

## LAVEROVITE, $K_2NaMn_7Zr_2(Si_4O_{12})_2O_2(OH)_4F$ , A NEW ASTROPHYLLITE-SUPERGROUP MINERAL FROM MONT SAINT-HILAIRE, QUÉBEC, CANADA

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### ABSTRACT

Laverovite (IMA 2017-009b), ideally  $K_2NaMn_7Zr_2(Si_4O_{12})_2O_2(OH)_4F$ , is a kupletskite-group (astrophyllite-supergroup) mineral from Mont Saint-Hilaire, Québec, Canada. Associated minerals are zircophyllite, kupletskite, astrophyllite, aegirine, analcime, orthoclase, and albite. Laverovite is brown, transparent in thin grains, and has a vitreous luster. Mohs hardness is 3,  $D_{\text{calc.}} = 3.367 \text{ g/cm}^3$ . Laverovite is biaxial (–) with refractive indices ( $\lambda = 589 \text{ nm}$ )  $\alpha = 1.670(2)$ ,  $\beta = 1.710(5)$ ,  $\gamma = 1.740(5)$ ;  $2V_{\text{meas.}} = 82(2)^\circ$ ,  $2V_{\text{calc.}} = 80^\circ$ , strong dispersion:  $r > v$ . Cleavage is perfect parallel to  $\{001\}$ . Chemical analysis by electron microprobe gave Nb<sub>2</sub>O<sub>5</sub> 0.56, ZrO<sub>2</sub> 9.78, TiO<sub>2</sub> 4.69, SiO<sub>2</sub> 33.52, Al<sub>2</sub>O<sub>3</sub> 0.94, SrO 0.13, ZnO 0.07, FeO 13.94, MnO 20.51, CaO 0.48, MgO 0.76, Cs<sub>2</sub>O 0.05, K<sub>2</sub>O 6.00, Na<sub>2</sub>O 2.28, F 1.80, H<sub>2</sub>O<sub>calc.</sub> 2.57, sum 97.32 wt.%; H<sub>2</sub>O was calculated from crystal-structure analysis. The empirical formula based on 31.15 (O + F) *apfu* with [OH + F = 5 *pfu* and H<sub>2</sub>O = 0.15 *pfu*] is  $(K_{1.78}Sr_{0.02}Cs_{0.01}\square_{0.19})_{\Sigma 2}(\square_{1.85}Na_{0.15})_{\Sigma 2}(Na_{0.88}Ca_{0.12})_{\Sigma 1}(Mn_{4.03}Fe^{2+}_{2.71}Mg_{0.25}Zn_{0.01})_{\Sigma 7}(Zr_{1.11}Ti_{0.82}Nb_{0.06}Mg_{0.01})_{\Sigma 2}[(Si_{7.78}Al_{0.26})_{\Sigma 8.04}O_{24}]O_2[(OH)_{3.68}F_{0.32}]_{\Sigma 4}F[\square_{1.85}(H_2O)_{0.15}]_{\Sigma 2}$ ,  $Z = 1$ . The simplified formula is  $K_2Na(Mn,Fe^{2+})_7(Zr,Ti)_2(Si_4O_{12})_2O_2(OH)_4F$ . Laverovite is triclinic, space group  $P\bar{1}$ ,  $a$  5.4329(1),  $b$  11.9232(3),  $c$  11.7491(3) Å,  $\alpha$  112.905(2),  $\beta$  94.696(1),  $\gamma$  103.178(1)°,  $V$  670.14(5) Å<sup>3</sup>. The six strongest lines in the X-ray powder diffraction data [ $d$  (Å)( $hkl$ )] are: 3.452(92)(003,111); 2.788(97)( $\bar{1}\bar{3}1$ ,  $\bar{1}\bar{4}2$ ); 2.680(68)( $\bar{2}11$ ); 2.589(100)(130,  $\bar{1}\bar{4}3$ ); 2.504(44)( $\bar{2}12$ ), and 1.590(50)( $\bar{3}\bar{5}1$ ,  $\bar{3}\bar{2}2$ ). The crystal structure has been refined to  $R_1 = 3.26\%$  for 3757 observed ( $F_o > 4\sigma F_o$ ) reflections. In the crystal structure of laverovite, there are four <sup>[4]</sup>*T* sites, with  $\langle T-O \rangle = 1.621 \text{ Å}$ , occupied mainly by Si, with minor Al. TO<sub>4</sub> tetrahedra constitute the T<sub>4</sub>O<sub>12</sub> astrophyllite ribbon. The Zr-dominant <sup>[6]</sup>*D* site is occupied mainly by Zr and Ti and minor Nb and Mg, with  $\langle D-\varphi \rangle = 2.002 \text{ Å}$  ( $\varphi = O, F$ ). The T<sub>4</sub>O<sub>12</sub> astrophyllite ribbons and D octahedra constitute the H (Heteropolyhedral) sheet. In the O (Octahedral) sheet, there are four Mn<sup>2+</sup>-dominant <sup>[6]</sup>*M*(1–4) sites, with  $\langle M(1-4)-\varphi \rangle = 2.187, 2.174, 2.161$ , and  $2.146 \text{ Å}$  ( $\varphi = O, OH$ ). Two H sheets and the central O sheet form the HOH block, and adjacent HOH blocks link *via* a common X<sup>*P*</sup><sub>D</sub> anion 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<sub>A</sub>* site, partly occupied by H<sub>2</sub>O. The *A* site splits into two partly occupied sites, <sup>[13]</sup>*A*(1) and <sup>[6]</sup>*A*(2), with  $A(1)-A(2) = 1.108 \text{ Å}$ . The <sup>[13]</sup>*A*(1) site is occupied at 90.5%: mainly by K, with minor Sr and Cs,  $\langle A(1)-\varphi \rangle = 3.326 \text{ Å}$ ; the <sup>[6]</sup>*A*(2) site is occupied at 7.5% by Na:  $[\square_{1.85}Na_{0.15}]$ ,  $\langle A(2)-\varphi \rangle = 2.29 \text{ Å}$  ( $\varphi = O, F, H_2O$ ). The aggregate content of the *A* site is  $(K_{1.78}Sr_{0.02}Cs_{0.01}Na_{0.15}\square_{0.04})_{\Sigma 2}$ , ideally K<sub>2</sub> *apfu*. The <sup>[10]</sup>*B* site is occupied by  $(Na_{0.88}Ca_{0.12})$ ,  $\langle B-\varphi \rangle = 2.646 \text{ Å}$ . The *W<sub>A</sub>* site is occupied at 7.5% by H<sub>2</sub>O:  $[\square_{1.85}(H_2O)_{0.15}]$  *pfu*. The presence of OH and H<sub>2</sub>O groups in the laverovite structure was confirmed by infrared spectroscopy. The mineral is named “laverovite” after Professor Nikolay Pavlovich Laverov (1930–2016), Academician of the Russian Academy of Sciences, a prominent Russian ore geologist and an expert in uranium ore deposits and radiogenic waste disposal. Laverovite is a Mn-analogue of zircophyllite,  $K_2NaFe^{2+}Zr_2(Si_4O_{12})_2O_2(OH)_4F$ .

**Keywords:** laverovite, new mineral, astrophyllite supergroup, Mont Saint-Hilaire, Québec, electron microprobe analysis, crystal structure, FTIR spectroscopy.

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## INTRODUCTION

Laverovite, ideally  $K_2NaMn_7Zr_2(Si_4O_{12})_2O_2(OH)_4F$ , is a new kupletskite-group (astrophyllite supergroup, IMA 2017D, Sokolova *et al.* 2017a) mineral. It was found in the sample R060216, which is the property of the RRUFF Database, University of Arizona, Tucson, U.S.A. The sample is from the Desourdy quarry which later became part of the Demix quarry which in turn was subsumed by the Poudrette quarry, Mont Saint-Hilaire, La Vallée-du-Richelieu RCM, Montérégie, Québec, Canada. The mineral is named “laverovite” (pronunciation: la-’vər-o-vait; Russian-Cyrillic: лавёровит) after Professor Nikolay Pavlovich Laverov (Cyrillic: Николай Павлович Лавёров) (1930–2016), Academician of the Russian Academy of Sciences, a prominent Russian ore geologist and an expert in uranium ore deposits and radiogenic waste disposal. Professor Laverov was a great scientist who had major impact both on the principal areas of his work and on the organization of science in Russia. Professor Laverov was President of the Academy of Sciences of the Kyrgyz SSR (1987–1988) and Vice-President of the Russian Academy of Sciences (1991–2013); he was also Director of the Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry of the Russian Academy of Sciences (IGEM RAS) (1991–2003). The new mineral species and its name were approved by the Commission on New Minerals, Nomenclature and Classification, International Mineralogical Association (IMA 2017–009b). The holotype specimen of laverovite has been deposited in the collections of Royal Ontario Museum, Toronto, Ontario, Canada; ROM accession number is M57542. Here we report the description and crystal structure of laverovite, a new mineral.

