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TWO ASTROPHYLLITE-SUPERGROUP MINERALS: BULGAKITE, A NEW MINERAL FROM THE DARAI-PIOZ ALKALINE MASSIF, TAJIKISTAN AND REVISION OF THE CRYSTAL STRUCTURE AND CHEMICAL FORMULA OF NALIVKINITE

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ABSTRACT

Bulgakite, ideally $Li_2(Ca,Na)Fe^{2+}_7Ti_2(Si_4O_{12})_2O_2(OH)_4(O,F)(H_2O)_2$, and nalivkinite, ideally $Li_2NaFe^{2+}_7Ti_2(Si_4O_{12})_2O_2(OH)_4F(H_2O)_2$, are astrophyllite-supergroup minerals. Bulgakite is a new mineral from the Darai-Pioz alkaline massif in the upper reaches of the Darai-Pioz river, in the area of the joint Turkestansky, Zeravshansky, and Alaisky ridges, Tajikistan. Bulgakite was found in fenitized amphibole–quartz–feldspar rock with brannockite, sogdianite, bafertisite, albite, and titanite. Bulgakite is brownish orange, transparent in thin grains, and has a vitreous luster. Mohs hardness is 3, $D_{meas.} = 3.30(2)$ g/cm^3, $D_{calc.} = 3.326$ g/cm^3. Bulgakite is biaxial (+) with refractive indices ($\lambda = 589$ nm) $\alpha = 1.695(3)$, $\beta = 1.711(2)$, $\gamma = 1.750(3)$; $2V_{meas.} = 70(5)°$, $2V_{calc.} = 67°$, strong dispersion: $r > v$. Cleavage is perfect parallel to {001} and moderate parallel to {010}. Chemical analysis by electron microprobe gave SiO_2 35.63, Al_2O_3 0.95, Na_2O 1.04, K_2O 3.27, Cs_2O 0.31, CaO 2.56, MgO 0.16, ZnO 0.15, FeO 29.24, MnO 7.14, TiO_2 11.07, Nb_2O_5 0.49, ZrO_2 0.37, SnO_2 1.18, F 1.01, Li_2O 1.36 (AAS), Rb_2O 0.85 (AAS), $(H_2O)_{calc.}$ 4.04, sum 100.38 wt.%, H_2O was calculated from crystal-structure analysis. The empirical formula based on 31.94 (O + OH + F + H_2O) *pfu* is $(Li_{0.94}K_{0.91}Rb_{0.12}Cs_{0.03})_{\Sigma 2}(Ca_{0.60}Na_{0.40})_{\Sigma 1}(Fe^{2+}_{5.34}Mn_{1.32}Li_{0.25}Mg_{0.05}Na_{0.04}Zn_{0.02})_{\Sigma 7.02}$ $(Ti_{1.82}Sn_{0.10}Nb_{0.05}Zr_{0.04})_{\Sigma 2.01}[(Si_{7.78}Al_{0.24})_{\Sigma 8.02}O_{24}]O_2(OH)_4(F_{0.70}O_{0.30})[(H_2O)_{0.94}\square_{1.06}]_{\Sigma 2}$, $Z = 1$. Bulgakite is triclinic, space group $P\bar{1}$, *a* 5.374(1), *b* 11.965(2), *c* 11.65(3) Å, α 113.457(8), β 94.533(8), γ 103.08(1)°, *V* 657.5(8) Å^3. The six strongest reflections in the X-ray powder diffraction data [*d* (Å), I, (*hkl*)] are: 10.54, 100, (001); 3.50, 100, (003); 2.578, 100, (130); 2.783, 90, ($1\bar{4}2$); 1.576, 68, ($3\bar{5}1$,$\bar{3}\,\bar{2}2$); 2.647, 55, ($\bar{2}11$). The crystal structure has been refined to $R_1 = 2.6\%$ for 3592 unique $F_o > 4\sigma F$) reflections. In the crystal structure of bulgakite, there are four $^{[4]}T$ sites, with $<T–O> = 1.626$ Å, occupied mainly by Si, with minor Al. The TO_4 tetrahedra constitute the T_4O_{12} astrophyllite ribbon. The $^{[6]}D$ site is occupied mainly by Ti, with $<D–\varphi> = 1.965$ Å (φ = O, F). The T_4O_{12} astrophyllite ribbons and D octahedra constitute the H (Heteropolyhedral) sheet. In the O (Octahedral) sheet, there are four Fe^{2+}-dominant $^{[6]}M(1–4)$ sites, with $<M–\varphi> = 2.159$ Å (φ = O, OH). Two H and the central O sheets form the HOH block, and adjacent HOH blocks link *via* a common anion (X^P_D) of two D octahedra. In the **I** (Intermediate) block between adjacent HOH blocks, there are two interstitial cation sites, *A* and *B*, and a *W* site, partly occupied by H_2O. The *A* site splits into two partly occupied sites, $^{[13]}A(1)$ and $^{[6]}A(2)$, with A(1)–A(2) = 1.16 Å. The $^{[6]}A(2)$ site is occupied by Li with $<A(2)–\varphi> = 2.285$ Å (φ = O, F, H_2O), and the $^{[13]}A(1)$ site is occupied by K, Rb, and Cs with $<A(1)–\varphi> = 3.298$ Å. The aggregate content of the *A* site is $(Li_{0.94}K_{0.91}Rb_{0.12}Cs_{0.03})_{\Sigma 2}$, ideally Li_2 *apfu*. The $^{[10]}B$ site is occupied by $(Ca_{0.60}Na_{0.40})$ with $<B–\varphi> = 2.593$ Å. The *W* site is occupied by $[(H_2O)_{0.94}\square_{1.06}]_{\Sigma 2}$ *pfu*. The mineral is named *bulgakite* after

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Lev Vasil'evich Bulgak (born 1955), Russian mineralogist, gemologist, and discoverer of several new minerals. The crystal structure of nalivkinite has been revised and refined to $R_1 = 4.52\%$ for 3546 unique ($F_o > 4\sigma F$) reflections: space group $P\bar{1}$, a 5.374(3), b 11.948(5), c 11.676(5) Å, α 113.360(6), β 94.538(8), γ 103.01(1)°, V 658.7(9) $Å^3$, $Z = 1$, $D_{calc.} = 3.347$ g/cm^3. The revised empirical formula of nalivkinite is based on 32.14 (O + OH + F + H_2O) *pfu*: $(Li_{1.14}K_{0.75}Cs_{0.09}Pb_{0.02})_{\Sigma2}(Na_{0.71}Ca_{0.29})_{\Sigma1}(Fe^{2+}_{5.62}Mn_{0.90}Zr_{0.08}Na_{0.08}Mg_{0.04}Zn_{0.04})_{\Sigma6.76}(Ti_{1.56}Nb_{0.24}Sn_{0.09}Zr_{0.08}Ta_{0.04})_{\Sigma2}[(Si_{7.86}Al_{0.15})_{\Sigma8.01}O_{24}]O_2(OH)_4F[(H_2O)_{1.14}\square_{0.86}]_{\Sigma2}$. The presence of H_2O groups in the bulgakite and nalivkinite structures was confirmed by infrared spectroscopy. Bulgakite is a Ca-analogue of nalivkinite. Bulgakite and nalivkinite are related by the following substitution: 0.3 $^{B}Ca^{2+} + 0.3\ ^{X}O^{2-} \leftrightarrow 0.3\ ^{B}Na^{+} + 0.3\ ^{X}F^{-}$.

Keywords: bulgakite, new mineral species, nalivkinite, astrophyllite supergroup, *A*(2) site, Darai-Pioz massif, Tajikistan, electron microprobe analysis, crystal structure, FTIR spectroscopy.

INTRODUCTION

Bulgakite, ideally $Li_2(Ca,Na)Fe^{2+}_7Ti_2(Si_4O_{12})_2O_2(OH)_4(O,F)(H_2O)_2$, is a new astrophyllite-supergroup mineral. It occurs in the moraine of the Darai-Pioz glacier in the upper Darai-Pioz alkaline massif (Darai-Pioz massif further in the paper) in the upper reaches of the Darai-Pioz river, in the area of the joint Turkestansky, Zeravshansky, and Alaisky ridges, Tajikistan. The mineral is named *bulgakite* (Russian Cyrillic: *булгакит*) after Lev Vasil'evich Bulgak (born 1955), Russian mineralogist, gemologist, translator of geological literature, and discoverer of several new minerals who worked at the A.E. Fersman Mineralogical Museum (Moscow, Russia) from 1975 to 2003. The new mineral species and its name were approved by the Commission on New Minerals, Nomenclature and Classification, International Mineralogical Association (IMA 2014-041). The holotype specimen has been deposited in the mineral collection of the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow, Russia, registration # 4572/1.

During our work, we located an H_2O group in the **I** (Intermediate) block of bulgakite; this H_2O group is a ligand of the Li atom at the [6]-coordinated *A*(2) site. This new development in the crystal chemistry of the astrophyllite-supergroup minerals required reinvestigation of the crystal structure of nalivkinite, ideally $Li_2NaFe^{2+}_7Ti_2(Si_4O_{12})_2O_2(OH)_4F$ (Agakhanov *et al.* 2008, Uvarova *et al.* 2008), where Uvarova *et al.* (2008) reported [5]-coordinated Li at the *A*(2) site. In our proposal on bulgakite (IMA 2014-041), we outlined the issue of the [6]-coordinated *A*(2) site in bulgakite and suggested that the revision of the crystal structure of nalivkinite would result in the following ideal formula: $Li_2NaFe^{2+}_7Ti_2(Si_4O_{12})_2O_2(OH)_4F(H_2O)_2$, and this proposal was approved by the CNMNC (Agakhanov *et al.* 2014). Here we report the description and crystal structure of bulgakite, a new mineral, and revision of the crystal structure and chemical formula of nalivkinite (Table 1).

