

Fluorlamprophyllite, $\text{Na}_3(\text{SrNa})\text{Ti}_3(\text{Si}_2\text{O}_7)_2\text{O}_2\text{F}_2$, a new mineral from Poços de Caldas alkaline massif, Morro do Serrote, Minas Gerais, Brazil

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ABSTRACT

A new mineral species, fluorlamprophyllite (IMA2013-102), ideally $\text{Na}_3(\text{SrNa})\text{Ti}_3(\text{Si}_2\text{O}_7)_2\text{O}_2\text{F}_2$, has been found in the Poços de Caldas alkaline massif, Morro do Serrote, Minas Gerais, Brazil. Alternatively, the idealized chemical formula could be written as $(\text{SrNa})[(\text{Na}_3\text{Ti})\text{F}_2][\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_2]$, setting the large interlayer cations before the cations of the layer. Fluorlamprophyllite is the F-analogue of lamprophyllite. It is associated with aegirine, analcime, natrolite, nepheline and microcline. Fluorlamprophyllite crystals are brownish-orange and bladed. The mineral is transparent with a pale yellow streak and an adamantine lustre. It is brittle and has a Mohs hardness of ~ 3 ; cleavage is perfect on $\{100\}$ and no parting was observed. The calculated density is 3.484 g/cm^3 . Optically, fluorlamprophyllite is biaxial (+), with $\alpha = 1.735(7)$, $\beta = 1.749(7)$ and $\gamma = 1.775(9)$ and $2V_{\text{meas}} = 72(3)^\circ$. An electron microprobe analysis produced an average composition (wt.%) (9 points) of Na_2O 10.63(30), K_2O 0.47(3), SiO_2 30.51(13), SrO 18.30(24), MgO 0.81(17), Al_2O_3 0.23(2), CaO 1.11(7), MnO 5.03(38), TiO_2 27.41(87), Fe_2O_3 2.45(37), F 2.86(23), plus H_2O 1.00 (added to bring the total close to 100%), $-\text{O}=\text{F}$ -1.20 , with the total = 98.61%. The elements Nb and Ba were sought, but contents were below microprobe detection limits. The resultant chemical formula was calculated on the basis of 18 (O + F) atoms per formula unit. The addition of 1.00 wt.% H_2O brought $[\text{F}+(\text{OH})] = 2$ pfu, yielding $(\text{Na}_{2.63}\text{Sr}_{1.35}\text{Mn}_{0.54}\text{Ca}_{0.15}\text{Mg}_{0.15}\text{K}_{0.08})_{\Sigma 4.90}(\text{Ti}_{2.63}\text{Fe}_{0.24}\text{Al}_{0.04})_{\Sigma 2.91}\text{Si}_{3.89}\text{O}_{16}[\text{F}_{1.15}(\text{OH})_{0.85}]_{\Sigma 2.00}$. The mineral is monoclinic, with space group $C2/m$ and unit-cell parameters $a = 19.255(2)$, $b = 7.0715(7)$, $c = 5.3807(6)$ Å, $\beta = 96.794(2)^\circ$ and $V = 727.5(1)$ Å³. The structure is a layered silicate inasmuch as the O atoms are arranged in well-defined, though not necessarily close-packed layers.

KEYWORDS: fluorlamprophyllite, $\text{Na}_3(\text{SrNa})\text{Ti}_3(\text{Si}_2\text{O}_7)_2\text{O}_2\text{F}_2$, crystal structure, X-ray diffraction, lamprophyllite group.

Introduction

A new mineral species, fluorlamprophyllite, ideally $\text{Na}_3(\text{SrNa})\text{Ti}_3(\text{Si}_2\text{O}_7)_2\text{O}_2\text{F}_2$, has been found in the Poços de Caldas alkaline massif, Morro do Serrote (Serrote Hill), Minas Gerais, Brazil. Alternatively, the idealized chemical formula could be written as

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(SrNa)[(Na₃Ti)F₂][Ti₂(Si₂O₇)₂O₂], setting the large interlayer cations before the cations of the layer (Rastsvetaeva *et al.*, 2016). The new mineral and its name have been approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA2013-102). The holotype and part of the co-type sample have been deposited at the University of Arizona Mineral Museum (catalogue no. 19589) and the RRUFF Project (deposition no. R130421: <http://ruff.info/fluorlamprophyllite>), respectively.