## THE ASTROPHYLLITE SUPERGROUP

Here we give general information on the astrophyllite supergroup (Sokolova *et al.* 2017a), so that the site nomenclature and details of the structure are explained prior to their use in the sections on chemical analysis and structure refinement. The astrophyllite supergroup is divided into three groups: the astrophyllite group, the kupletskite group, and the devitoite group (Table 1).

The HOH block is the main structural unit in all astrophyllite-supergroup structures; it consists of two H (Heteropolyhedral) and one O (Octahedral) sheets where the  $T_4O_{12}$  astrophyllite ribbons occur in the H sheets. The term “astrophyllite ribbon” was introduced by Belov (1963, 1976). In each structure, HOH blocks alternate with **I** (Intermediate) blocks along [001]. The

14 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.

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,  $Sn^{4+}$ ,  $^{15}Fe^{3+}$ , Mg, Al; T = Si, minor Al; the **I** (Intermediate) block is composed of the peripheral layers of the form  $A_{2p}B_rW_{A2}$  where  $p = 1, 2$ ;  $r = 1, 2$ ; A = K, Cs, Ba,  $H_2O$ , Li, Rb,  $Pb^{2+}$ , Na,  $\square$ ; B = Na, Ca, Ba,  $H_2O$  (only in *veinbergeite*),  $\square$ ;  $W_A = H_2O$ ,  $\square$ , and I represents the composition of the central part of the **I** block, *e.g.*,  $(PO_4)_2(CO_3)$  in devitoite;  $X^O_D = O$ ;  $X^O_A = OH, F$ ;  $X^P_D = F, O, OH, H_2O, \square$ , where  $n = 0, 1, 2$  for  $(X^P_D)_n$ . The A site can split into A(1) and A(2) sites. Table 1 lists ideal structural formulae for the 14 astrophyllite-supergroup minerals.

## OCCURRENCE AND MINERAL ASSOCIATION

The laverovite studied in this work is a part of sample R060216, which is the property of the RRUFF Database, University of Arizona, Tucson, U.S.A. Sample R060216 came from the Royal Ontario Museum (ROM accession number M26526), Toronto, Canada. The sample is from the Desourdy quarry which later became part of the Demix quarry which in turn was subsumed by the Poudrette quarry, Mont Saint-Hilaire, La Vallée-du-Richelieu RCM, Montérégie, Québec, Canada. Associated minerals are zircophyllite, kupletskite, astrophyllite, aegirine, analcime, orthoclase, and albite. Laverovite formed as a late-stage hydrothermal mineral in a nepheline-syenite pegmatite.

In sample R060216, astrophyllite-supergroup minerals occur as transparent pale-brown to dark-brown elongated lath-like crystals. Each grain of sample R060216 is an intergrowth of four minerals: laverovite, zircophyllite, astrophyllite, and kupletskite. Laverovite occurs as a narrow rim on one side of grain 5 from sample R060216 (Fig. 1).

## PHYSICAL PROPERTIES

Laverovite is brown and has a vitreous luster and a light-brown streak. Laverovite is visually indistin-

TABLE 1. IDEAL STRUCTURAL FORMULAE OF THE FORM  $A_{2p}B_rC_7D_2(T_4O_{12})_2X^O_{D_2}X^O_{A_4}X^P_{Dn}W_{A_2}$  FOR THE ASTROPHYLLITE-SUPERGROUP MINERALS\*

Mineral	Ideal structural formula										Z	Ref.***	
	$A_{2p}$	$B_r$	$C_7$	$D_2$	$(T_4O_{12})_2$	$X^O_{D_2}$	$X^O_{A_4}$	$X^P_{Dn}$	$W_{A_2}$	$p$			$r$
<i>Astrophyllite group</i>													
Astrophyllite	$K_2$	Na	$Fe^{2+}_7$	$Ti_2$	$(Si_4O_{12})_2$	$O_2$	$(OH)_4$	F		1	1	1	(1,2)
Niobophyllite	$K_2$	Na	$Fe^{2+}_7$	$(Nb, Ti)_2$	$(Si_4O_{12})_2$	$O_2$	$(OH)_4$	(O,F)		1	1	1	(3,2)
Zircophyllite	$K_2$	Na	$Fe^{2+}_7$	$Zr_2$	$(Si_4O_{12})_2$	$O_2$	$(OH)_4$	F		1	1	1	(4,5)
Tarbagataite	( $K\Box$ )	Ca	$Fe^{2+}_7$	$Ti_2$	$(Si_4O_{12})_2$	$O_2$	$(OH)_4$	(OH)		1	1	1	(6)
Nalivkinite	$Li_2$	Na	$Fe^{2+}_7$	$Ti_2$	$(Si_4O_{12})_2$	$O_2$	$(OH)_4$	F	$(H_2O)_2$	1	1	1	(7,8)
Bulgakite	$Li_2$	(Ca,Na)	$Fe^{2+}_7$	$Ti_2$	$(Si_4O_{12})_2$	$O_2$	$(OH)_4$	(O,F)	$(H_2O)_2$	1	1	1	(8)
<i>Kupletskite group</i>													
Kupletskite	$K_2$	Na	$Mn_7$	$Ti_2$	$(Si_4O_{12})_2$	$O_2$	$(OH)_4$	F		1	1	1,4**	(9,10)
Kupletskite-(Cs)	$Cs_2$	Na	$Mn_7$	$Ti_2$	$(Si_4O_{12})_2$	$O_2$	$(OH)_4$	F		1	1	1	(11,2)
Niobokupletskite	$K_2$	Na	$Mn_7$	$(Nb, Ti)_2$	$(Si_4O_{12})_2$	$O_2$	$(OH)_4$	(O,F)		1	1	1	(12)
Laverovite	$K_2$	Na	$Mn_7$	$Zr_2$	$(Si_4O_{12})_2$	$O_2$	$(OH)_4$	F		1	1	1	(13)
Heyerdahlite	$Na_2$	Na	$Mn_7$	$Ti_2$	$(Si_4O_{12})_2$	$O_2$	$(OH)_4$	F	$(H_2O)_2$	1	1	1	(14)
<i>Devitoite group</i>													
Devitoite	$Ba_4$	$Ba_2$	$Fe^{2+}_7$	$Fe^{3+}_2$	$(Si_4O_{12})_2$	$O_2$	$(OH)_4$	$\Box_2$		2	2	0	(15)
Sveinbergeite	$(H_2O)_2$	$[Ca(H_2O)]$	$(Fe^{2+}_6Fe^{3+})$	$Ti_2$	$(Si_4O_{12})_2$	$O_2$	$(OH)_4$	$[(OH)(H_2O)]$		1	2	2	(16)
Lobanovite	$K_2$	Na	$(Fe^{2+}_4Mg_2Na)$	$Ti_2$	$(Si_4O_{12})_2$	$O_2$	$(OH)_4$	$\Box$		1	1	0	(17,18)

\* After Sokolova et al. (2017a);

\*\* Z = 1 and 4 for kupletskite-1A and kupletskite-2M, respectively;

\*\*\* References (description of a new mineral, the latest work on the structure): (1) Weibye (1848); (2) Cámara et al. (2010); (3) Nickel et al. (1964); (4) Kapustin (1972, 1973); (5) Sokolova & Hawthorne (2016); (6) Stepanov et al. (2012); (7) Agakhanov et al. (2008); (8) Agakhanov et al. (2016); (9) Semenov (1956); (10) Piilonen et al. (2001); (11) Yefimov et al. (1971); (12) Piilonen et al. (2000); (13) This work; (14) Sokolova et al. (2018b); (15) Kampf et al. (2010); (16) Khomyakov et al. (2011); (17) Sokolova et al. (2017b); (18) Sokolova & Cámara (2008).