GENERAL INFORMATION ON THE ASTROPHYLLITE SUPERGROUP

The crystal chemistry of the astrophyllite group was discussed by Belov (1963, 1976), Peng & Ma (1963), Piilonen *et al.* (2003a, b), Cámara *et al.* (2010), and Sokolova (2012). Based on the work of Sokolova (2012), the nomenclature and classification of the astrophyllite-supergroup minerals were reconsidered by Sokolova *et al.* (2016b). The Nomenclature Voting proposal 15-B – "*Magnesioastrophyllite*" *validated under the name* "*lobanovite*"*, and astrophyllite supergroup classification* – was approved by the CNMNC-IMA with the following two conclusions: (1) "magnesioastrophyllite" has been validated under the name lobanovite, $K_2Na(Fe^{2+}_4Mg_2Na)Ti_2(Si_4O_{12})_2O_2(OH)_4$ (Sokolova *et al.* 2016a); (2) according to the new classification scheme, the astrophyllite supergroup is now divided into three groups: the astrophyllite group, the kupletskite group, and the devitoite group (Sokolova *et al.* 2015b).

The HOH block is the main structural unit in all astrophyllite-supergroup structures; it consists of three H–O–H sheets where the T_4O_{12} astrophyllite ribbons occur in the H sheets. In each structure, HOH blocks alternate with **I** (Intermediate) blocks along [001]. The minerals of the astrophyllite supergroup are divided into three groups based on (1) the type of self-linkage of HOH blocks, *i.e.*, (a) HOH blocks link directly *via* D–X^{P}_{D}–D bridges, or (b) HOH blocks do not link directly; and (2) the dominant cation of the O sheet [the C group: C_7 *apfu* (atoms per formula unit)]. In the astrophyllite group, HOH blocks connect *via* D–X^{P}_{D}–D bridges, Fe^{2+} is dominant at C_7; in the kupletskite group, HOH blocks connect *via* D–X^{P}_{D}–D bridges, Mn^{2+} is dominant at C_7; in the devitoite group, HOH blocks do not connect *via* D–X^{P}_{D}–D bridges. There are 12 minerals in the astrophyllite supergroup: (1) the astrophyllite group comprises astrophyllite, $K_2NaFe^{2+}_7Ti_2(Si_4O_{12})_2O_2(OH)_4F$ (Weibye 1848, Cámara *et al.* 2010); niobophyllite, $K_2NaFe^{2+}_7(Nb,Ti)_2(Si_4O_{12})_2O_2(OH)_4(O,F)$ (Nickel *et*

TABLE 1. COMPARISON OF BULGAKITE AND NALIVKINITE

	bulgakite	nalivkinite*
Formula	$Li_2(Ca,Na)Fe^{2+}{}_7Ti_2(Si_4O_{12})_2O_2(OH)_4(O,F)(H_2O)_2$	$Li_2NaFe^{2+}{}_7Ti_2(Si_4O_{12})_2O_2(OH)_4F(H_2O)_2$
System	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	5.374(1)	5.374(1)
b	11.965(2)	11.948(5)
c	11.65(3)	11.676(5)
α (°)	113.457(8)	113.360(6)
β	94.533(8)	94.538(8)
γ	103.08(1)	103.01(1)
V (Å^3)	657.5(1)	658.7(9)
Z	1	1
$D_{meas.}$, g/cm^3	3.30(2)	3.32(2)
$D_{calc.}$, g/cm^3	3.326	3.347
Strongest reflections in the X-ray powder data $d_{obs.}$ (Å) (I)	10.54 (100), 3.50(100), 2.578 (100), 2.783 (90), 1.576 (68), 2.647 (55)	10.56 (100), 3.50 (100), 2.780 (80), 2.578 (70), 2.648 (45), 2.106 (35)
Color	brownish orange	brownish orange
Optical character	biaxial (+)	biaxial (+)
α	1.695	1.703
β	1.711	1.716
γ	1.750	1.745
2V (°)	70	68

* This work except for: $D_{meas.}$, X-ray powder data and optics (Agakhanov *et al.* 2008).

al. 1964, Cámara *et al.* 2010); zircophyllite, $K_2NaFe^{2+}{}_7Zr_2(Si_4O_{12})_2O_2(OH)_4F$ [Kapustin 1973, Sokolova & Hawthorne (2016)]; tarbagataite, (K□)$CaFe^{2+}{}_7Ti_2(Si_4O_{12})_2O_2(OH)_5$ (Stepanov *et al.* 2012); nalivkinite, $Li_2NaFe^{2+}{}_7Ti_2(Si_4O_{12})_2O_2(OH)_4F(H_2O)_2$ (Agakhanov *et al.* 2008, Uvarova *et al.* 2008, this work); and bulgakite, $Li_2(Ca,Na)Fe^{2+}{}_7Ti_2(Si_4O_{12})_2O_2(OH)_4(O,F)(H_2O)_2$ (this work); (2) the kupletskite group consists of kupletskite, $K_2NaMn^{2+}{}_7Ti_2(Si_4O_{12})_2O_2(OH)_4F$ (Semenov 1956; Piilonen *et al.* 2001: triclinic and monoclinic polytypes); niobokupletskite, $K_2NaMn^{2+}{}_7(Nb,Ti)_2(Si_4O_{12})_2O_2(OH)_4(O,F)$ (Piilonen *et al.* 2000); and kupletskite-(Cs), $Cs_2NaMn_7Ti_2(Si_4O_{12})_2O_2(OH)_4F$ (Yefimov *et al.* 1971, Cámara *et al.* 2010); (3) the devitoite group includes sveinbergeite, $(H_2O)_2[Ca(H_2O)](Fe^{2+}{}_6Fe^{3+})Ti_2(Si_4O_{12})_2O_2(OH)_4[(OH)(H_2O)]$ (Khomyakov *et al.* 2011); devitoite, $Ba_6Fe^{2+}{}_7Fe^{3+}{}_2(Si_4O_{12})_2(PO_4)_2(CO_3)O_2(OH)_4$ (Kampf *et al.* 2010); and lobanovite, $K_2Na(Fe^{2+}{}_4Mg_2Na)Ti_2(Si_4O_{12})_2O_2(OH)_4$ (Sokolova *et al.* 2016a, Sokolova & Cámara 2008).

The general formula for the astrophyllite-supergroup minerals is of the form $A_{2p}B_rC_7D_2(T_4O_{12})_2IX^O{}_{D2}X^O{}_{A4}X^P{}_{Dn}W_{A2}$, where C [cations at the *M*(1–4) sites in the O sheet] = Fe^{2+}, Mn, Na, Mg, Zn, Fe^{3+}, Ca, Zr, Li; D (cations in the H sheets) = $^{[6,5]}$Ti, Nb, Zr, Sn^{4+}, $^{[5]}Fe^{3+}$, Mg, Al; T = Si, minor Al; $A_{2p}B_rIW_{A2}$ (**I** block) where p = 1,2; r = 1,2; A = K, Cs, Ba, H_2O, Li, Rb, Pb^{2+}, Na, □; B = Na, Ca, Ba, H_2O, □; I represents the composition of the central part of the **I** block, excluding peripheral layers, and is of the form $A_{2p}B_rW_{A2}$, *e.g.*, $(PO_4)_2(CO_3)$ (devitoite); $X^O{}_D$ = O; $X^O{}_A$ = OH, F; $X^P{}_D$ = F, O, OH, H_2O, □, where $n = 0$, 1, 2 for $(X^P{}_D)_n$; W_A = H_2O, □ (Sokolova *et al.* 2016b).

OCCURRENCE

Bulgakite was found in the moraine of the Darai-Pioz glacier covering the Darai-Pioz alkaline massif (39°30′N 70°40′E). The massif is located at the intersection of the Turkestansky, Zeravshansky, and Alaisky ridges in the Rasht (formerly Garm) district, Tajikistan. In plan, the Darai-Pioz massif is equant, slightly extended in the NW direction and occupies ~16 km². The glacier covers most of the massif and the rock outcrops form steep valley walls that can be reached only by using special equipment. Most mineralogical and petrological studies of the massif have been done on material deposited in its moraine and that is why our knowledge of the geology of the massif is not complete. The mineralogy and geology of the Darai-Pioz massif was described by Moskvin

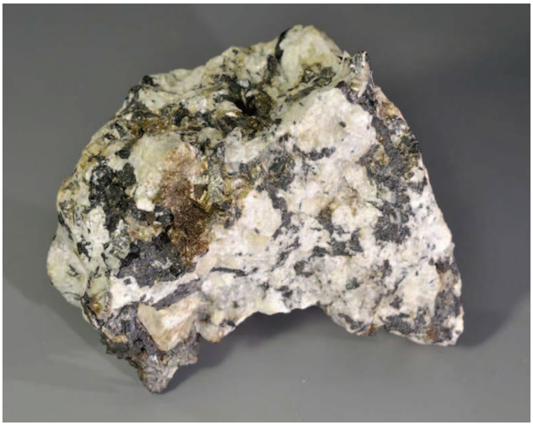

FIG. 1. General view of the amphibole–quartz–feldspar rock (6 × 5 × 3 cm) in which bulgakite was found. Crystals of bulgakite, brownish orange, form intergrowths with black alkali amphibole, quartz, and microcline.

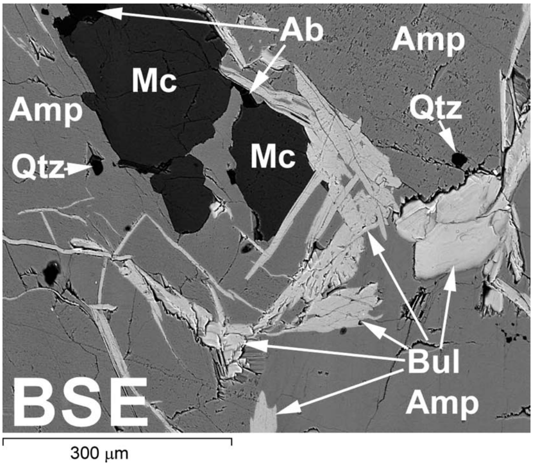

FIG. 2. BSE image of the intergrowth of flakes of bulgakite (Bul) with alkali amphibole (Amp), microcline (Mc), albite (Ab), and quartz (Qtz).

