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Lavinskyite, $K(LiCu)Cu_6(Si_4O_{11})_2(OH)_4$, isotypic with plancheite, a new mineral from the Wessels mine, Kalahari Manganese Fields, South Africa

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ABSTRACT

A new mineral species, lavinskyite, ideally $K(LiCu^{2+})Cu^{2+}_6(Si_4O_{11})_2(OH)_4$ (IMA 2012-028), has been found in the Wessels mine, Kalahari Manganese Fields, Northern Cape Province, South Africa. Associated minerals include wesselsite, pectolite, richterite, sugilite, and scottyite. Lavinskyite crystals are tabular [parallel to (010)]. The mineral is light blue, transparent with very pale blue streak and vitreous luster. It is brittle and has a Mohs hardness of ~5; cleavage is perfect on {010} and no parting was observed. The measured and calculated densities are 3.61(3) and 3.62 g/cm^3, respectively. Optically, lavinskyite is biaxial (+), with α = 1.675(1), β = 1.686(1), γ = 1.715(1), $2V_{meas}$ = 64(2)°. An electron microprobe analysis produced an average composition (wt%) of SiO_2 42.85(10), CuO 46.13(23), K_2O 4.16(2), MgO 1.53(17), Na_2O 0.27(4), BaO 0.18(6), and MnO 0.08(1), plus Li_2O 1.38 from the LA-ICP-MS measurement and H_2O 3.22 (added to bring the analytical total close to 100%), yielding a total of 99.79% and an empirical chemical formula $(K_{0.99}Ba_{0.01})_{\Sigma=1.00}(Li_{1.04}Cu_{0.93}Na_{0.10})_{\Sigma=2.07}(Cu_{5.57}Mg_{0.43}Mn_{0.01})_{\Sigma=6.01}(Si_{4.00}O_{11})_2(OH)_4$.

Lavinskyite is isotypic with plancheite, $Cu_8(Si_4O_{11})_2(OH)_4·H_2O$, an amphibole derivative. It is orthorhombic, with space group *Pcnb* and unit-cell parameters a = 19.046(2), b = 20.377(2), c = 5.2497(6) Å, and V = 2037.4(4) Å^3. The key difference between lavinskyite and plancheite lies in the coupled substitution of K^+ and Li^+ in the former for H_2O and Cu^{2+} in the latter, respectively. The structure of lavinskyite is characterized by the undulating, brucite-like layers consisting of three distinct octahedral sites occupied mainly by Cu. These layers are sandwiched by the amphibole-type double silicate chains extending along the c axis, forming a sheet structure of compact silicate-Cu-silicate triple layers. Adjacent sheets are linked together by K and M4 (= Cu + Li) cations, as well as hydrogen bonding. The M4 site is split, with Cu and Li occupying two different sites. Lavinskyite exhibits more amphibole-like structural features than plancheite, as a consequence of K in the large cavity between the two back-to-back double silicate chains.

Keywords: Lavinskyite, $K(LiCu)Cu_6(Si_4O_{11})_2(OH)_4$, plancheite, crystal structure, X-ray diffraction, Raman spectra

INTRODUCTION

A new mineral species, lavinskyite, ideally $K(LiCu)Cu_6(Si_4O_{11})_2(OH)_4$, has been found in the Wessels mine, Kalahari Manganese Fields, Northern Cape Province, Republic of South Africa. It is named in honor of Robert Matthew Lavinsky (born in 1973), the founder and manager of Arkenstone, a sole proprietorship for dealing in collectible mineral specimens and crystals. The Arkenstone web site (www.iRocks.com) was one of the first to bring mineral specimens to sale over the Internet. Lavinsky has been a donor of important mineral specimens to the Smithsonian Institution, Harvard University, California Institute of Technology, University of Arizona, and other institutions. He is also the largest contributor of information and photography to Mindat (an online public-access database of mineralogical information) and the sponsor of the Tucson Mineral and Gem Show Juniors' Award. Lavinsky recognized that some mineral specimens he brought to the U.S.A. from South Africa appeared to represent new mineral species and provided samples to our laboratory. The new mineral and its name have been approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA 2012-028). Part of the co-type sample has been deposited at the University of Arizona Mineral Museum (Catalog 19335) and the RRUFF Project (deposition R120057). The holotype sample is in the collection of W.W. Pinch.