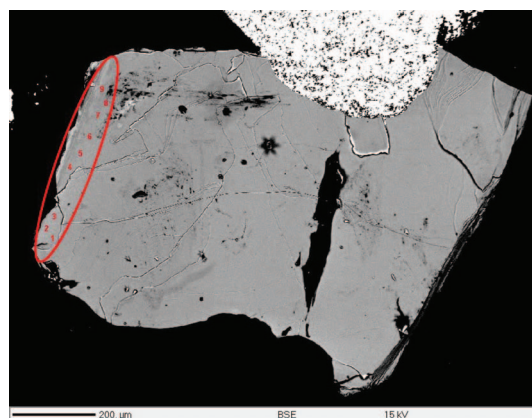


FIG. 1. BSE image of grain 5 from sample R060216; the laverovite zone is enclosed by a red ellipse.

guishable from other astrophyllite-supergroup minerals. Cleavage is perfect parallel to  $\{001\}$ ; it is brittle and has a hackly fracture. The Mohs hardness is 3. Laverovite does not fluoresce under ultraviolet light.  $D_{\text{calc.}} = 3.367 \text{ g/cm}^3$  (from the empirical formula). Laverovite is biaxial (–) with refractive indices ( $\lambda = 589 \text{ nm}$ )  $\alpha = 1.670(2)$ ,  $\beta = 1.710(5)$ ,  $\gamma = 1.740(5)$ ;  $2V_{\text{meas.}} = 82(2)^\circ$ ,  $2V_{\text{calc.}} = 80^\circ$ . The dispersion is strong,  $r > v$ . It is pleochroic according to the scheme  $X > Y > Z$ , where  $X =$  yellowish brown,  $Y =$  brownish yellow,  $Z =$  pale yellow. The compatibility index ( $1 - Kp/Kc$ ) = 0.007 (for  $D_{\text{calc.}}$ ) is rated as superior (Mandarino 1981).

#### INFRARED SPECTROSCOPY

The FTIR spectra of laverovite (Fig. 2) were collected from crystal fragments using a Bruker Hyperion 2000 IR microscope equipped with a liquid nitrogen-cooled MCT detector (University of Manitoba). The spectrum shown in Figures 2a, 2b, and 2d was collected from a single-crystal fragment pressed into a homogenous film with a thickness of 10  $\mu\text{m}$  using a diamond anvil. The spectrum in Figure 2c was collected from single-crystal fragments with thicknesses of  $\sim 35$ –50  $\mu\text{m}$ . Data over the range 4800–620  $\text{cm}^{-1}$  were obtained by averaging 100 scans with a resolution of 4  $\text{cm}^{-1}$ . Base-line corrections were done using the OPUS spectroscopic software (Bruker Optic GmbH).

The complete FTIR spectrum of laverovite is shown in Figure 2a and parts of this spectrum are shown at higher resolution in Figures 2b and 2d. There a single sharp band at  $\sim 3612 \text{ cm}^{-1}$  (Fig. 2b) that may be assigned to an OH-stretching band and an extremely broad  $\text{H}_2\text{O}$  stretching band centered at  $\sim 3432 \text{ cm}^{-1}$  (Fig. 2b). Figure 2c shows a weak broad band centered at  $\sim 1645 \text{ cm}^{-1}$ ; this band may be assigned to an H–O–H

TABLE 2. CHEMICAL COMPOSITION AND UNIT FORMULA\* FOR LAVEROVITE

Constituent	wt. %	Range		<i>apfu</i>
$\text{Nb}_2\text{O}_5$	0.56	0.29–0.69	Si	7.78
$\text{ZrO}_2$	9.78	9.34–10.67	Al	0.26
$\text{TiO}_2$	4.69	4.03–5.03	$\Sigma\text{T}$	8.04
$\text{SiO}_2$	33.52	33.34–33.80		
$\text{Al}_2\text{O}_3$	0.94	0.91–0.97	Mn	4.03
SrO	0.13	0.09–0.18	$\text{Fe}^{2+}$	2.71
ZnO	0.07	0.05–0.12	Mg	0.25
FeO	20.51	13.23–14.44	Zn	0.01
MnO	17.19	20.09–21.03	$\Sigma\text{M}$	7.00
CaO	0.48	0.46–0.49		
MgO	0.76	0.73–0.79	Zr	1.11
$\text{Cs}_2\text{O}$	0.05	0.03–0.06	Ti	0.82
$\text{K}_2\text{O}$	6.00	5.97–6.05	Nb	0.06
$\text{Na}_2\text{O}$	2.28	2.23–2.35	Mg	0.01
$\text{H}_2\text{O}$	2.57**		$\Sigma\text{D}$	2.00
F	1.80	1.56–2.26		
F=O	<u>–0.76</u>		Na	0.88
Total	97.32		Ca	0.12
			$\Sigma\text{B}$	1.00
			K	1.78
			Sr	0.02
			Cs	0.01
			$\Sigma\text{A}(1)$	1.81
			Na	0.15
			$\Sigma\text{A}(2)$	0.15
			$\Sigma\text{A}(1,2)$	1.96
			F	1.32
			OH	3.68
			$\text{H}_2\text{O}$	0.15

\* Formula unit calculated based on 31.15 (O + F) *pfu*;

\*\* calculated from crystal-structure analysis: OH + F = 5 *pfu* and  $\text{H}_2\text{O} = 0.15 \text{ pfu}$ .

bending mode. In Figure 2d, there is a strong band at  $\sim 962 \text{ cm}^{-1}$  (with a shoulder at  $\sim 1042 \text{ cm}^{-1}$ ) that may be assigned to symmetric and asymmetric stretching modes of the  $\text{SiO}_4$  group. A less intense, broad band at  $\sim 646 \text{ cm}^{-1}$  (with a shoulder at  $\sim 694 \text{ cm}^{-1}$ ) may be assigned to an Si–O–Si bending mode. In Figure 2b, three low-intensity bands in the range 2800–3000  $\text{cm}^{-1}$  are likely due to C–H stretching from grease used during sample preparation. In Figure 2c, low-intensity bands in the range 2060–2420  $\text{cm}^{-1}$  are due to atmospheric  $\text{CO}_2$  transitions. An additional low-intensity band at  $\sim 1260 \text{ cm}^{-1}$  in Figure 2d is due to epoxy attached to the sample after removal from the EMPA slide.

#### CHEMICAL COMPOSITION

A narrow zone in grain 5 (Fig. 1) was analyzed with a Cameca SX-100 electron microprobe operating