Fluorlamprophyllite is the F-analogue of lamprophyllite and the fourth reported F-dominant member of the lamprophyllite group, the others being schüllerite (Chukanov *et al.*, 2011), lileyite (Chukanov *et al.*, 2012) and emmerichite (Aksenov *et al.*, 2014). It is also part of the family of heterophyllosilicates (Ferraris and Gula, 2005). Also, the term ‘heteropolyhedral (H) sheet’ has been used instead of heterophyllosilicates, which emphasizes the fact that the H sheet consists of different cation polyhedra (Sokolova, 2006). The general chemical formula can be expressed as $[M1M2]_2A_2[M3L_2](Si_2O_7)_2O_2Y_2$, where $M1 = Na, Mn^{2+}, Mg$ or Fe^{2+} ; $M2 = Na$ or Mn^{2+}, Mg, Fe^{2+} or Ca ; $A = Ba, Sr, K, Na, Ca$ or \square ; $M3 = Ti, Mn^{2+}, Mg, Fe^{3+}$ or Fe^{2+} ; $L = Ti$ or Fe^{3+} and $Y = OH, O$ or F , according to the ion occupancies suggested by Chukanov *et al.* (2012) and Rastsvetaeva *et al.* (2016). In fluorlamprophyllite, the Y site is dominated by F. There are other eight members of this group, including monoclinic (2M) and orthorhombic (2O) polytypes: lamprophyllite-2M and -2O, Na₃(SrNa)Ti₃(Si₂O₇)₂O₂(OH)₂ (Woodrow, 1964; Saf'yanov *et al.*, 1983; Krivovichev *et al.*, 2003), ericssonite-2M and -2O, Ba₂Mn₄Fe₂³⁺(Si₂O₇)₂O₂(OH)₂ (Moore, 1971; Matsubara, 1980), nabalamprophyllite-2M and -2O, Na₃(BaNa)Ti₃(Si₂O₇)₂O₂(OH)₂ (Chukanov *et al.*, 2004; Sokolova and Hawthorne, 2008), barytolamprophyllite-2M, Na₃(BaK)Ti₃(Si₂O₇)₂O₂(OH)₂ (Sokolova and Cámara, 2008), ferroericssonite-2M, Ba₂Fe₄²⁺Fe₂³⁺(Si₂O₇)₂O₂(OH)₂ (Kampf *et al.*, 2011), schüllerite-1T, Ba₂NaMnFe²⁺Fe³⁺Ti₂(Si₂O₇)₂O₂F₂ (Rastsvetaeva *et al.*, 2011; Chukanov *et al.*, 2011; Rastsvetaeva *et al.*, 2016), lileyite-2M, Ba₂Na(Na,Fe,Ca)₂MgTi₂(Si₂O₇)₂O₂F₂ (Chukanov *et al.*, 2012) and emmerichite-2M, Ba₂Na₃Fe³⁺Ti₂(Si₂O₇)₂O₂F₂ (Aksenov *et al.*, 2014; Chukanov *et al.*, 2014; Rastsvetaeva *et al.*, 2016). This paper describes the physical and chemical properties of fluorlamprophyllite and its crystal structure



FIG. 1. A piece of the specimen in which fluorlamprophyllite was found.

determined from single-crystal X-ray diffraction data.

Sample description and experimental procedure

Occurrence, chemical composition and Raman spectra

Fluorlamprophyllite was found embedded in the mass of a sample of nepheline syenite (Fig. 1) collected from Morro do Serrote, Minas Gerais (21° 53'05"S, 46°38'45"W). Associated minerals include aegirine, analcime, natrolite, nepheline and microcline. The nepheline syenite at Morro do Serrote is an intrusive body (9 km², 60–65 Ma) in phonolites, located in the central-western portion of the subcircular Mid-Cretaceous Poços de Caldas alkaline massif (800 km²). The massif's geology and petrology have been studied since the 19th



FIG. 2. A microscopic view of brownish-orange, bladed fluorlamprophyllite crystals.

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TABLE 1. Powder X-ray diffraction data for fluorlamprophyllite.*

Experimental		Theoretical				
I_{obs}	d_{obs} (Å)	I_{calc}	d_{calc} (Å)	h	k	l
7	4.722 (2 overlaps)	23	4.7799	4	0	0
		5	4.7342	3	1	0
63	4.120	27	4.0798	1	1	1
40	3.704	31	3.7088	$\bar{3}$	1	1
22	3.363 (4 overlaps)	11	3.3982	3	1	1
		5	3.3698	4	0	1
		26	3.3637	5	1	0
		14	3.3162	2	2	0
23	3.185	34	3.1866	6	0	0
15	2.983 (2 overlaps)	18	2.9903	$\bar{5}$	1	1
		8	2.9486	0	2	1
26	2.857 (2 overlaps)	13	2.8914	$\bar{6}$	0	1
		6	2.8426	4	2	0
100	2.762 (2 overlaps)	100	2.7672	2	2	1
		25	2.7217	5	1	1
25	2.655	35	2.6556	$\bar{2}$	0	2
24	2.587 (3 overlaps)	5	2.6046	6	0	1
		34	2.5861	$\bar{4}$	2	1
		13	2.5479	7	1	0
		5	2.4974	2	0	2
15	2.448 (6 overlaps)	8	2.4591	$\bar{4}$	0	2
		9	2.4394	4	2	1
		4	2.4194	$\bar{3}$	1	2
		5	2.4053	$\bar{7}$	1	1
		6	2.3671	6	2	0
		8	2.2437	3	1	2
9	2.224 (2 overlaps)	9	2.178	$\bar{6}$	0	2
		9	2.1317	1	3	1
33	2.126 (6 overlaps)	21	2.1315	0	2	2
		7	2.1234	$\bar{2}$	2	2
		24	2.0971	6	2	1
		4	2.0914	8	0	1
		4	2.0731	$\bar{3}$	3	1
		10	2.0346	9	1	0
15	2.014 (3 overlaps)	7	2.0189	$\bar{4}$	2	2
		13	2.0066	5	3	0
		14	1.9547	$\bar{7}$	1	2
		5	1.9375	6	0	2
10	1.945 (4 overlaps)	9	1.919	$\bar{8}$	2	1
		4	1.8961	$\bar{8}$	0	2
		8	1.8412	5	3	1
		5	1.8001	8	2	1
25	1.764 (4 overlaps)	6	1.7845	7	3	0
		22	1.7679	0	4	0
		9	1.7499	7	1	2
		9	1.7499	7	1	2
10	1.645 (4 overlaps)	4	1.6581	$\bar{4}$	4	0
		5	1.6499	$\bar{10}$	0	2
		6	1.6464	$\bar{5}$	1	3
		4	1.6207	3	1	3
28	1.595 (4 overlaps)	11	1.5966	$\bar{2}$	2	3
		14	1.5906	0	2	3