Lavinskyite is a Cu-bearing silicate with amphibole-type double chains. Cu-bearing chain silicates are relatively rare in nature. In addition to lavinskyite, plancheite $Cu_8(Si_4O_{11})_2(OH)_4·H_2O$ (Evans and Mrose 1977), shattuckite $Cu_5(Si_2O_6)_2(OH)_2$ (Evans and Mrose 1966, 1977; Kawahawa 1976) and liebauite $Ca_6Cu_{10}(Si_{18}O_{52})$ (Zöller et al. 1992) also belong to this group. Nonetheless, there have been several reports on synthetic Cu-bearing chain silicates, such as $Na_2Cu_3(Si_4O_{12})$ (Kawamura and Kawahara 1976), $Na_4Cu_2(Si_8O_{20})$ (Kawamura and Kawahara 1977), $CuMg(Si_2O_6)$ (Breuer et al. 1986), $CaBa_3Cu(Si_6O_{17})$

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(Angel et al. 1990), and $Li_2(Mg,Cu)Cu_2(Si_2O_6)_2$ (Horiuchi et al. 1997). Moreover, Kawamura et al. (1976) successfully synthesized plancheite under hydrothermal conditions at 350–500 °C and 1–2 kbars. This paper describes the physical and chemical properties of lavinskyite and its structure determination using single-crystal X-ray diffraction.

SAMPLE DESCRIPTION AND EXPERIMENTAL METHODS

Occurrence, physical and chemical properties, and Raman spectra

Lavinskyite was found on two specimens originating from the central-eastern ore body of the Wessels mine, Kalahari Manganese Fields, Northern Cape Province, Republic of South Africa. It is in a massive assemblage associated with wesselsite $SrCuSi_4O_{10}$, scottyite $BaCu_2Si_2O_7$, pectolite $NaCa_2Si_3O_8(OH)$, richterite $Na(CaNa)Mg_5Si_8O_{22}(OH)_2$, and sugilite $KNa_2Fe^{3+}_2(Li_3Si_{12})O_{30}$ (Figs. 1 and 2). The mineral assemblage probably formed as a result of a hydrothermal event. Conditions during metamorphism were in the range of 270–420 °C at 0.2–1.0 kbar (Kleyenstuber 1984; Gutzmer and Beukes 1996). Detailed reviews of the geology and mineralogy of the Kalahari Manganese Fields have been given by Kleyenstuber (1984), Von Bezing et al. (1991), and Gutzmer and Beukes (1996).

Lavinskyite crystals are tabular [parallel to (010); broken pieces are usually bladed, elongated along [001], up to 0.5 × 0.3 × 0.1 mm. No twinning is observed. The mineral is light blue, transparent with very pale blue streak and vitreous luster. It is brittle and has a Mohs hardness of ~5; cleavage is perfect on {010} and no parting is observed. The measured and calculated densities are 3.61(3) and 3.62 g/cm³, respectively. Optically, lavinskyite is biaxial (+), with $\alpha = 1.675(1)$, $\beta = 1.686(1)$, $\gamma = 1.715(1)$ (white light), $2V$ (meas.) = 64(2)°, $2V$ (calc.) = 64.2°, and the orientation $X = a$, $Y = b$, $Z = c$. The pleochroism is X = dark blue, Y = light blue, and Z = light blue, and the absorption $X > Y = Z$. No dispersion was observed. Lavinskyite is insoluble in water, acetone, or hydrochloric acid.

The chemical composition of lavinskyite was determined using a CAMECA SX-100 electron microprobe (15 kV, 20 nA, <1 μm beam diameter). The standards included chalcopyrite (Cu), NBS_K458 (Ba), diopside (Si, Mg), rhodonite (Mn), orthoclase (K), and albite (Na), yielding an average composition (wt%) (8 points) of SiO_2 42.85(10), CuO 46.13(23), K_2O 4.16(2), MgO 1.53(17), Na_2O 0.27(4), BaO 0.18(6), and MnO 0.08(1), and total = 95.19(26). The content of Li_2O (1.38 wt%) was measured with a LA-ICP-MS mass spectrometer. The H_2O content (3.22 wt%) was added to bring the analytical total close to 100%. The resultant chemical formula, calculated on the basis of 26 O apfu (from the structure determination), is $(K_{0.99}Ba_{0.01})_{\Sigma=1.00}(Li_{1.04}Cu_{0.93}Na_{0.10})_{\Sigma=2.07}(Cu_{5.57}Mg_{0.43}Mn_{0.01})_{\Sigma=6.01}(Si_{4.00}O_{11})_2(OH)_4$, which can be simplified to $K(LiCu^{2+})Cu^{2+}_6(Si_4O_{11})_2(OH)_4$.

