The Canadian Mineralogist
Vol. 46, pp. 447-453 (2008)
DOI: 10.3749/canmin.46.2.447

KNASIBFITE, $K_3Na_4[SiF_6]_3[BF_4]$, A NEW HEXAFLUOROSILICATE–TETRAFLUOROBORATE FROM LA FOSSA CRATER, VULCANO, AEOLIAN ISLANDS, ITALY

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Abstract

Knasibfite, ideally $K_3Na_4[SiF_6]_3[BF_4]$, is a newly discovered mineral species that can be considered a potassium and sodium hexafluorosilicate–tetrafluoroborate. It occurs in an altered pyroclastic breccia associated with hieratite, avogadrite and demartinite in a low-temperature fumarole at the rim of La Fossa crater, Vulcano Island, Aeolian Archipelago, Sicily, Italy. The mineral is orthorhombic, space group *Imm*2, with *a* 5.522(1), *b* 17.106(3), *c* 9.175(2) Å, *V* 866.7(3) Å^3, Z = 2. The crystals are colorless, prismatic up to 0.1 mm, most commonly showing the forms {001}, {100}, {010}, {110}, {011} and {101}. The mean analytical results are: K 16.78, Na 13.14, Si 11.36, F 57.83, B 1.50, for a total of 100.61 wt%. The boron content has been estimated from results of the crystal-structure analysis. The empirical formula (based on 33 *apfu*) is: $K_{3.09}Na_{4.11}Si_{2.91}B_{1.00}F_{21.89}$; the simplified formula is $K_3Na_4[SiF_6]_3[BF_4]$, which requires: K 16.24, Na 12.73, Si 11.67, F 57.87, B 1.50, for a total of 100.00 wt%. The crystal structure has been refined to a final R index of 0.0272 for 660 observed reflections. The asymmetric unit contains two twelve-coordinated independent K^+ ions, located on *m*.. and on *mm*2 sites, respectively [K–F distances in the range 2.756(3)–3.332(2) Å], two independent Na^+ ions, of which one is nine-coordinated [Na–F distances in the range 2.254(5)–2.949(3) Å], and the other one displays instead octahedral coordination [Na–F distances in the range 2.224(3)–2.387(3) Å]. There are also two crystallographically independent octahedral SiF_6^{2-} anions with Si–F distances in the range 1.640(6)–1.684(4) Å, and a tetrahedral BF_4^- anion, with B–F distances ranging from 1.385(6) to 1.386(7) Å. The calculated density is 2.77 g/cm^3, the measured density is 2.75(1) g/cm^3. The mineral is optically nearly isotropic, with n = 1.32(1). The strongest six lines in the X-ray powder-diffraction pattern [d_{obs} in Å(*I*)*hkl*] are: 4.044(100)(022), 8.558(50)(020), 2.280(50)(222), 3.175(30)(141), 8.107(25)(011) and 2.094(25)(251). The name reflects its chemical composition.

Keywords: knasibfite, new mineral species, hexafluorosilicate–tetrafluoroborate, silicofluoride, borofluoride, crystal structure, fumarole minerals, Vulcano Island, Aeolian Islands, Italy.

