

Kyawthuite, $\text{Bi}^{3+}\text{Sb}^{5+}\text{O}_4$, a new gem mineral from Mogok, Burma (Myanmar)

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ABSTRACT

Kyawthuite, $\text{Bi}^{3+}\text{Sb}^{5+}\text{O}_4$, is a new gem mineral found as a waterworn crystal in alluvium at Chaung-gyi-ah-le-ywa in the Chaung-gyi valley, near Mogok, Burma (Myanmar). Its description is based upon a single sample, which was faceted into a 1.61-carat gem. The composition suggests that the mineral formed in a pegmatite. Kyawthuite is monoclinic, space group $I2/c$, with unit cell dimensions $a = 5.4624(4)$, $b = 4.88519(17)$, $c = 11.8520(8)$ Å, $\beta = 101.195(7)^\circ$, $V = 310.25(3)$ Å³ and $Z = 4$. The colour is reddish orange and the streak is white. It is transparent with adamantine lustre. The Mohs hardness is 5½. Kyawthuite is brittle with a conchoidal fracture and three cleavages: {001} perfect, {110} and {110} good. The measured density is 8.256(5) g cm⁻³ and the calculated density is 8.127 g cm⁻³. The mineral is optically biaxial with $2V = 90(2)^\circ$. The predicted indices of refraction are $\alpha = 2.194$, $\beta = 2.268$, $\gamma = 2.350$. Pleochroism is imperceptible and the optical orientation is $X = \mathbf{b}$; $Y \approx c$; $Z \approx \mathbf{a}$. Electron microprobe analyses, provided the empirical formula $(\text{Bi}_{0.82}^{3+}, \text{Sb}_{0.18}^{3+})_{\Sigma 1.00}(\text{Sb}_{0.99}^{5+}, \text{Ta}_{0.01}^{5+})_{\Sigma 1.00}\text{O}_4$. The Raman spectrum is similar to that of synthetic $\text{Bi}^{3+}\text{Sb}^{5+}\text{O}_4$. The infrared spectrum shows a trace amount of OH/H₂O. The eight strongest powder X-ray diffraction lines are [d_{obs} in Å(I)(hkl)]: 3.266(100)($\bar{1}12$), 2.900(66)(112), 2.678(24)(200), 2.437(22)(020, $\bar{1}14$), 1.8663(21)(024), 1.8026(43)($\bar{1}16, 220, 204$), 1.6264(23)($\bar{2}24, 116$) and 1.5288(28)(312, $\bar{1}32$). In the crystal structure of kyawthuite ($R_1 = 0.0269$ for 593 reflections with $F_o > 4\sigma F$), Sb^{5+}O_6 octahedra share corners to form chequerboard-like sheets parallel to {001}. Atoms of Bi^{3+} , located above and below the open squares in the sheets, form bonds to the O atoms in the sheets, thereby linking adjacent sheets into a framework. The Bi^{3+} atom is in lopsided 8 coordination, typical of a cation with stereoactive lone electron pairs. Kyawthuite is isostructural with synthetic $\beta\text{-Sb}_2\text{O}_4$ and clinocervantite (natural $\beta\text{-Sb}_2\text{O}_4$).

KEYWORDS: kyawthuite, new mineral, gemstone, antimonate, crystal structure, Mogok, Burma (Myanmar).

Introduction

In January of 2010, while visiting the alluvial gem area at Chaung-gyi (Big Stream) just north of Mogok, Burma, Dr. Kyaw Thu purchased two waterworn crystals, one yellow and one orange, from a miner called ‘Kha-ne-say’. Kyaw Thu suspected that the stones were scheelite because

of their high density and lustre. After he faceted the two stones, he confirmed that the yellow one was scheelite; however, the orange gem had a different lustre and much higher density. Being unable to match its properties to those of any known gem, he sent the stone to the Gemological Institute of America (GIA) Laboratory in Bangkok, Thailand. Lab personnel there were also unable to identify the gem, and arranged for X-ray diffraction of the gem by Sunan Rangseekansong and Manop Tirattanasompt at the GIA Laboratory in Bangkok; their examination indicated that the orange gem

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matched synthetic BiSbO_4 . Subsequently, Dr. Kyaw Thu provided the gem to the authors for its detailed description as a new mineral species.