(1937), Dusmatov *et al*. (1963), Dusmatov (1968, 1971), Semenov *et al*. (1973), and Belakovskiy (1991).

The Darai-Pioz massif is a multiphase intrusion and occupies the core of a large synclinal fold of Carboniferous (Pennsylvanian series) slates. The core of the massif consists of alkaline rocks of the Alaisky (Matchaisky) Upper Paleozoic intrusive complex of Permian age, and the outer part of the massif consists of granites of the second phase of the Turkestan complex. Rocks of the massif have been intruded by fine-grained dikes of biotite tourmaline granites and veins of calcite carbonatites and fenites. The principal metasomatic rocks are fenites and baratovite- and miserite-containing quartz–albite–aegirine rocks.

The Darai-Pioz mineralization is enriched in Li. There are 17 Li minerals that occur in the Darai-Pioz massif, eight of which have been described as new species. Lithium has been found in astrophyllite-supergroup minerals that are common in the massif: kupletskite-(Cs) (0.5 wt.% Li_2O, Yefimov *et al*. 1971), nalivkinite (Agakhanov *et al*. 2008, Uvarova *et al*. 2008, this work), and bulgakite (this work).

MINERAL ASSOCIATION

Bulgakite was found in a rounded amphibole–quartz–feldspar boulder (0.3 × 0.5 × 0.6 m) of spotty texture due to accumulations of amphiboles and bulgakite (Fig. 1). Boulders of similar rocks occur at the right front part of the moraine, but we did not find outcrops of this particular rock. Bulgakite occurs as individual crystals and intergrowths in small cavities (up to 0.5 cm) and as intergrowths (up to 1 cm) of platy crystals and aggregates of poorly crystallized grains (Fig. 2). Associated minerals are alkali amphibole, quartz, microcline, bafertisite, aegirine, calcybeborosilite-(Y), thorite, and fluorite. Microcline occurs as large (1–5 cm) grains of grayish and yellowish color. An alkali amphibole has prismatic crystals (often deformed) up to 2 cm. Secondary minerals are brannockite and sogdianite which form zoned platy agglomerates up to 1 cm that luminesce bright white under short-wave ultraviolet light. In the agglomerates, brannockite and sogdianite form the central and peripheral parts, respectively. Minor associated minerals are albite (granular aggregate), bafertisite (small plates), and titanite (poorly crystallized grains).

PHYSICAL PROPERTIES

Bulgakite is brownish orange, and it has a vitreous luster and a pale brown streak. Cleavage is perfect parallel to {001} and moderate parallel to {010}, and elongation relative to the plane of perfect cleavage is positive; it is brittle and has a hackly fracture. The microhardness of bulgakite is VHN = 204 (with a range of 165–221), which corresponds to Mohs hardness of 3; measurements were done with a PMT-3 instrument, calibrated on NaCl at a loading of 50 g. Bulgakite does not fluoresce under ultraviolet light. $D_{\text{meas.}} = 3.30(2)$ g/cm^3 was determined by flotation in Clerici liquid, $D_{\text{calc.}} = 3.326$ g/cm^3 was determined from the empirical formula. Bulgakite is biaxial (+) with refractive indices ($\lambda = 589$ nm) $\alpha = 1.695(3)$, $\beta = 1.711(2)$, $\gamma = 1.750(3)$. The optical axial angle, measured with a Fedorov stage, is 70(5)°; $2V_{calc.} = 67°$. The dispersion is strong, $r > v$. It is pleochroic according to the scheme $X < Z < Y$, where X = intensive reddish brown, Y = light brown, Z = greenish light brown. The compatibility index $(1 - Kp/Kc) = 0.030$ (for $D_{meas.}$) is rated as superior (Mandarino 1981).

INFRARED AND RAMAN SPECTROSCOPY

The FTIR spectra of bulgakite (Fig. 3a) and nalivkinite (Fig. 3b) were collected from crystal fragments using a Bruker Hyperion 2000 IR microscope equipped with a liquid-nitrogen-cooled MCT detector. Data over the range 4000–650 cm^{-1} were obtained by averaging 100 scans with a resolution of 4 cm^{-1}. Baseline correction was done using the OPUS spectroscopic software (Bruker Optic GmbH). The Raman spectrum of bulgakite in the region 100–1200 cm^{-1} (Fig. 3c) was collected in backscattered mode with a HORIBA JobinYvon-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 ~1 μm, a 1800 gr/mm grating, and a 532 nm excitation laser. The wavenumber was calibrated using the 520.7 cm^{-1} line of Si metal.

In the OH-stretching region (4000–3000 cm^{-1}), the FTIR spectra of both bulgakite and nalivkinite show sharp absorption peaks that are characteristic of stretching vibrations of OH groups. These peaks occur at ~3639 cm^{-1} (with a shoulder at ~3655 cm^{-1}) and 3589 cm^{-1} (with a shoulder at ~3600 cm^{-1}) for bulgakite and at ~3630 cm^{-1} (with a shoulder at ~3650 cm^{-1}) and 3590 cm^{-1} (with a shoulder at ~3600 cm^{-1}) for nalivkinite. The spectra also show a broad band at ~3490 cm^{-1} that is attributed to H_2O stretches. The H_2O bend peak is observed at 1622 cm^{-1}. In the low-frequency region, the bulgakite spectrum (Fig. 3a) shows a strong band at ~1041 cm^{-1}, a broad band centered at ~940 cm^{-1} showing some saturation, and a small peak at 695 cm^{-1} that may be assigned to Si–O stretches. The weak peaks at 2950–2850 cm^{-1} are due to C–H stretching vibrations, probably from a hydrocarbon contaminant.

In the Raman spectrum of bulgakite (Fig. 3c), the strong peak at 910 cm^{-1} along with peaks at 733 (with a shoulder at ~785 cm^{-1}) and 1041 cm^{-1} are due to Si–O stretches. Peaks at 660, 569, 420, 395, and 367 may be assigned to bending vibrations of the silicate groups, and those at 258, 233, 170, and 133 cm^{-1} are mainly due to lattice modes.

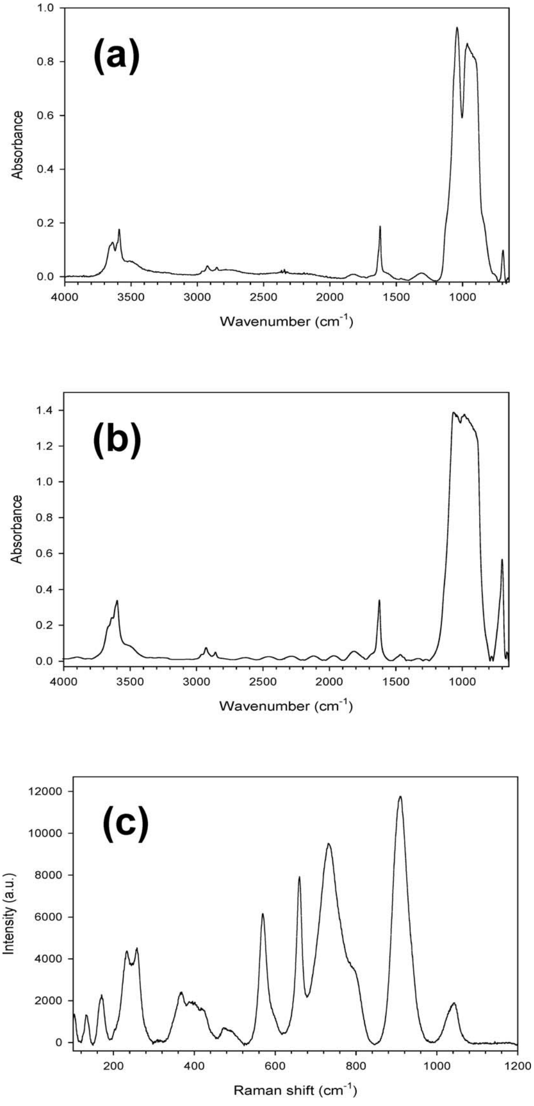

FIG. 3. The FTIR spectra of bulgakite (a) and nalivkinite (b). (c) The Raman spectrum of bulgakite.

CHEMICAL COMPOSITION

The chemical composition of bulgakite was determined using a JEOL Superprobe JCXA-733 electron microprobe equipped with an energy-dispersive spectrometer (EDS), an ultrathin ATW2 window, an INCA control system, and wavelength-dispersive spectrometers (WDS). Measurements were done using EDS with an accelerating voltage of 20 kV, a specimen current of 2 nA, and a beam diameter of 5 μm. To avoid damage of the very thin bulgakite flakes under the electron beam, we chose EDS as a less

TABLE 2. CHEMICAL COMPOSITION AND UNIT FORMULA FOR BULGAKITE AND NALIVKINITE

	wt.%			*apfu*	
Constituent	bulgakite[1]	nalivkinite[2]		bulgakite[1]	nalivkinite[2]
Ta_2O_5	n.d.	0.61	Si	7.78	7.86
Nb_2O_5	0.49	2.40	Al	0.24	0.15
SnO_2	1.18	0.89	ΣT	8.02	8.01
ZrO_2	0.37	1.47			
TiO_2	11.07	9.48	Fe^{2+}	5.34	5.62
SiO_2	35.63	36.11	Mn	1.32	0.90
Al_2O_3	0.95	0.58	Li	0.25	0
PbO	n.d.	0.39	Mg	0.05	0.04
ZnO	0.15	0.23	Na	0.04	0.08
FeO	29.24	30.84	Zn	0.02	0.04
MnO	7.14	4.86	Zr	0	0.08
CaO	2.56	1.24	ΣM	7.02	6.76
MgO	0.16	0.11			
Rb_2O*	0.84	n.d.	Ti	1.82	1.56
Cs_2O	0.31	0.93	Sn	0.10	0.09
K_2O	3.27	2.68	Nb	0.05	0.24
Na_2O	1.04	1.88	Zr	0.04	0.08
Li_2O*	1.36	1.30	Ta	0	0.04
F	1.01	1.45	ΣD	2.01	2.00
H_2O**	4.04	4.32			
F=O	–0.43	–0.61	Ca	0.60	0.29
Total	100.38	101.27	Na	0.40	0.71
			ΣB	1.00	1.00
			Li	0.94	1.14
			K	0.91	0.75
			Rb	0.12	0
			Cs	0.03	0.09
			Pb	0	0.02
			ΣA	2.00	2.00
			F	0.70	1.00
			OH	4.00	4.00
			H_2O	0.94	1.14