The Raman spectrum of lavinskyite was collected from a randomly oriented crystal on a Thermo-Almega microRaman system, using a 532 nm solid-state laser with a thermoelectric cooled CCD detector. The laser is partially polarized with 4 cm⁻¹ resolution and a spot size of 1 μm.

X-ray crystallography

The powder X-ray diffraction data of lavinskyite were collected on a Bruker D8 Advance diffractometer with CuKα radiation. Listed in Table 1 are the experimental d-spacing and relative intensity data for observed strong peaks, along with the corresponding values calculated from the determined structure using the program XPOW (Downs et al. 1993). Single-crystal X-ray diffraction data of lavinskyite were collected on a Bruker X8 APEX2 CCD X-ray diffractometer equipped with graphite-monochromatized MoKα radiation, with frame widths of 0.5° in ω and 30 s counting time per frame. All reflections were indexed on the basis of an orthorhombic unit-cell (Table 2). The intensity data were corrected for

TABLE 1. Powder diffraction data for strong peaks of lavinskyite

Experimental		Theoretical		
I	*d* (Å)	*I*	*d* (Å)	*h k l*
100	10.291	100	10.189	0 2 0
13	9.608	9	9.523	2 0 0
8	9.006	16	8.984	1 2 0
18	6.994	5	6.957	2 2 0
18	4.984	24	4.921	1 4 0
6	4.057	11	4.046	3 0 1
11	3.964	19	3.973	3 4 0
2	3.578	11	3.590	1 4 1
27	3.321	30	3.343	1 6 0
6	2.979	9	2.995	3 6 0
3	1.571	11	1.568	12 2 0

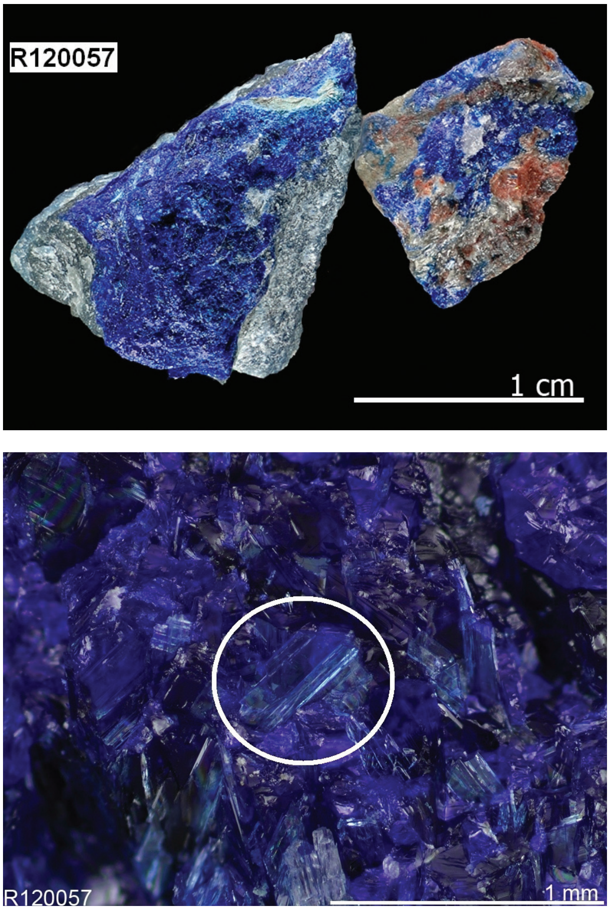

FIGURE 1. (**a**) Rock samples on which lavinskyite crystals are found; (**b**) a microscopic view of lavinskyite, associated with dark blue scottyite.

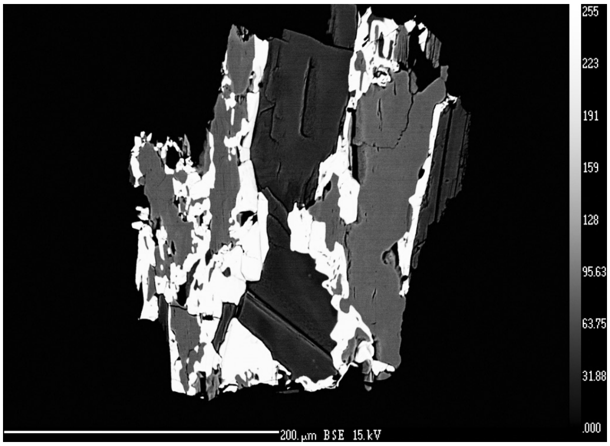

FIGURE 2. A backscattered electron image, showing the assemblage of scottyite (light gray), wesselsite (medium gray), and lavinskyite (dark gray).