Kyawthuite (/cha: 'tu: ait/) is named for Dr. Kyaw Thu (b. 1973), a Burmese mineralogist-petrologist-gemologist with a PhD from Yangon University (2007). He was on the staff of the Geology Department of Yangon University from 1998 to 2005 and has been the owner/operator of the Macle Gem Trade Laboratory since 2003. His PhD dissertation 'The igneous rocks of the Mogok Stone Tract: Their distributions, petrography, petrochemistry, sequence, geochronology and economic geology' is a seminal work on the subject. Kyaw Thu has provided guidance for a number of scientific expeditions to the Mogok area and elsewhere in Myanmar, including those by two of the authors (ARK and GRR). Kyaw Thu has agreed to the naming of the mineral in his honour.

The new mineral and name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA2015-078). The holotype specimen, a 1.61-carat faceted gem, is deposited in the Natural History Museum of Los Angeles County under catalogue number 65602.

Occurrence

Kyawthuite was found as a waterworn crystal in alluvium at Chaung-gyi-ah-le-ywa (Middle Village at Chaung-gyi; $22^{\circ}57'50''\text{N}$, $96^{\circ}30'35''\text{E}$) in the Chaung-gyi (Big Stream) valley, ~5 km north-northeast of the town of Mogok, Pyin-Oo-Lwin district, Mandalay division, Burma (Myanmar).



FIG. 1. Faceted kyawthuite gem; 1.61 carats; 5.80 mm \times 4.58 mm \times 3.00 mm.

The waterworn crystal was faceted into a 1.61-carat gem (Fig. 1). The foregoing description is based upon the study of that gemstone and small fragments removed from its culet.

The rocks of the area are igneous (leucogranite, syenite) and metamorphic (marble, calc-silicate, gneiss). The gemstones are found both in the alluvium on the valley floor and in adjacent primary deposits (marbles, skarns and pegmatites). The minerals reported from the area include almandine, beryl, cordierite, corundum, feldspar, kornorupine, magnesioataffeite-2N'2S, pyrite, quartz, schorl, spinel, topaz and tourmaline.

BiSbO_4 is known as a synthetic phase and has seen use in ceramics and catalysts (Wang *et al.*, 2013; You *et al.*, 2011). Ito *et al.* (1975) grew single crystals of BiSbO_4 up to 1 mm wide and 14 mm long by vapour growth at $900\text{--}1200^{\circ}$ and noted that the Bi^{3+} sites in the crystal could be partially substituted by Sb^{3+} in the presence of excess Sb in the synthesis mixtures. Enjalbert *et al.* (1995) synthesized 125 μm crystals of BiSbO_4 at 800°C in a $\text{Bi}_2\text{O}_3\text{--Sb}_2\text{O}_3\text{--V}_2\text{O}_5$ flux system. Popolitov (1996) subsequently grew BiSbO_4 crystals up to 2 mm \times 4 mm \times 18 mm with a hydrothermal method in the $450\text{--}520^{\circ}\text{C}$ range. These temperatures of formation suggest that the natural phase formed from a high-temperature melt or fluid. Although kyawthuite is only known from alluvium, the presence of Bi, Sb and small amounts of Ta, as well as trace amounts of Ti, Nb, W and U (see below), suggest that it probably crystallized in a pegmatite.