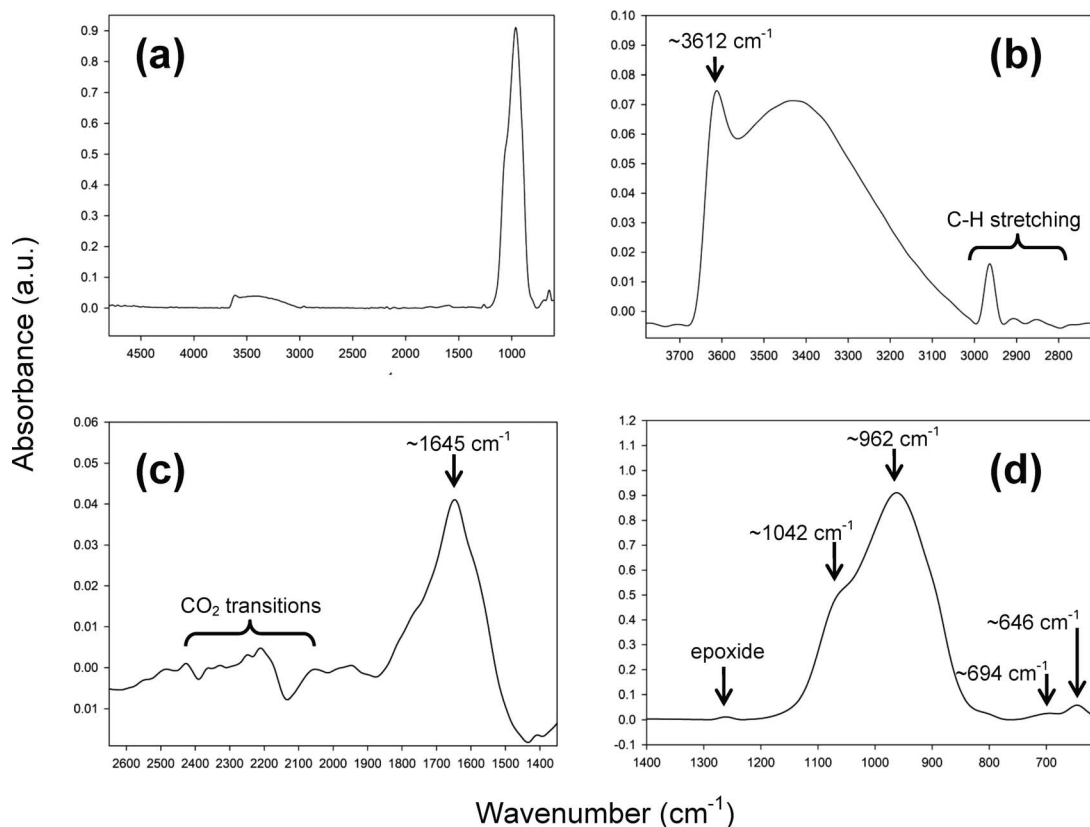


FIG. 2. The FTIR spectrum of laverovite: (a) the spectrum from 4600 to 600  $\text{cm}^{-1}$ ; (b) the spectrum from  $\sim 3800$  to 2700  $\text{cm}^{-1}$  with an expanded absorbance scale; (c) the region from 2650 to 1350  $\text{cm}^{-1}$  with an expanded absorbance scale; (d) the region from 1400 to 605  $\text{cm}^{-1}$  with an expanded absorbance scale.

in wavelength-dispersive mode with an accelerating voltage of 15 kV, a specimen current of 20 nA, and a beam diameter of 10  $\mu\text{m}$ . The following standards were used: Si, Ca: diopside; Na: albite; Al: andalusite; Nb:  $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ ; Zr: zircon; Ti: titanite; Fe: fayalite; Mn: spessartine; Mg: forsterite; Zn: gahnite; Sr:  $\text{SrTiO}_3$ ; Cs: pollucite; K: orthoclase; F: fluororibeckite. The elements Pb, Rb, and Sn were sought but not detected. The data were reduced and corrected by the PAP method of Pouchou & Pichoir (1985). Water was calculated from the results of the crystal-structure analysis so that  $\text{OH} + \text{F} = 5 \text{ apfu}$  and  $\text{H}_2\text{O} = 0.15 \text{ pfu}$ . Table 2 gives the chemical composition of laverovite (mean of nine points). The empirical formula calculated on the basis of 31.15 (O + F) is  $(\text{K}_{1.78}\text{Sr}_{0.02}\text{Cs}_{0.01}\square_{0.19})_{\Sigma 2}(\square_{1.85}\text{Na}_{0.15})_{\Sigma 2}(\text{Na}_{0.88}\text{Ca}_{0.12})_{\Sigma 1}(\text{Mn}_{4.03}\text{Fe}^{2+}_{2.71}\text{Mg}_{0.25}\text{Zn}_{0.01})_{\Sigma 7}(\text{Zr}_{1.11}\text{Ti}_{0.82}\text{Nb}_{0.06}\text{Mg}_{0.01})_{\Sigma 2}[(\text{Si}_{7.78}\text{Al}_{0.26})_{\Sigma 8.04}\text{O}_{24}]\text{O}_2[(\text{OH})_{3.68}\text{F}_{0.32}]_{\Sigma 4}\text{F}[\square_{1.85}(\text{H}_2\text{O})_{0.15}]_{\Sigma 2}$ ,  $Z = 1$ . The basis of 31.15 (O + F) for calculation of the empirical formula unit

was derived from the structure-refinement results: 31 (O + F) anions (established basis for calculation of the formula unit for the astrophyllite and kupletskite groups of the astrophyllite-supergroup minerals) plus 0.15 O [from 0.15  $\text{H}_2\text{O}$  pfu at the  $W_A$  site] as determined by crystal-structure refinement. Note that 0.15  $\text{H}_2\text{O}$  pfu at the  $W_A$  site is necessary to complete the coordination of  $\text{Na}_{0.15}$  apfu at the  $A(2)$  site. The presence of OH and  $\text{H}_2\text{O}$  groups was confirmed by IR spectroscopy (see above).

The ideal formula is  $\text{K}_2\text{NaMn}_7\text{Zr}_2(\text{Si}_4\text{O}_{12})_2\text{O}_2(\text{OH})_4\text{F}$  which requires (wt.%):  $\text{K}_2\text{O}$  6.75,  $\text{Na}_2\text{O}$  2.22,  $\text{MnO}$  35.57,  $\text{ZrO}_2$  17.65,  $\text{SiO}_2$  34.44, F 1.36,  $\text{H}_2\text{O}$  2.58,  $\text{O} = \text{F} - 0.57$ , total 100.

#### DATA COLLECTION AND STRUCTURE REFINEMENT

Single-crystal X-ray data for laverovite were collected with a Bruker D8 QUEST ECO CMOS diffractometer equipped with a fine-focus tube ( $\text{MoK}\alpha$ ) and a PHOTON 50 detector. X-ray powder diffraction

TABLE 3. X-RAY POWDER DIFFRACTION DATA\* FOR LAVEROVITE

$l_{\text{est.}}$	$d_{\text{calc}}$ (Å)	$h$	$k$	$l$	$l_{\text{est.}}$	$d_{\text{calc}}$ (Å)	$h$	$k$	$l$
20	3.761	0	$\bar{2}$	3	16	2.027	1	3	2
	3.737	1	$\bar{2}$	2		2.018	1	$\bar{4}$	5
92	3.542	0	0	3	39	1.776	1	3	3
	3.542	1	1	1		1.771	0	0	6
28	3.280	$\bar{1}$	$\bar{1}$	3		1.768	1	$\bar{4}$	6
	3.275	0	$\bar{3}$	3	30	1.750	$\bar{2}$	1	5
21	3.100	$\bar{1}$	$\bar{2}$	2	35	1.658	0	$\bar{7}$	3
24	3.046	1	$\bar{2}$	3	29	1.640	0	$\bar{7}$	2
15	2.998	0	1	3		1.637	0	$\bar{7}$	4
	2.993	$\bar{1}$	3	1		1.635	$\bar{1}$	4	4
	2.982	0	3	1	50	1.5895	3	$\bar{5}$	1
29	2.892	0	$\bar{4}$	2		1.5894	$\bar{3}$	$\bar{2}$	2
	2.887	1	$\bar{3}$	3	33	1.5737	$\bar{3}$	5	0
	2.879	1	1	2		1.5726	$\bar{3}$	$\bar{2}$	3
	2.878	0	$\bar{1}$	4		1.5714	$\bar{3}$	$\bar{2}$	1
97	2.788	$\bar{1}$	$\bar{3}$	1		1.5704	3	$\bar{5}$	2
	2.784	1	$\bar{4}$	2	23	1.4513	$\bar{3}$	$\bar{2}$	5
68	2.680	$\bar{2}$	1	1		1.4510	$\bar{1}$	5	4
100	2.589	1	3	0		1.4488	3	2	1
	2.581	1	$\bar{4}$	3		1.4478	$\bar{1}$	4	5
44	2.504	$\bar{2}$	1	2		1.4463	3	$\bar{5}$	4
27	2.412	$\bar{1}$	4	1	16	1.4240	2	$\bar{1}$	6
	2.403	$\bar{1}$	$\bar{3}$	4		1.4227	$\bar{1}$	$\bar{4}$	8
34	2.309	1	3	1	23	1.4109	2	$\bar{8}$	2
	2.300	1	$\bar{4}$	4		1.4100	0	7	1
28	2.271	$\bar{2}$	1	3		1.4097	$\bar{2}$	$\bar{6}$	4
26	2.125	0	0	5	15	1.3840	2	$\bar{8}$	1
	2.124	$\bar{1}$	4	2		1.3813	$\bar{2}$	$\bar{6}$	5
	2.115	$\bar{1}$	$\bar{3}$	5	17	1.3527	$\bar{4}$	2	0
19	2.062	2	$\bar{1}$	3		1.3522	$\bar{2}$	$\bar{6}$	1