X-ray absorption using the Bruker program SADABS. The systematic absences of reflections suggest the unique space group *Pcnb* (no. 60). The crystal structure was solved and refined using SHELX97 (Sheldrick 2008).

During the structure refinements, for simplicity, the small amounts of Na, Ba, and Mn, detected from the electron microprobe analysis, were ignored. A preliminary refinement indicated that the M2 and M3 sites are filled with Cu only, whereas the M1 and M4 sites show the mixed occupations by (Cu+Mg) and (Cu+Li), respectively. The A site is fully occupied by K. Furthermore, the M4 site appears to be split, with the M4a and M4b sites separated by about 0.9 Å. Thereby, the following assignments of atoms into different sites were made in the subsequent refinements: A = K, M1 = (0.775 Cu + 0.225 Mg), M2 = Cu, M3 = Cu, M4a = (0.5 Li + □), and M4b = (0.5Cu + □), giving rise to the structure formula ${}^{A}K^{M4}(LiCu)^{M1}(Cu_{1.57}Mg_{0.43})^{M2M3}Cu_4(Si_4O_{11})_2(OH)_4$. The positions of all atoms were refined with anisotropic displacement parameters, except for H and Li atoms, the former being refined with a fixed U_{iso} parameter (= 0.04) and the latter with U_{iso} varied. Final coordinates and displacement parameters of atoms in lavinskyite are listed in Table 3, and selected bond-distances in Table 4. (A CIF[1] file is on deposit.)

TABLE 2. Summary of crystal data and refinement results for lavinskyite

Ideal chemical formula	$K(LiCu)Cu_6(Si_4O_{11})_2(OH)_4$
Crystal symmetry	Orthorhombic
Space group	*Pcnb* (no. 60)
a (Å)	19.046(2)
b (Å)	20.377(2)
c (Å)	5.2497(6)
V (Å^3)	2037.4(4)
Z	4
ρ_{cal} (g/cm^3)	3.616
λ (Å, Mo*K*α)	0.71073
μ (mm^{-1})	7.403
$2\theta_{max}$ (°)for data collection	65.36
No. of reflections collected	16336
No. of independent reflections	3702
No. of reflections with $I > 2\sigma(I)$	2639
No. of parameters refined	214
R(int)	0.048
Final R_1, wR_2 factors [$I > 2\sigma(I)$]	0.031, 0.057
Final R_1, wR_2 factors (all data)	0.058, 0.064
Goodness-of-fit	0.971

DISCUSSION

Crystal structure

Lavinskyite is isotypic with plancheite, demonstrated to be an amphibole derivative by Evans and Mrose (1977). Table 5 compares some mineralogical data for the two minerals. The key difference between lavinskyite and plancheite lies in the coupled chemical substitution of K^+ and Li^+ in the former for H_2O and Cu^{2+} in the latter, respectively. The crystal structure of lavinskyite is characterized by the undulating, brucite-like layers consisting of M1, M2, and M3 octahedra. These layers are parallel to (010) and are sandwiched by the amphibole-type double silicate chains extending along the **c** axis, forming a sheet structure in terms of the compact silicate-Cu-silicate triple layers (Figs. 3 and 4). Adjacent sheets are linked together by the A and M4 cations. Interestingly, our structure refinement shows that Cu and Li at the M4 site are split, occupying different M4a and M4b sites, respectively. The compact silicate-Cu-silicate triple layer in lavinskyite explains its perfect {010} cleavage and elongation along [001].

Each double silicate chain in lavinskyite is composed of four unique SiO_4 tetrahedra (Si1, Si2, Si3, and Si4), with Si1 and Si2 forming the single silicate A chain and Si3 and Si4 the B chain (Fig. 3). Thus far, such a conformation of double silicate chains has only been observed in monoclinic *P*2/*a* amphibole (joesmithite) (Moore et al. 1993). In comparison, each double silicate chain in most common *C*2/*m*, *P*2$_1$/*m*, and *Pnma* amphiboles comprises only two unique SiO_4 tetrahedra. The kinking angle, defined by the bridging oxygen atoms, of the B chain (∠O9-O10-O9 = 172.5°) is greater than that of the A chain (∠O6-O7-O6 = 168.3°). Moreover, the two SiO_4 tetrahedra in the B chain are both more distorted than those in the A chain, as measured by the tetrahedral angle variance (TAV) and quadratic elongation (TQE) (Robinson et al. 1971) (Table 4).

