# FROM STRUCTURE TOPOLOGY TO CHEMICAL COMPOSITION. XIX. TITANIUM SILICATES: REVISION OF THE CRYSTAL STRUCTURE AND CHEMICAL FORMULA OF BAFERTISITE, Ba<sub>2</sub>Fe<sup>2+</sup><sub>4</sub>Ti<sub>2</sub>(Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub>O<sub>2</sub>(OH)<sub>2</sub>F<sub>2</sub>, A GROUP-II TS-BLOCK MINERAL

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# Abstract

The crystal structure and chemical formula of bafertisite,  $Ba_2Fe^{2+}_4Ti_2(Si_2O_7)_2O_2(OH)_2F_2$ , have been revised. Three samples of bafertisite were studied using electron-microprobe analysis, Mössbauer spectroscopy, IR and Raman spectroscopy, and single-crystal X-ray diffraction. These samples are from (1) the Bayan Obo REE deposit, Inner Mongolia, China (holotype); (2) the Gremyakha-Vyrmes alkaline complex, Kola Peninsula, Russia; and (3) the Darai-Pioz alkaline massif, Tajikistan. Bafertisite is a TS-block mineral of Group II, Ti = 2 apfu (atoms per formula unit) per  $(Si_2O_7)_2$  (Sokolova 2006). Bafertisite is triclinic, CĪ, a 10.677(6), b 13.767(7), c 11.737(5) Å, α 90.12(1), β 112.28(4), γ 90.02(1)°, V 1596(3) Å<sup>3</sup> (unit-cell parameters are for bafertisite from Kola, sample 2). Chemical analysis was done by electron microprobe, the H<sub>2</sub>O content was calculated from the crystal-structure solution and refinement, and the occurrence of Fe<sup>2+</sup> and lack of Fe<sup>3+</sup> were confirmed by Mössbauer spectroscopy. The empirical formulae were calculated on the basis of 20 (O+F) anions, with (OH+F) = 4 apfu, and they are of the form  $A^{P}_{2}M^{O}_{4}M^{H}_{2}(Si_{2}O_{7})_{2}(X^{O})_{4}(X^{P})_{2}, Z = 4: (1) (Ba_{1.89}K_{0.03})_{\Sigma_{1}.92}(Fe^{2+}_{3.33}Mn_{0.47}Mg_{0.11})_{\Sigma_{3}.91}(Ti_{1.86}Nb_{0.07}Zr_{0.02}Mg_{0.05})_{\Sigma_{2}}$  $(Si_{2.05}O_7)_2O_2[(OH)_{1.82}F_{0.18}]_{\Sigma 2}F_2; (2) (Ba_{1.82}Sr_{0.02}X_{0.02})_{\Sigma 1.86}(Fe^{2+}_{3.24}Mn_{0.57}Al_{0.06}Mg_{0.03}Ca_{0.01}Zr_{0.01}Zn_{0.01}Na_{0.02})_{\Sigma 3.95}$  $(Ti_{1.96}Nb_{0.03}Zr_{0.01})_{\Sigma 2}(Si_{2.05}O_7)_2O_2[(OH)_{1.59}F_{0.41}]_{\Sigma 2}F_2; \text{ and } (3) \quad (Ba_{1.90}K_{0.02})_{\Sigma 1.92}(Fe^{2+}_{2.23}Mn_{1.61}Mg_{0.02}Zr_{0.04}Zn_{0.03})_{\Sigma 3.93})_{\Sigma 3.93}$  $(Ti_{1.90}Nb_{0.09}Zr_{0.01})_{\Sigma_2}(Si_{2.03}O_7)_2O_2[(OH)_{1.75}F_{0.25}]_{\Sigma_2}F_2. The crystal structures of (1), (2), and (3) were solved and refined from the solved for the solved$ twinned crystals to  $R_1 = 2.90, 2.46, \text{ and } 2.74\%$  on the basis of 4538, 4685, and 4692 unique reflections ( $|F| > 4\sigma|F|$ ) and can be described as a combination of a TS (Titanium Silicate) block and an I (Intermediate) block. The TS block consists of HOH sheets (H-heteropolyhedral, O-octahedral). The topology of the TS block is as in Group II of the Ti disilicates: Ti + Nb = 2 apfuper (Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub> (as defined by Sokolova 2006). Here we report structure-refinement results for bafertisite from Kola, sample (2), with the lowest value of  $R_1 = 2.46\%$ . In the O sheet, five <sup>[6]</sup> $M^{O}$  sites are occupied mainly by Fe<sup>2+</sup>, less Mn, and minor Mg, Al, Zr, Zn, and Ca, with  $\langle M^{O}-\phi \rangle = 2.179$  Å ( $\phi = O,OH$ ), and they ideally give Fe<sup>2+</sup><sub>4</sub> *apfu*. In the H sheet, two <sup>[6]</sup>M<sup>H</sup> sites are occupied mainly by Ti, with  $\langle M^{H}-\phi \rangle = 1.963$  Å ( $\phi = O,F$ ), and they ideally give Fe<sup>2+</sup><sub>4</sub> *apfu*; four <sup>[4]</sup>Si sites are occupied by Si, with  $\langle Si-O \rangle = 1.626$  Å. The M<sup>H</sup> octahedra and Si<sub>2</sub>O<sub>7</sub> groups constitute the H sheet. The two <sup>[12]</sup>Ba-dominant A<sup>P</sup>(1,2) sites, with  $\langle A^{P}-\phi \rangle = 2.979$  Å ( $\phi = O,F$ ), ideally give Ba<sub>2</sub> *apfu*. Two X<sup>O</sup><sub>M</sub>(1,2) and two X<sup>O</sup><sub>A</sub>(1,2) sites are occupied by O atoms and OH groups with minor F, respectively, ideally giving  $(X^{O})_{4} = (X^{O}_{M})_{2} + (X^{O}_{A})_{2} = O_{2}(OH)_{2} pfu$ . Two  $X^{P}_{M}(1,2)$  sites are occupied by F, giving F<sub>2</sub> apfu. TS blocks link via a layer of Ba atoms which constitute the I block. Simplified and endmember formulae of bafertisite are  $Ba_2(Fe^{2+},Mn)_4Ti_2(Si_2O_7)_2O_2(OH,F)_2F_2$  and  $Ba_2Fe^{2+}_4Ti_2(Si_2O_7)_2O_2(OH)_2F_2$ , Z = 4.

*Keywords*: bafertisite, holotype, electron microprobe, Mössbauer spectroscopy, IR and Raman spectroscopy, single-crystal X-ray diffraction, crystal structure, chemical formula, TS block, Group II.

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## INTRODUCTION

Bafertisite, Ba<sub>2</sub>Fe<sup>2+</sup><sub>4</sub>Ti<sub>2</sub>(Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub>O<sub>2</sub>(OH)<sub>2</sub>F<sub>2</sub>, is a TS-block mineral of Group II where Ti (+ Nb) = 2*apfu* (atoms per formula unit) per  $(Si_2O_7)_2$  (Sokolova 2006). The TS (Titanium Silicate) block is the main structural unit in 40 minerals: 34 are listed in Sokolova & Cámara (2013), and information on six minerals, kolskyite, emmerichite, saamite, betalomonosovite, bobshannonite, and fogoite-(Y) can be found in Cámara et al. (2013), Aksenov et al. (2014), Cámara et al. (2014), Sokolova et al. (2015a), Sokolova et al. (2015b), and Cámara et al. (2016a), respectively. In the fast-growing supergroup of TS-block minerals (cf. 24 TS-block minerals, Sokolova 2006), the TS block consists of a central trioctahedral (O) sheet and two adjacent heteropolyhedral (H) sheets of [5-7]-coordinated polyhedra and Si<sub>2</sub>O<sub>7</sub> groups. The TS block is characterized by a planar cell based on minimal lengths of translational vectors,  $t_1 \sim 5.5$  and  $t_2 \sim 7$  Å, and  $t_1 \wedge t_2 \approx 90^\circ$ . The general formula of the TS block is  $A^P_2 B^P_2 M^H_2 M^O_4 (Si_2 O_7)_2 X_{4+n}$ , where  $M^H_2$  and  $M^O_4$ = cations of the H and O sheets;  $M^H$  = Ti, Nb, Zr, Y, Mn, Ca + REE, Ca;  $M^{O} = Ti$ , Zr, Nb,  $Fe^{2+}$ ,  $Fe^{3+}$ , Mg, Mn, Ca, Na;  $A^{P}$  and  $B^{P}$  = cations at the peripheral (P) sites = Na, Ca + REE, Ca, Ba, Sr, K; X = anions, O, OH, F, and H<sub>2</sub>O groups;  $X_{4+n} = X_{4}^{O} + X_{n}^{P}$ , n = 0, 1, 11.5, 2, 4 (Sokolova & Cámara 2013). Sokolova (2006) developed general structural principles for the TSblock minerals. There are three topologically distinct TS blocks based on three types of linkage of H and O sheets. In the crystal structures of TS-block minerals, TS blocks either link directly or alternate with intermediate (I) blocks. The I block consists of alkali and alkaline-earth cations, oxyanions  $(PO_4)$ ,  $(SO_4)$ , and (CO<sub>3</sub>), and H<sub>2</sub>O groups. Sokolova (2006) divided TS-block structures into four Groups, based on the topology and stereochemistry of the TS block. Each group of structures has a different linkage, content, and stereochemistry of Ti (+ Nb +  $Zr + Fe^{3+} + Mg + Mn$ ) per  $(Si_2O_7)_2$ . In Group I, Ti (+Nb + Zr) = 1 apfu; in Group II, Ti (+ Nb) = 2 apfu; in Group III, Ti (+ Nb + $Fe^{3+} + Mg = 3 apfu$ ; in Group IV, Ti (+Mg + Mn) = 4apfu. In a TS-block structure, four types of self-linkage between adjacent TS blocks occur. Sokolova & Cámara (2013) introduced the concept of basic and derivative structures for TS-block minerals. A basic structure has the following four characteristics: (1) there is only one type of TS block; (2) the two H sheets of the TS block are identical; (3) there is only one type of I block or it is absent; (4) there is only one type of self-linkage of TS blocks. Basic structures obey the general structural principles of Sokolova (2006). A derivative structure has one or more of the three following characteristics: (1) there is more than one type of TS block; (2) there is more than one type of **I** block; (3) there is more than one type of self-linkage of TS blocks. A *derivative structure* is related to two or more *basic structures* of the same Group; it can be derived by adding these structures via sharing the central O sheet of the TS blocks of adjacent structural fragments that represent *basic structures*. There are 35 basic TS-block and five derivative TS-block structures. In the crystal structure of bafertisite, the TS block has the stereochemistry and topology of Group II where Ti (+ Nb) = 2 apfu. Bafertisite is the Fe<sup>2+</sup>-analogue of hejtmanite and is related to cámaraite (Table 1).