[1] this work, formula unit calculated on the basis of 31.94 ($O + OH + F + H_2O$) *pfu*;
[2] H_2O added to the chemical analysis of nalivkinite from Uvarova *et al.* (2008), formula unit calculated on the basis of 32.14 ($O + OH + F + H_2O$) *pfu*;
n.d. = not detected; * determined by AAS for bulgakite and ICP-OES for nalivkinite; ** calculated from crystal-structure analysis.

destructive method of chemical analysis due to the lower current (when compared to WDS). Elements F, Na, and Zn were analyzed subsequently with WDS. The following standards were used: USNM 143966 microcline (Si, K, Al), USNM 96189 ilmenite (Ti, Fe), anorthite USNM 137041 (Ca), $LiNbO_3$ (Nb), ZrO_2 (Zr), SnO_2 (Sn), $MnTiO_3$ (Mn), MgO (Mg), ZnO (Zn), $CsTbP_4O_{12}$ (Cs), jadeite (Na), and MgF_2 (F). The data (10 analyses) were reduced and corrected by the PAP method of Pouchou & Pichoir (1985). The amount of H_2O was calculated from the structure refinement. The amounts of Li_2O and Rb_2O were determined by Atomic Absorption Spectroscopy (AAS). Grains of bulgakite were dissolved in $HF + HNO_3$, then that solution was twice evaporated with HNO_3 and the residue was put in nitric solution (with a final concentration of 3% HNO_3). This solution was used for qualitative ICP-MS analysis. After adding a Cs-ionizing buffer solution, Li and Rb were analyzed by AAS and those results were confirmed by measurement with the flame-emission method. For bulgakite, Table 2 gives the chemical composition and empirical formula unit based on 31.94 ($O + OH + F + H_2O$) *pfu* (per formula unit): $(Li_{0.94}K_{0.91}Rb_{0.12}Cs_{0.03})_{\Sigma 2}$

TABLE 3. POWDER X-RAY DATA FOR BULGAKITE

$I_{obs.}$	$d_{obs.}$ (Å)	$d_{calc.}$ (Å)	*h*	*k*	*l*	$I_{obs.}$	$d_{obs.}$ (Å)	$d_{calc.}$ (Å)	*h*	*k*	*l*
100	10.54	10.52	0	0	1	28	2.399	2.400	$\bar{1}$	4	1
4	9.83	9.83	0	$\bar{1}$	1			2.396	$\bar{1}$	$\bar{3}$	4
28	5.80	5.809	0	$\bar{2}$	1	43	2.296	2.296	1	3	1
5	5.26	5.256	0	2	0	24	2.223	2.223	$\bar{2}$	1	3
26	4.39	4.403	$\bar{1}$	$\bar{1}$	1	27	2.107	2.109	$\bar{1}$	4	2
6	4.31	4.338	$\bar{1}$	2	0			2.105	$\bar{1}$	$\bar{3}$	5
		4.316	1	$\bar{2}$	1	20	2.041	2.041	2	$\bar{1}$	3
9	4.05	4.060	0	2	1			2.011	1	$\bar{4}$	5
21	3.76	3.761	$\bar{1}$	2	1	7	1.963	1.962	$\bar{2}$	1	4
		3.748	0	$\bar{2}$	3	9	1.933	1.935	0	$\bar{6}$	3
100	3.50	3.500	0	0	3	52	1.760	1.761	1	3	3
31	3.26	3.277	0	$\bar{3}$	3		1.757	1.758	1	$\bar{4}$	6
		3.250	$\bar{1}$	$\bar{1}$	3	23	1.728	1.728	$\bar{2}$	1	5
15	3.07	3.066	$\bar{1}$	2	2	46	1.660	1.660	0	$\bar{7}$	3
16	3.03	3.024	1	$\bar{2}$	3	27	1.620	1.619	$\bar{1}$	4	4
8	2.853	2.850	1	1	2	10	1.595	1.594	$\bar{2}$	0	6
90	2.783	2.785	1	$\bar{4}$	2	68	1.576	1.577	3	$\bar{5}$	1
		2.780	$\bar{1}$	$\bar{3}$	1			1.576	$\bar{3}$	$\bar{2}$	2
55	2.647	2.650	$\bar{2}$	1	1	33	1.432	1.433	$\bar{1}$	4	5
37	2.625	2.625	0	0	4			1.430	$\bar{1}$	$\bar{3}$	8
100	2.578	2.580	1	3	0	41	1.407	1.408	2	$\bar{8}$	2
		2.579	1	$\bar{4}$	3			1.406	$\bar{2}$	$\bar{6}$	4
45	2.475	2.474	$\bar{2}$	1	2						

$(Ca_{0.60}Na_{0.40})_{\Sigma 1}Fe^{2+}_{5.34}Mn_{1.32}Li_{0.25}Mg_{0.05}Na_{0.04}Zn_{0.02})_{\Sigma 7.02}(Ti_{1.82}Sn_{0.10}Nb_{0.05}Zr_{0.04})_{\Sigma 2.01}[(Si_{7.78}Al_{0.24})_{\Sigma 8.02}O_{24}]O_2(OH)_4(F_{0.70}O_{0.30})[(H_2O)_{0.94}\square_{1.06}]_{\Sigma 2}$, $Z = 1$. The basis of 31.94 (anions + H_2O groups) for calculation of the empirical formula unit was derived from the structure-refinement results: 31 anions (established basis for calculation of the formula unit for the astrophyllite and kupletskite groups of the astrophyllite-supergroup minerals) plus 0.94 H_2O *pfu* as determined by crystal-structure refinement. Note that 0.94 H_2O *pfu* at the *W* site is necessary to complete the coordination of $Li_{0.94}$ *apfu* at the *A*(2) site (see below). The same situation occurs in nalivkinite where $Li_{1.14}$ *apfu* at the *A*(2) site requires 1.14 H_2O *pfu* at the *W* site.

For nalivkinite, details of the original chemical analysis are given in Uvarova *et al*. (2008) and Agakhanov *et al*. (2008). Here we consider a modified chemical analysis of nalivkinite: in accord with 1.14 Li *apfu* at the *A*(2) site, we added 1.14 H_2O *pfu* (at the *W* site) to achieve the [6]-coordinated environment of Li [*A*(2)] and thus recalculated the amount of H_2O as 4.32 wt.% (Table 2) (*cf*. 2.75 wt.%, Uvarova *et al*. 2008). Table 2 gives the chemical composition and empirical formula unit of nalivkinite based on 32.14 (O + OH + F + H_2O) *pfu*, derived from the structure-refinement results: $(Li_{1.14}K_{0.75}Cs_{0.09}Pb_{0.02})_{\Sigma 2}(Na_{0.71}Ca_{0.29})_{\Sigma 1}(Fe^{2+}_{5.62}Mn_{0.90}Zr_{0.08}Na_{0.08}Mg_{0.04}Zn_{0.04})_{\Sigma 6.76}(Ti_{1.56}Nb_{0.24}Sn_{0.09}Zr_{0.08}Ta_{0.04})_{\Sigma 2}[(Si_{7.86}Al_{0.15})_{\Sigma 8.01}O_{24}]O_2(OH)_4F[(H_2O)_{1.14}\square_{0.86}]_{\Sigma 2}$, $Z = 1$, $D_{calc.} = 3.347$ g/cm^3.

X-Ray Powder Diffraction

X-ray powder diffraction data for bulgakite were collected with a Rigaku R-AXIS Rapid II single-crystal diffractometer (Cu*K*α) equipped with a cylindrical image-plate detector and using Debye-Scherrer geometry (*D* = 127.4 mm). The X-ray powder diffraction data for bulgakite are given in Table 3. Unit-cell parameters refined from the powder data are as follows: *a* 5.3729(8), *b* 11.926(2), *c* 11.638(2) Å, α 113.284(4), β 94.560(4), γ 103.085(4)°, *V* 657.5(1) Å^3.