Sommaire

Nous décrivons la knasibfite, de formule idéale $K_3Na_4[SiF_6]_3[BF_4]$, nouvelle espèce minérale considérée un hexafluorosilicate–tétrafluoroborate de potassium et sodium. Elle est présente dans une brèche pyroclastique altérée, associée à la hiératite, l'avogadrite et la demartinite dans une fumerolle active à basse température au cratère La Fossa, île de Vulcano dans l'archipel Aeolien, en Sicile, Italie. Il s'agit d'un minéral orthorhombique, groupe spatial *Imm*2, *a* 5.522(1), *b* 17.106(3), *c* 9.175(2) Å, *V* 866.7(3) Å^3, Z = 2. Les cristaux sont des prismes incolores atteignant 0.1 mm, montrant en général les formes {001}, {100}, {010}, {110}, {011} et {101}. Les analyses ont donné, en moyenne, K 16.78, Na 13.14, Si 11.36, F 57.83, B 1.50, pour un total de 100.61% (poids). La teneur en bore est évaluée à partir des résultats de l'ébauche de la structure cristalline. La formule empirique, fondée sur trente-trois atomes par formule unitaire, est: $K_{3.09}Na_{4.11}Si_{2.91}B_{1.00}F_{21.89}$; la formule simplifiée est $K_3Na_4[SiF_6]_3[BF_4]$, ce qui requiert: K 16.24, Na 12.73, Si 11.67, F 57.87, B 1.50, pour un total de 100.00%. La structure cristalline a été affinée jusqu'à un résidu R de 0.0272 pour 660 réflexions observées. L'unité assymétrique contient deux ions indépendants de K^+ à coordinence 12, situés sur les sites *m*.. et *mm*2, respectivement [distances K–F dans l'intervalle 2.756(3)–3.332(2) Å], deux ions Na^+ indépendants, un à coordinence neuf [distances Na–F dans l'intervalle 2.254(5)–2.949(3) Å], et l'autre à coordinence octaédrique [distances Na–F dans l'intervalle 2.224(3)–2.387(3) Å]. Il y a aussi deux octaèdres SiF_6^{2-} cristallographiquement indépendants ayant des distances Si–F dans l'intervalle 1.640(6)–1.684(4) Å, et un tétraèdre BF_4^- ayant des distances B–F entre

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1.385(6) et 1.386(7) Å. La densité calculée est 2.77 g/cm^3, et la densité mesurée est 2.75(1) g/cm^3. Le minéral est presque isotrope optiquement, avec n = 1.32(1). Les six raies les plus intenses du spectre de diffraction, méthode des poudres [d_{obs} en Å(*I*)*hkl*], sont: 4.044(100)(022), 8.558(50)(020), 2.280(50)(222), 3.175(30)(141), 8.107(25)(011) et 2.094(25)(251). Le nom choisi est inspiré de sa composition chimique.

(Traduit par la Rédaction)

Keywords: knasibfite, nouvelle espèce minérale, hexafluorosilicate–tétrafluoroborate, silicofluorure, borofluorure, structure cristalline, minéraux de fumerolles, île de Vulcano, îles Aeoliennes, Italie.

INTRODUCTION

The fumarolic system of La Fossa crater, Vulcano Island in the Aeolian Archipelago, Sicily, Italy, seems to be a promising source of new and rare minerals. Already more than one century ago, hieratite, a cubic modification of K_2SiF_6, was described for the first time by Alfonso Cossa (1881–1882, 1882, 1884), and forty years later, the lead–bismuth sulfosalt cannizzarite $Pb_{45}Bi_{54}S_{127}$ was discovered by Zambonini *et al.* (1924). The discovery of hieratite raised attention to the particular importance of fluorides in this locality, since it preceded even the discovery of the same species at Vesuvius (Zambonini & Carobbi 1926). Later on, the presence of another rare fluoride, gearksutite $CaAlF_4(OH)•H_2O$, was also observed at Vulcano (Bernauer 1941).

In more recent times, renewed interest in this locality led to the discovery of additional new lead–bismuth sulfosalts such as mozgovaite $PbBi_4(S,Se)_7$ and vurroite $Pb_{20}Sn_2(Bi,As)_{22}S_{54}Cl_6$ (Vurro *et al.* 1999, Garavelli *et al.* 2005, and references therein). Moreover, La Fossa crater is the type locality of thallium halides such as lafossaite, TlCl (Roberts *et al.* 2006) and hephaistosite $TlPb_2Cl_5$ (Campostrini *et al.* 2008; see there for additional references and historical details). Among fluorides, barberiite, NH_4BF_4 (Garavelli & Vurro 1994) and a new hexagonal polymorph of K_2SiF_6, demartinite (Gramaccioli & Campostrini 2007) were also discovered in these fumaroles.