Bafertisite from the Bayan Obo REE deposit, Inner Mongolia, China, was described as a new mineral by Semenov & Zhang Peishan (1959). Guan *et al.* (1963) solved the crystal structure of bafertisite in space group *Cm*, outlined details of its general topology, and gave the chemical formula as follows: BaFe<sub>2</sub>TiO [Si<sub>2</sub>O<sub>7</sub>](OH)<sub>2</sub>, Z = 8. However, they reported very short Si–O bond-lengths, *e.g.*, 1.43 Å (the same applies for all bafertisite structure refinements, see PREVIOUS WORK below). Semenov & Zhang Peishan (1959) did not report any F in bafertisite, whereas chemical analyses of bafertisite from all other localities give F ~2 *apfu* per (Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub>.

Given our continuous interest in TS-block minerals, we felt strongly that the chemical composition and crystal structure of bafertisite needed to be revised. We studied three samples of bafertisite by electronmicroprobe analysis, Mössbauer spectroscopy, IR and Raman spectroscopy, and single-crystal X-ray diffraction. These samples are from (1) the Bayan Obo REE deposit, Inner Mongolia, China (holotype, sample 61513, Fersman Mineralogical Museum, Moscow, Russia); (2) the Gremyakha-Vyrmes alkaline complex, Kola Peninsula, Russia (sample from the mineral collection of Renato and Adriana Pagano, Milan, Italy); and (3) the Darai-Pioz alkaline massif, Tajikistan (sample M49249\_2, Royal Ontario Museum, Toronto, Canada). Based on our work, the revised chemical formula of bafertisite, Ba<sub>2</sub>Fe<sup>2+</sup><sub>4</sub>Ti<sub>2</sub> (Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub>O<sub>2</sub>(OH)<sub>2</sub>F<sub>2</sub>, and its revised crystallographic symmetry, triclinic, and the space group, C1, have been accepted by the CNMNC (Commission on New Minerals, Nomenclature, and Classification) (nomenclature voting proposal 15-I, 2015). The current paper reports the revised crystal structure and chemical formula of bafertisite.

# PREVIOUS WORK

Semenov & Zhang Peishan (1959) described bafertisite, BaFe<sub>2</sub>TiSi<sub>2</sub>O<sub>9</sub>, Z = 2, as a new mineral from the Bayan Obo REE deposit, Inner Mongolia, China. They reported  $D_{\text{meas.}} = 4.25-3.96 \text{ g/cm}^3$  and the

Mineral				Ш.	ormula					<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	ů.		
Structure type**	$A^{P}_{1-i}$	2 B <sup>P</sup> 0-2	$M^{H}_{2}$	$M^{O}_{4}$	(Si <sub>2</sub> 0 <sub>7</sub> ) <sub>2</sub>		(X <sup>O</sup> M)2	(X <sup>O</sup> A)2	$(X^{P}_{M})_{0-2}$	α (₀)	β (°)	(₀) λ	gr.	Ν	Ref.
bafertisite	Ba <sub>2</sub>		Ti <sub>2</sub>	Fe <sup>2+</sup> 4	(Si <sub>2</sub> 0 <sub>7</sub> ) <sub>2</sub>		02	(OH) <sub>2</sub>	$F_2$	10.677	13.767	11.737	<u>1</u>	4	(I
B2(GII)										90.11	112.28	90.02			
hejtmanite	$Ba_2$		$TI_2$	$Mn_4$	(Si <sub>2</sub> O <sub>7</sub> ) <sub>2</sub>		02	(OH) <sub>2</sub>	$F_2$	10.716	13.795	11.778	<u>5</u>	4	(2)
B2(GII)										90.07	112.24	90.03			
cámaraite <sup>1</sup>	Ba <sub>3</sub>	Na	Ti <sub>4</sub>	$Fe^{2+}_{8}$	(Si <sub>2</sub> O <sub>7</sub> ) <sub>4</sub>		04	(OH)4	F <sub>3</sub>	10.6965	13.7861	21.478	5	4	(3)
D1(GII)										99.345	92.315	89.993			
jinshajiangite	Ba	Na	$TI_2$	$Fe^{2+}_4$	$(Si_2O_7)_2$		03	(OH) <sub>2</sub>	ш	10.7059	13.7992	20.7603	5	ω	(4)
B1(GII)										90.008	94.972	89.984			
perraultite	Ba	Na	$TI_2$	Mn <sub>4</sub>	$(Si_2O_7)_2$		03	(OH) <sub>2</sub>	ш	10.731	13.841	20.845	С С	ω	(2)
B1(GII)										06	95.06	06			
bobshannonite <sup>1</sup>	Ba K	Na2	(Nb,Ti)4	(Mn,Na) <sub>8</sub>	$(Si_2O_7)_4$		04	(OH)4	(O,F) <sub>2</sub>	10.839	13.912	20.98	5	4	(9)
B1(GII)										89.99	95.02	89.998			
yoshimuraite <sup>2</sup>	Ba <sub>2</sub>	$Ba_2$	<sup>[5]</sup> Ti <sub>2</sub>	$Mn_4$	(Si <sub>2</sub> 0 <sub>7</sub> ) <sub>2</sub>	(PO <sub>4</sub> ) <sub>2</sub>	02	(OH) <sub>2</sub>		5.386	6.999	14.748	P	2	(
B3(GII)										95.50	93.62	89.98			
bussenite <sup>3</sup>	(Na⊡)₂ Ba₂	$Ba_2$	$Ti_2$	(M <sup>2+</sup> Na) <sub>2</sub>	$(Si_2O_7)_2$	(CO <sub>3</sub> )2	02	(OH) <sub>2</sub>	(H <sub>2</sub> O) <sub>2</sub>	<sup>2</sup> 5.399	7.016	16.254	P.	2	(8)
B4(GII)										102.44	93.18	90.10			
* The general sti	uctural formula	of the T	S-block is	A <sup>P</sup> <sub>2</sub> B <sup>P</sup> <sub>2</sub> M <sup>H</sup> <sub>2</sub> N	1 <sup>0</sup> 4(Si <sub>2</sub> O <sub>7</sub> )2	X <sub>4+n</sub> , who	ere M <sup>H</sup> 2	and M <sup>o</sup>	$_{4} = cations$	of the H and (	) sheets; A	<sup>P</sup> and B <sup>P</sup> =	= catio	ns ai	the
peripheral (P) sit	es; X = anions;	$X_{4+n} = X$	$V_4 + X_n$ , n	=0, 1, 1.5, 2	, 4 (Sokolo	va & Cám	ara 201:	3). X <sup>4</sup> =	$= (X_{M})_{2} + (X_{M})_{2}$	$(A)_2$ : $X^{O}_M = a$	nions at con	nmon verti	ces of	3MC	and
M <sup>rr</sup> polyneara an Mock The stoich	d X <sup>oren</sup> a anions iometry of the o	at comr	non vertice: of the TS-h	ot טוט anc וההג M <sup>H</sup> ,M <sup>O</sup>	A' polyne, ג'נ <b>כו₀D</b> , א'	dra (wner o , is inva	e A' – A' riant in g	A < 3 A	$(); X'_{M} = aple$	cal anions or r in hold) In Gr	1'' cations a	it the perip אל B <sup>P</sup> catio	nery o ns nlı	f the	ה - כ
	10111041 y <1 41.4 v	- 22 2 2 2	2)->======		4/() /Zi / /Zi / /H	4, 10, 11, 4					S C S An		2	2	(4)Z

\*\* Bn(GII) and Dn(GII) denote B for basic and D for derivative structures of Group II (Sokolova & Cámara 2013). (in yoshimuraite) and (Na□)<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub>F<sub>2</sub> (in bussenite) constitute the I block.