Among four symmetrically non-equivalent Cu-dominant sites, the octahedrally coordinated M1, M2, and M3 sites in the

TABLE 3. Atomic coordinates and displacement parameters for lavinskyite

Atom	*x*	*y*	*z*	U_{iso}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
A	0.5	0.25	0.9725(2)	0.0239(2)	0.0200(5)	0.0279(6)	0.0238(5)	0	0	–0.0094(5)
M1	0.45964(3)	0.00661(3)	0.25459(9)	0.0085(2)	0.0092(3)	0.0096(3)	0.0065(3)	0.0029(2)	–0.0024(2)	–0.0029(2)
M2	0.37544(2)	0.02733(2)	0.77970(7)	0.0096(1)	0.0094(2)	0.0117(2)	0.0077(2)	0.0030(1)	–0.0018(1)	–0.0022(1)
M3	0.29265(2)	0.05185(2)	0.29637(6)	0.0092(1)	0.0095(2)	0.0122(2)	0.0058(2)	0.0027(1)	–0.0019(1)	–0.0034(1)
M4a	0.25019(3)	0.30433(3)	0.7061(1)	0.0145(2)	0.0116(3)	0.0074(3)	0.0244(4)	0.0003(2)	–0.0074(3)	0.0001(2)
M4b	0.208(2)	0.301(1)	0.814(7)	0.061(7)						
Si1	0.64168(4)	0.10879(4)	0.9294(1)	0.0066(2)	0.008(4)	0.0068(4)	0.0052(3)	0.0001(3)	–0.0007(3)	–0.0009(3)
Si2	0.56233(4)	0.12204(4)	0.4315(1)	0.0066(2)	0.008(4)	0.0068(4)	0.0050(3)	0.0002(3)	0.0000(3)	–0.0004(3)
Si3	0.40602(4)	0.15778(4)	0.4751(1)	0.0065(2)	0.007(3)	0.0075(4)	0.0052(3)	0.0004(3)	0.0003(3)	–0.0011(3)
Si4	0.32834(4)	0.18205(4)	0.9822(1)	0.0070(2)	0.009(4)	0.0075(4)	0.0048(3)	0.0002(3)	–0.0002(3)	–0.0008(3)
O1	0.6279(1)	0.0311(1)	0.9193(4)	0.0088(4)	0.0103(10)	0.0074(10)	0.0087(9)	–0.0001(8)	–0.0010(8)	–0.0016(8)
O2	0.5459(1)	0.0455(1)	0.4319(4)	0.0095(4)	0.0128(11)	0.0080(11)	0.0076(9)	0.0016(8)	0.0003(8)	–0.0020(8)
O3	0.3809(1)	0.0825(1)	0.4653(4)	0.0086(4)	0.0108(10)	0.0078(10)	0.0071(9)	–0.0002(7)	–0.0017(8)	–0.0033(8)
O4	0.2997(1)	0.1082(1)	0.9986(4)	0.0116(4)	0.0145(11)	0.0117(11)	0.0087(9)	0.0003(8)	–0.0022(8)	–0.0022(8)
O5	0.7237(1)	0.1273(1)	0.9552(4)	0.0127(4)	0.0081(10)	0.0149(12)	0.0148(10)	0.0000(8)	–0.0022(8)	–0.0035(8)
O6	0.5984(1)	0.1442(1)	0.1638(4)	0.0111(4)	0.0156(11)	0.0089(11)	0.0086(9)	0.0001(8)	0.0040(8)	0.0006(8)
O7	0.6125(1)	0.1432(1)	0.6677(4)	0.0115(4)	0.0161(12)	0.0104(11)	0.0081(9)	0.0007(8)	–0.0041(8)	–0.0022(8)
O8	0.4913(1)	0.1659(1)	0.4616(4)	0.0122(4)	0.0070(10)	0.0088(11)	0.0206(11)	–0.0007(8)	0.0018(8)	–0.0009(8)
O9	0.3834(1)	0.1913(1)	0.7418(4)	0.0110(4)	0.0147(11)	0.0111(11)	0.0069(9)	–0.0016(8)	0.0044(8)	–0.0027(8)
O10	0.3782(1)	0.1982(1)	0.2306(4)	0.0108(4)	0.0170(11)	0.0085(11)	0.0068(9)	0.0013(8)	–0.0032(8)	–0.0031(9)
O11	0.2709(1)	0.2388(1)	0.9597(4)	0.0161(5)	0.0151(11)	0.0172(13)	0.0160(11)	–0.0019(9)	–0.0028(9)	0.0059(9)
O12	0.4609(1)	0.0603(1)	0.9434(4)	0.0127(5)	0.0141(11)	0.0108(11)	0.0134(10)	0.0025(9)	–0.0033(9)	–0.0049(9)
O13	0.2851(1)	0.0020(1)	0.6192(4)	0.0082(4)	0.0084(10)	0.0096(11)	0.0069(9)	0.0014(8)	–0.0002(7)	–0.0011(8)
H1	0.274(3)	–0.032(3)	0.593(9)	0.04						
H2	0.469(3)	0.096(2)	0.916(9)	0.04						