\* Powder data were obtained by collapsing experimental single-crystal data into two dimensions. Reflection (001) was covered by the beam stop. Reflections with  $l_{\text{est.}} < 15$  are not listed.

data were obtained by collapsing single-crystal experimental data into two dimensions (Table 3). Unit-cell parameters from the single-crystal data were determined by least-squares refinement of 9935 reflections with  $I > 10\sigma I$  and are given in Table 4, together with miscellaneous information regarding data collection and structure refinement. For laverovite, the intensities of 58,385 reflections were measured using 30 s per  $0.5^\circ$  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 laverovite was refined using atom coordinates of zircophyllite (Sokolova & Hawthorne 2016) as a starting model, except for those of the Na atom at the  $A(2)$  site and the O atom of the  $H_2O$  group at the  $W_A$  site, which were found in the

difference-Fourier map. The crystal structure of laverovite was refined to  $R_1 = 3.26\%$  based on 3757 unique reflections with ( $F_o > 4\sigma F$ ). 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 Mn),  $D$  site (scattering curve of Zr),  $A(1)$  site (scattering curve of K),  $A(2)$  and  $B$  sites (scattering curve of Na), and  $W_A$  site (scattering curve of O). For laverovite, we observed disorder at the  $A(1)$ ,  $A(2)$ , and  $W_A$  sites, which are partly occupied by K, Na, and  $H_2O$  and separated by short distances:  $A(1)-A(2) = 1.108$  and  $A(1)-W_A = 1.030$  Å. For the final refinement, the occupancies of the  $A(2)$  and  $W_A$  sites were adjusted in accord with the chemical analysis and constrained to be equal (see text below). The  $D(\text{donor})-H(1,2)$  distances were softly constrained to 0.98 Å.

TABLE 4. MISCELLANEOUS REFINEMENT DATA FOR LAVEROVITE

<i>a</i> (Å)	5.4329(1)
<i>b</i>	11.9232(3)
<i>c</i>	11.7491(3)
$\alpha$ (°)	112.905(2)
$\beta$	94.696(1)
$\gamma$	103.178(1)
<i>V</i> (Å <sup>3</sup> )	670.14(5)
Space group	<i>P</i> $\bar{1}$
<i>Z</i>	1
Reflections ( <i>I</i> > 10 $\sigma$ <i>I</i> )	9935
Absorption coefficient (mm <sup>-1</sup> )	4.80
<i>F</i> (000)	655.2
<i>D</i> <sub>calc.</sub> (g/cm <sup>3</sup> )	3.367
Crystal size (mm)	0.22 × 0.11 × 0.016
Radiation/monochromator	MoK $\alpha$ /graphite
2 $\theta$ -range for data collection (°)	61.98
<i>h</i>	-7 ≤ <i>h</i> ≤ 7
<i>k</i>	-17 ≤ <i>k</i> ≤ 17
<i>l</i>	-16 ≤ <i>l</i> ≤ 16
<i>R</i> (int) (%)	3.99
Reflections collected	58,385
Independent reflections	4232
<i>F</i> <sub>o</sub> > 4 $\sigma$ <i>F</i>	3757
Refinement method	Full-matrix least squares on <i>F</i> <sup>2</sup> , fixed weights proportional to 1/ $\sigma$ <i>F</i> <sub>o</sub> <sup>2</sup>
Final <i>R</i> (obs) (%)	
<i>R</i> <sub>1</sub> ( <i>F</i> <sub>o</sub> > 4 $\sigma$ <i>F</i> )	3.26
<i>R</i> <sub>1</sub>	3.92
<i>wR</i> <sub>2</sub>	8.02
Highest peak, deepest hole (e Å <sup>-3</sup> )	1.22, -0.67
Goodness of fit on <i>F</i> <sup>2</sup>	1.049

Final atom coordinates and anisotropic displacement parameters are listed in Table 5, selected interatomic distances and Si–O–Si angles are given in Table 6, refined site-scattering and assigned site-populations for selected cation and anion sites are given in Table 7, bond-valence values for selected anions are given in Table 8, and details of hydrogen bonding in Table 9. A list of observed and calculated structure factors and a Crystallography Information File (CIF) may be obtained from The Depository of Unpublished Data on the MAC website<sup>1</sup> (documents Laverovite CM57, 18-00071).

#### STRUCTURE DESCRIPTION

In the crystal structure of laverovite (Fig. 3), there are four *T* sites occupied by Si and minor Al (Table 5)

and tetrahedrally coordinated by O atoms with  $\langle T-O \rangle = 1.621$  Å (Table 6). There is one Zr-dominant *D* site coordinated by five O atoms and an *X*<sup>*P*</sup><sub>*D*</sub> anion [*X*<sup>*P*</sup><sub>*D*</sub> = *F*], with  $\langle D-\varphi \rangle = 2.002$  Å ( $\varphi = O, F$ ). The *D* site contains (Zr<sub>1.11</sub>Ti<sub>0.82</sub>Nb<sub>0.06</sub>Mg<sub>0.01</sub>) $\Sigma$ <sub>2</sub>, ideally Zr<sub>2</sub> *apfu* (Table 7). There are four *M* sites octahedrally coordinated by O atoms and *X*<sup>*O*</sup><sub>*A*</sub>(1,2) anions occupied mainly by O atoms of OH groups and minor F (Tables 5–9);  $\langle M-\varphi \rangle = 2.159$  Å ( $\varphi = O, OH$ ). These four *M* sites contain (Mn<sub>4.03</sub>Fe<sup>2+</sup><sub>2.71</sub>Mg<sub>0.25</sub>Zn<sub>0.01</sub>) $\Sigma$ <sub>7</sub>, ideally Mn<sub>7</sub> *apfu*. In the O sheet, Mn > Fe<sup>2+</sup>, hence laverovite is a kupletskite-group mineral (Table 1). 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). M(1–4) octahedra share common edges to form a trioctahedral O sheet. The T tetrahedra share vertices to form the T<sub>4</sub>O<sub>12</sub> (ideally Si<sub>4</sub>O<sub>12</sub>) astrophyllite ribbon along [100]. Astrophyllite ribbons and D octahedra share common vertices to form an H sheet. Two H

<sup>1</sup> The MAC website may be found at <http://mineralogicalassociation.ca>