For yoshimuraite and bussenite, ideal structural formulae are from Sokolova (2006). Surkhobite (Rastsvetaeva et al. 2008) is not listed here as there are problems with its crystal structure.

<sup>1</sup> The formulae for cámaraite and bobshannonite are per double minimal cell based on  $2t_1$  and  $2t_2$  translations  $[(S_{i2}O_{7})_4]$ ;

 $^2$  There are misprints in McDonald *et al.* (2000):  $\alpha = 89.98, \ \gamma = 95.50^\circ;$ 

<sup>3</sup>  $M^{2+} = Fe^{2+}$ , Mn;

References (the most recent reference on the structure): (1) this work, bafertisite from Kola; (2) Sokolova *et al.* (2016); (3) Cámara *et al.* (2009); (4) Cámara *et al.* (2016b); (5) Yamnova *et al.* (1998); (6) Sokolova *et al.* (2015b); (7) McDonald *et al.* (2000); (8) Zhou *et al.* (2002).

presence of H<sub>2</sub>O and stated that the optical properties of bafertisite indicate monoclinic symmetry (although in the paper, the symmetry was given as orthorhombic, a 7.55, b 10.98, c 5.36 Å). The crystal structure of bafertisite from the Bayan Obo deposit was determined using diffraction data from Weissenberg films by (1) Guan et al. (1963) and (2) Peng Zhizhong & Shen Jinchuan (1963): (1) monoclinic, space group *Cm*, *a* 10.60, *b* 13.64, *c* 12.47 Å,  $\beta$  119.5°,  $R_{0kl,h0l,hkl} =$ 15.3, 16.6, and 18.5%, respectively; (2) monoclinic, space group  $P2_1/m$ , a 10.98, b 6.80, c 5.36 Å,  $\beta$  94°, R = 26%. No atom coordinates were given in (2). Guan et al. (1963) described the main structural unit in the bafertisite structure as a block of three sheets: the central sheet of Fe<sup>2+</sup> octahedra and two adjacent sheets composed of Si<sub>2</sub>O<sub>7</sub> groups and Ti octahedra. They described linkage of those blocks via a layer of Ba atoms. Based on the structure-refinement results, Guan et al. (1963) and Peng Zhizhong & Shen Jinchuan (1963) gave the chemical formula of bafertisite as follows: BaFe<sub>2</sub>Ti[Si<sub>2</sub>O<sub>7</sub>]O(OH)<sub>2</sub>, Z = 8. However, both structure refinements reported very short Si-O bondlengths, e.g., (1) 1.43 Å and (2) 1.23 Å, indicating problems with the crystallographic symmetry used for the structure refinements.

Yakovlevskaya & Mineev (1965) studied the optical properties of bafertisite from the Verkhnee Espe deposit, Kazakhstan, and concluded that all of the crystals are twinned. Vrána et al. (1992) described hejtmanite, a manganese-dominant analogue of bafertisite: monoclinic, diffraction symbol C\*/\*, a 10.698, b 13.768, c 11.748 Å,  $\beta$  112.27°, Z = 8, with simplified and endmember formulae Ba(Mn,Fe)<sub>2</sub>TiO(Si<sub>2</sub>O<sub>7</sub>)  $(OH,F)_2$  and  $BaMn_2TiO(Si_2O_7)(OH,F)_2$  (Table 1). Vrána et al. (1992) compared the chemical compositions of heitmanite, holotype bafertisite (Semenov & Zhang Peishan 1959), and bafertisite from Kazakhstan (Yakovlevskava & Mineev 1965), Jiangsu province, China (Zhang et al. 1982), and the Burpala massif, northern Baikal, Russia (Ganzeev et al. 1971): the heitmanite and all bafertisite samples contain F  $\sim$ 1 apfu per Si<sub>2</sub>O<sub>7</sub>, except for the holotype sample of bafertisite (Semenov & Zhang Peishan 1959). There has been more X-ray diffraction work on bafertisite. Yang et al. (1999) used powder X-ray diffraction to study bafertisite from two localities in China: the original Bayan Obo locality in Inner Mongolia, and a locality in Jiangsu province. They confirmed the monoclinic unit-cell, space group Cm (in accordance with Guan et al. 1963) and ruled out the monoclinic space group  $P2_1/m$  reported by Peng Zhizhong & Shen Jinchuan (1963). Li et al. (2011) refined a monoclinic superstructure of bafertisite from single-crystal X-ray data (a 10.6502, b 13.7233, c 21.6897 Å, β 94.698°, space group Cm, R = 6.3%) and reported a monoclinic subcell (space group  $P2_1/m$ , a 5.3249, b 6.8669, c 10.8709 Å,  $\beta$  94.740°). Li *et al.* (2011) did not mention any twinning or intergrowth (which is very unlikely not to occur) and their models (again) have short Si–O bond-lengths, *e.g.*, 1.546 Å, which tells us that the crystallographic symmetries used for those structure models are not correct. Sokolova (2006) and Sokolova & Cámara (2013) considered bafertisite a TS-block mineral of Group II (see above).

We conclude that two issues need to be addressed: Crystal structure of bafertisite—All structure-refinement results give very short Si–O bond-lengths in the crystal structure of bafertisite, *e.g.*, 1.43, 1.23, and 1.546 Å, indicating that both established crystallographic symmetries, space group *Cm* and space group  $P2_1/m$ , are not correct. The problems with the crystal structure of bafertisite arise from the poor quality of its crystals, which is related to extensive twinning and intergrowth. Bafertisite crystals often form intergrowths with related minerals (see HRTEM image of an intergrowth of bafertisite and cámaraite in Fig. 1).

Chemical composition of bafertisite—It is very unlikely that bafertisite (holotype sample) does not have F, whereas all other bafertisites and hejtmanite, a Mn-analogue of bafertisite, do have F.

# MÖSSBAUER SPECTROSCOPY

Mössbauer spectroscopy was done in transmission geometry at room temperature using a <sup>57</sup>Co point source. The Mössbauer spectrum of bafertisite from Kola (sample 2) (Fig. 2a) was collected from several crystal fragments stuck to a thin glass slide that was mounted on a Pb disk with a  $\sim$ 300 µm aperture. The spectrum shows an asymmetric doublet located at  $\sim 0.1$  and 2.1 mm/s arising from the presence of Fe<sup>2+</sup>. The asymmetry in the spectrum is due to preferred orientation and the overlap of the two Fe<sup>2+</sup> components (see below) and hence the ratio of the spectral areas of the low-velocity peak to the high-velocity peak was allowed to vary during spectrum fitting. The spectrum was fitted using a Voigt-based quadrupolesplitting-distribution (QSD) method to a model having only one generalized Fe<sup>2+</sup> QSD site with two Gaussian components. The  $Fe^{2+}$  QSD profile is shown in Figure 2b. The refined parameters for the center shift (CS) relative to  $\alpha$ -Fe at room temperature, quadrupole splitting (QS), and relative area (A) are as follows: CS = 1.13 mm/s, QS = 1.99 mm/s, and A = 88% for component (1); CS = 1.14 mm/s, QS = 2.46 mm/s, and A = 12% for component (2). The two components, both assigned to Fe<sup>2+</sup> in the O sheet, have CS values that are characteristic of high-spin Fe<sup>2+</sup> in octahedral coordination. Our Mössbauer results are in agreement with those reported for bafertisite from Jiansu, China,



FIG. 1. High-resolution TEM image of cámaraite (Cam) slices in a bafertisite (Baf) matrix. The zone axis is [110]. The upper right inset shows an SAED (selected area electron diffraction) image of bafertisite (after Cámara *et al.* 2009).



Fig. 2. Mössbauer spectrum of bafertisite from Kola (a) and  $Fe^{2+}$  QSD profile (b).



FIG. 3. FTIR spectrum of bafertisite from Kola.

where two  $Fe^{2+}$  doublets having QS values of 2.34 and 1.89 mm/s were used to fit its Mössbauer spectrum, and no  $Fe^{3+}$  was detected (Wu *et al.* 1982).

# FTIR AND RAMAN SPECTROSCOPY

Both FTIR and Raman spectroscopy measurements were done using the same crystal of bafertisite from Kola (sample 2) used for the collection of the X-ray diffraction data.

# FTIR spectroscopy

The single-crystal FTIR spectrum of bafertisite (Fig. 3) was collected using a Hyperion 2000 IR microscope equipped with a liquid-nitrogen-cooled MCT detector. Data over the range 4000–650  $\text{cm}^{-1}$ were obtained by averaging 100 scans with a resolution of 4 cm<sup>-1</sup>. In the OH-stretching region  $(4000-3000 \text{ cm}^{-1})$ , there are two sharp peaks at 3639 and 3588  $\text{cm}^{-1}$  (Fig. 3) that are attributed to the presence of OH groups in the structure of bafertisite, in accord with structure refinement and previous IR work on bafertisite from Jiansu, China (Zhang et al. 1982). At low frequency, two strong absorption bands were observed at 1025 and 930  $\text{cm}^{-1}$  (with a shoulder at  $\sim$ 865 cm<sup>-1</sup>), that are due to Si–O stretches. The peaks at 725 and 688 cm<sup>-1</sup> may be assigned to stretching vibrations of Si-O-Si bridges and/or M-O-H bends.