Data Collection and Structure Refinement

Single-crystal X-ray data for bulgakite and nalivkinite were collected using a Bruker APEX II ULTRA three-circle diffractometer equipped with a rotating-anode generator (Mo*K*α), multilayer optics, and an APEX II 4K CCD detector. Unit-cell parameters were determined by least-squares refinement of reflections with $I > 10\sigma I$ and are given in Table 4, together with miscellaneous information on data collection and structure refinement. The crystal structures of bulgakite and nalivkinite were refined using the atom coordinates of nalivkinite (Uvarova *et al*. 2008) as a

TABLE 4. MISCELLANEOUS REFINEMENT DATA FOR BULGAKITE AND NALIVKINITE

	bulgakite	nalivkinite*
a (Å)	5.374(1)	5.374(3)
b	11.965(2)	11.948(5)
c	11.65(3)	11.676(5)
α (°)	113.457(8)	113.360(6)
β	94.533(8)	94.538(8)
γ	103.08(1)	103.01(1)
V (Å^3)	657.5(8)	658.7(9)
Space group	$P\bar{1}$	$P\bar{1}$
Z	1	1
Reflections ($I > 10\sigma I$)	9897	7876
Absorption coefficient (mm^{-1})	5.17	5.25
F(000)	639.7	643.2
$D_{\text{calc.}}$ (g/cm^3)	3.326	3.347
Second component (%)	0	28.7(3)
Crystal size (mm)	0.12 × 0.10 × 0.004	0.08 × 0.08 × 0.007
Radiation/monochromator	Mo$K\alpha$/graphite	
2θ-range for data collection (°)	60.22	60.29
h	$-7 \leq h \leq 7$	$-7 \leq h \leq 7$
k	$-16 \leq k \leq 16$	$-16 \leq k \leq 15$
l	$-16 \leq l \leq 16$	$0 \leq l \leq 16$
R(int) (%)	1.53	6.47
Reflections collected	24961	29583
Independent reflections	3877	3885
$F_o > 4\sigma F$	3592	3546
Refinement method	Full-matrix least squares on F^2, fixed weights proportional to $1/\sigma F_o^2$	
Final R(obs) (%)		
$F_o > 4\sigma F$	2.60	4.52
R_1	2.87	4.99
wR_2	8.10	13.10
Highest peak, deepest hole (e Å^{-3})	1.79, −0.77	2.50, −1.36
Goodness of fit on F^2	1.137	1.106

* Structure refinement using HKLF5 dataset containing reflections that belong to the first component and overlap with reflections from the second component.

starting model, except for those of the O atom of the H_2O group at the *W* site that was found in the difference-Fourier map. Scattering curves for neutral atoms were taken from the International Tables for Crystallography (Wilson 1992). Site-scattering values were refined for the *M*(1–4) sites (scattering curve of Fe), *D* site (scattering curve of Ti), *A*(1) site (scattering curve of K), *A*(2) site (scattering curve of Li), *B* site (bulgakite: scattering curve of Ca; nalivkinite: scattering curve of Na), and *W* site (scattering curve of O). For bulgakite and nalivkinite, we observed disorder at the *A*(1), *A*(2), and *W* sites, partly occupied by K, Li, and H_2O and separated by short distances: [bulgakite: A(1)–A(2) = 1.16 and A(1)–W = 0.644 Å; nalivkinite: A(1)–A(2) = 1.26 and A(1)–W = 0.512 Å]. For the final refinement, the occupancies of the *A*(2) and *W* sites were adjusted in accord with the chemical analysis and constrained to be equal (see text below); the A(2)–W distance was softly constrained to 1.80 Å. The D(donor)–H(1,2) distances were softly constrained to 0.98 Å.

For bulgakite, the intensities of 24961 reflections were measured using 17 s per 0.3° frame. 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 of bulgakite was refined to $R_1 = 2.60\%$ based on 3592 unique reflections with ($F_o > 4\sigma F$).

For nalivkinite, the intensities of 29583 reflections were measured from a twinned crystal using 6 s per 0.3° frame. An absorption correction was done using the TWINABS program (Sheldrick 2008). CELL_NOW (Sheldrick 2004) was used to obtain an HKLF5 file, and with the Bruker SHELXTL Version 5.1 system of programs (Sheldrick 2008), the crystal structure of nalivkinite was refined to $R_1 = 4.52\%$ based on 3546 unique reflections with ($F_o > 4\sigma F$), the twin ratio being 0.713(3):0.287(3).

For bulgakite and nalivkinite, final atom coordinates and anisotropic-displacement parameters are listed in Table 5, selected interatomic distances and framework angles are given in Table 6, refined site-scattering and assigned site-populations for selected cation and anion sites are given in Table 7, and bond-valence values for selected atoms are given in Table 8. A list of observed and calculated structure factors, Crystallography Information Files (CIF) and anisotropic displacement parameters for both minerals may be obtained from The Depository of Unpublished Data on the MAC website [documents Bulgakite CM54_1500085 and Nalivkinite CM54_1500085].

STRUCTURE DESCRIPTION

Bulgakite and nalivkinite are topologically identical astrophyllite-group minerals. Here we describe the crystal structure of bulgakite. This description is applicable to the refined crystal structure of nalivkinite, and numerical details of the topology and crystal chemistry of the nalivkinite structure are given in Tables 5–9.

In the crystal structure of bulgakite, there are four *T* sites occupied by Si and minor Al (Table 5) and tetrahedrally coordinated by O atoms with $<T–O> =$ 1.626 Å (Table 6). There is one Ti-dominant *D* site coordinated by five O atoms and an X^P_D anion ($X^P_D = F_{0.70}O_{0.30}$), with $<D–\varphi>$ 1.965 Å (φ = O, F), which gives ($Ti_{1.82}Sn_{0.10}Nb_{0.05}Zr_{0.03}$), ideally Ti_2 *apfu* (Table 7). There are four Fe^{2+}-dominant *M* sites octahedrally coordinated by O atoms and OH groups [$(X^O_A)_2$ = O(4) + O(5) = O atoms of OH groups, Tables 5–9], with $<M–\varphi> = 2.159$ Å (φ = O, OH). These four *M* sites give $(Fe^{2+}_{5.34}Mn_{1.32}Li_{0.25}Mg_{0.05}Na_{0.04})_{\Sigma 7}$, ideally Fe^{2+}_7 *apfu* ($Zn_{0.02}$ *apfu* is not taken into account as the smallest constituent of the O-sheet cations, see Table 2). As in most astrophyllite-supergroup structures, the sizes of M octahedra follow the pattern M(1) > M(2) > M(3) > M(4) due to the different linkages of M octahedra and the polyhedra of the H sheets (Sokolova 2012). The M(1–4) octahedra share common edges to form a trioctahedral O sheet. The T tetrahedra share vertices to form the T_4O_{12} (ideally Si_4O_{12}) astrophyllite ribbon along [100]. Astrophyllite ribbons and D octahedra share common vertices to form an H sheet. Two H and one O sheets form an HOH block identical to that in astrophyllite (Fig. 4a). In the bulgakite structure, D octahedra share a common X^P_D anion, which has the composition $F_{0.70}O_{0.30}$ (Table 7).

In the **I** block between adjacent HOH blocks, there are two interstitial cation sites, *A* and *B*, and a *W* site partly occupied by H_2O. The *A* site splits into two sites, [13]-coordinated *A*(1) and [6]-coordinated *A*(2), separated by a short distance of 1.16 Å (Table 6). The *A*(1) site is coordinated by 12 O atoms and the X^P_D anion of composition $F_{0.70}O_{0.30}$, and the *A*(2) site is coordinated by four O atoms, the X^P_D anion, and an H_2O group at the *W* site. There is a short distance A(1)–W = 0.64 Å (Table 6) and hence the *W* and *A*(1) sites cannot both be locally occupied. The *A*(1) and *A*(2) sites are occupied by $(K_{0.91}Rb_{0.12}Cs_{0.03}\square_{0.94})$ *pfu* (53% occupancy) and $(Li_{0.94}\square_{1.06})$ *pfu* (47% occupancy) (Table 7). As the *A*(1) site is occupied at 53%, the *W* site can be occupied by H_2O at 47%, *i.e.*, by 0.94 H_2O *pfu,* which is in accord with 0.94 Li *apfu* at the *A*(2) site (Table 7). Figure 4b shows a possible short-range-order (SRO) arrangement of K and Li atoms where they fully occupy the *A*(1) and *A*(2) sites, respectively. The aggregate content of the *A* site is $(Li_{0.94}K_{0.91}Rb_{0.12}Cs_{0.03})_{\Sigma 2.00}$, ideally Li_2 *apfu*. Note that the ideal composition of the *A* site, Li_2 *apfu* (where it is fully occupied by Li), requires full occupancy of the *W* site: $(H_2O)_2$ *pfu*; otherwise the coordination of the Li atom is not complete. The [10]-coordinated *B* site is occupied by $(Ca_{0.60}Na_{0.40})$ (Table 5), ideally (Ca,Na) *apfu*.

ON THE IDEAL FORMULA OF BULGAKITE

The general formula for the astrophyllite-group minerals nalivkinite and bulgakite is of the form $A_2BC_7D_2(T_4O_{12})_2X^O_{D2}X^O_{A4}X^P_DW_{A2}$ (Sokolova *et al.* 2015b). For the ideal formula of nalivkinite, we sum the ideal compositions of the following sites: $C_7 = Fe^{2+}$; $D = {}^{[6]}Ti$; T = Si; A = Li; B = Na; $X^O_D = O$; $X^O_A = OH$; $X^P_D = F$; $W_A = H_2O$ (Table 7). Hence the ideal formula of nalivkinite is $Li_2NaFe^{2+}_7Ti_2(Si_4O_{12})_2O_2(OH)_4F(H_2O)_2$; the two ($H_2O$) groups were added to the ideal formula of nalivkinite by Uvarova *et al.* (2008).

Bulgakite and nalivkinite are two distinct mineral species: at the *B* site, Ca is dominant in bulgakite and Na is dominant in nalivkinite. However, when we write the ideal formula of bulgakite as the sum of cation and anion sites using the principle of dominant cation and anion at each site (Table 7) the ideal formula is not neutral: $Li_2(Ca,Na)Fe^{2+}_7Ti_2(Si_4O_{12})_2O_2(OH)_4(F,O)(H_2O)_2$. Below we explain how to write an ideal formula for bulgakite that does not have an excess charge.