Certainly, there are no likely sources for synthetic BiSbO_4 in the relatively remote Mogok area, particularly in large crystals of gem quality. The aforementioned chemical impurities are consistent

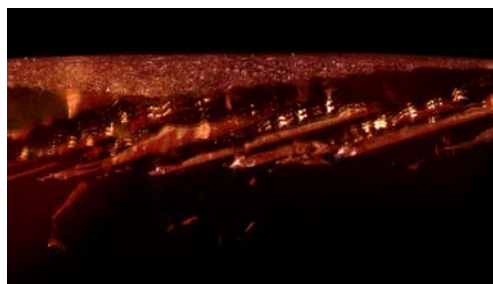


FIG. 2. A series of *en echelon* hollow tube inclusions near the girdle of the kyawthuite gem. These can also be seen along the top of the gem in Fig. 1. The field of view is 2 mm across.

with a natural rather than synthetic origin. In addition, a series of *en echelon* hollow tubes near the girdle of the faceted gem (Fig. 2) are further evidence that the material described here is of natural origin.

Physical and optical properties

The original crystal of kyawthuite was a waterworn, roughly rectangular prism weighing 3.66 carats. There were no images taken or other measurements made of the original crystal. The gem faceted from the crystal is a rectangular cushion weighing 1.61 carats and measuring 5.80 mm × 4.58 mm × 3.00 mm (Fig. 1). No fragments were saved from the cutting process; however, several small fragments were successfully removed from the culet of the gem without compromising its general appearance. These were used for the ensuing description, whereas the entire stone was used for the density determination and infrared spectroscopy.

No twinning was observed optically under crossed polars or based upon single-crystal X-ray diffraction. The gem has a saturated orange colour with a red overtone. The streak is white. Kyawthuite is transparent and has adamantine lustre. It does not fluoresce under longwave or shortwave ultraviolet light. The Mohs hardness is 5. The mineral is brittle with conchoidal fracture. Cleavage is perfect on {001} and good on {110 and $\bar{1}10$ }. The density measured by the buoyancy method in water is 8.256(5) g cm⁻³ and the density calculated using the empirical formula and single-crystal cell is

8.127 g cm⁻³. Kyawthuite is unreactive in room temperature concentrated HCl, H₂SO₄ and HNO₃.

The Gladstone–Dale relationship predicts an average index of refraction of 2.271 (Mandarino, 2007). The unavailability of index liquids with $n > 2$ precluded the measurement of the mineral's indexes of refraction. Examination of a crystal fragment mounted on a spindle stage provided a measured 2V of 90(2)° obtained from extinction data using *EXCALIBUR* (Gunter *et al.*, 2004). The mineral is clearly biaxial, but the optical sign is ambiguous. The retardation ($\gamma - \alpha$) measured with a Berek compensator is 0.156. Based upon this, the measured 2V and the average index of refraction calculated using the Gladstone–Dale relationship, the following hypothetical indices of refraction are proposed: $\alpha = 2.194$, $\beta = 2.268$, $\gamma = 2.350$. The dispersion could not be observed, the pleochroism is imperceptible and the optical orientation is $X = \mathbf{b}$; $Y \approx \mathbf{c}$; $Z \approx \mathbf{a}$.

Chemical composition

Chemical analyses (nine) of kyawthuite were carried out using a JEOL 8200 electron microprobe (wavelength-dispersive mode, 15 kV, 25 nA and focused beam) at the Division of Geological and Planetary Sciences, California Institute of Technology. The standards used were: synthetic AgBiS₂ (for Bi), synthetic Sb₂S₃ (for Sb) and Ta metal (for Ta). The analytical results [mean (range) (s.d.)] are Bi₂O₃ 50.64 (50.34–50.96) (0.22), Sb₂O₅ 50.10 (49.85–50.57) (0.23) [apportioned as Sb₂O₃