TABLE 5. ATOM COORDINATES AND ANISOTROPIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ ) FOR LAVEROVITE

Atom	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$	$U_{\text{eq}}$
M(1)	0.85063(7)	0.20604(3)	0.48065(4)	0.00981(19)	0.01047(19)	0.0165(2)	0.00670(14)	0.00372(13)	0.00396(13)	0.01164(13)
M(2)	0.28040(7)	0.06801(3)	0.48929(4)	0.01040(19)	0.0122(2)	0.0174(2)	0.00852(15)	0.00463(13)	0.00488(13)	0.01215(13)
M(3)	0.42267(7)	0.35204(3)	0.48528(4)	0.01045(19)	0.01104(19)	0.0180(2)	0.00770(15)	0.00465(13)	0.00480(13)	0.01221(13)
M(4)	0	1/2	1/2	0.0097(3)	0.0091(3)	0.0162(3)	0.0056(2)	0.00229(19)	0.00346(18)	0.01147(17)
D	0.07905(6)	0.08676(3)	0.19818(3)	0.00890(14)	0.01224(15)	0.01470(16)	0.00583(11)	0.00260(10)	0.00433(10)	0.01163(10)
T(1)	0.67846(13)	0.27352(6)	0.23139(7)	0.0128(3)	0.0101(3)	0.0133(3)	0.0059(2)	0.0024(2)	0.0036(2)	0.01167(14)
T(2)	0.81262(15)	0.54743(7)	0.25413(7)	0.0187(3)	0.0099(3)	0.0153(3)	0.0059(3)	0.0026(3)	0.0039(3)	0.01452(15)
T(3)	0.37628(14)	0.67447(7)	0.25645(7)	0.0174(3)	0.0109(3)	0.0144(3)	0.0068(3)	0.0026(3)	0.0044(3)	0.01371(15)
T(4)	0.50576(13)	0.92977(6)	0.23572(7)	0.0137(3)	0.0099(3)	0.0132(3)	0.0063(2)	0.0026(2)	0.0039(2)	0.01168(14)
A(1)	0.1368(3)	0.27097(11)	0.99556(11)	0.0857(10)	0.0476(7)	0.0365(6)	0.0160(5)	0.0064(5)	0.0132(6)	0.0585(5)
A(2)	0.089(3)	0.1761(9)	0.9968(14)	0.024(7)	0.012(6)	0.027(8)	0.015(6)	0.002(6)	0.005(5)	0.019(3)
B	1/2	0	0	0.0221(6)	0.0124(5)	0.0078(5)	0.0032(4)	0.0018(4)	0.0047(4)	0.0145(3)
O(1)	0.7260(3)	0.31781(17)	0.38291(17)	0.0121(8)	0.0122(8)	0.0137(8)	0.0055(7)	0.0023(6)	0.0039(6)	0.0126(3)
O(2)	0.1276(4)	0.39176(17)	0.59358(17)	0.0140(8)	0.0113(8)	0.0137(8)	0.0054(7)	0.0026(6)	0.0039(6)	0.0129(3)
O(3)	0.5617(4)	0.25740(17)	0.58977(17)	0.0142(8)	0.0136(8)	0.0135(8)	0.0063(7)	0.0027(6)	0.0052(7)	0.0133(3)
O(4)	0.5730(4)	0.01377(17)	0.38758(17)	0.0131(8)	0.0138(8)	0.0130(8)	0.0055(7)	0.0025(6)	0.0046(7)	0.0132(3)
O(5)	0.0705(5)	0.5916(3)	0.2018(2)	0.0300(12)	0.0379(13)	0.0200(11)	0.0078(10)	0.0046(9)	-0.0076(10)	0.0338(6)
O(6)	0.2521(5)	0.0429(3)	0.8277(2)	0.0360(14)	0.0466(16)	0.0240(12)	-0.0012(11)	0.0158(11)	-0.0183(12)	0.0455(8)
O(7)	0.4302(5)	0.4141(3)	0.7976(2)	0.0463(15)	0.0390(14)	0.0208(11)	0.0088(10)	0.0022(10)	0.0293(12)	0.0338(6)
O(8)	0.1307(6)	0.8054(3)	0.8317(2)	0.075(2)	0.0666(19)	0.0239(12)	0.0222(13)	0.0218(13)	0.0621(18)	0.0456(8)
O(9)	0.2660(6)	0.9550(3)	0.1719(2)	0.0612(18)	0.0458(15)	0.0243(12)	-0.0022(11)	-0.0132(12)	0.0432(15)	0.0456(8)
O(10)	0.2669(6)	0.6051(2)	0.8047(2)	0.0672(18)	0.0110(9)	0.0189(10)	0.0069(8)	0.0045(11)	0.0051(10)	0.0335(6)
O(11)	0.5734(6)	0.2218(2)	0.8012(2)	0.0706(19)	0.0127(9)	0.0207(11)	0.0096(8)	0.0060(11)	0.0057(11)	0.0351(6)
O(12)	0.3873(5)	0.1934(3)	0.1680(2)	0.0275(12)	0.0638(19)	0.0252(12)	0.0225(13)	-0.0083(10)	-0.0227(12)	0.0448(8)
X <sup>O</sup> <sub>D</sub>	0.1483(4)	0.16281(18)	0.37645(18)	0.0127(8)	0.0137(8)	0.0191(9)	0.0072(7)	0.0041(7)	0.0054(7)	0.0147(4)
X <sup>O</sup> <sub>A</sub> (1)	0.2981(4)	0.46365(18)	0.40167(18)	0.0159(9)	0.0166(9)	0.0162(9)	0.0067(7)	0.0035(7)	0.0057(7)	0.0160(4)
X <sup>O</sup> <sub>A</sub> (2)	0.9893(4)	0.11668(18)	0.59206(18)	0.0168(9)	0.0165(9)	0.0152(9)	0.0078(7)	0.0037(7)	0.0063(7)	0.0155(4)
X <sup>P</sup> <sub>D</sub>	0	0	0	0.0259(12)	0.0237(12)	0.0165(11)	0.0073(9)	0.0038(9)	0.0071(10)	0.0224(5)
W <sub>A</sub>	0.175(13)	0.3650(18)	0.011(5)	0.09(2)*						
H(1)	0.257(7)	0.425(3)	0.3094(10)	0.01925*						
H(2)	1.022(7)	0.156(3)	0.6845(10)	0.01854*						

\*  $U_{\text{iso}}$



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

M(1)–(X <sup>O</sup> <sub>D</sub> )a	2.143(2)	M(2)–X <sup>O</sup> <sub>A</sub> (2)b	2.117(2)	M(3)–X <sup>O</sup> <sub>A</sub> (1)	2.124(2)
M(1)–O(3)	2.154(2)	M(2)–O(4)	2.133(2)	M(3)–O(1)	2.140(2)
M(1)–X <sup>O</sup> <sub>A</sub> (2)	2.170(2)	M(2)–X <sup>O</sup> <sub>A</sub> (2)c	2.138(2)	M(3)–O(2)	2.151(2)
M(1)–O(2)a	2.190(2)	M(2)–O(3)	2.210(2)	M(3)–O(3)	2.160(2)
M(1)–O(4)	2.220(2)	M(2)–X <sup>O</sup> <sub>D</sub>	2.221(2)	M(3)–X <sup>O</sup> <sub>A</sub> (1)d	2.185(2)
M(1)–O(1)	2.242(2)	M(2)–O(4)c	2.223(2)	M(3)–X <sup>O</sup> <sub>D</sub>	2.204(2)
<M(1)–φ>	2.187	<M(2)–φ>	2.174	<M(3)–φ>	2.161
M(4)–X <sup>O</sup> <sub>A</sub> (1) ×2	2.094(2)	T(1)–O(12)	1.592(3)	T(2)–O(10)d	1.608(2)
M(4)–O(1)b ×2	2.166(2)	T(1)–O(8)d	1.593(2)	T(2)–O(2)d	1.619(2)
M(4)–O(2) ×2	2.178(2)	T(1)–O(1)	1.627(2)	T(2)–O(5)a	1.636(3)
<M(4)–φ>	2.146	T(1)–O(10)d	1.632(2)	T(2)–O(7)d	1.638(2)
		<T(1)–O>	1.611	<T(2)–O>	1.625
T(3)–O(11)d	1.610(2)	T(4)–O(6)d	1.594(2)	T(1)d–O(10)–T(2)d	143.5(2)
T(3)–O(3)d	1.634(2)	T(4)–O(9)	1.595(3)	T(2)b–O(5)–T(3)	139.4(2)
T(3)–O(7)d	1.649(2)	T(4)–O(11)d	1.626(2)	T(2)d–O(7)–T(3)d	139.9(2)
T(3)–O(5)	1.653(3)	T(4)–O(4)e	1.630(2)	T(3)d–O(11)–T(4)d	143.6(2)
<T(3)–O>	1.637	<T(4)–O>	1.611	<T–O–T>	141.6
D–X <sup>O</sup> <sub>D</sub>	1.894(2)	A(1)–O(8)k	2.895(3)	A(2)–X <sup>P</sup> <sub>D</sub>	2.060(8)
D–O(6)f	1.999(2)	A(1)–O(12)l	2.897(3)	A(2)–W <sub>A</sub> l	2.129(1)
D–O(9)g	2.000(2)	A(1)–O(9)h	2.898(3)	A(2)–O(9)h	2.38(1)
D–O(12)	2.006(2)	A(1)–O(6)	2.912(3)	A(2)–O(8)k	2.39(2)
D–O(8)h	2.007(2)	A(1)–(X <sup>P</sup> <sub>D</sub> )l	3.168(1)	A(2)–O(12)l	2.39(1)
D–X <sup>P</sup> <sub>D</sub>	2.1059(3)	A(1)–O(11)	3.415(3)	A(2)–O(6)	2.40(2)
<D–φ>	2.002	A(1)–O(11)b	3.453(3)	<A(2)–φ>	2.29
		A(1)–O(10)m	3.473(3)		
Short distances		A(1)–O(10)k	3.482(3)	B–O(6)c ×2	2.617(4)
A(1)–A(2)	1.108(8)	A(1)–O(5)h	3.564(3)	B–O(12) ×2	2.624(4)
A(1)–W <sub>A</sub> l	1.030(9)	A(1)–O(7)	3.649(3)	B–O(9)g ×2	2.634(4)
		A(1)–O(7)m	3.670(3)	B–O(8)d ×2	2.641(4)
		A(1)–O(5)l	3.765(3)	B–X <sup>P</sup> <sub>D</sub> ×2	2.7164(0)
		<A(1)–φ>	3.326	<B–φ>	2.646