Here, we report a description of a newly discovered potassium and sodium hexafluorosilicate–tetrafluoroborate, knasibfite, $K_3Na_4[SiF_6]_3[BF_4]$, as a further example of the presence of unusual complex fluorides at this locality. [We name knasibfite a hexafluorosilicate-tetrafluoroborate to conform to IUPAC rules; some prefer to consider minerals containing these anions as silicofluorides and borofluorides, respectively.] The mineral was found in an altered pyroclastic breccia associated with hieratite, avogadrite and demartinite in a low-temperature fumarole at the rim of the crater. The mineral has been named according to its chemical composition; both the mineral and the name have been approved by the Commission on New Minerals and Mineral Names of the IMA (No. 2006–042). The holotype is deposited (no. 2006–03) in the Reference Collection of Dipartimento di Chimica Strutturale e Stereochimica Inorganica of Università degli Studi di Milano.

TABLE 1. CHEMICAL COMPOSITION OF KNASIBFITE

Constituent	wt%	Range of 10 determinations	Standard deviation	Microprobe standard
K	16.78	16.70 - 16.91	0.1	KF
Si	11.36	11.05 - 11.98	0.1	Si
F	57.83	55.23 - 58.50	0.2	KF
Na	13.14	11.09 - 14.18	0.2	NaF
B	1.50			calculated*
Total	100.61			

* The boron content has been deduced from the crystal-structure determination.

APPEARANCE AND PHYSICAL PROPERTIES

Knasibfite crystals are prismatic, colorless and transparent, with maximum dimension about 0.1 mm. An electron microscope photograph of the mineral and drawings of the crystals based on the forms {001}, {100}, {010}, {110}, {011} and {101} are shown in Figures 1 and 2, respectively. The luster is vitreous, and the streak is white. The mineral is brittle; the hardness could not be determined because of the small size of the crystals. We did not observe signs of a distinct cleavage and fracture. The mineral is non-fluorescent either under short-wave (254 nm) or long-wave (366 nm) ultraviolet light. The density [2.75(1) g/cm^3] was measured by flotation in methylene iodide – monobromonaphthalene; the corresponding value calculated from the empirical formula and single-crystal data is 2.77 g/cm^3. The crystals are optically nearly isotropic, and the index of refraction, which is inferior to that of water, almost matches that of 2,2,3,3-tetrafluoro-1-propanol [n = 1.32(1) for λ = 589 nm]; on this basis, the compatibility index 1 – (K_P/K_C), – 0.030, is excellent according to Mandarino (1981).

CHEMICAL DATA

Chemical analyses were carried out by means of a JEOL JSM 5500 LV scanning electron microscope equipped with an IXRF EDS 2000 microprobe (20 kV, 10^{-11}A, 1 μm beam diameter); the mean analytical results are reported in Table 1. A wavelength-dispersion analysis was also performed using a JEOL JXA 8200

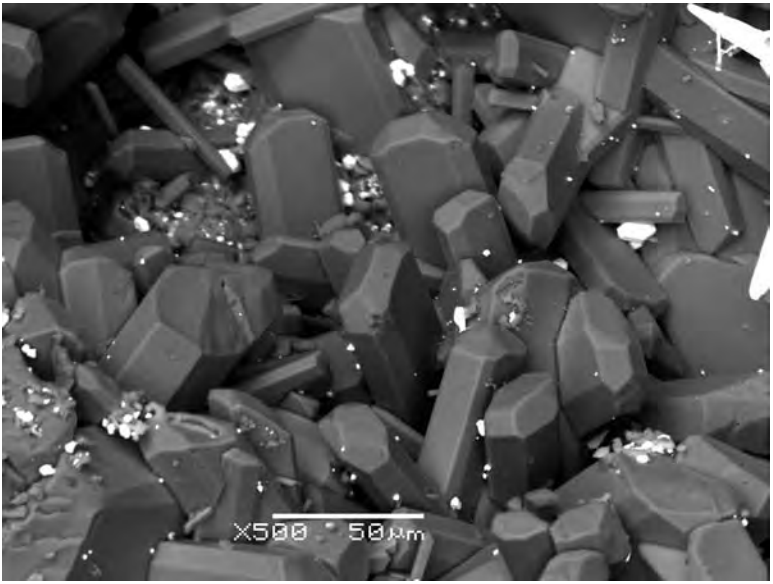

FIG. 1. An SEM image of knasibfite crystals.