Note: The site occupancies are A = K, M1= (0.775Cu + 0.225Mg), M2 = Cu, M3 = Cu, M4a = 0.5Cu, M4b = 0.5Li.

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[1] Deposit item AM-14-205, CIF. Deposit items are stored on the MSA web site and available via the *American Mineralogist* Table of Contents. Find the article in the table of contents at GSW (ammin.geoscienceworld.org) or MSA (www.minsocam.org), and then click on the deposit link.

TABLE 4. Selected bond distances in lavinskyite and plancheite

	Lavinskyite Distance (Å)	Plancheite Distance (Å)
Si1-O1	1.606(2)	1.608
-O5	1.613(2)	1.629
-O7	1.640(2)	1.646
-O6	1.648(2)	1.637
Avg.	1.630	1.630
TAV[a]	7.93	
TQE[a]	1.002	
Si2-O2	1.592(2)	1.635
-O7	1.624(2)	1.704
-O6	1.628(2)	1.530
-O8	1.629(2)	1.612
Avg.	1.630	1.620
TAV		7.98
TQE		1.002
Si3-O3	1.607(2)	1.617
-O10	1.615(2)	1.626
-O9	1.617(2)	1.580
-O8	1.635(2)	1.636
Avg.	1.618	1.615
TAV		15.80
TQE		1.004
Si4-O11	1.596(2)	1.649
-O4	1.603(2)	1.637
-O10	1.647(2)	1.659
-O9	1.652(2)	1.585
Avg.	1.624	1.633
TAV		22.77
TQE		1.005
M1-O2	1.961(2)	1.690
-OH12	1.966(2)	1.844
-O2	2.047(2)	2.158
-O1	2.050(2)	2.155
-OH12	2.287(2)	2.467
-O3	2.422(2)	2.469
Avg.	2.122	2.130
M2-OH12	1.960(2)	2.029
-O1	1.979(2)	1.867
-OH13	1.985(2)	2.079
-O3	2.000(2)	1.869
-O2	2.383(2)	2.687
-O4	2.473(2)	2.279
Avg.	2.130	2.135
M3-O4	1.944(2)	2.220
-OH13	1.982(2)	1.736
-O3	2.000(2)	2.063
-OH13	2.023(2)	2.215
-O4	2.353(2)	2.242
-O1	2.535(2)	2.641
Avg.	2.140	2.186
M4a-O11	1.902(2)	1.945
-O11	1.927(2)	1.798
-O5	1.975(2)	1.839
-O5	1.983(2)	2.022
Avg.	1.947	1.901
M4-O11	1.907(2)	
-O5	2.091(2)	
-O11	2.286(2)	
-O5	2.399(2)	
-O6	2.494(2)	
-O10	2.699(2)	
Avg.	2.313	
A-O9 x2	2.797(2)	
-O10 x2	2.886(2)	
-O6 x2	3.027(2)	
-O8 x2	3.091(2)	
-O8 x2	3.197(2)	
Avg.	2.998	

Note: According to Evans and Mrose (1977), "The bond lengths in plancheite are poorly determined ($\sigma > 0.1$ Å) and are not amenable to detailed interpretation."
[a] TAV = tetrahedral angle variance; TQE = tetrahedral quadratic elongation (Robinson et al. 1971).

