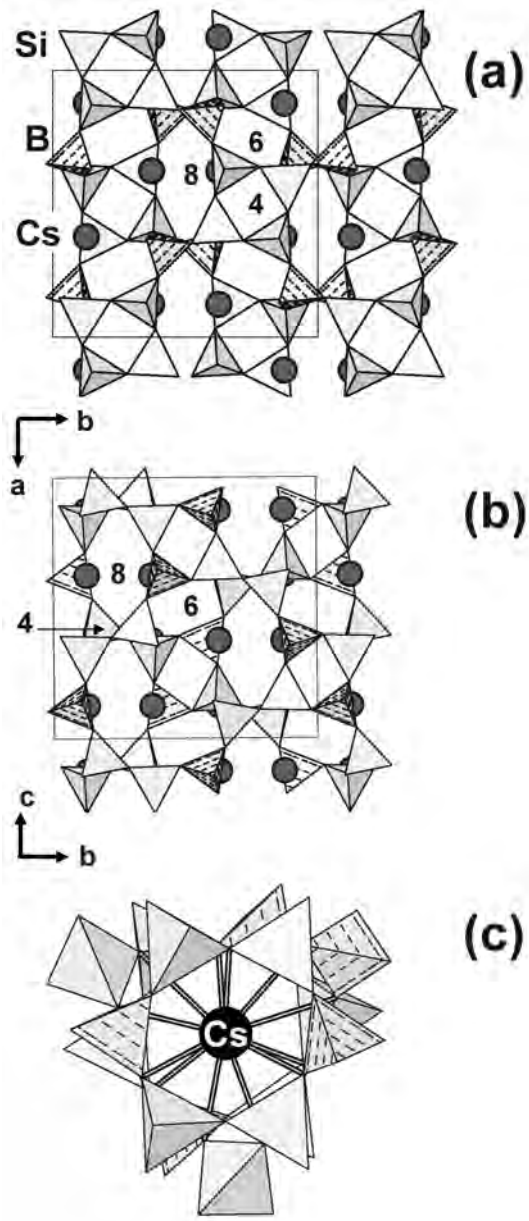

FIG. 2. The crystal structure of kirchhoffite: (a) general view of the structure projected onto (001); (b) general view of the structure projected onto (100); (c) [12]-coordinated Cs atom in a channel of six-membered-rings along [111]. The Si and B tetrahedra are white and striped, Cs atoms are shown as black spheres, four-membered, six-membered and eight-membered rings are labeled 4, 6 and 8, respectively.

TABLE 6. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN KIRCHHOFFITE

Si-O(1)$_a$	1.594(4)		B-O(1)$_d$	1.460(7)	×2
Si-O(3)$_b$	1.596(4)		B-O(3)$_d$	1.471(6)	×2
Si-O(2)$_c$	1.618(4)		<B-O>	1.465	
Si-O(2)	1.631(4)				
<Si-O>	1.610				
Cs-O(1)	3.163(4)	×2	B$_h$-O(1)-Si$_a$	145.2(4)	
Cs-O(2)$_e$	3.267(4)	×2	Si-O(2)-Si$_e$	151.3(3)	
Cs-O(3)$_d$	3.272(4)	×2	B$_h$-O(3)-Si$_i$	135.5(3)	
Cs-O(3)$_f$	3.273(4)	×2			
Cs-O(2)$_f$	3.337(4)	×2			
Cs-O(1)$_g$	3.494(4)	×2			
<Cs-O>	3.301				

a: $-y + ¼$, $-x + ¼$, $-z + ¼$; b: $-y + ¼$, $x - ¼$, $z + ¼$; c: $y - ¼$, $-x + ¼$, $-z + ¾$; d: $y + ¼$, $-x + ¾$, $-z + ¼$; e: $-y + ¼$, $x + ¼$, $-z + ¾$; f: $-x + ½$, $-y + ½$, $-z + ½$; g: $-x$, $-y + ½$, z; h: $-y + ¾$, $x - ¼$, $-z + ¼$.

TABLE 7. BOND-VALENCE* (*vu*) VALUES FOR KIRCHHOFFITE

Atom	Si	B	Cs	Σ
O(1)	1.08	0.79 ×2↓	0.13 ×2↓ 0.07 ×2↓	2.07
O(2)	1.01 0.98		0.11 ×2↓ 0.09 ×2↓	2.19
O(3)	1.07	0.77 ×2↓	0.11 ×2↓ 0.11 ×2↓	2.06
Total	4.14	3.12	1.24	
Charge	4.00	3.00	1.00	

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

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