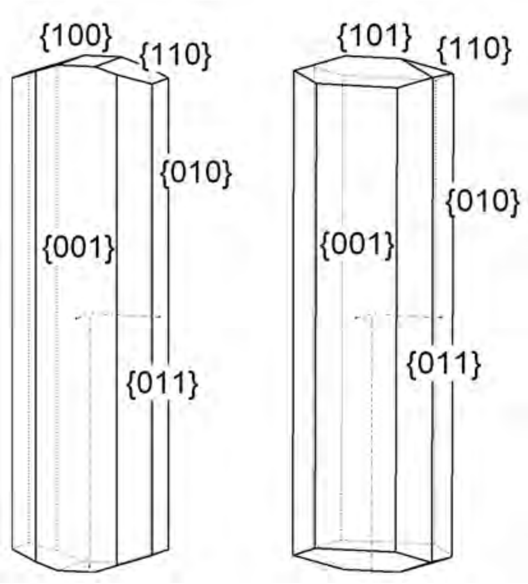

FIG. 2. Idealized drawings of typical crystals of knasibfite.

electron microprobe, but the results were less satisfactory, owing to fusion and partial volatilization under the electron beam; in any case, the *K*α peak of boron was clearly evident working at 10 kV, with a beam current of 2 × 10^{-8}A, beam diameter of 10 µm and a LDEB spectrometer.

The empirical formula (based on 33 *apfu*) is: $K_{3.09}Na_{4.11}Si_{2.91}B_{1.00}F_{21.89}$. The simplified formula is $K_3Na_4[SiF_6]_3[BF_4]$, which requires: K 16.24, Na 12.73, Si 11.67, F 57.87, B 1.50, for a total of 100.00 wt.%.

X-RAY DATA AND STRUCTURE REFINEMENT

X-ray powder-diffraction data have been obtained using a Gandolfi camera 114.6 mm in diameter, with Cu*K*α radiation (Table 2); from these data, the unit-cell parameters *a* 5.521(1), *b* 17.115(4), *c* 9.186(2) Å, and *V* = 868.1(2) Å^3 have been obtained using the program UNIT CELL (Holland & Redfern 1997).

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR KNASIBFITE

I/I_o	*d* (Å) obs.	*d* (Å) calc.*	*h k l*	I/I_o	*d* (Å) obs.	*d* (Å) calc.*	*h k l*
50	8.558	8.557	0 2 0	15	3.015	3.014	0 1 3
25	8.107	8.094	0 1 1	25	3.004	3.002	1 3 2
20	4.854	4.846	0 3 1	15	2.366	2.366	2 0 2
25	4.726	4.732	1 0 1	20	2.361	2.363	0 7 1
25	4.134	4.141	1 2 1	10	2.296	2.297	0 0 4
100	4.044	4.047	0 2 2	50	2.280	2.281	2 2 2
20	3.458	3.458	1 1 2	25	2.094	2.092	2 5 1
30	3.175	3.174	1 4 1	25	1.795	1.795	2 7 1

* Calculated from the refined unit-cell data: *a* 5.521(1), b 17.115(4), *c* 9.186(2) Å, *V* 868.1(2) Å^3. Pattern recorded with a Gandolfi camera 114.6 mm in diameter, Cu*K*α radiation.