TABLE 5. Mineralogical data for lavinskyite and plancheite

	Lavinskyite	Plancheite
Chemical formula	$K(LiCu)Cu_6(Si_4O_{11})_2(OH)_4$	$Cu_8(Si_4O_{11})_2(OH)_4{\cdot}H_2O$
a (Å)	19.046(2)	19.043(3)
b (Å)	20.377(2)	20.129(5)
c (Å)	5.2497(6)	5.269(1)
V (Å^3)	2037.4(4)	2019.5(5)
Space group	*Pcnb*(no. 60)	*Pcnb*(no. 60)
Z	4	4
ρ_{cal} (g/cm^3)	3.62	3.82
Strong powder lines	10.188(100)	10.064(100)
	3.343(32)	4.865(53)
	2.693(29)	2.694(47)
	2.522(27)	6.917(43)
	4.921(25)	3.943(31)
	2.316(22)	2.520(31)
	3.973(19)	3.304(27)
n_α	1.675	1.697
n_β	1.686	1.718
n_γ	1.715	1.741
2*V* (°)	64(+)	88.5(+)
Reference	(1)	(2)

Note: (1) This work; (2) Evans and Mrose (1977).

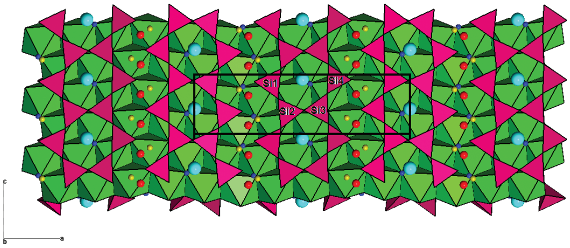

FIGURE 3. Crystal structure of lavinskyite.

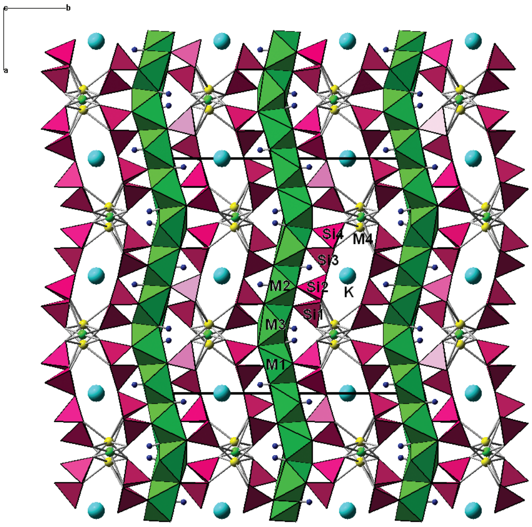

FIGURE 4. Crystal structure of lavinskyite. The aquamarine, yellow, green, and blue spheres represent K, Cu(M4), Li(M4), and H atoms, respectively.

brucite-like layers are all distorted, with two M-O bonds noticeably longer than the other four bonds (Table 4). The M4a site, however, is in a nearly square-planar coordination. In contrast, the M4b site, partially occupied by Li, is in a markedly distorted octahedral coordination, with the Li-O bond distances ranging from 1.907(2) to 2.699(2) Å. The A site, occupied by K^+, is situated in a large cavity between the back-to-back double tetrahedral chains (Fig. 3), resembling that in amphiboles containing the A-type cations. The A site in plancheite is occupied by H_2O (Evans and Mrose 1977).

There are two OH groups in the lavinskyite structure, O12-H1 and O13-H2. The H1 and H2 atoms are 0.76 and 0.74 Å away from OH12 and OH13, respectively. The bonding environment of the O12-H1 group is quite analogous to that of the OH groups in amphiboles, with two O12-H1 bonds pointing nearly to the A site from opposite directions (∠H1-A-H1 = 169.4°) (Fig. 4). The nearest O atom (O8) to O12 is 3.37 Å away, indicating that O12-H forms little or no hydrogen bonding with other O atoms. In contrast, the O13-H2 group forms a relatively strong hydrogen bond with O5 (O13-O5 = 2.91 Å, ∠O13-H2···O5 = 170.7°). However, this hydrogen bond is only found on one side of the M4 site, not on the opposite (Fig. 4). Such an unbalanced distribution of the hydrogen bond around the M4 site may account in part for the corrugation of the brucite-like octahedral layers. The hydrogen bonds are reported to be responsible for the corrugation of the $CoO_4(H_2O)_2$ octahedral layers in the synthetic compound $Co_{2.39}Cu_{0.61}(PO_4)_2 \cdot H_2O$ (Assani et al. 2010), as well as the Ca-polyhedral layers in vladimirite $Ca_4(AsO_3OH)(AsO_4)_2 \cdot 4H_2O$ (Yang et al. 2011).