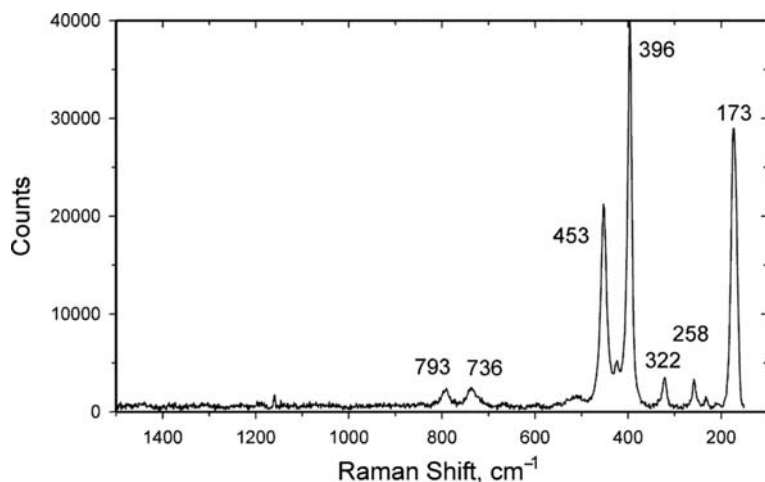


FIG. 3. Raman spectrum of kyawthuite.

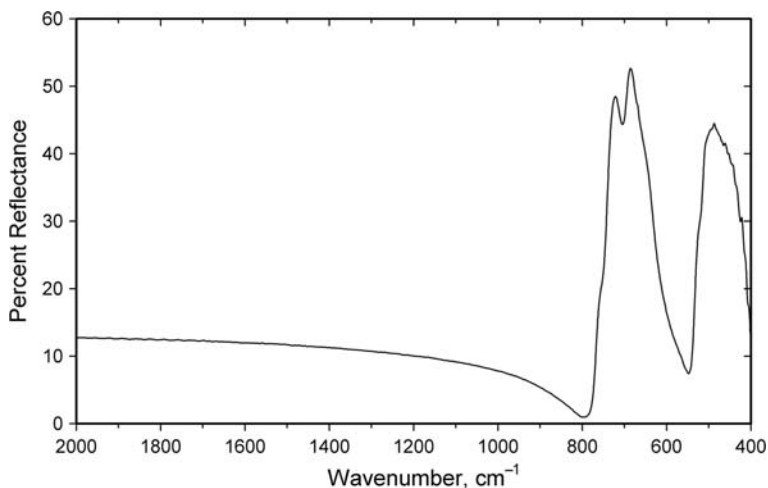


FIG. 4. Infrared specular reflection spectrum of kyawthuite taken from the culet of the gemstone compared to an aluminium standard.

6.90 and Sb₂O₅ 42.44, based on the structure], Ta₂O₅ 0.52 (0.33–0.67) (0.11), total 100.50 wt.%. The empirical formula (based on 4 O atoms per formula unit) is (Bi_{0.82}Sb_{0.18})_{Σ1.00}(Sb_{0.99}Ta_{0.01})_{Σ1.00}O₄. The simplified end-member formula is Bi³⁺Sb⁵⁺O₄, which requires Bi₂O₃ 59.02, Sb₂O₅ 40.98, total 100 wt.%. Note that the earlier chemical analyses using laser ablation inductively coupled plasma mass spectrometry performed at Chulalongkorn University also indicated TiO₂ 0.09, Nb₂O₅ 0.05, WO₃ 0.09 and UO₂ 0.03 wt.%; however, Ti, Nb, W and U were all

found to be below detection limits in our electron microprobe analyses.

Raman spectroscopy

Raman spectroscopic microanalyses were carried out using a Renishaw M1000 micro-Raman spectrometer system. Light from a 514.5 nm solid-state laser was focused onto the sample with a 100× objective lens. Approximately 6 mW of laser power was available at the sample in a spot