(continued)

TABLE 1. (*contd.*)

Experimental		Theoretical				
I_{obs}	d_{obs} (Å)	I_{calc}	d_{calc} (Å)	h	k	l
		4	1.5589	11	1	1
		13	1.5585	10	2	1
10	1.546 (2 overlaps)	4	1.5459	6	4	0
		5	1.5399	7	3	2
16	1.475 (3 overlaps)	6	1.4873	6	2	3
		13	1.4716	2	4	2
		4	1.4636	4	2	3
11	1.440 (3 overlaps)	17	1.4417	12	2	1
		7	1.4336	7	3	2
		4	1.4142	9	3	2

*Theoretical data were calculated from the determined structure model using the *XPOW* program (Downs *et al.*, 1993).

century and a systematic study of its structure, mineralogy and petrology has been presented by Ulbrich (1984), including a comprehensive classification of the different nepheline syenite facies from Morro do Serrote. Also, Morro do Serrote is an important bauxite deposit (Leonardi *et al.*, 2011).

Fluorlamprophyllite crystals are orange and bladed, up to 3 mm long, 0.3 mm wide and 0.2 mm thick (Figs 1 and 2). The mineral is transparent with a pale yellow streak and an adamantine lustre. It is brittle and has a Mohs hardness of ~3; cleavage is perfect on {100} and no

TABLE 2. Summary of crystal data and refinement results for fluorlamprophyllite and lamprophyllite.

	Fluorlamprophyllite	Lamprophyllite
Ideal chemical formula	$\text{Na}_3(\text{SrNa})\text{Ti}_3(\text{Si}_2\text{O}_7)_2\text{O}_2\text{F}_2$	$\text{Na}_3(\text{SrNa})\text{Ti}_3(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2$
Crystal chemistry	Monoclinic	Monoclinic
Space group	$C2/m$ (No. 12)	$C2/m$ (No. 12)
a (Å)	19.255(2)	19.215(5)
b (Å)	7.0715(7)	7.061(2)
c (Å)	5.3807(6)	5.3719(15)
β (°)	96.794(2)°	96.797(4)
V (Å ³)	727.5(1)	723.7(4)
Z	2	2
ρ_{cal} (g/cm ³)	3.496	3.49
λ (Å, MoK α)	0.71073	0.71073
μ (mm ⁻¹)	7.331	7.036
2 θ max. for data collection(°)	≤65	≤55
No. of reflections collected	5188	1607
No. of independent reflections	1397	688
No. of reflections with $I > 2\sigma(I)$	1202	
No. of parameters refined	89	84
R_{int}	0.026	0.045
Final R_1 , wR_2 factors [$I > 2\sigma(I)$]	0.0232, 0.0520	0.040, 0.103
Final R_1 , wR_2 factors (all data)	0.0316, 0.0545	
Goodness-of-fit	1.08	1.05
Reference	This work	Krivovichev <i>et al.</i> (2003)

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 TABLE 3. Coordinates, Wyckoff positions (W), refined number of electrons (e_{ref}^-), equivalent displacement parameters (U_{eq} , \AA^2) and site population (s.p.) in fluorlampoptyllite.

Cationic site	Atom	x	y	z	W	Occ.	e_{ref}^-	U_{eq}	s.p.
<i>A</i>	Sr	0.2849(1)	0	0.2621(1)	4i	0.640(3)	48.6	0.0098(1)	Sr _{1.28}
	Na3	0.2749(5)	0	0.2596(17)	4i	0.360(3)	8.0	0.038(5)	Na _{0.73}
<i>M2</i>	Na1	½	0.24126(9)	½	4h	0.667(3)	14.6	0.0119(2)	Na _{1.33}
	Mn1	½	0.24126(9)	½	4h	0.333(3)	16.8	0.0119(2)	Mn _{0.67}
<i>M1</i>	Na2	0	0	0	2a	1	11.0	0.0169(3)	Na
<i>L</i>	Ti1	0.15061(2)	0	0.7077(1)	4i	1	44.0	0.0069(1)	Ti ₂
<i>M3</i>	Ti2	-0.0062(2)	½	0.0263(5)	4i	0.4939(17)	21.8	0.0068(4)	Ti _{0.99}
<i>Si</i>	Si	0.14368(2)	0.28440(6)	0.2049(1)	8j	1	56.0	0.0067(1)	Si ₄
	O1H	0.4453(6)	0	0.2862(19)	4i	0.44(4)		0.0145(22)	
	O1F	0.4392(4)	0	0.2617(15)	4i	0.56(4)		0.0249(21)	
	O2	0.17485(7)	0.1893(2)	0.4675(2)	8j	1		0.0138(3)	
	O3	0.17533(7)	0.1878(2)	0.9719(2)	8j	1		0.0132(3)	
	O4	0.17725(9)	½	0.2196(3)	4i	1		0.0109(3)	
	O5	0.05953(7)	0.2951(2)	0.1724(2)	8j	1		0.0115(2)	
	O6	0.0625(1)	0	0.6678(3)	4i	1		0.0182(4)	