\*φ = O, OH, F, H<sub>2</sub>O. Symmetry operators: 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 + 2; l: x, y, z + 1; m: –x + 1, –y + 1, –z + 2.

sheets and one O sheet form an HOH block identical to that in astrophyllite- and kupletskite-group minerals. In the laverovite structure, D octahedra share a common X<sup>P</sup><sub>D</sub> anion which has the composition 1 F *apfu* (Table 7).

In the I block between adjacent HOH blocks, there are two interstitial cation sites, A and B, and a W<sub>A</sub> site partly occupied by H<sub>2</sub>O. The A site splits into two sites, <sup>[13]</sup>A(1) and <sup>[6]</sup>A(2), separated by 1.108 Å (Table 6), and hence the A(1) and A(2) sites cannot both be locally occupied. The A(1) site is coordinated by 12 O atoms and one F atom (X<sup>P</sup><sub>D</sub> site), <A(1)–φ> = 3.326 Å (φ = O, F), and the A(2) site is coordinated by four O atoms, one F atom (X<sup>P</sup><sub>D</sub> site), and an H<sub>2</sub>O group at the W<sub>A</sub> site, <A(2)–φ> = 2.29 Å (φ = O, F, H<sub>2</sub>O). There is a short distance A(1)–W<sub>A</sub> = 1.030 Å (Table 6) and hence the W<sub>A</sub> and A(1) sites cannot both be locally occupied. The A(1) and A(2) sites are occupied by

(K<sub>1.78</sub>Sr<sub>0.02</sub>Cs<sub>0.01</sub>□<sub>0.19</sub>)<sub>Σ2</sub> *pfu* (90.5% occupancy) and (□<sub>1.85</sub>Na<sub>0.15</sub>)<sub>Σ2</sub> *pfu* (7.5% occupancy) (Table 7). As the A(1) site is occupied at 90.5%, the W<sub>A</sub> site can be occupied by H<sub>2</sub>O at less than 9.5%, *i.e.*, by 0.15 H<sub>2</sub>O *pfu* (7.5% occupancy), which is in accord with 0.15 Na *apfu* at the A(2) site (Table 7). Note that the ideal compositions of the A(2) and W<sub>A</sub> sites are □<sub>2</sub> and □<sub>2</sub>, respectively, and we will not count them in the ideal formula of laverovite. The aggregate content of the A site is (K<sub>1.78</sub>Na<sub>0.15</sub>Sr<sub>0.02</sub>Cs<sub>0.01</sub>□<sub>0.04</sub>)<sub>Σ2</sub>, ideally K<sub>2</sub> *apfu*. The <sup>[10]</sup>B site is occupied by (Na<sub>0.88</sub>Ca<sub>0.12</sub>), ideally Na *apfu* (Table 7).

#### ON THE [6]-COORDINATED A(2) SITE IN LAVEROVITE

Sodium at the A(2) site was reported for heyerdahlite, Na<sub>3</sub>Mn<sub>7</sub>Ti<sub>2</sub>(Si<sub>4</sub>O<sub>12</sub>)<sub>2</sub>O<sub>2</sub>(OH)<sub>4</sub>F(H<sub>2</sub>O)<sub>2</sub> (Sokolova *et al.* 2018b), another kupletskite-group mineral; the

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

Site*	Refined site-scattering (epfu)	Site-population (apfu)	Calculated site-scattering (epfu)	<Ct-φ> <sub>obs.</sub> (Å)**	Ideal composition (apfu)
Cations					
M(1)	50.3(1)			2.187	
M(2)	50.6(1)	Mn <sub>4.03</sub> Fe <sup>2+</sup> <sub>2.71</sub> Mg <sub>0.25</sub> Zn <sub>0.01</sub>		2.174	
M(3)	50.1(1)			2.161	
M(4)	24.78(9)			2.146	
ΣM	175.78		174.51		Mn <sub>7</sub>
D	63.3(2)	Zr <sub>1.11</sub> Ti <sub>0.82</sub> Nb <sub>0.06</sub> Mg <sub>0.01</sub>	65.02	2.002	Zr <sub>2</sub>
[ <sup>13</sup> ]A(1)	35.8(2)	K <sub>1.78</sub> Sr <sub>0.02</sub> Cs <sub>0.01</sub> □ <sub>0.19</sub>	35.13	3.326	K <sub>2</sub>
A(2)	1.65	□ <sub>1.85</sub> Na <sub>0.15</sub>	1.65	2.29	□ <sub>2</sub>
ΣA	37.45	K <sub>1.78</sub> Na <sub>0.15</sub> Sr <sub>0.02</sub> Cs <sub>0.01</sub> □ <sub>0.04</sub>	36.78		K <sub>2</sub>
[ <sup>10</sup> ]B	15.40(9)	Na <sub>0.88</sub> Ca <sub>0.12</sub>	12.08	2.646	Na
Anions and H <sub>2</sub> O groups					
[ <sup>4</sup> ]X <sub>D</sub> <sup>O</sup>		O <sub>2.00</sub>			O <sub>2</sub>
[ <sup>3</sup> ]X <sub>A(1,2)</sub> <sup>O</sup>		(OH) <sub>3.68</sub> F <sub>0.32</sub>			(OH) <sub>4</sub>
X <sub>D</sub> <sup>P</sup>		F <sub>1.00</sub>			F
[ <sup>1</sup> ]W <sub>A</sub>		□ <sub>1.85</sub> (H <sub>2</sub> O) <sub>0.15</sub>			□ <sub>2</sub>

\* Coordination number is given for non-[6]-coordinated sites; \*\* Ct = cation, φ = O, OH, F, H<sub>2</sub>O.

Na–W<sub>A</sub> bond-length of 2.15 Å is the shortest bond-length compared to other A(2)–φ (φ = O, F) bond lengths in heyerdahlite: 2.344–2.498 Å. The short Na–W<sub>A</sub> bond-length of 2.15 Å allows the O atom of an H<sub>2</sub>O group to provide Na at the A(2) site with a significant bond-valence compared to the aggregate bond-valences from five other anions. Similar disorder at the A site has been reported for nafertisite, ideally Na<sub>3</sub>Fe<sup>2+</sup><sub>10</sub>Ti<sub>2</sub>(Si<sub>6</sub>O<sub>17</sub>)<sub>2</sub>O<sub>2</sub>(OH)<sub>6</sub>F(H<sub>2</sub>O)<sub>2</sub> (Cámara *et al.* 2014), which is topologically related to the astrophyllite-supergrupp minerals. At the A(2) site, Na is coordinated by four O atoms, with <Na–O> = 2.464 Å, the X<sub>D</sub><sup>P</sup> anion (F<sub>0.86</sub>O<sub>0.14</sub>), with Na–X<sub>D</sub><sup>P</sup> = 2.309 Å, and an H<sub>2</sub>O group at the W<sub>A</sub> site, with Na–W<sub>A</sub> = 2.21 Å, the shortest (Na–φ) bond-length, where φ = O, F, H<sub>2</sub>O.