Single-crystal diffraction data were collected from a prismatic crystal (0.10 × 0.06 × 0.05 mm) with Mo$K\alpha$ radiation (λ = 0.71073 Å), using a BRUKER Apex II diffractometer equipped with a 2K CCD detector. A one-minute frame-time and 0.3° frame-width were used. A total of 2477 reflections were measured up to 2θ = 47.62°, of which 780 were considered unique. The unit-cell dimensions were refined by least-squares from 790 reflections with $I > 5\sigma(I)$; the refined values are given in Table 3, together with other details concerning the data collection and refinement. An absorption correction was applied using the SADABS program (Sheldrick 2000). The structure was solved by direct methods with SIR97 (Altomare *et al.* 1999) and refined with the SHELXL97 program (Sheldrick 1997) implemented in the WINGX suite (Farrugia 1999). An extinction parameter x was also refined to the value of 0.028(7), where F_c is multiplied by $k\ [1+ 0.001xF_c^2\lambda^3/\sin(2\theta)]^{-1/4}$, k being the overall scale-factor. The final values of the refined occupancies of the alkali ions do not differ significantly from unity (within three estimated standard deviations). The final coordinates and displacement parameters of the atoms are reported in Tables 4 and 5, respectively. Projections of the crystal structure are provided as Figures 3, 4 and 5, respectively. Selected interatomic distances and angles are reported in Table 6.

Observed and calculated structure-factors tables may be obtained from The Depository of Unpublished Data, on the MAC web site [document Knasibfite CM46_447].

TABLE 3. KNASIBFITE: SINGLE-CRYSTAL DATA

Crystal system	orthorhombic	D_{calc} (g/cm^3)	2.77
Space group	*Imm*2 (no. 44)	μ (Mo$K\alpha$) (mm^{-1})	1.312
a (Å)	5.522(1)	Scan mode	ω
b (Å)	17.106(3)	θ range (°)	2.38 -23.81
c (Å)	9.175(2)	Measured reflections	2477
V (Å^3)	866.7(3)	Independent reflections	780
Z	2	Observed reflections [$I > 2\sigma(I)$]	660
Minimum transmission-factor		0.729	
Parameters refined		97	
Final R and wR2 $^\$$		0.0272, 0.0491	
Largest diffraction peak and hole (e Å^{-3})		0.24, -0.29	

$^\$$ $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - Fc^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$.

TABLE 4. KNASIBFITE: FRACTIONAL COORDINATES AND U_{eq} OF ATOMS

Atom	*X / a*	*Y / b*	*Z / c*	U_{eq}
K(1)	½	0.37387(8)	0.2826(2)	0.0353(4)
K(2)	½	0	0.4448(2)	0.0266(5)
Na(1)	0	0.1714(1)	0.3514(3)	0.0333(7)
Na(2)	0	0.3583(1)	0.6039(3)	0.0226(6)
Si(1)	0	0	0.2030(3)	0.0187(6)
Si(2)	½	0.2142(1)	0.5193(2)	0.0192(4)
F(1)	0	0	0.3864(5)	0.0334(14)
F(2)	0	0	0.0242(6)	0.0393(14)
F(3)	-0.2144(5)	0.0697(13)	0.2094(3)	0.0368(7)
F(4)	½	0.2254(2)	0.6987(4)	0.0473(11)
F(5)	½	0.2038(2)	0.3369(4)	0.0328(11)
F(6)	0.7156(4)	0.14567(14)	0.5318(3)	0.0350(7)
F(7)	0.2853(5)	0.28234(14)	0.5000(3)	0.0423(9)
F(8)	0.2043(6)	½	0.2255(4)	0.0314(9)
F(9)	0	0.4332(2)	0.3987(4)	0.0412(11)
B	0	½	0.3131(11)	0.0260(30)

U_{eq} = ⅓ (U_{11} + U_{22} + U_{33}).