parting was observed. The calculated density is 3.484 g/cm³. Optically, fluorlampoptyllite is biaxial (+), with $\alpha = 1.735(7)$, $\beta = 1.749(7)$ and $\gamma = 1.775(9)$ (white light), $2V_{\text{meas}} = 72(3)^\circ$, $2V_{\text{calc}} = 74^\circ$, and the orientation $X \perp b$, $Z \wedge c \cong 5^\circ$. The pleochroism is $X = \text{yellow-green}$, $Y = \text{yellow-brown}$ and $Z = \text{brown}$.

The chemical composition of fluorlampoptyllite was determined using a CAMECA SX-100 electron microprobe with an operating current of 15 kV and 10 nA and 10 μm beam diameter. The

standards included albite (Na), microcline (K), wollastonite (Si), SrTiO₃ (Sr), diopside (Ca and Mg), anorthite (Al), rhodonite (Mn), rutile (Ti), fayalite (Fe) and MgF₂ (F), yielding an average composition (wt.%) (9 analytical points) of: Na₂O 10.63(30), K₂O 0.47(3), SiO₂ 30.51(13), SrO 18.30(24), MgO 0.81(17), Al₂O₃ 0.23(2), CaO 1.11(7), MnO 5.03(38), TiO₂ 27.41(87), Fe₂O₃ 2.45(37), F 2.86(23) and O = F -1.20, with the total = 98.61%. The elements Nb and Ba were sought, but contents were below microprobe detection

 TABLE 4. Anisotropic displacement parameters of atoms in fluorlampoptyllite (\AA^2).

Cationic site	Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
<i>A</i>	Sr	0.0135(3)	0.0086(2)	0.0072(2)	0	0.0004(2)	0
	Na3	0	0	0	0	0	0
<i>M2</i>	Na1	0.0155(4)	0.0107(3)	0.0100(3)	0	0.0039(2)	0
	Mn1	0.0155(4)	0.0107(3)	0.0100(3)	0	0.0039(2)	0
<i>M1</i>	Na2	0.0175(8)	0.0187(8)	0.0158(7)	0	0.0064(6)	0
<i>L</i>	Ti1	0.0079(2)	0.0076(2)	0.0052(2)	0	0.0005(1)	0
<i>M3</i>	Ti2	0.0068(11)	0.0065(3)	0.0067(12)	0	-0.0005(5)	0
<i>Si</i>	Si	0.0080(2)	0.0054(2)	0.0065(2)	0.0002(1)	0.0004(2)	0.0002(2)
	O1H	0	0	0	0	0	0
	O1F	0	0	0	0	0	0
	O2	0.0156(7)	0.0150(6)	0.0103(5)	0.0058(4)	-0.0002(5)	-0.0030(5)
	O3	0.0148(6)	0.0131(6)	0.0120(5)	-0.0054(4)	0.0030(5)	-0.0015(5)
	O4	0.0117(9)	0.0053(7)	0.0155(8)	0	0.0009(6)	0
	O5	0.0097(6)	0.0099(6)	0.0146(6)	0.0002(4)	0.0002(4)	0.0001(5)
	O6	0.0097(9)	0.0340(11)	0.0106(8)	0	-0.0002(7)	0

TABLE 5. Selected bond distances (Å) in fluorlamprophyllite.

Sr–O1F	2.971(8)
Sr–O2 × 2	2.839(2)
Sr–O2 × 2	2.698(1)
Sr–O3 × 2	2.806(2)
Sr–O3 × 2	2.697(1)
Sr–O4	2.774(2)
Sr–O4	<u>2.798(2)</u>
<Sr–O>	2.784
Na3–O2 × 2	2.696(8)
Na3–O2 × 2	2.753(6)
Na3–O3 × 2	2.672(8)
Na3–O3 × 2	2.761(6)
Na3–O4	2.838(9)
Na3–O4	<u>2.844(9)</u>
<Na3–O>	2.745
(Na1,Mn1)–O1H × 2	2.249(7)
(Na1,Mn1)–O1H × 2	2.360(6)
(Na1,Mn1)–O5 × 2	2.228(1)
(Na1,Mn1)–O6 × 2	<u>2.314(1)</u>
<(Na1,Mn1)–O>	2.288
Na2–O5 × 4	2.506(1)
Na2–O6 × 2	<u>2.270(2)</u>
<Na2–O>	2.427
Ti1–O2 × 2	1.956(1)
Ti1–O3 × 2	1.962(1)
Ti1–O6	<u>1.684(2)</u>
<Ti1–O>	1.904
Ti2–O1H	1.772(10)
Ti2–O1H	2.161(10)
Ti2–O1F	1.740(8)
Ti2–O1F	2.131(8)
Ti2–O5 × 2	2.021(3)
Ti2–O5 × 2	<u>2.009(3)</u>
<Ti2–O>	1.983
Si–O2	1.615(1)
Si–O3	1.610(1)
Si–O4	1.654(1)
Si–O5	<u>1.611(1)</u>
<Si–O>	1.622