Gagné & Hawthorne (2016) reported bond-length distributions for alkali and alkaline-earth metals bonded to oxygen and gave the shortest recorded [<sup>6</sup>]Na–O bond-length as 2.129 Å.

For the A(2) site in laverovite, the shortest Na–W<sub>A</sub> bond-length is 2.060(8) Å, *i.e.*, it is very short. However, we did not constrain the Na–W<sub>A</sub> distance at 2.129 Å, as the A(2) and W<sub>A</sub> sites are only 7.5% occupied by Na and H<sub>2</sub>O and hence the refined coordinates of Na and O atoms at the A(2) and W<sub>A</sub> sites are not very accurate.

#### THE IDEAL FORMULA OF LAVEROVITE

The general formula for the kupletskite-group (astrophyllite-supergrupp) mineral laverovite is of the form A<sub>2</sub>BC<sub>7</sub>D<sub>2</sub>(T<sub>4</sub>O<sub>12</sub>)<sub>2</sub>X<sub>D2</sub><sup>O</sup>X<sub>A4</sub><sup>P</sup>DW<sub>A2</sub> (Table 1). For the ideal formula of laverovite, we sum the ideal compositions of the following sites: C<sub>7</sub> = Mn<sub>7</sub>; D = [<sup>6</sup>]Zr; T = Si; A<sub>2</sub> = K<sub>2</sub>; B = Na; (X<sub>D</sub><sup>O</sup>)<sub>2</sub> = O<sub>2</sub>; (X<sub>A</sub><sup>O</sup>)<sub>4</sub> = (OH)<sub>4</sub>; X<sub>D</sub><sup>P</sup> = F, (W<sub>A</sub>)<sub>2</sub> = □<sub>2</sub> (Table 7). Hence the ideal formula of laverovite is K<sub>2</sub>NaMn<sub>7</sub>Zr<sub>2</sub>(Si<sub>4</sub>O<sub>12</sub>)<sub>2</sub>O<sub>2</sub>(OH)<sub>4</sub>F.

Laverovite, ideally K<sub>2</sub>NaMn<sub>7</sub>Zr<sub>2</sub>(Si<sub>4</sub>O<sub>12</sub>)<sub>2</sub>O<sub>2</sub>(OH)<sub>4</sub>F, is a Mn analogue of zircophyllite, ideally

TABLE 8. HYDROGEN BONDING IN LAVEROVITE

D–H...A	D–H (Å)	H...A (Å)	D...A (Å)	∠DHA (°)
X <sub>A</sub> <sup>O</sup> (1)–H(1)...O(8)a	0.98(1)	2.82(3)	3.455(4)	123(3)
X <sub>A</sub> <sup>O</sup> (1)–H(1)...O(12)	0.98(1)	2.90(3)	3.493(4)	120(3)
X <sub>A</sub> <sup>O</sup> (2)–H(2)...O(6)b	0.98(1)	2.90(3)	3.506(4)	121(2)
X <sub>A</sub> <sup>O</sup> (2)–H(2)...O(9)c	0.98(1)	2.88(3)	3.504(4)	122(2)

a: –x, –y + 1, –z + 1; b: x + 1, y, z; c: –x + 1, –y + 1, –z + 1.

TABLE 9. SELECTED BOND-VALENCE VALUES\* FOR LAVEROVITE

Atom**	M(1–4)	D	A(1)	A(2)	B	Σ
$X_D^O$	0.96	1.01				1.97
$X_{A(1)}^O$	1.10					1.10
$X_{A(2)}^O$	1.12					1.12
$X_D^P$		0.25 $\times 2 \rightarrow$	0.07 $\times 2 \rightarrow$	0.02 $\times 2 \rightarrow$	0.09 $\times 2 \rightarrow$	0.86

\* Bond-valence parameters ( $\nu u$ ) are from Brown (1981), except Brown & Altermatt (1985) for Zr–F;

\*\*  $M_7 = Mn_4Fe^{2+}_3$ ;  $D = Zr_{0.55}Ti_{0.45}$ ;  $A(1) = K_{0.90}\square_{0.10}$ ;  $A(2) = Na_{0.08}\square_{0.92}$ ;  $B = Na$ ;  $X_D^O = O$ ;  $X_{A(1,2)}^O = OH$ ;  $X_D^P = F$ .

$K_2NaFe^{2+}_7Zr_2(Si_4O_{12})_2O_2(OH)_4F$  (Kapustin 1972, 1973, Sokolova & Hawthorne 2016). Zircophyllite,  $K_2NaFe^{2+}_7Zr_2(Si_4O_{12})_2O_2(OH)_4F$ , was redefined as an astrophyllite-group mineral (IMA 15B, Sokolova *et al.* 2018a).

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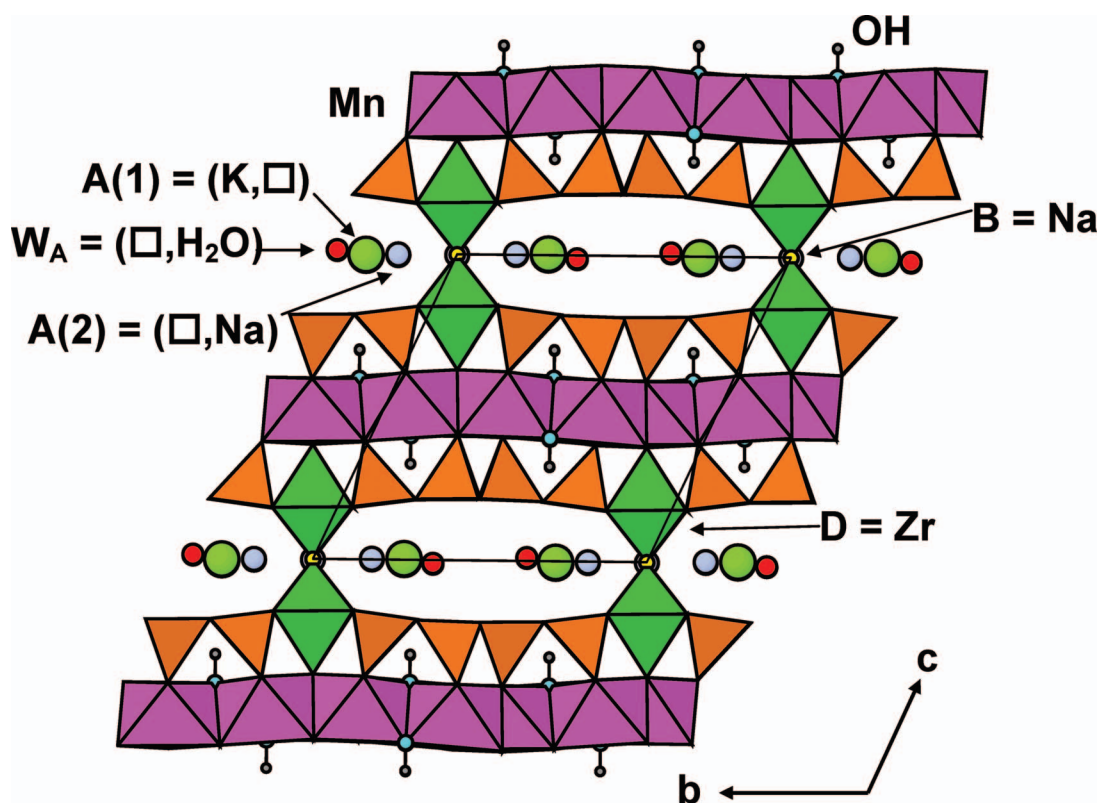


FIG. 3. General view of the crystal structure of laverovite. Mn-dominant M and Zr-dominant D octahedra are magenta and green, respectively; Si tetrahedra are orange; K atoms at the A(1) site are shown as large green spheres; Na atoms at A(2) and B sites are shown as medium navy blue spheres; F atoms ( $X_D^P$  site) and O atoms of OH groups ( $X_A^O$  sites) are shown as small yellow and turquoise spheres, respectively; H atoms of OH groups are shown as small gray spheres; H<sub>2</sub>O groups ( $W_A$  site) are shown as medium red spheres; the unit cell is shown with thin black lines.

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