#### Raman spectroscopy

The Raman spectrum of bafertisite (100–1200 cm<sup>-1</sup>, Fig. 4) was acquired with a HORIBA Jobin Yvon-LabRAM ARAMIS integrated confocal micro-Raman system equipped with a 460 mm focal-length spectrograph and a multichannel air-cooled (-70 °C) CCD detector. A magnification of 100× was used with an estimated spot size of  $\sim 1 \mu m$ , a 1800 gr/mm



FIG. 4. Raman spectrum of bafertisite from Kola.

grating, and a 532 nm excitation laser. The wavenumber was calibrated using the 520.7 cm<sup>-1</sup> line of Si. In the 800–1200 cm<sup>-1</sup> region, the two strong peaks at 812 and 917 cm<sup>-1</sup> and weak peaks at 966, 988, 1027, 1116, and 1184 cm<sup>-1</sup> are assigned to Si–O stretching vibrations of the Si<sub>2</sub>O<sub>7</sub> group. The broad and intense peak at 688 cm<sup>-1</sup> may be assigned to stretching vibrations of Si–O–Si bridges. The strong peak at 593 cm<sup>-1</sup> and weak peaks at 478 and 418 cm<sup>-1</sup> are due to bending vibrations of the Si<sub>2</sub>O<sub>7</sub> group, and peaks below 400 cm<sup>-1</sup> (355, 336, 264, 230, 178, 163, and 135 cm<sup>-1</sup>) are mainly due to lattice vibrations.

#### CHEMICAL COMPOSITION

Crystals of bafertisite from three localities—(1) the Bayan Obo REE deposit, Inner Mongolia, China (holotype); (2) the Gremyakha-Vyrmes alkaline complex, Kola Peninsula, Russia; and (3) the Darai-Pioz alkaline massif, Tajikistan-were analyzed using a Cameca SX-100 electron microprobe operating in wavelength-dispersive mode with an accelerating voltage of 15 kV, a specimen current of 10 nA, and a beam diameter of 10 µm. The following standards were used: Si, Ca: diopside; Nb, Ba: Ba2NaNb5O15; Zr: zircon; Ti: titanite; Al: andalusite; Fe: fayalite; Mn: spessartine; Mg: forsterite; Zn: gahnite; Sr: SrTiO<sub>3</sub>; Cs: pollucite; Na: albite; K: orthoclase; F: fluorite (1B) and fluor-riebeckite (2,3). The elements Ta, Sn, Pb, and Rb were sought but not detected. The data were reduced and corrected by the PAP method of Pouchou & Pichoir (1985). All Fe was considered Fe<sup>2+</sup> (see results of Mössbauer spectroscopy above). The H<sub>2</sub>O (presence of OH groups confirmed by IR spectroscopy, see above) was calculated from the results of the crystal-structure analysis on the basis of F + OH = 4 apfu. Table 2 gives the chemical composition of bafertisite from three localities—(1B, holotype), (2), and (3) (mean of 10

determinations)-and the original chemical analysis of the holotype (1A) (Semenov & Zhang Peishan 1959). The empirical formulae of bafertisite on the basis of 20 (O + F) anions are of the form  $A_2^P M_4^O M_2^H$  $(Si_2O_7)_2(X^O)_4(X^P)_2$ , Z = 4: (1B)  $(Ba_{1.89}K_{0.03})_{\Sigma 1.92}$  $(Fe^{2+}_{3.33}Mn_{0.47}Mg_{0.11})_{\Sigma 3.91}(Ti_{1.86}Nb_{0.07}Zr_{0.02}Mg_{0.05})_{\Sigma 2}$  $(Si_{2.05}O_7)_2O_2[(OH)_{1.82}F_{0.18}]_{\Sigma 2}F_2, D_{calc.} = 4.251 \text{ g/cm}^3;$ (2)  $(Ba_{1.82}Sr_{0.02}K_{0.02})_{\Sigma 1.86}(Fe^{2+}_{3.24}Mn_{0.57}Al_{0.06}Mg_{0.03})$  $Ca_{0.01}Zr_{0.01}Zn_{0.01}Na_{0.02})_{\Sigma 3.95}(Ti_{1.96}Nb_{0.03}Zr_{0.01})_{\Sigma 2}$  $(Si_{2.05}O_7)_2O_2[(OH)_{1.59}F_{0.41}]_{\Sigma 2}F_2, D_{calc.} = 4.205 \text{ g/cm}^3;$ and (3)  $(Ba_{1.90}K_{0.02})_{\Sigma 1.92}(Fe^{2+}_{2.23}Mn_{1.61}Mg_{0.02})$  $Zr_{0.04}Zn_{0.03})_{\Sigma 3.93}(Ti_{1.90}Nb_{0.09}Zr_{0.01})_{\Sigma 2}(Si_{2.03}O_7)_2O_2$  $[(OH)_{1.75}F_{0.25}]_{\Sigma 2}F_2$ ,  $D_{calc.} = 4.236$  g/cm<sup>3</sup>. There is a good correlation between density values calculated from the empirical formula for samples (1-3) and  $D_{\text{meas.}} = 4.25 - 3.96 \text{ g/cm}^3$  (Semenov & Zhang Peishan 1959). Simplified and endmember formulae of bafertisite are  $Ba_2(Fe^{2+},Mn)_4Ti_2(Si_2O_7)_2O_2(OH,F)_2F_2$  and  $Ba_2Fe^{2+}_{4}Ti_2(Si_2O_7)_2O_2(OH)_2 F_2, Z = 4.$ 

# CRYSTAL STRUCTURE

We solved and refined the crystal structure of bafertisite from twinned crystals of three bafertisite samples: (1) holotype, (2) bafertisite from Kola, and (3) bafertisite from Darai-Pioz, using single-crystal X-ray diffraction data (Table 3). The best structure-refinement results,  $R_1 = 2.46\%$ , and the lowest magnitude of the highest peak in the difference Fourier map, 2.18 e/Å<sup>-3</sup>, are for the bafertisite from Kola. Hence in this paper, we present the structure-refinement results for bafertisite from Kola.

#### Data collection and structure refinement

Single-crystal X-ray data for bafertisite from Kola were collected using a Bruker APEX II ULTRA threecircle diffractometer with a rotating-anode generator (MoKa), multilayer optics, and an APEX II 4K CCD detector. The intensities of 9369 reflections with -15 < h < 15, -19 < k < 19, -16 < l < 16, measured to 60.47° 20 using 10 s per 0.2° frame. Unit-cell dimensions were determined by least-squares refinement of 9984 reflections with  $I > 10\sigma I$ , and are given in Table 3 (column 2), together with other miscellaneous information on data collection and structure refinement. An absorption correction was done using the SADABS program (Sheldrick 2008). All calculations were done with the Bruker SHELXTL version 5.1 system of programs (Sheldrick 2008). The crystal structure was solved in space group  $C\overline{1}$  and refined to  $R_1 = 2.46\%$  for a twinned crystal with two components related by the twin matrix  $[100 \ 0\overline{1}0 \ 001]$  and a twin ratio of 0.694(1) : 0.306(1). The (Niggli) reduced unit cell is: a 8.710(2), b 8.713(2), c 11.737(2) Å, a 103.34(3),  $\beta$  103.53(3),  $\gamma$  104.41(3)°, V 798(2) Å<sup>3</sup>,  $P\overline{1}$ ,

		(wt.%)				Form	ula unit (	apfu)	
	Semenov & Zhang Peishan (1959)		This work	<		Semenov & Zhang Peishan (1959)		This wor	k
	·,	Holotype					Holotype		
Component	(1A)	(1B)	(2)	(3)		(1A)	(1B)	(2)	(3)
Nb <sub>2</sub> O <sub>5</sub>	0.84	0.89	0.34	1.08	Si	4.00	4.10	4.09	4.05
ZrO <sub>2</sub>	n.d.	0.25	0.18	0.60					
TiO <sub>2</sub>	15.39	14.15	15.06	14.44	Fe <sup>2+</sup>	3.19	3.33	3.24	2.23
SiO <sub>2</sub>	23.68	23.48	23.71	23.17	Mn	0.23	0.47	0.57	1.61
Al <sub>2</sub> O <sub>3</sub>	0.29	n.d.	0.31	n.d.	Fe <sup>3+</sup>	0.14	0	0	0
Fe <sub>2</sub> O <sub>3</sub>	1.08	n.d.	n.d.	n.d.	Mg	0.13	0.11	0.03	0.02
FeO	22.56	22.81	22.41	15.27	Al	0.06	0	0.06	0
BaO	29.98	27.56	26.82	27.68	Ca	0.07	0	0.01	0
SrO	n.d.	n.d.	0.20	n.d.	Zr	0	0	0.01	0.04
ZnO	n.d.	n.d.	0.09	0.22	Zn	0	0	0.01	0.03
MnO	1.62	3.18	3.87	10.88	Na	0.16	0	0.02	0
CaO	0.37	n.d.	0.04	n.d.	Σ4Μ <sup>Ο</sup>	3.98	3.91	3.95	3.93
MgO	0.50	0.60	0.12	0.06					
Cs <sub>2</sub> O	n.a.	0.05	n.d.	0.05	Ti	1.96	1.86	1.96	1.90
K₂Ō	0.12	0.15	0.10	0.07	Nb	0.06	0.07	0.03	0.09
Na <sub>2</sub> O	0.49	n.d.	0.07	n.d.	Zr	0	0.02	0.01	0.01
F	n.a.	3.94	4.42	4.07	Mg	0	0.05	0	0
CI	0.63	n.d.	n.d.	n.d.	Σ2M <sup>H</sup>	2.02	2.00	2.00	2.00
H₂O	2.79	1.57	1.38	1.50					
0=F	0.00	-1.66	-1.86	-1.71	Ва	1.98	1.89	1.82	1.90
O=Cl <sub>2</sub>	-0.14	0	0	0	Sr	0	0	0.02	0
Total	100.20	96.97	97.26	97.38	К	0.03	0.03	0.02	0.02
					$\Sigma 2A^{P}$	2.01	1.92	1.86	1.92
					$\Sigma$ cations	12.01	11.93	11.90	11.90
					F	0	2.18	2.41	2.25
					ОН	1.86	1.82	1.59	1.75
					$\Sigma 2 X^{P}_{M} + \Sigma 2 X^{O}_{A}$	1.86	4.00	4.00	4.00
					CI	0.18	0	0	0
					$\Sigma$ anions	19.07	20.00	20.00	20.00