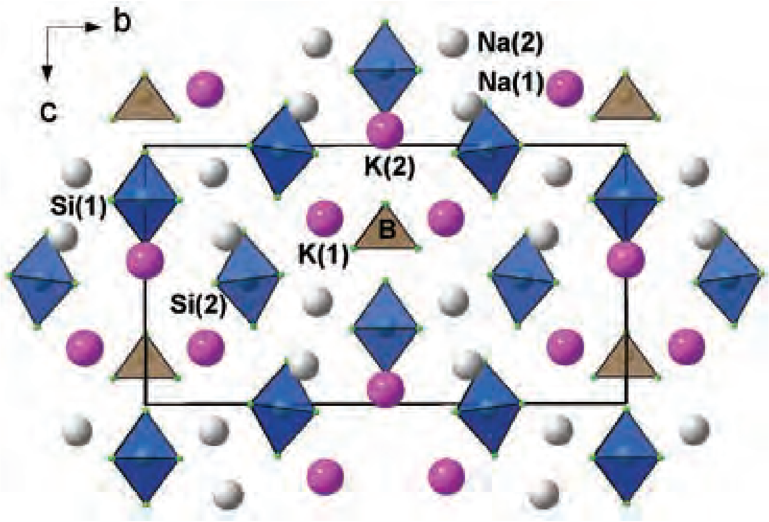

FIG. 3. A projection of the crystal structure of knasibfite along [1 0 0]. The blue octahedra and the tan tetrahedra are SiF_6^{2-} and BF_4^- anions, respectively. The K and Na ions are represented as magenta and light gray balls, respectively.

RESULTS AND DISCUSSION

The asymmetric unit contains two twelve-coordinated K^+ ions, located on *m*.. and on *mm*2 crystallographic sites, respectively. Their coordination polyhedra are far from being regular. The polyhedron around K(1) displays K–F distances in the range 2.756(3)–3.332(2) Å with an average value of 2.974 Å, whereas the corresponding distances in the polyhedron around K(2) are instead in the range 2.811(4)–2.928(3) Å, with an average of 2.872 Å. The situation is entirely different from that occurring in hieratite, the cubic form of K_2SiF_6, where the coordination polyhedron around K is in contrast an almost undistorted cuboctahedron with an average K–F distance of 2.897(1) Å; it also differs from that observed in demartinite, the hexagonal polymorph

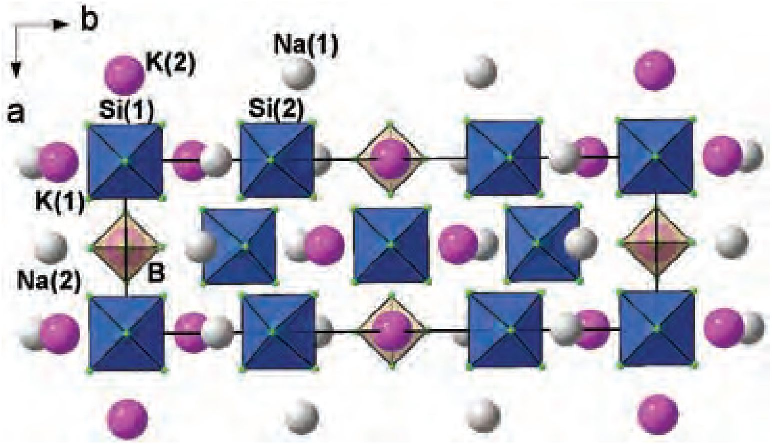

FIG. 4. A projection of the crystal structure of knasibfite along [0 0 1]. Atom representation as in Figure 2.