Bulgakite and nalivkinite are related by multiple substitutions (Table 7): (1) in the O sheet, ~0.2 Li

TABLE 5. ATOM COORDINATES AND EQUIVALENT* DISPLACEMENT PARAMETERS (Å^2) FOR BULGAKITE AND NALIVKINITE

bulgakite					nalivkinite				
Atom	*x*	*y*	*z*	U_{eq}	Atom	*x*	*y*	*z*	U_{eq}
M(1)	0.84863(5)	0.20579(3)	0.48033(3)	0.00901(11)	M(1)	0.84895(11)	0.20526(7)	0.47922(6)	0.0080(2)
M(2)	0.28090(5)	0.06747(2)	0.48997(3)	0.00930(11)	M(2)	0.28017(12)	0.06732(6)	0.48925(6)	0.0084(2)
M(3)	0.42327(5)	0.35244(2)	0.48579(3)	0.00931(11)	M(3)	0.42240(13)	0.35182(6)	0.48461(7)	0.0085(2)
M(4)	0	½	½	0.00871(13)	M(4)	0	½	½	0.0080(3)
D	0.07915(5)	0.08698(3)	0.20016(3)	0.00733(10)	D	0.07795(9)	0.08577(6)	0.19761(5)	0.00736(16)
A(1)	0.1424(3)	0.27355(14)	–0.00369(12)	0.0383(4)	A(1)	0.1397(12)	0.2752(3)	–0.0044(5)	0.0358(7)
A(2)	0.087(2)	0.1754(9)	–0.0003(9)	0.032(2)	A(2)	0.088(5)	0.1678(13)	–0.003(2)	0.033(3)
B	½	0	0	0.0142(2)	B	½	0	0	0.0104(3)
T(1)	0.67803(9)	0.27133(5)	0.23068(5)	0.00806(11)	T(1)	0.6775(2)	0.27131(11)	0.23117(12)	0.0077(3)
T(2)	0.81387(9)	0.54627(5)	0.25457(5)	0.00848(11)	T(2)	0.8142(2)	0.54701(11)	0.25631(12)	0.0071(2)
T(3)	0.37967(9)	0.67555(5)	0.25675(5)	0.00811(11)	T(3)	0.3798(2)	0.67629(12)	0.25836(10)	0.0065(2)
T(4)	0.50403(9)	0.93051(5)	0.23419(5)	0.00773(11)	T(4)	0.5046(2)	0.93076(11)	0.23509(12)	0.0073(2)
O(1)	0.7254(3)	0.31688(13)	0.38407(13)	0.0099(3)	O(1)	0.7256(6)	0.3174(3)	0.3845(3)	0.0092(6)
O(2)	0.1454(3)	0.16003(13)	0.37135(13)	0.0109(3)	O(2)	0.1457(5)	0.1610(4)	0.3722(3)	0.0097(5)
O(3)	0.1263(3)	0.39055(13)	0.59159(13)	0.0095(3)	O(3)	0.1260(6)	0.3894(3)	0.5904(3)	0.0084(6)
O(4)	0.2997(3)	0.46191(13)	0.39991(13)	0.0116(3)	O(4)	0.3003(7)	0.4628(4)	0.3999(3)	0.0111(7)
O(5)	0.9897(3)	0.11727(14)	0.59203(13)	0.0118(3)	O(5)	0.9904(6)	0.1170(4)	0.5910(3)	0.0099(6)
O(6)	0.5569(3)	0.25633(13)	0.58834(12)	0.0093(3)	O(6)	0.5579(5)	0.2560(4)	0.5874(3)	0.0082(5)
O(7)	0.5725(3)	0.01551(13)	0.38792(13)	0.0100(3)	O(7)	0.5737(6)	0.0161(4)	0.3891(3)	0.0093(6)
O(8)	0.0744(3)	0.58976(14)	0.20102(13)	0.0172(3)	O(8)	0.0749(6)	0.5901(3)	0.2029(3)	0.0140(7)
O(9)	0.2519(3)	0.04194(14)	0.83233(14)	0.0176(3)	O(9)	0.2487(7)	0.0420(4)	0.8298(4)	0.0217(8)
O(10)	0.4270(3)	0.41416(14)	0.79949(13)	0.0170(3)	O(10)	0.4255(7)	0.4126(3)	0.7967(3)	0.0158(7)
O(11)	0.1275(3)	0.80899(15)	0.83470(14)	0.0177(3)	O(11)	0.1269(8)	0.8078(4)	0.8326(4)	0.0216(8)
O(12)	0.2600(3)	0.95444(14)	0.16707(14)	0.0174(3)	O(12)	0.2616(7)	0.9550(4)	0.1696(4)	0.0212(8)
O(13)	0.2695(3)	0.60686(13)	0.80496(14)	0.0170(3)	O(13)	0.2697(8)	0.6062(3)	0.8033(4)	0.0166(7)
O(14)	0.5723(3)	0.22118(13)	0.80189(14)	0.0175(3)	O(14)	0.5727(8)	0.2209(3)	0.7997(3)	0.0167(7)
O(15)	0.3831(3)	0.18705(14)	0.16364(14)	0.0168(3)	O(15)	0.3815(7)	0.1890(4)	0.1660(4)	0.0210(8)
X^P_D	0	0	0	0.0114(3)	X^P_D	0	0	0	0.0129(6)
W	0.1686(11)	0.3304(7)	0.0005(5)	0.0383(13)	W	0.165(3)	0.3210(7)	0.0003(14)	0.0194(17)
H(1)	0.254(5)	0.424(2)	0.3067(2)	0.01392(0)	H(1)	0.250(11)	0.425(5)	0.3072(6)	0.01326(0)
H(2)	1.035(5)	0.160(2)	0.6853(2)	0.01416(0)	H(2)	1.046(11)	0.176(4)	0.6811(14)	0.0119(0)

* U_{iso} for H(1) and H(2) atoms.

TABLE 6. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR BULGAKITE AND NALIVKINITE

	bulgakite	nalivkinite		bulgakite	nalivkinite
M(1)–O(6)	2.132(2)	2.131(3)	M(2)–O(5)b	2.091(2)	2.083(3)
M(1)–O(2)a	2.149(2)	2.134(3)	M(2)–O(7)	2.098(2)	2.095(3)
M(1)–O(5)	2.167(3)	2.165(4)	M(2)–O(5)c	2.135(2)	2.133(4)
M(1)–O(3)a	2.171(2)	2.167(4)	M(2)–O(6)	2.184(1)	2.189(4)
M(1)–O(7)	2.193(2)	2.183(4)	M(2)–O(7)c	2.221(3)	2.220(4)
M(1)–O(1)	2.221(3)	2.217(4)	M(2)–O(2)	2.257(3)	2.250(4)
<M(1)–φ>	2.172	2.166	<M(2)–φ>	2.164	2.162
M(3)–O(1)	2.107(2)	2.101(4)	M(4)–O(4) ×2	2.090(2)	2.092(4)
M(3)–O(3)	2.114(2)	2.112(3)	M(4)–O(1)b ×2	2.160(2)	2.158(4)
M(3)–O(4)	2.119(2)	2.121(4)	M(4)–O(3) ×2	2.172(2)	2.172(4)
M(3)–O(6)	2.144(3)	2.146(4)	<M(4)–φ>	2.141	2.141
M(3)–O(4)d	2.181(2)	2.185(4)			
M(3)–O(2)	2.234(2)	2.219(4)			
<M(3)–φ>	2.150	2.147			
T(1)–O(15)	1.610(2)	1.609(4)	T(2)–O(13)d	1.614(2)	1.615(3)
T(1)–O(11)d	1.611(2)	1.602(4)	T(2)–O(3)d	1.615(5)	1.614(4)
T(1)–O(1)	1.627(5)	1.630(4)	T(2)–O(10)d	1.638(2)	1.633(4)
T(1)–O(13)d	1.640(6)	1.638(3)	T(2)–O(8)a	1.639(2)	1.638(4)
<T(1)–O>	1.622	1.620	<T(2)–O>	1.627	1.625
T(3)–O(14)d	1.617(2)	1.607(4)	T(4)–O(9)d	1.612(2)	1.612(4)
T(3)–O(6)d	1.626(4)	1.624(3)	T(4)–O(12)	1.612(2)	1.600(4)
T(3)–O(8)	1.645(2)	1.643(4)	T(4)–O(7)e	1.629(4)	1.637(4)
T(3)–O(10)d	1.647(2)	1.646(3)	T(4)–O(14)d	1.633(2)	1.634(3)
<T(3)–O>	1.634	1.630	<T(4)–O>	1.622	1.621
T(1)d–O(13)–T(2)d	144.0(1)	144.3(2)	D–O(2)	1.797(5)	1.839(3)
T(2)b–O(8)–T(3)	139.1(1)	139.2(2)	D–O(9)f	1.968(1)	1.958(4)
T(2)d–O(10)–T(3)d	138.7(1)	139.3(2)	D–O(12)g	1.969(1)	1.966(4)
T(3)d–O(14)–T(4)d	144.1(1)	144.6(3)	D–O(11)h	1.976(2)	1.969(4)
<T–O–T>	141.5	141.9	D–O(15)	1.978(2)	1.967(4)
			D–X^{P}_{D}	2.101(6)	2.080(1)
			<D–φ>	1.965	1.963
A(1)–O(12)k	2.879(2)	2.898(6)	A(2)–W	1.80(1)	1.767(9)
A(1)–O(11)h	2.883(5)	2.907(7)	A(2)–X^{P}_{D}	2.05(1)	1.97(1)
A(1)–O(15)	2.891(5)	2.920(7)	A(2)–O(11)h	2.29(1)	2.33(2)
A(1)–O(9)l	2.894(3)	2.914(6)	A(2)–O(12)k	2.32(1)	2.32(2)
A(1)–X^{P}_{D}	3.207(2)	3.226(4)	A(2)–O(15)	2.32(1)	2.32(2)
A(1)–O(14)l	3.349(4)	3.378(7)	A(2)–O(9)l	2.36(1)	2.31(2)
A(1)–O(13)d	3.399(3)	3.428(7)	<A(2)–φ>	2.19	2.17
A(1)–O(14)m	3.438(4)	3.430(8)			
A(1)–O(13)h	3.452(4)	3.456(7)	B–O(15) ×2	2.543(3)	2.575(4)
A(1)–O(8)k	3.571(5)	3.559(6)	B–O(9)c ×2	2.553(4)	2.588(4)
A(1)–O(10)l	3.591(6)	3.591(6)	B–O(12)n ×2	2.584(5)	2.606(4)
A(1)–O(10)d	3.622(3)	3.642(6)	B–O(11)d ×2	2.599(2)	2.620(4)
A(1)–O(8)	3.704(3)	3.693(6)	B–X^{P}_{D} ×2	2.6870(5)	2.687(1)
<A(1)–φ>	3.298	3.311	<B–φ>	2.593	2.615
A(1)–A(2)	1.16(1)	1.26(1)	A(1)–W	0.644(6)	0.512(6)

* φ = O, OH, F, H_2O.