TABLE 2. CHEMICAL ANALYSIS AND FORMULA UNIT FOR BAFERTISITE

Localities: (1A) and (1B) Bayan Obo REE deposit, Inner Mongolia, China; (2) Gremyakha-Vyrmes alkaline complex, Kola Peninsula, Russia; (3) Darai-Pioz alkaline massif, Tajikistan.

n.a. = not analyzed; n.d. = not detected.

Chemical analysis. (1A) wet chemistry; minor Sr, Zn, and Sn were detected by "spectral" analysis;  $H_2O^+ = 1.65$  wt.%,  $H_2O^- = 1.14$  wt.%;  $H_2O^+ + H_2O^- = H_2O = 2.79$  wt.%;  $H_2O^+ = 1.65$  wt.% has been used to calculate the formula on cation basis: Si = 4 *apfu*.

(1B,2,3) This work, EMPA, FeO determined by Mössbauer spectroscopy;  $H_2O$  calculated from structure-refinement results where (OH + F) = 4 *apfu*. For (1B,2,3), formulae were calculated on anion basis: 20 (O + F) *apfu*.

Z = 2. The  $P\overline{1}$  unit cell can be derived from the  $\overline{1}$  unit cell *via* the transformation matrix  $[-\frac{1}{2}-\frac{1}{2}0 -\frac{1}{2}\frac{1}{2}0 0 -\frac{1}{2}\frac{1}{2}0 0 -\frac{1}{2}\frac{1}{2}0 0 -\frac{1}{2}\frac{1}{2}0 0 -\frac{1}{2}\frac{1}{2}0 0 -\frac{1}{2}\frac{1}{2}0 0 -\frac{1}{2}\frac{1}{2}\frac{1}{2}0 0 -\frac{1}{2}\frac{1}{2}\frac{1}{2}0 0 -\frac{1}{2}\frac{1}{2}\frac{1}{2}0 0 -\frac{1}{2}\frac{1}{2}\frac{1}{2}0 0 -\frac{1}{2}\frac{1}{2}\frac{1}{2}0 0 -\frac{1}{2}\frac{1$ 

content, all unit-cell parameters and the cell volume increase while the  $\beta$  angle does not change within the observed errors (Tables 2 and 3). Scattering curves for neutral atoms were taken from the International Tables for Crystallography (Wilson 1992). In the crystal structure of bafertisite, we identify three groups of cation sites:  $M^{O}$  sites of the O sheet,  $M^{H}$  and Si sites of

Sample	(1)	(2)	(3)
a (Å)	10.665(2)	10.677(6)	10.695(8)
b	13.743(2)	13.767(7)	13.788(10)
С	11.721(3)	11.737(5)	11.758(7)
α (°)	90.30(4)	90.12(1)	90.22(1)
β	112.27(2)	112.28(4)	112.22(5)
γ	90.00(3)	90.02(1)	90.01(1)
<i>V</i> (Å <sup>3</sup> )	1589.8(8)	1596(3)	1605(3)
Space group	CĪ	CĪ	CĪ
Z	4	4	4
Absorption coefficient (mm <sup>-1</sup> )	9.31	9.19	9.23
F(000)	1890.6	1878.8	1897.4
$D_{\text{calc.}}$ (g/cm <sup>3</sup> )	4.251	4.205	4.236
Crystal size (mm)	0.02 imes 0.05 imes 0.07	0.03 imes 0.12 imes 0.20	0.03 imes 0.09 imes 0.14
Second component*	0.095(1)	0.306(1)	0.144(1)
Radiation/monochromator	MoKa/graphite	MoKa/graphite	MoKa/graphite
20-range for data collection (°)	60.24	60.47	60.21
<i>R</i> (int) (%)	4.08	1.95	1.33
Reflections collected	9226	9369	9393
Independent reflections	4617	4707	4715
$F_{o} > 4\sigma F$	4538	4685	4692
Refinement method	Full-matrix least squares o	n F <sup>2</sup> , fixed weights proportio	nal to $1/\sigma F_o^2$
No. of refined parameters	308	308	308
Final R indices (%)			
$R_1 (F_o > 4\sigma F)$	2.90	2.46	2.74
$R_1$	2.93	2.47	2.74
wR <sub>2</sub>	8.64	6.91	7.78
Highest peak, deepest hole	3.15	2.18	3.20
(e Å <sup>-3</sup> )	-0.88	-1.04	-1.47
Goodness of fit on $F^2$	1.076	1.065	1.081

TABLE 3. MISCELLANEOUS REFINEMENT DATA FOR BAFERTISITE

Samples: (1) Holotype, Bayan Obo REE deposit, Inner Mongolia, China; (2) Gremyakha-Vyrmes alkaline complex, Kola Peninsula, Russia; (3) Darai-Pioz alkaline massif, Tajikistan.

\* Second component of the crystal is related to the first component by the twin matrix [100 010 001].

the H sheet, and peripheral  $A^P$  sites which occur in the I block. Site labeling is in accord with Sokolova (2006). Site-scattering values were refined for the  $M^{\rm O}(1-5)$  sites using the scattering curve for Fe,  $M^{\rm H}(1,2)$  sites (scattering curve for Ti), and  $A^{\rm P}(1,2)$ sites (scattering curve for Ba). In the last stages of the refinement, two peaks were found in the difference-Fourier map which were included in the refinement as the H(1,2) atoms. The D (donor)-H distances were softly constrained to 0.98 Å and the coordinates of the H atoms were refined. Final atom coordinates and anisotropic-displacement parameters for the bafertisite from Kola are listed in Table 4, selected interatomic distances and angles are given in Table 5, refined sitescattering values and assigned site-populations for selected cation and anion sites are given in Table 6, bond-valence values for selected anions in Table 7, and details of the hydrogen bonding in Table 8. Tables of structure factors and CIFs for three bafertisite

samples (1, holotype; 2, from Kola; and 3, from Darai-Pioz) may be obtained from The Depository of Unpublished Data on the MAC website [documents bafertisite CM54\_10.3749/canmin.1500059].

#### Description of the structure

The crystal structure of bafertisite can be described as a combination of a TS block and an I block (Fig. 5a). The TS block consists of HOH sheets (Hheteropolyhedral, O-octahedral). In the O sheet, there are four Fe<sup>2+</sup>-dominant <sup>[6]</sup> $M^{O}(1-4)$  sites, with  $< M^{O}-\phi > = 2.176$  Å, and one Mn-dominant <sup>[6]</sup> $M^{O}(5)$  site, with  $< M^{O}-\phi > = 2.200$  Å ( $\phi = O$ , OH) (Tables 5, 6, Fig. 5b). Five  $M^{O}$  sites ideally give Fe<sup>2+</sup><sub>4</sub> *apfu* (Table 6). In the H sheet, the two <sup>[6]</sup> $M^{H}(1,2)$  sites are occupied mainly by Ti and minor Nb, Mg, and Zr, ideally giving Ti<sub>2</sub> *apfu*, with  $< M^{H}-\phi > = 1.963$  Å ( $\phi = O$ , F). Four <sup>[4]</sup>Si sites are occupied solely by Si, with < Si-O > =1.626 Å (Tables 5, 6). The M<sup>H</sup> octahedra and Si<sub>2</sub>O<sub>7</sub>