limits. The resultant chemical formula was calculated on the basis of 18 (O + F) atoms per formula unit, yielding $(\text{Na}_{2.63}\text{Sr}_{1.35}\text{Mn}_{0.54}\text{Ca}_{0.15}\text{Mg}_{0.15}\text{K}_{0.08})_{\Sigma 4.90}(\text{Ti}_{2.63}\text{Fe}_{0.24}^{3+}\text{Al}_{0.04})_{\Sigma 2.91}\text{Si}_{3.89}\text{O}_{16}[\text{F}_{1.15}(\text{OH})_{0.85}]_{\Sigma 2.00}$, which can be simplified to the following ideal formula $\text{Na}_3(\text{SrNa})\text{Ti}_3(\text{Si}_2\text{O}_7)_2\text{O}_2\text{F}_2$. The total is brought close to 100% by adding 1.00 H_2O .

The Raman spectra of fluorlamprophyllite were collected from a randomly oriented crystal on a Thermo-Almega microRaman system, using a 532 nm solid-state laser with a thermoelectric cooled CCD detector. The laser was partially polarized with 4 cm^{-1} resolution and a spot-size of 1 μm .

X-ray crystallography

The powder and single-crystal X-ray diffraction data of fluorlamprophyllite were collected on a Bruker APEX2 CCD X-ray diffractometer equipped with graphite-monochromatized $\text{MoK}\alpha$ radiation. Listed in Table 1, are the measured powder X-ray diffraction data, along with those calculated from the determined structure using the program *XPOW* (Downs *et al.*, 1993). It was not possible to determine unambiguously the unit-cell parameters from the powder diffraction data because of severe overlapping of reflections.

The single-crystal X-ray intensity data were collected from a nearly equi-dimensional crystal (0.06 mm × 0.05 mm × 0.05 mm) with frame widths of 0.5° in ω and 30 s counting time per frame. All reflections were indexed on the basis of a monoclinic unit-cell. The intensity data were corrected for X-ray absorption with the software *SADABS* (Sheldrick, 2007). The summary of crystal data and refinement results for fluorlamprophyllite (this work) and lamprophyllite (Krivovichev *et al.*, 2003) are presented in Table 2. It is the monoclinic $2M$ polytype, with space group $C2/m$. The crystal structure was solved and refined using *SHELX97* (Sheldrick, 2008). A preliminary structure refinement based on the ideal chemical formula of fluorlamprophyllite revealed an unusual size of the displacement ellipsoid of the F/OH site, suggesting positional disorder. It was therefore modelled as two split nonequivalent sites, O1F and O1H, displaced 0.165 Å from each other. Also, we could identify by difference-Fourier maps that Sr was split in two partially occupied nonequivalent sites, identified as Na3 and Sr. Furthermore, the occupancies at the two sites were allowed to vary. In contrast to previous studies (e.g. Krivovichev *et al.*, 2003), Ti2 was displaced from the special position of site symmetry $2/m$ at (0, $\frac{1}{2}$, 0) and refined assuming a split Ti-site with site symmetry m based on difference-Fourier maps. For simplicity, during the structure refinements, minor Mg was treated as Mn, (Ca + K) as Na, and (Fe + Al) as Ti. During the refinements, the correspondence between the sites indicated in

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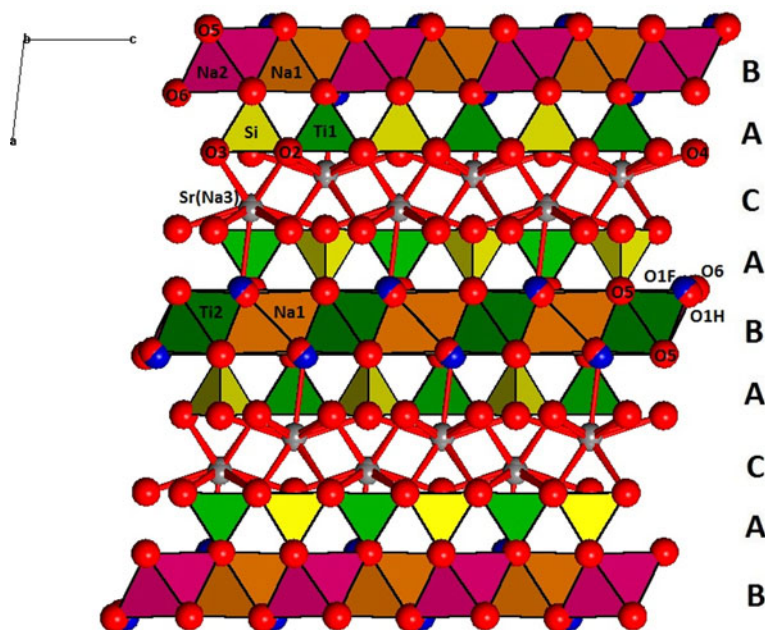