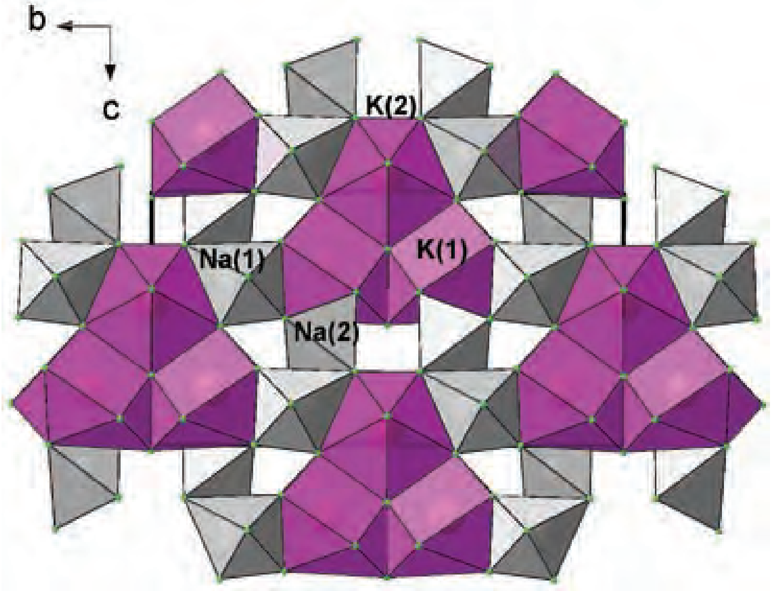

FIG. 5. A projection of the crystal structure showing the coordination polyhedra of the K^+ (magenta) and Na^+ (light gray) ions.

TABLE 5. KNASIBFITE: ANISOTROPIC DISPLACEMENT PARAMETERS *U*(*i,j*)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
K(1)	0.0399(10)	0.0283(8)	0.0376(9)	0.0088(8)	0	0
K(2)	0.0273(12)	0.0242(11)	0.0282(12)	0	0	0
Na(1)	0.0375(16)	0.0319(16)	0.0304(14)	0.0011(14)	0	0
Na(2)	0.0247(13)	0.0195(12)	0.0235(14)	-0.0036(11)	0	0
Si(1)	0.0172(14)	0.0147(13)	0.0242(15)	0	0	0
Si(2)	0.0192(10)	0.0182(10)	0.0201(10)	-0.0015(8)	0	0
F(1)	0.027(3)	0.050(4)	0.023(3)	0	0	0
F(2)	0.038(3)	0.057(4)	0.023(3)	0	0	0
F(3)	0.0312(17)	0.0285(15)	0.0507(19)	0.0035(16)	-0.0014(13)	0.0153(12)
F(4)	0.079(3)	0.044(2)	0.019(2)	-0.009(2)	0	0
F(5)	0.048(3)	0.028(2)	0.023(2)	-0.005(2)	0	0
F(6)	0.0299(16)	0.0298(15)	0.0455(17)	0.0063(15)	0.0043(14)	0.0131(12)
F(7)	0.0410(18)	0.0359(17)	0.050(2)	0.0064(16)	0.0111(14)	0.0183(14)
F(8)	0.027(2)	0.032(2)	0.035(2)	0	0.0042(18)	0
F(9)	0.053(3)	0.034(2)	0.036(3)	0.016(2)	0	0
B	0.030(6)	0.022(6)	0.025(7)	0	0	0

The anisotropic displacement factor exponent takes the form: $-2\pi^2(U_{11}h^2(a^*)^2 + \ldots + 2U_{12}hka^*b^* + \ldots)$

TABLE 6. KNASIBFITE: INTERATOMIC DISTANCES (Å) AND ANGLES (°)