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Atom	x	У	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$	$U_{ m eq}$
M <sup>O</sup> (1)	0	0	0	0.0067(4)	0.0081(4)	0.0126(4)	-0.0006(3)	0.0043(3)	-0.0003(3)	0.0090(3)
M <sup>O</sup> (2)	0.24428(4)	0.12334(5)	-0.01220(4)	0.0063(2)	0.0086(2)	0.0106(2)	-0.0000(2)	0.00367(16)	-0.0011(2)	0.00840(15)
M <sup>O</sup> (3)	0.25574(4)	0.87305(5)	0.00842(4)	0.0068(2)	0.0079(2)	0.0105(2)	-0.0006(2)	0.00400(16)	-0.0011(2)	0.00819(15)
M <sup>O</sup> (4)	0.99526(5)	0.75210(4)	0.99381(5)	0.0061(3)	0.0096(3)	0.0142(4)	0.0017(2)	0.0036(3)	-0.0014(2)	0.0100(2)
M <sup>O</sup> (5)	1/2	0	0	0.0055(4)	0.0162(5)	0.0195(5)	-0.0088(3)	0.0016(3)	0.0005(3)	0.0147(3)
M <sup>H</sup> (1)	0.46521(6)	0.60392(4)	0.71645(6)	0.0031(3)	0.0076(3)	0.0053(3)	-0.00023(18)	0.00209(18)	-0.00066(18)	0.00517(18)
M <sup>H</sup> (2)	0.53602(6)	0.85602(4)	0.28617(5)	0.0029(3)	0.0073(3)	0.0053(3)	0.00013(19)	0.00225(19)	-0.00042(18)	0.00499(18)
Si(1)	0.28268(11)	0.01517(7)	0.24709(10)	0.0053(4)	0.0052(4)	0.0066(4)	-0.0008(3)	0.0026(3)	-0.0011(3)	0.0056(2)
Si(2)	0.71702(11)	0.76397(7)	0.75114(10)	0.0052(4)	0.0061(4)	0.0063(4)	0.0005(3)	0.0026(3)	-0.0014(3)	0.0057(2)
Si(3)	0.74186(11)	0.48299(7)	0.75141(10)	0.0049(4)	0.0051(4)	0.0067(4)	-0.0006(3)	0.0025(3)	-0.0015(3)	0.0055(2)
Si(4)	0.25880(11)	0.73729(8)	0.24802(10)	0.0054(4)	0.0058(4)	0.0068(4)	0.0004(3)	0.0029(3)	0.0002(3)	0.0058(2)
$A^{P}(1)$	0.61159(2)	0.62480(2)	0.46836(2)	0.00763(10)	0.01100(10)	0.00860(10)	-0.00037(11)	0.00349(7)	-0.00062(11)	0.00895(7)
$A^{P}(2)$	0.38933(2)	0.87896(2)	0.53534(2)	0.00896(11)	0.03347(15)	0.01079(12)	-0.00081(14)	0.00459(8)	-0.00237(14)	0.01749(8)
O(1)	0.4165(3)	0.9509(2)	0.3207(3)	0.0088(11)	0.0122(12)	0.0126(12)	0.0026(10)	0.0051(9)	0.0036(9)	0.0109(5)
O(2)	0.6699(3)	0.5012(2)	0.3056(3)	0.0098(12)	0.0137(13)	0.0157(13)	-0.0041(10)	0.0087(10)	-0.0048(10)	0.0119(5)
O(3)	0.2175(3)	0.9999(2)	0.0986(3)	0.0079(12)	0.0099(12)	0.0054(12)	-0.0009(10)	0.0013(10)	-0.0020(9)	0.0081(5)
O(4)	0.6548(2)	0.8746(2)	0.7252(2)	0.0087(10)	0.0078(10)	0.0115(10)	0.0003(10)	0.0045(8)	0.0010(9)	0.0091(4)
O(5)	0.6715(3)	0.7524(2)	0.3084(3)	0.0103(11)	0.0105(12)	0.0153(12)	0.0032(10)	0.0087(10)	0.0017(9)	0.0109(5)
O(6)	0.7847(3)	0.7509(2)	0.9002(3)	0.0076(12)	0.0116(12)	0.0066(12)	0.0017(10)	0.0034(10)	0.0003(9)	0.0084(5)
0(7)	0.5825(3)	0.6987(2)	0.6828(3)	0.0092(11)	0.0140(12)	0.0114(12)	-0.0011(10)	0.0054(9)	-0.0046(9)	0.0111(5)
O(8)	0.8190(3)	0.5479(2)	0.6833(3)	0.0080(11)	0.0122(12)	0.0113(12)	-0.0000(10)	0.0030(9)	-0.0045(9)	0.0107(5)
O(9)	0.5813(3)	0.4992(2)	0.6953(3)	0.0058(11)	0.0125(12)	0.0143(13)	-0.0047(10)	0.0030(10)	-0.0007(9)	0.0111(5)
O(10)	0.7983(3)	0.4960(2)	0.9008(3)	0.0060(11)	0.0100(12)	0.0052(12)	-0.0006(9)	0.0012(10)	0.0001(9)	0.0073(5)
O(11)	0.2802(2)	0.8726(2)	0.7230(2)	0.0103(10)	0.0078(10)	0.0111(10)	0.0003(10)	0.0056(8)	0.0003(10)	0.0093(4)
O(12)	0.2040(3)	0.7505(2)	0.0987(3)	0.0076(12)	0.0103(12)	0.0062(12)	0.0012(10)	0.0025(10)	-0.0008(9)	0.0081(5)
O(13)	0.4198(3)	0.7521(2)	0.3108(3)	0.0065(11)	0.0110(12)	0.0131(12)	0.0024(10)	0.0024(9)	-0.0014(9)	0.0106(5)
O(14)	0.3165(3)	0.6964(2)	0.6819(3)	0.0107(12)	0.0102(11)	0.0132(12)	-0.0012(10)	0.0063(10)	0.0024(9)	0.0108(5)
Х <sup>о</sup> <sub>M</sub> (1)	0.5368(2)	0.6160(2)	0.8821(2)	0.0079(10)	0.0132(12)	0.0081(10)	-0.0009(10)	0.0038(8)	-0.0026(10)	0.0095(5)
Х <sup>о</sup> <sub>M</sub> (2)	0.4637(2)	0.8660(2)	0.1220(2)	0.0070(10)	0.0154(13)	0.0096(10)	-0.0029(11)	0.0040(8)	-0.0013(10)	0.0104(5)
X <sup>O</sup> A(1)	-0.0441(2)	0.1242(3)	0.0848(2)	0.0090(10)	0.0107(10)	0.0080(9)	0.0013(11)	0.0029(8)	0.0010(12)	0.0093(4)
X <sup>O</sup> A(2)	0.4533(2)	0.1278(2)	0.0770(2)	0.0079(9)	0.0094(10)	0.0093(10)	0.0024(11)	0.0036(8)	0.0018(11)	0.0088(4)
$X^{P}_{M}(1)$	0.6176(2)	0.40617(19)	0.4769(2)	0.0102(10)	0.0276(12)	0.0068(9)	-0.0004(8)	0.0023(8)	-0.0013(8)	0.0151(5)
$X^{P}_{M}(2)$	0.6147(2)	0.8524(2)	0.4797(2)	0.0097(10)	0.0361(16)	0.0076(9)	-0.0010(9)	0.0023(8)	-0.0009(9)	0.0181(5)
H(1)	0.002(4)	0.143(4)	0.1712(17)	0.01118*						
H(2)	0.486(5)	0.145(4)	0.1647(15)	0.01052*						