FIG. 3. The crystal structure of fluorlamprophyllite. Na1 [brown], Na2 [purple], Si [yellow], Ti1 [light green], Sr(Na3) [grey], Ti2 [dark green], O [red], O1H [red] and O1F [blue].

the general formula and the atoms site positions is the following: $M1 = Na2$; $M2 = Na1 + Mn1$; $A = Sr + Na3$; $M3 = Ti2$; $L = Ti1$; and $Y = F + OH$. The divalent cations are ordered in the A site and present in the $M2$ site. The position of most of the atoms were refined with anisotropic displacement parameters, except for the partially occupied O1F, O1H and Na3 sites, giving rise to the refined structure

formula $(Na_{2.33}Mn_{0.67})_{\Sigma 3.00}(Sr_{1.28}Na_{0.73})_{\Sigma = 2.01}Ti_{2.99}Si_4O_{16}[F_{1.12}(OH)_{0.88}]_{\Sigma 2.00}$. Final coordinates and displacement parameters of atoms in fluorlamprophyllite are listed in Table 3 and 4 and selected bond distances in Table 5. Additional structural information is provided in the crystallographic information file (available as supplementary material, see below).

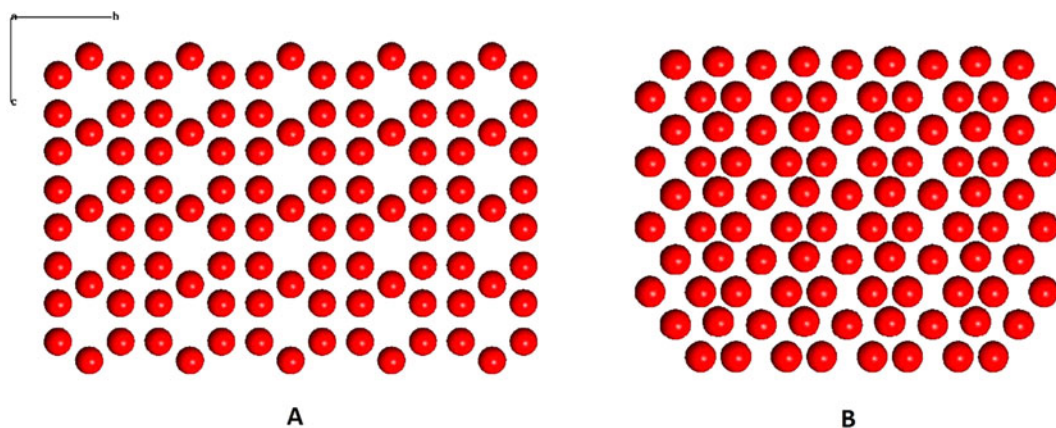


FIG. 4. The O layers of the A and B sheets in fluorlamprophyllite showing that the oxygens are not arranged in hexagonal close-packed layers

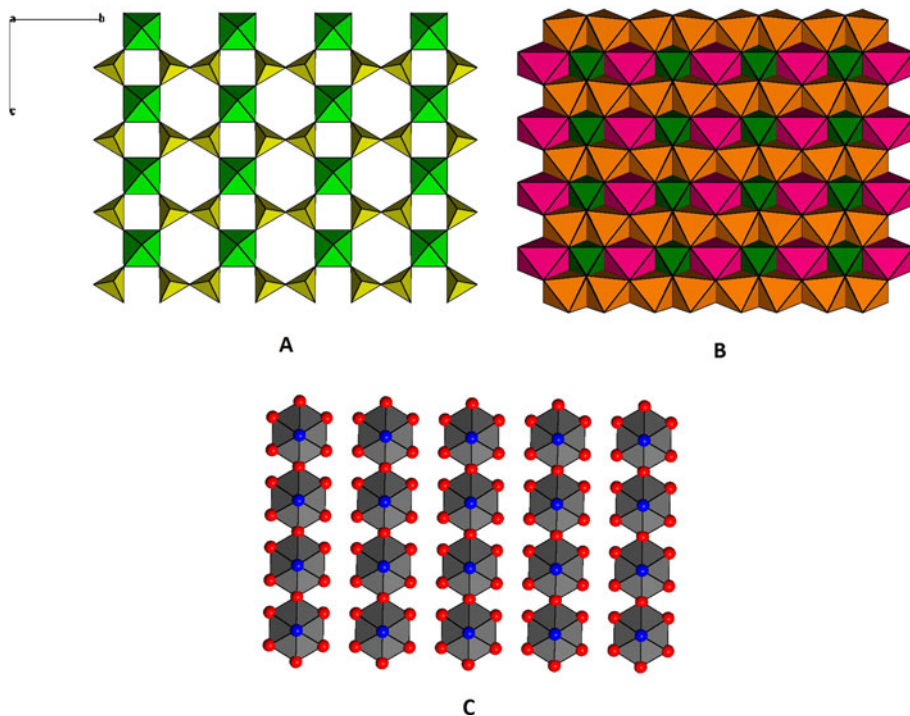


FIG. 5. The layers in fluorlamprophyllite: A = (Si_2O_7) dimers connected by TiO_5 polyhedra; B = brucite-type layer of $(\text{Na}1)\text{O}_6$, $(\text{Na}2)\text{O}_6$ and $(\text{Ti}2)\text{O}_6$ edge-sharing octahedra; and C = $\text{Sr}(\text{Na}3)$.