	Coordination of the K^+ ions		
K(1)-F(2)	3.093(4)	K(2)-F(1) × 2	2.813(2)
K(1)-F(4) × 2	3.332(2)	K(2)-F(3) × 4	2.928(3)
K(1)-F(5)	2.952(4)	K(2)-F(6) × 4	2.875(3)
K(1)-F(6) × 2	2.806(3)	K(2)-F(8) × 2	2.811(4)
K(1)-F(7) × 2	2.799(3)		
K(1)-F(8) × 2	2.756(3)		
K(1)-F(9) × 2	3.129(2)		
K(1)-F *average*	2.974	K(2)-F *average*	2.872
	Coordination of the Na^+ ions		
Na(1)-F(1)	2.949(3)	Na(2)-F(3) × 2	2.224(3)
Na(1)-F(3) × 2	2.475(3)	Na(2)-F(5)	2.387(4)
Na(1)-F(4)	2.254(5)	Na(2)-F(7) × 2	2.253(3)
Na(1)-F(5) × 2	2.819(1)	Na(2)-F(9)	2.278(4)
Na(1)-F(6) × 2	2.324(3)		
Na(1)-F(7)	2.818(3)		
Na(1)-F *average*	2.584	Na(2)-F *average*	2.270
	The SiF_6^{2-} ions		
Si(1)-F(1)	1.683(5)	Si(2)-F(4)	1.656(4)
Si(1)-F(2)	1.640(6)	Si(2)-F(5)	1.684(4)
Si(1)-F(3) × 4	1.681(2)	Si(2)-F(6) × 2	1.675(3)
		Si(2)-F(7) × 2	1.672(3)
Si(1)-F *average*	1.675	Si(2)-F *average*	1.672
F(1)-Si(1)-F(2)	180	F(4)-Si(2)-F(5)	179.4(2)
F(3)-Si(1)-F(3) × 2	176.0(3)	F(6)-Si(2)-F(7) × 2	177.8(2)
F(1)-Si(1)-F(3) × 4	88.0(2)	F(4)-Si(2)-F(6) × 2	90.8(2)
F(2)-Si(1)-F(3) × 4	92.0(2)	F(4)-Si(2)-F(7) × 2	91.4(2)
F(3)-Si(1)-F(3) × 2	89.5(2)	F(5)-Si(2)-F(6) × 2	89.7(2)
F(3)-Si(1)-F(3) × 2	90.3(2)	F(5)-Si(2)-F(7) × 2	88.2(2)
		F(6)-Si(2)-F(6)	90.6(2)
		F(6)-Si(2)-F(7) × 2	89.5(2)
		F(7)-Si(2)-F(7)	90.3(2)
	The BF_4^- ion		
B-F(8) × 2	1.385(6)	B-F(9) × 2	1.386(7)
F(8)-B-F(8)	109.1(7)	F(8)-B-F(9) × 4	109.2(11)
F(9)-B-F(9)	111.0(8)		

of K_2SiF_6, where two independent K^+ ions displaying cuboctahedral or trigonal dodecahedral geometry are present; for these, the average K–F distances are 2.928 and 2.842 Å, respectively (Gramaccioli & Campostrini 2007). Two Na^+ ions also are present, both located on a mirror plane, but with different coordination. One [Na(1)] is surrounded by nine fluoride ions and is enclosed in a very distorted polyhedron where six Na–F distances are in the range 2.254(5)–2.475(3) Å, and three longer ones range from 2.818(3) to 2.949(3) Å. The other ion [Na(2)] displays instead octahedral coordination, with Na–F distances ranging from 2.224(3) to 2.387(4) Å. Similar Na–F distances, in the range 2.18–2.45 Å, have also been observed in malladrite, Na_2SiF_6 (Zalkin *et al.* 1964). The arrangement of the coordination polyhedra of the alkali ions in the crystal structure is shown in Figure 5. The absence of Na – K disorder is confirmed by the occupancies of the alkali-ion sites (see above) and is in agreement with the low temperature of formation.

The two SiF_6^{2-} ions are not symmetry-related. They both display significant deviation from the idealized octahedral geometry; the average Si–F distances, 1.675 and 1.672 Å, are slightly shorter than those observed for hieratite and demartinite [1.685(1) Å for both].

The BF_4^- ion is located on a *mm*2 crystallographic site, and its geometry is similar to that occurring for other fluoroborates. For instance, here the four B–F distances are practically identical (1.386 Å) and coincide with the average [1.386(2) Å] observed for KBF_4 (Brunton 1969); the F–B–F angles are not significantly different from the ideal tetrahedral angle (see Table 6).

As a conclusion, the first example of a mineral containing both hexafluorosilicate and tetrafluoroborate ions as a representative of a new class of complex fluorides has been discovered in the fumaroles at Vulcano. The unique characteristics of such an environment of formation may lead to the discovery of further very interesting mineralogical species and chemical compounds in general.

ACKNOWLEDGEMENTS

The authors are indebted to the Editor, Prof. Robert. F. Martin and to the referees, one of which is Prof. Anna Garavelli, for useful suggestions. The courteous assistance of Mr. Andrea Risplendente of Dipartimento di Scienze della Terra of our University is also gratefully acknowledged.

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Received June 15, 2007, revised manuscript accepted March 8, 2008.