\* U<sub>iso</sub>

$M^{O}(1) - X^{O}_{A}(1)$	2.118(3)	×2 ×2	$M^{O}(2) - X^{O}_{A}(2)$ $M^{O}(2) - X^{O}_{A}(2)$	2.076(3)		$M^{O}(3) - X^{O}_{A}(1)d$ $M^{O}(3) - X^{O}_{A}(2)$	2.105(3)
$M^{o}(1)=O(3)a$ $M^{o}(1)=X^{o}_{M}(1)b$ $$	2.167(3) 2.246(3) 2.177	×2 ×2	$M^{O}(2) - O(6)b$ $M^{O}(2) - O(10)b$ $M^{O}(2) - O(3)a$ $M^{O}(2) - O(6)c$	2.091(3) 2.162(3) 2.211(3) 2.225(3) 2.263(3)		$M^{O}(3)-O(3)$ $M^{O}(3)-O(12)$ $M^{O}(3)-O(12)$ $M^{O}(3)-O(12)e$ $M^{O}(3)-O(10)f$	2.115(3) 2.157(3) 2.249(3) 2.261(3)
$M^{O}(4) = O(6)$	2 095(3)		<Μ <sup>ο</sup> (2)–φ> M <sup>0</sup> (5)–Ω(10)b	2.171 2.024(3)	×2	M <sup>ο</sup> (3)–φ>	2.177
$M^{O}(4) - X^{O}(1)c$	2.095(3)		$M^{O}(5) - X^{O}_{A}(2)$	2.121(3)	×2		
$M^{O}(4) - O(12)h$	2.098(3)		$M^{O}(5) - X^{O}_{M}(2)a$	2.456(2)	×2		
$M^{O}(4) - X^{O}_{A}(2)q$	2.102(3)		$< M^{O}(5) - \phi >$	2.200			
$M^{O}(4) - X^{O}_{M}(2)i$	2.264(3)		(-) +				
$M^{O}(4) - X^{O}_{M}(1)i$	2.430(3)						
<m<sup>O(4)-φ&gt;</m<sup>	2.180						
$M^{H}(1) - X^{O}_{M}(1)$	1.806(3)		M <sup>H</sup> (2)–X <sup>O</sup> <sub>M</sub> (2)	1.789(3)			
M <sup>H</sup> (1)–O(7)	1.950(3)		M <sup>H</sup> (2)–O(8)j	1.962(3)			
M <sup>H</sup> (1)–O(14)	1.955(3)		M <sup>H</sup> (2)–O(1)	1.972(3)			
M <sup>H</sup> (1)–O(9)	1.977(3)		M <sup>H</sup> (2)–O(5)	1.978(3)			
M <sup>H</sup> (1)–O(2)c	1.989(3)		M <sup>H</sup> (2)–O(13)	1.986(3)			
M <sup>H</sup> (1)–X <sup>P</sup> <sub>M</sub> (1)c	2.105(3)		$M^{H}(2) - X^{P}_{M}(2)$	2.102(3)			
<Μ <sup>H</sup> (1)–φ>	1.963		<Μ <sup>н</sup> (2)–φ>	1.963			
Si(1)–O(2)k	1.609(3)		Si(2)–O(5)j	1.608(3)		Si(3)–O(9)	1.602(3)
Si(1)–O(1)a	1.625(3)		Si(2)–O(7)	1.624(3)		Si(3)–O(8)	1.618(3)
Si(1)–O(3)a	1.627(3)		Si(2)–O(6)	1.630(3)		Si(3)–O(10)	1.633(3)
Si(1) - O(4)c	1.639(3)		SI(2) = O(4)	1.644(3)		SI(3)-O(11)I	1.640(3)
<si(1)-o></si(1)-o>	1.625		<Si(2)–O>	1.627	105 7(0)	<Si(3)–O>	1.623
SI(4) = O(13)	1.606(3)		SI(1)C-O(4)-SI(2)	) 1) m	135.7(2)		
S(4) = O(14) m	1.030(3)			4)[[]	135.3(2)		
Si(4) = O(12) Si(4) = O(11)m	1.000(0)		<31-0-31>		135.5		
$\leq Si(4) = O(11) III$	1.009(0)						
$A^{P}(1) - X^{P} (2)i$	2 768(3)		$A^{P}(2) - X^{P}_{M}(1)n$	2 743(3)			
$A^{P}(1) - X^{P}_{M}(1)c$	2,788(3)		$A^{P}(2) - X^{P}_{M}(2)$	2.746(3)			
$A^{P}(1) - O(2)$	2.797(3)		$A^{P}(2) - O(1)$	2.825(3)			
$A^{P}(1) - O(13)$	2.798(3)		$A^{P}(2) - O(14)m$	2.854(3)			
$A^{P}(1) - O(9)c$	2.798(3)		A <sup>P</sup> (2)–O(11)	2.857(3)			
$A^{P(1)} - O(5)$	2.818(3)		$A^{P}(2) - O(4)$	2.866(3)			
$A^{P}(1) - O(7)$	2.836(3)		A <sup>P</sup> (2)–O(8)n	3.156(3)			
$A^{P}(1) - O(8)$	2.857(3)		A <sup>P</sup> (2)–O(1)o	3.157(3)			
$A^{P}(1) - X^{P}_{M}(1)$	3.012(3)		A <sup>P</sup> (2)–O(13)	3.275(3)			
$A^{P}(1)-X^{P}_{M}(2)$	3.135(3)		A <sup>P</sup> (2)–O(7)	3.275(3)			
A <sup>P</sup> (1)–O(5)j	3.236(3)		A <sup>P</sup> (2)–O(2)n	3.290(3)			
A <sup>P</sup> (1)–O(9)	3.295(3)		A <sup>P</sup> (2)–O(14)	3.304(3)			
< <b>Α</b> <sup><i>P</i></sup> (1)–φ>	2.928		< <b>Α</b> <sup><i>P</i></sup> (2)–φ>	3.029			

TABLE 5. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN BAFERTISITE FROM KOLA

a: x, y-1, z; b: x-1/2, y-1/2, z-1; c: -x+1, -y+1, -z+1; d: -x, -y+1, -z; e: -x+1/2, -y(3)2, -z; f: x-1/2, y+1/2, z-1; g: x+1/2, y+1/2, z+1; h: x+1, y, z+1; i: -x(3)2, -y(3)2, -z+2; j: -x(3)2, -y(3)2, -z+1; h: x-1/2, y-1/2, z; l: x+1/2, y-1/2, z; m: -x+1/2, -y(3)2, -z+1; n: x-1/2, y+1/2, z; o: -x+1, -y+2, -z+1

groups constitute the H sheet (Fig. 5c). Two H sheets and the central O sheet link *via* common vertices of  $M^H$  octahedra and Si<sub>2</sub>O<sub>7</sub> groups with  $M^O$  octahedra to form the TS block. In Group II, the TS block exhibits linkage 2 where the Si<sub>2</sub>O<sub>7</sub> groups of two H sheets link to  $M^O$  octahedra adjacent along  $\mathbf{t}_2$  (|| **b**) in the O sheet (Fig. 5a), as defined by Sokolova (2006). There are two <sup>[12]</sup>Ba-dominant  $A^{P}(1,2)$  sites, with  $\langle A^{P}(1)-\phi \rangle =$  2.928 Å and  $\langle A^{P}(2)-\phi \rangle =$  3.029 Å ( $\phi = O$ , F). The two  $A^{P}$  sites ideally give Ba<sub>2</sub> *apfu* (Table 6). In the crystal structure of bafertisite, TS blocks link *via* a layer of Ba atoms that constitute the I block (Fig. 5a).

Site*	Refined site-scattering ( <i>epfu</i> )	Assigned site-population ( <i>apfu</i> )	Calculated site-scattering ( <i>epfu</i> )	<x-<math>\phi&gt;_{obs}^{**} (Å)</x-<math>	Ideal composition ( <i>apfu</i> )
Cations					
<i>M</i> <sup>O</sup> (1)	13.00(7)	0.47 $\text{Fe}^{2+}$ + 0.02 Mg + 0.01 $\Box$	12.35	2.177	Fe <sup>2+</sup> 0.5
$M^{O}(2)$	26.3(1)	0.93 Fe <sup>2+</sup> + 0.07 Mg	25.02	2.171	Fe <sup>2+</sup>
M <sup>O</sup> (3)	26.1(1)	0.94 Fe <sup>2+</sup> + 0.02 Mg + 0.06 □	24.68	2.177	Fe <sup>2+</sup>
$M^{O}(4)$	26.2(1)	0.96 Fe <sup>2+</sup> + 0.04 □	24.96	2.180	Fe <sup>2+</sup>
$M^{O}(5)$	13.16(7)	0.47 Mn <sup>2+</sup> + 0.03 Fe <sup>2+</sup>	12.53	2.200	Mn <sub>0.5</sub>
Σ <i>M</i> <sup>O</sup> (1–5)	104.76	$3.33 \text{ Fe}^{2+} + 0.47 \text{ Mn} + 0.11 \text{ Mg} + 0.09 \square$	99.65		Fe <sup>2+</sup> 4
М <sup>н</sup> (1)	22.1(1)	1.86  Ti + 0.07  Nb + 0.05  Mg + 0.02  Zr		1.963	Ti
М <sup>Н</sup> (2)	21.88(9)			1.963	Ti
Σ <i>M</i> <sup>H</sup> (1,2)	43.98	$1.86 \; Ti + 0.07 \; Nb + 0.05 \; Mg + 0.02 \; Zr$	45.19		Ti <sub>2</sub>
$^{[12]}A^{P}(1)$	56.4(1)	0.95 Ba + 0.05 □	53.20	2.928	Ba
$^{[12]}A^{P}(2)$	56.4(1)	0.94 Ba + 0.03 K + 0.03 □	53.21	3.029	Ba
Σ <i>A<sup>P</sup></i> (1,2)	112.8	1.89 Ba + 0.03 K + 0.08 □	106.41		Ba <sub>2</sub>
Anions					
$\Sigma X^{O}_{M}(1,2)$		2.00 O			O <sub>2</sub>
$\Sigma X^{O}_{A}(1,2)$		1.59 (OH) + 0.41 F			(OH) <sub>2</sub>
$\Sigma X^{P}{}_{M}(1,2)$		2.00 F			F <sub>2</sub>

TABLE 6. REFINED SITE-SCATTERING VALUES AND ASSIGNED SITE-POPULATIONS FOR BAFERTISITE FROM KOLA

\* coordination number is given only for non-[6]-coordinated sites; \*\* X = cation,  $\phi$  = O, OH, F.

The general topology of the bafertisite structure is in accord with Guan *et al.* (1963).