Operators for generating equivalent atoms: a: *x*+1, *y*, *z*; b: *x*–1, *y*, *z*; c: –*x*+1, –*y*, –*z*+1; d: –*x*+1, –*y*+1, –*z*+1; e: *x*, *y*+1, *z*; f: –*x*, –*y*, –*z*+1; g: *x*, *y*–1, *z*; h: –*x*, –*y*+1, –*z*+1; k: –*x*, –*y*+1, –*z*; l: *x*, *y*, *z*–1; m: *x*–1, *y*, *z*–1; n: –*x*+1, –*y*+1, –*z*.

TABLE 7. REFINED SITE-SCATTERING VALUES AND ASSIGNED SITE-POPULATIONS FOR BULGAKITE AND NALIVKINITE

Site*	Refined site-scattering (*epfu*)	Site population (*apfu*)	Calculated site-scattering (*epfu*)	$<X–\varphi>_{obs.}$** (Å)	Ideal composition (*apfu*)
		bulgakite			
M(1)	45.9(1)	$1.52\ Fe^{2+} + 0.23\ Li + 0.21\ Mn + 0.04\ Na$	45.90	2.172	Fe^{2+}_2
M(2)	50.3(1)	$1.19\ Fe^{2+} + 0.81\ Mn$	51.19	2.164	Fe^{2+}_2
M(3)	50.1(1)	$1.65\ Fe^{2+} + 0.30\ Mn + 0.05\ Mg$	51.0	2.150	Fe^{2+}_2
M(4)	25.58(6)	$0.98\ Fe^{2+} + 0.02\ Li$	25.54	2.141	Fe^{2+}
Σ*M*	171.88	$5.34\ Fe^{2+} + 1.32\ Mn + 0.25\ Li + 0.05\ Mg + 0.04\ Na$	173.63		Fe^{2+}_7
D	47.92(9)	$1.82\ Ti + 0.10\ Sn + 0.05\ Nb + 0.03\ Zr$	48.29	1.965	Ti_2
$^{[13]}A(1)$	25.0(1)	$0.91\ K + 0.12\ Rb + 0.03\ Cs + 0.94\ \square$	23.38	3.298	
A(2)	2.82	$0.94\ Li + 1.06\ \square$	2.82	2.19	
Σ*A*	27.82	$0.94\ Li + 0.91\ K + 0.12\ Rb + 0.03\ Cs$	26.20		Li_2
$^{[10]}B$	16.64(6)	$0.60\ Ca + 0.40\ Na$	16.40	2.593	(Ca,Na)
X^P_D		$0.70\ F + 0.30\ O$			(O,F)***
W		$0.94\ H_2O + 1.06\ \square$			$(H_2O)_2$****
		nalivkinite			
M(1)	47.8(2)	$1.46\ Fe^{2+} + 0.22\ Mn + 0.08\ Zr + 0.08\ Na + 0.16\ \square$	47.54	2.166	Fe^{2+}_2
M(2)	50.9(2)	$1.56\ Fe^{2+} + 0.40\ Mn + 0.04\ \square$	50.56	2.162	Fe^{2+}_2
M(3)	51.1(2)	$1.66\ Fe^{2+} + 0.28\ Mn + 0.04\ Mg + 0.02\ \square$	50.64	2.147	Fe^{2+}_2
M(4)	26.1(1)	$0.94\ Fe^{2+} + 0.04\ Zn + 0.02\ \square$	25.64	2.141	Fe^{2+}
Σ*M*	175.9	$5.62\ Fe^{2+} + 0.90\ Mn + 0.08\ Zr + 0.08\ Na + 0.04\ Zn + 0.04\ Mg + 0.24\ \square$	174.41		Fe^{2+}_7
D	53.1(2)	$1.55Ti + 0.24\ Nb + 0.09\ Sn + 0.08\ Zr + 0.04\ Ta$	54.56	1.963	Ti_2
$^{[13]}A(1)$	20.84	$0.75\ K + 0.09\ Cs + 0.02\ Pb + 1.14\ \square$	20.84	3.311	
A(2)	3.42	$1.14\ Li + 0.86\ \square$	3.42	2.17	
Σ*A*	24.26	$1.14\ Li + 0.75\ K + 0.09\ Cs + 0.02\ Pb$	24.26		Li_2
$^{[10]}B$	13.27(4)	$0.71\ Na + 0.29\ Ca$	13.61	2.615	Na
X^P_D		$1.00\ F$			F
W		$1.14\ H_2O + 0.86\ \square$			$(H_2O)_2$****

* coordination number is given for non-[6]-coordinated sites;

** X = cation, φ = O, OH, F, H_2O;

*** for explanation, see section "On the ideal formula of bulgakite";

**** Note that the ideal composition of the *A* site, Li_2 *apfu*, [where it is fully occupied by Li] requires full occupancy of the *W* site: $(H_2O)_2$ *pfu*; otherwise the coordination of the Li atom is not complete.

(Bul) substitutes for ~0.2 □ (Nal); (2) in the H sheet, ~0.2 Ti^{4+} (Bul) substitutes for ~0.2 ($Nb^{5+} + Ta^{5+}$) (Nal) at the *D* site; and (3) in the **I** block, ~0.3 Ca (Bul) substitutes for ~0.3 Na (Nal) at the *B* site and ~0.3 O^{2-} (Bul) substitutes for ~0.3 F^- (Nal) at the X^P_D site. However in bulgakite, O^{2-} is not a dominant cation at the X^P_D site. How can we justify the writing of the ideal formula of bulgakite where X^P_D = (O,F)? Consider charges of specific groups of cations and anions using empirical formulae for both minerals. Here we present these formulae as $A_2C_7D_2(T_4O_{12})_2X^O_{D2}X^O_{A4}X^P_DW_{A2} + BX^P_D$: (1) bulgakite, $\{(Li_{0.94}K_{0.91}Rb_{0.12}Cs_{0.03})_{\Sigma2}(Fe^{2+}_{5.34}Mn_{1.32}Li_{0.25}Mg_{0.05}Na_{0.04}Zn_{0.02})_{\Sigma7.02}(Ti_{1.82}Sn_{0.10}Nb_{0.05}Zr_{0.04})_{\Sigma2.01}(Si_{7.78}Al_{0.24})_{\Sigma8.02}O_{24}O_2(OH)_4(H_2O)_{0.94}]_{\Sigma2}]^{0.32-} + [(Ca_{0.60}Na_{0.40})_{\Sigma1}(F_{0.70}O_{0.30})_{\Sigma1}]^{0.30-}\}$ and (2) nalivkinite $\{(Li_{1.14}K_{0.75}Cs_{0.09}Pb_{0.02})_{\Sigma2}(Fe^{2+}_{5.62}Mn_{0.90}Zr_{0.08}Na_{0.08}Mg_{0.04}Zn_{0.04})_{\Sigma6.76}(Ti_{1.56}Nb_{0.24}Sn_{0.09}Zr_{0.08}Ta_{0.04})_{\Sigma2}(Si_{7.86}Al_{0.15})_{\Sigma8.01}O_{24}O_2(OH)_4(H_2O)_{1.14}]^{0.26-} + [(Na_{0.71}Ca_{0.29})_{\Sigma1}F]^{0.29+}\}$. Inspection of these formulae shows that (1) in spite of several substitutions and therefore the slightly different compositions of several

TABLE 8. HYDROGEN BONDING IN BULGAKITE AND NALIVKINITE

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	∠DHA (°)
bulgakite				
O(4)OH–H(1)···O(11)a	0.980(3)	2.81(2)	3.440(3)	123(2)
O(4)OH–H(1)···O(13)a	0.980(3)	2.88(2)	3.446(4)	117(2)
O(5)OH–H(2)···O(14)b	0.980(3)	2.89(2)	3.455(4)	117(2)
O(5)OH–H(2)···O(14)	0.980(3)	3.02(2)	3.502(4)	112(2)
nalivkinite				
O(4)OH–H(1)···O(11)a	0.98(1)	2.80(5)	3.436(6)	123(4)
O(4)OH–H(1)···O(13)a	0.98(1)	2.86(5)	3.443(5)	119(4)
O(5)OH–H(2)···O(14)b	0.98(1)	2.88(5)	3.453(5)	118(4)
O(5)OH–H(2)···O(14)	0.98(1)	3.04(5)	3.498(5)	110(4)

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

cation and anion groups in bulgakite and nalivkinite, the larger parts of their structures, $[A_2C_7D_2(T_4O_{12})_2X^O_{D2}X^O_{A4}X^P_DW_{A2}]$, have the same charge: $\sim 0.3^-$ (see above) and (2) accordingly, the $[BX^P_D]$ parts of the formulae have the same charge: $\sim 0.3^+$ for the rest of the formulae. We conclude that the bulgakite ↔ nalivkinite cation and anion substitutions at the *B* and X^P_D sites are not affected by other substitutions

TABLE 9. SELECTED BOND-VALENCE VALUES* FOR BULGAKITE AND NALIVKINITE

Atom	M(1–4)	D	A(2)**	B**	Σ
bulgakite					
O(4)OH	1.08				1.08
O(5)OH	1.08				1.08
O(9)			0.11	$0.18^{x2\downarrow}$	
O(11)			0.13	$0.16^{x2\downarrow}$	
O(12)			0.12	$0.17^{x2\downarrow}$	
O(15)			0.12	$0.19^{x2\downarrow}$	
X^P_D**		$0.37^{x2\rightarrow}$	$0.17^{x2\rightarrow}$	$0.10^{x2\downarrow\rightarrow}$	1.28
W**			0.34		0.34
Total			0.99	1.60	
Aggregate charge			1.00	1.60	
nalivkinite					
O(4)OH	1.06				1.06
O(5)OH	1.07				1.07
O(9)			0.12	$0.18^{x2\downarrow}$	
O(11)			0.12	$0.16^{x2\downarrow}$	
O(12)			0.12	$0.17^{x2\downarrow}$	
O(15)			0.12	$0.19^{x2\downarrow}$	
X^P_D**		$0.35^{x2\rightarrow}$	$0.19^{x2\rightarrow}$	$0.10^{x2\downarrow\rightarrow}$	1.28
W**			0.36		0.36
Total			1.03	1.40	
Aggregate charge			1.00	1.25	

* bond-valence parameters (*vu*) are from Brown (1981);
** A(2) = Li, W = H_2O; bulgakite: $X^P_D = F_{0.70}O_{0.30}$, B = $Ca_{0.60}Na_{0.40}$; nalivkinite: X^P_D = F, B = $Na_{0.71}Ca_{0.29}$.