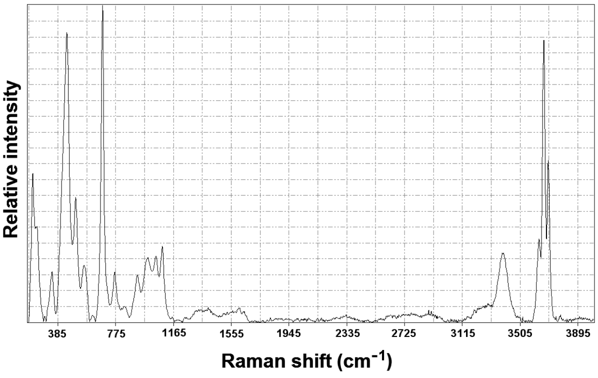

FIGURE 5. Raman spectrum of lavinskyite.

Raman spectra

The Raman spectrum of lavinskyite is displayed in Figure 5. Based on previous Raman spectroscopic studies on plancheite (Frost and Xi 2012) and various amphiboles (Rinaudo et al. 2004; Makreshi et al. 2007; Apopei and Buzgar 2010, and references therein), we made a tentative assignment of major Raman bands for lavinskyite (Table 6). As expected, the Raman spectrum of lavinskyite shows some features similar to those for both amphiboles and plancheite, especially in the O-H stretching region. Specifically, whereas all O-H stretching bands (at least five obvious ones) in plancheite are between 2800 and 3500 cm^{-1} (Frost and Xi 2012), those (1 to 4 obvious ones, depending on chemical compositions) in hydroxyl amphiboles (Rinaudo et al. 2004; Makreshi et al. 2007) generally fall between 3600 and 3700 cm^{-1}. For lavinskyite, we observe three apparent, sharp O-H stretching bands between 3600 and 3700 cm^{-1}, as those in amphiboles, and a relatively weak and broad band (with a shoulder) at 3390 cm^{-1}. Consequently, we attribute the three O-H stretching bands between 3600 and 3700 cm^{-1} to the vibrations of the amphibole-like O12-H1 group and the band at 3390 cm^{-1} to the OH13-H2 vibration. According to the correlation between O-H stretching frequencies and O-H ···O hydrogen bond lengths in minerals (Libowitzky 1999), the O-H stretching band at 3390 cm^{-1} would correspond to an O-H···O distance of ~2.90 Å, in accordance with the value from our structural determination. For plancheite, the presence of the multiple O-H stretching bands between 2800 and 3500 cm^{-1} and the lack of the amphibole-like bands above 3600 cm^{-1} are apparently due to the existence of H_2O in the A site and may suggest that all H atoms are likely engaged in hydrogen bonding.

The discovery of lavinskyite adds a new member to the amphibole derivative group, and it evidently exhibits more amphibole-like structural features than plancheite, due to the presence of K in its large cavity between the two back-to-back double silicate chains. Furthermore, the crystal-chemical relationship between lavinskyite and plancheite begs the question whether the amphibole structure can incorporate H_2O in its A site as well, with the composition $^A(H_2O)M_7Si_8O_{22}(OH)_2$, where M represents divalent cations found in amphiboles. From the crystal structure point of view, there seems no obstacle for H_2O to enter the A site in the amphibole structure, given its strong resemblance to that in plancheite. Based on the Raman spectroscopic measurement by Frost and Xi (2012), it appears that the occupation of H_2O in the A site in plancheite result in the formation of multiple hydrogen bonds, as indicated by several obvious Raman bands between 2800 and 3500 cm^{-1}. The three shortest distances between O_{water}

TABLE 6. Tentative assignments of major Raman bands for lavinskyite

Bands (cm^{-1})	Intensity	Assignment
3694, 3662, 3630 3390	Weak to strong, sharp	O-H stretching vibrations
1090, 1043, 991 919, 891	Relatively weak and broad	Si-O symmetric and anti-symmetric stretching modes within SiO_4 tetrahedra
685	Strong, sharp	Si-O-Si bending
580, 562, 503, 445 424, 401	Relatively strong	O-Si-O symmetric and anti-symmetric bending modes within SiO_4 tetrahedra
<400	Strong to weak	SiO_4 rotational modes, lattice vibrational modes, and Cu-O interactions

in the A site and nearest O$_{\text{bridging}}$ are 2.62, 2.99, and 3.04 Å in plancheite (Evans and Mrose 1977). Accordingly, similar Raman spectral features in the OH stretching vibration region can be expected for H$_2$O-bearing amphiboles if they could be found in nature or synthesized eventually.

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