Anion considerations. The O(1–14) atoms coordinate Si atoms of Si<sub>2</sub>O<sub>7</sub> groups, giving (Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub> pfu. Two  $X^{O}_{M}(1,2)$  anions are bonded to one M<sup>H</sup> (Ti) cation and three M<sup>O</sup> (Fe<sup>2+</sup> and Mn) cations, receive 1.82 and 1.84 vu (valence units), and hence they are O atoms, giving O<sub>2</sub> apfu (Tables 5–7). Two  $X^{P}_{M}(1,2)$  anions are bonded to one M<sup>H</sup> (Ti) cation and three A<sup>P</sup> (Ba) cations (Fig. 5d); they receive 0.82 and 0.84 vu (Table 7). We conclude that the  $X^{P}_{M}(1,2)$  anions are monovalent. The two  $X^{P}_{M}$  sites are coordinated by four cations and hence there is no space to accommodate an OH group plus a hydrogen bond at those sites. Therefore we assign F to the  $X_M^P(1,2)$  sites, and they give F<sub>2</sub> *apfu* (Table 6). Two  $X_A^O(1,2)$  anions are bonded to three M<sup>O</sup> (Fe<sup>2+</sup>) cations, with incident valence sums of 1.17 and 1.19 *vu* (Table 7), hence they are monovalent anions. Chemical analysis gives 2.41 F *apfu* for the bafertisite from Kola (Table 2) and we assign 1.59 OH + (2.41 - 2.00 = 0.41) F to the  $X_A^O(1,2)$  sites, ideally (OH)<sub>2</sub> *apfu* (Table 6). Details of hydrogen bonding are given in Table 8.

TABLE 7. BOND-VALENCE VALUES\* FOR SELECTED ANIONS IN BAFERTISITE FROM KOLA

Atom	M <sup>O</sup> (1)	M <sup>O</sup> (2)	M <sup>O</sup> (3)	M <sup>O</sup> (4)	M <sup>O</sup> (5)	M <sup>H</sup> (1)	M <sup>H</sup> (2)	A <sup>P</sup> (1)	A <sup>P</sup> (2)	Σ
X <sup>O</sup> <sub>M</sub> (1)	0.26	0.39		0.17		1.00				1.82
$X^{O}_{M}(2)$			0.37	0.25	0.17		1.05			1.84
$^{[3]}X^{O}_{A}(1)$	0.37		0.41	0.39						1.17
<sup>[3]</sup> X <sup>O</sup> <sub>A</sub> (2)		0.41		0.38	0.40					1.19
$X^{P}_{M}(1)$						0.32		0.18	0.19	0.82
								0.13		
X <sup>P</sup> <sub>M</sub> (2)						0.32		0.19	0.19	0.81
								0.11		

\* Bond-valence parameters (*vu*) are from Brown (1981); bond-valence values calculated for  $M^{O}(1-4) = Fe^{2+}$ ,  $M^{O}(5) = Mn$ ;  $M^{H} = Ti$ ;  $A^{P} = Ba$ ; coordination numbers are shown for non-4-coordinated anions.

D–H····A	D–H (Å)	H⊷∙A (Å)	D· · ·A (Å)	∠ DHA (°)
X <sup>O</sup> <sub>A</sub> (1)OH−H(1)····O(5)a	0.98(1)	2.43(3)	3.270(4)	143(4)
X <sup>O</sup> <sub>A</sub> (1)OH−H(1)···O(9)a	0.98(1)	2.60(4)	3.323(4)	131(4)
X <sup>O</sup> <sub>A</sub> (2)OH–H(2)···O(11)b	0.98(1)	2.35(4)	2.923(4)	117(3)
$X^{O}_{A}(2)OH-H(2)\cdots O(4)b$	0.98(1)	2.34(4)	2.959(3)	120(4)

TABLE 8. HYDROGEN BONDING IN BAFERTISITE FROM KOLA

a: x-1/2, y-1/2, z; b: -x+1, -y+1, -z+1.

The infrared spectrum (Fig. 3) shows two bands at two sharp peaks at 3639 and 3588  $\text{cm}^{-1}$ . This could be related to short-range order (SRO) at the  $X^{O}_{A}$  anion sites. There are two hydrogen sites in the bafertisite structure, H(1) and H(2). The hydrogen bonding reported in Table 8 shows that these two hydrogen atoms have different bonding environments, with apparent stronger bifurcated bonding for the H(2)atom, which should cause a shift to shorter frequencies. In addition, each X<sup>O</sup><sub>A</sub> anion has two different next-nearest-neighbor (NNN) environments: the  $X^{O}_{A}(1)$  anion is bonded to three  $Fe^{2+}$  cations at  $^{[6]}M^{O}(1,3,4)$  sites; the X<sup>O</sup><sub>A</sub>(2) anion is locally bonded to three  $\text{Fe}^{2+}$  cations at  ${}^{[6]}M^{O}(2,4,5)$  sites, and locally (45%) to two Fe<sup>2+</sup> cations at  ${}^{[6]}M^{O}(2,4)$  sites, and to a  $Mn^{2+}$  cation at the <sup>[6]</sup> $M^{O}(5)$  site.

Endmember formula. We write the endmember formula of bafertisite as the sum of groups of cation and anion sites: Ba<sub>2</sub>  $(A^{P}_{2}) + Fe^{2+}_{4} (M^{O}_{4}) + Ti_{2} (M^{H}_{2}) + (Si_{2}O_{7})_{2} + O_{2} [(X^{O}_{M})_{2}] + (OH)_{2} [(X^{O}_{A})_{2}] + F_{2} [(X^{P}_{M})_{2}] = Ba_{2}Fe^{2+}_{4}Ti_{2}(Si_{2}O_{7})_{2}O_{2}(OH)_{2}F_{2}, Z = 4.$ 

*Basic TS-block structure*. In the crystal structure of bafertisite, (1) there is only one type of TS block of composition  $[Fe^{2+}_{4}Ti_2(Si_2O_7)_2O_2(OH)_2F_2]^{4-}$ ; (2) the two H sheets of the TS block are identical; (3) there is only one type of I block of composition  $[Ba_2]^{4+}$ ; and (4) there is only one type of self-linkage of TS blocks, *via* a layer of Ba atoms in the I block. Points (1)–(4) are in accord with the definition of a basic structure as given by Sokolova & Cámara (2013).

# SUMMARY

(1) Bafertisite, ideally  $Ba_2Fe^{2+}_4Ti_2(Si_2O_7)_2O_2$ (OH)<sub>2</sub>F<sub>2</sub>, is a Group-II TS-block mineral Ti = 2 *apfu* in accord with Sokolova (2006). The crystal structure of bafertisite [*a* 10.677(6), *b* 13.767(7), *c* 11.737(5) Å,  $\alpha$  90.12(1),  $\beta$  112.28(4),  $\gamma$  90.02(1)°, *V* 1596(3) Å<sup>3</sup>, space group *C*I] is of basic type [B2(GII)] and is an alternation of TS and I blocks of compositions [Fe<sup>2+</sup><sub>4</sub>Ti<sub>2</sub>(Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub>O<sub>2</sub>(OH)<sub>2</sub>F<sub>2</sub>]<sup>4–</sup> and [Ba<sub>2</sub>]<sup>4+</sup>, respectively. The crystal structure of bafertisite has the same topology as that of hejtmanite,  $Ba_2Mn^{2+}_4Ti_2(Si_2O_7)_2O_2(OH)_2F_2$ .

- (2) In the O sheet of the TS block, Fe<sup>2+</sup> is the dominant cation, and the lack of Fe<sup>3+</sup> has been confirmed by Mössbauer spectroscopy.
- (3) In the crystal structure of bafertisite, OH groups and F atoms are ordered at the  $X^{O}_{A}$  sites in the O sheet and  $X^{P}_{M}$  sites on the periphery of the TS block. The two  $X^{P}_{M}$  sites are coordinated by four cations and hence there is no space to accommodate an OH group plus a hydrogen bond at those sites. The presence of OH groups in the O sheet of the TS block is supported by IR spectroscopy and bond-valence calculations for anions.
- (4) The endmember formula of bafertisite is of the form  $A^{P}_{2}M^{O}_{4}M^{H}_{2}(Si_{2}O_{7})_{2}(X^{O})_{4}(X^{P})_{2}$ : Ba<sub>2</sub>Fe<sup>2+<sub>4</sub></sup> Ti<sub>2</sub>(Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub>O<sub>2</sub>(OH)<sub>2</sub>F<sub>2</sub>, Z = 4 where  $A^{P}_{2}$  = Ba<sub>2</sub>,  $M^{O}_{4}$  = Fe<sup>2+<sub>4</sub></sup>,  $M^{H}_{2}$  = Ti<sub>2</sub>,  $(X^{O})_{4}$  =  $(X^{O}_{M})_{2}$  +  $(X^{O}_{A})_{2}$ = O<sub>2</sub>(OH)<sub>2</sub>,  $(X^{P}_{M})_{2}$  = F<sub>2</sub>.

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FIG. 5. A general view of the crystal structure of bafertisite which consists of TS (Titanium Silicate) and I (intermediate) blocks (a) and the details of the TS block: the close-packed O sheet of  $Fe^{2+}$  and Mn-dominant  $M^O$  octahedra (b), the H sheet of Tidominant  $M^H$  octahedra and Si<sub>2</sub>O<sub>7</sub> groups (c), and the F atom at the  $X^P_M$  site coordinated by the four cations (d). SiO<sub>4</sub> tetrahedra are orange, Ti-,  $Fe^{2+}$ , and Mn-dominant octahedra are yellow, green, and magenta, respectively; Ba atoms at the  $A^P$  sites in the I block are shown as raspberry spheres; O and H atoms of OH groups at the  $X^O_A$  sites are shown as red and small grey spheres; F atoms at the  $X^P_M$  sites are shown as yellow spheres. The unit cell is shown by thin black lines.

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