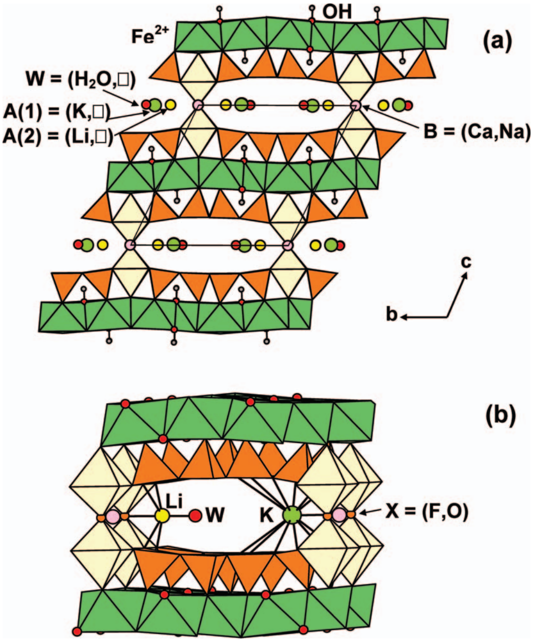

FIG. 4. The crystal structure of bulgakite: (a) general view, (b) a possible short-range-order (SRO) arrangement of K and Li atoms at the *A*(1) and *A*(2) sites, respectively. The Fe^{2+}-dominant and Ti octahedra are green and yellow, respectively; Si tetrahedra are orange; Ca, K, and Li atoms at *B*, *A*(1), and *A*(2) sites are shown as medium pink, large green, and medium yellow spheres; X^P_D anions, OH groups [X^O_A sites], and H_2O groups [*W* site] are shown as small orange, small red, and medium red spheres, respectively; H atoms of OH groups are shown as small gray spheres, O–H bonds are shown as black lines; the unit cell is shown with thin black lines.

elsewhere in the structure. In bulgakite and nalivkinite, BX^P_D = $[(Ca_{0.60}Na_{0.40})(F_{0.70}O_{0.30})]$ and $[(Na_{0.71}Ca_{0.29})F]$, respectively. Hence bulgakite and nalivkinite are related by the following substitution: 0.3 $^BCa^{2+}$ + 0.3 $^XO^{2-}$ ↔ 0.3 $^BNa^+$ + 0.3 $^XF^-$. The latter substitution shows that the dominance of Ca at the *B* site must be accompanied by partial substitution of O for F at the X^P_D site. To indicate the relation between Ca^{2+} and O^{2-} and in spite of the dominance of F^- over O^{2-} at the X^P_D site in bulgakite (Table 7), we must write the ideal formula of bulgakite as follows: $Li_2(Ca,Na)Fe^{2+}_7Ti_2(Si_4O_{12})_2O_2(OH)_4(O,F)(H_2O)_2$.

ON THE [6]-COORDINATED *A*(2) SITE IN THE ASTROPHYLLITE-SUPERGROUP MINERALS

Previous work

Piilonen *et al.* (2003b) reviewed the stereochemistry of the *A* site and the positional disorder that could occur around the *A* site. They concluded that the *A* site could split into two subsites, the [11]-coordinated *A*(1) site and the [5–7]-coordinated *A*(2) site. Cámara *et al.* (2010) further discussed positional disorder of the *A* site and stated that the *A*(1) site is usually partly occupied by K. There were several reports on the [5]-coordinated *A*(2) site in the astrophyllite-supergroup structures, *e.g.*, Piilonen *et al.* (2001) reported K at the *A*(2) site with 12% occupancy in the triclinic polytype of kupletskite (sample RUS12); Uvarova *et al.* (2008) reported Li at the *A*(2) site with ~50% occupancy in nalivkinite; and Cámara *et al.* (2010) reported (K,Ca,Pb) at the *A*(2) site with 23% occupancy in kupletskite-(Cs). In kupletskite, nalivkinite, and kupletskite-(Cs) (see above) the coordination of the cation at the [5]-coordinated *A*(2) site is not complete: all five anions occur on one side of the cation and hence the cation is not surrounded by anions.

Details of the topology

In bulgakite and nalivkinite, the [6]-coordinated *A*(2) site is partly occupied by Li. The Li atom is coordinated by four O atoms, an X^P_D anion [(F,O) in bulgakite and F in nalivkinite], and an H_2O group at the *W* site (Table 6). The presence of H_2O groups in the bulgakite and nalivkinite structures has been confirmed by infrared spectroscopy (Fig. 3a, 3b). The Li–W bond-length of 1.80 Å is the shortest bond-length if compared to other Li–φ (φ = O, F) bond-lengths in bulgakite and nalivkinite: 1.97–2.36 Å (Table 6). The short Li–W bond-length of 1.80 Å allows the O atom of an H_2O group to provide Li with a significant bond-valence of 0.34 *vu* (valence units) (bulgakite) and 0.36 *vu* (nalivkinite) if compared to the aggregate bond-valences from five other anions, 0.65 *vu* (bulgakite) and 0.67 *vu* (nalivkinite) (Table 9). The sums of bond-valence contributions from the six anions (including H_2O at the *W* site) are 0.99 *vu* for bulgakite and 1.03 *vu* for nalivkinite and they compensate for the positive charge of a monovalent Li at the *A*(2) site.

In the ICSD (Belsky *et al.* 2002), there are five structures (out of about 450 structures) with Li–O bonds shorter or equal to 1.80 Å (ICSD ##8238, 35162, 99481, 151878, 201980) (O. Gagne, *pers. commun.* 2014). However, only one entry, ICSD #151878, gives a bond-length from Li to an H_2O group in $LiNpO_2(CO_3)\cdot 2(H_2O)$ where Li is coordinated by three O atoms and an H_2O group: Li–H_2O = 1.80 Å (Charushnikova *et al.* 2004). The latter bond is the shortest compared to three other bond-lengths: Li–O = 2.01 Å.

Similar disorder at the *A* site has been reported for nafertisite (Cámara *et al.* 2014). The crystal structure of nafertisite, $Na_3Fe^{2+}_{10}Ti_2(Si_6O_{17})_2O_2(OH)_6F(H_2O)_2$, consists of HOH blocks that link *via* D–X^P_D–D bridges as in most of the astrophyllite-supergroup minerals. In the **I** block, the *A*+*B*, *C*, and *W* sites are occupied mainly by Na+Na, vacancy(□), and H_2O, respectively. The *A* site splits into $^{[9]}A(1)$ and $^{[6]}A(2)$ sites, occupied mainly by □ and Na, respectively. At the *A*(2) site, Na is coordinated by four O atoms, with <Na–O> = 2.464 Å; the X^P_D anion, with Na–(F,O) = 2.309 Å; and an H_2O group at the *W* site, with Na–W = 2.21 Å, the shortest (Na–φ) bond-length, where φ = O, F.

SUMMARY

Bulgakite, ideally $Li_2(Ca,Na)Fe^{2+}_7Ti_2(Si_4O_{12})_2O_2(OH)_4(O,F)(H_2O)_2$, is a new mineral of the astrophyllite group, a Ca-analogue of nalivkinite, $Li_2NaFe^{2+}_7Ti_2(Si_4O_{12})_2O_2(OH)_4F(H_2O)_2$ (Agakhanov *et al.* 2008, Uvarova *et al.* 2008, this work) (Table 1). The formula of bulgakite is of the form $A_2BC_7D_2(T_4O_{12})_2O_2(OH)_4X^P_DW_2$, where ideally C_7 = $^{[6]}Fe^{2+}_7$ at the *M*(1–4) sites; D = $^{[6]}Ti$; T = Si; A = Li; B = (Ca,Na); X^P_D = (O,F); W_2 = $(H_2O)_2$.

The bulgakite structure consists of HOH blocks which alternate with **I** blocks. In the crystal structure of bulgakite, the HOH block has the same topology and stereochemistry as in nalivkinite. The topology of the **I** block is the same as that in nalivkinite where Li is the dominant cation at the *A* site. Bulgakite and nalivkinite are two distinct mineral species: at the *B* site, Ca is dominant in bulgakite and Na is dominant in nalivkinite. Bulgakite and nalivkinite are related by the following substitution: 0.3 $^BCa^{2+}$ + 0.3 $^XO^{2-}$ ↔ 0.3 $^BNa^+$ + 0.3 $^XF^-$.

The crystal structure of nalivkinite, ideally $Li_2NaFe^{2+}_7Ti_2(Si_4O_{12})_2O_2(OH)_4F(H_2O)_2$, has been refined and its chemical formula has been revised. It is of the form $A_2BC_7D_2(T_4O_{12})_2O_2(OH)_4X^{P}{}_{D}W_2$, where ideally $C_7 = {}^{[6]}Fe^{2+}{}_7$ at the M(1–4) sites; $D = {}^{[6]}Ti$; $T = Si$; $A = Li$; $B = Na$; $X^{P}{}_{D} = F$; $W_2 = (H_2O)_2$.

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