Discussion

Details of lamprophyllite-type structures, including triclinic, monoclinic and orthorhombic structures have been discussed by Krivovichev *et al.* (2003) and Rastsvetaeva *et al.* (2011). The structure of fluorlamprophyllite is a layered silicate inasmuch as the O atoms are arranged in well-defined, though not necessarily close-packed layers, as shown in Figs 3 and 4. It can be seen that the oxygens are not arranged in hexagonal close-packed layers. The polyhedral

units also form three distinct layers parallel to (100) , designated as A = (Si_2O_7) dimers connected by TiO_5 polyhedra, B = brucite-type layer of $(\text{Na}1)\text{O}_6$, $(\text{Na}2)\text{O}_6$ and $(\text{Ti}2)\text{O}_6$ edge-sharing octahedra, with $(\text{Ti}2)\text{O}_6$ alternating in columns with $(\text{Na}1)\text{O}_6$ and C = $(\text{Sr} + \text{Na}3)$ (Figs 5 and 6). Sandwiches of strongly bonded ABA layers are separated by the weaker bonded C layers, responsible for the perfect cleavage on $\{100\}$. The cations in layer C ($\text{Sr} + \text{Na}$) are coordinated to 6 O atoms on one side of the layer and

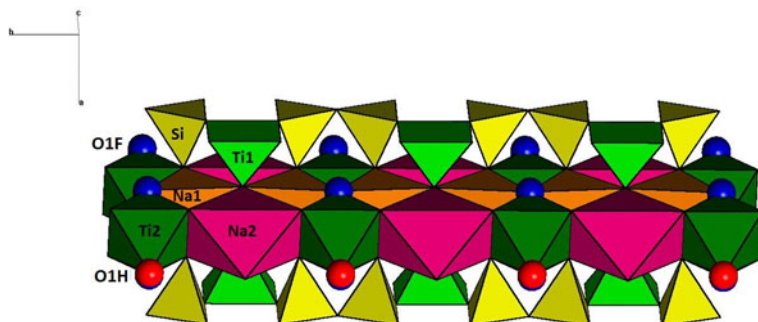


FIG. 6. The F/OH atoms, B and A layers in fluorlamprophyllite.

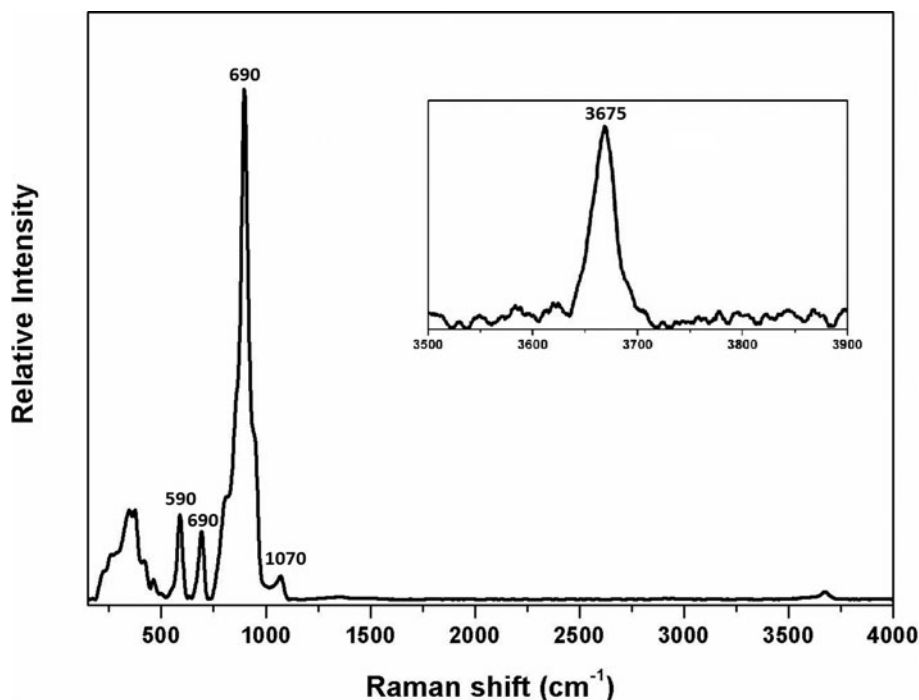


FIG. 7. The Raman spectrum of fluorlamprophyllite.

4 on the other (Fig. 6). The Si–O–Si angle within the Si_2O_7 dimer in fluorlamprophyllite, $134.33(12)^\circ$, is among the smallest of the lamprophyllite group, which exhibit Si–O–Si angles ranging from 134° to 148° for lamprophyllite (Krivovichev *et al.*, 2003) and ericssonite (Matsubara, 1980), respectively.

Raman spectra of fluorlamprophyllite are shown in Fig. 7. Tentative assignments of major Raman bands (cm^{-1}) are 3550–3700 O–H

stretching, 750–1200 Si–O stretching of SiO_4 groups, 690 Si–O–Si bending of Si_2O_7 groups, 590 Ti–O stretching in TiO_5 and TiO_6 groups, and < 500 lattice modes. As expected, the Raman spectra of fluorlamprophyllite (R130421) and lamprophyllite (R070200, R070284 and R130240) presented in the project RRUFF (<http://rruff.info/>) are pretty similar considering the similarities in their structures.

TABLE 6. Calculated bond-valence sums (in valence units) for fluorlamprophyllite.

	O1H	O1F	O2	O3	O4	O5	O6	SUM
Sr		0.027	$0.091 \times 2 \rightarrow$	$0.100 \times 2 \rightarrow$	0.109			1.156
			$0.134 \times 2 \rightarrow$	$0.134 \times 2 \rightarrow$	0.102			
Na3			$0.032 \times 2 \rightarrow$	$0.034 \times 2 \rightarrow$	$0.022 \times 2 \rightarrow \downarrow$			0.286
			$0.028 \times 2 \rightarrow$	$0.027 \times 2 \rightarrow$				
(Na1,Mn1)	$0.130 \times 2 \rightarrow \downarrow$	$0.090 \times 2 \rightarrow \downarrow$				$0.313 \times 2 \rightarrow$	$0.249 \times 2 \rightarrow \downarrow$	1.564
Na2						$0.150 \times 4 \rightarrow$	$0.283 \times 2 \rightarrow$	1.166
Ti1			$0.684 \times 2 \rightarrow$	$0.671 \times 2 \rightarrow$			1.425	4.135
Ti2	0.244	0.292				$0.283 \times 2 \rightarrow$		1.872
	0.085	0.101				$0.292 \times 2 \rightarrow$		
Si			1.025	1.039	$0.921 \times 2 \downarrow$	1.037		4.022
SUM	0.589	0.600	1.994	2.005	2.097	2.075	2.206	

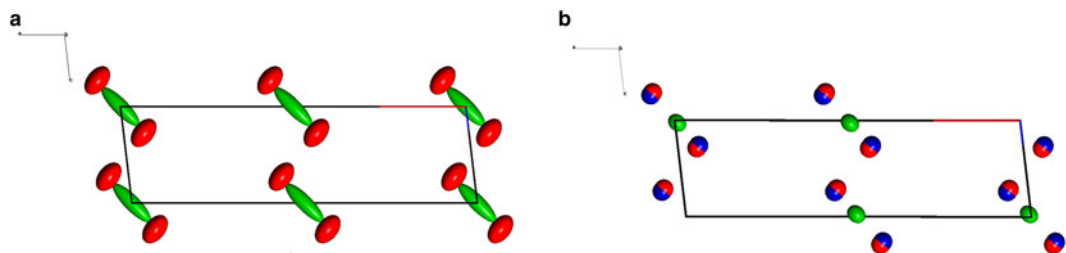


FIG. 8. Fluorlamprophyllite unit cell: (a) Ti2 at $(0, \frac{1}{2}, 0)$ (green) and O1H,O1F (red) at $(0.44190, 0, 0.2727)$ atoms; (b) Ti2 at $(-0.0062, \frac{1}{2}, 0.0263)$ (green), O1H (red) at $(0.4452, 0, 0.2862)$ and O1F (blue) at $(0.4392, 0, 0.2617)$ atoms. Displacement ellipsoids drawn at the 99.9% probability level.

Bond-valence sums (Table 6) for the fluorlamprophyllite structure were calculated using the parameters given by Brese and O’Keeffe (1991) and are consistent with structure refinement results. The Sr^{2+} cation in fluorlamprophyllite is bonded to ten O atoms and weakly to a F atom within 3.0 Å and the bond-valence sum for the site is 1.156 valence units (vu). Initially, Ti2 was located at $(0, \frac{1}{2}, 0)$ (Krivovichev *et al.*, 2003). However, we observed a significant increase in the *R*-factor and abnormal temperature factors for the Ti (Fig. 8). Using the difference-Fourier maps, it was possible to find the new position $(-0.0062, 0.0263, 0.494)$ and consequently the Ti-site splitting. Also, a more systematic and complete discussion on the Ti-site splitting in the lamprophyllite-type minerals is in preparation. The Ti1 and Ti2 positions by Ti are in good agreement with the bond-valence sums of 4.135 and 1.872 vu, respectively. The Ti2 calculation was obtained from anion contributions of O1H and O1F from the split-site *Y* and from O5. The Na1 position incorporates Na and bivalent cations (Mn^{2+}). The bond-valence sum for Na1 is 1.564 vu. The bond-valence sums for the partially occupied O1F and O1H positions in fluorlamprophyllite are 0.600 and 0.589 vu, respectively, which are in a good agreement with their assignment to fluorine and hydroxyl groups.

Crystal structure and physical properties of lamprophyllite-group minerals have been studied and new species characterized in recent years. However, there are no synthetic analogues of lamprophyllite-group minerals, representing a challenge to the development of new compounds based on layered mineral structures.

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Supplementary material

To view supplementary material for this article, please visit <https://doi.org/10.1180/minmag.2017.081.027>

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