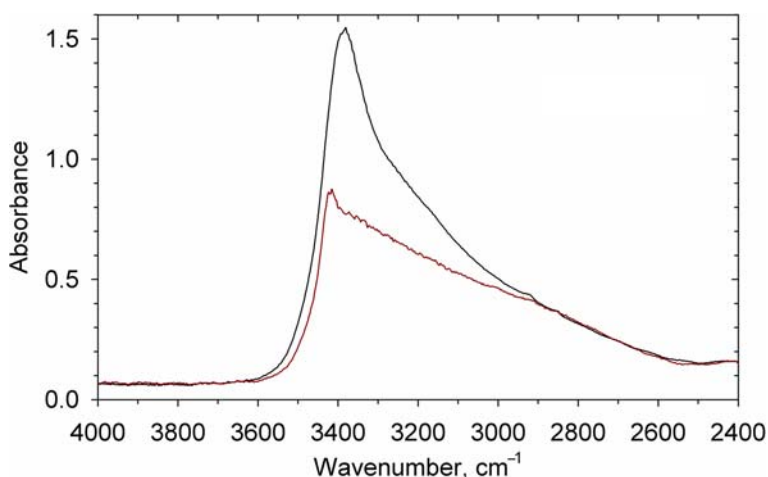


FIG. 5. Single-crystal polarized infrared spectrum of kyawthuite taken in the two extinction directions through the culet of the 3.02 mm thick gemstone in the OH region.

size of $\sim 1 \mu\text{m}$ diameter. Peak positions were calibrated against a silicon (520.5 cm^{-1}) standard. All spectra were obtained with a dual-wedge polarization scrambler inserted directly above the objective lens to minimize the effects of polarization. Prominent Raman features were observed at shifts of 793, 736, 453, 396, 322, 258 and 173 cm^{-1} (Fig. 3).

There is a report of the Raman spectrum of synthetic end-member BiSbO_4 by Loubbidi *et al.* (2014). Their spectrum is similar, with features at 790, 740, 450, 425, 395, 325, 250, 155 and 140 cm^{-1} , but the bands have some relative intensity differences and are displaced from those in the kyawthuite spectrum. The differences in band positions are consistent with the partial substitution of antimony into the bismuth site that is observed in the structure of kyawthuite.

Infrared spectroscopy

A specular reflectance Fourier transform infrared spectroscopy (FTIR) spectrum (Fig. 4) was obtained from the piece of the stone in the electron microprobe mount using a Thermo-Nicolet iS50 FTIR and a Nicolet Continuum FTIR microscope in reflectance mode. The sample's reflectivity was compared to a front-surface aluminium mirror standard. The spectrum displayed distinct maxima at 685 and 722 cm^{-1} , a broader band of reflectance in the $430\text{--}510 \text{ cm}^{-1}$ region, but no features in the OH region. Additionally, shoulders appear at approximately 760 , 641 and 527 cm^{-1} .

To address the possibility that there was a hydroxide or water component in the mineral, a transmission spectrum was obtained through the culet to the table of the stone with a Nicolet Continuum FTIR microscope. The spectrum was obtained with linearly polarized light in the two extinction directions, neither of which was the principal direction of the indicatrix. The spectrum (Fig. 5) shows a prominent OH feature at $\sim 3419 \text{ cm}^{-1}$ in one polarization and a less prominent maximum at 3386 cm^{-1} in the other polarization superimposed on a broader feature that is reminiscent of the water spectrum. A weak feature is present at 4385 cm^{-1} .

To estimate the OH or water content, a spectrum in the third, orthogonal polarization direction is needed, but was not possible to obtain. The third direction is estimated to be the average intensity of the two polarizations obtained. From these, a total integrated absorbance of 4524 per cm is obtained.

TABLE 1. Powder X-ray diffraction data for kyawthuite.

Kyawthuite					Syn. BiSbO_4^*	
I_{obs}	d_{obs}	d_{calc}	I_{calc}	hkl	I_{obs}	d_{obs}
		5.8132	5	0 0 2	8	5.8053
		4.5038	2	0 1 1		
100	3.266	3.6101	3	1 1 0	4	3.6101
		3.2642	100	$\bar{1}$ 1 2	100	3.2653
		3.0361	1	0 1 3		
		2.9066	32	0 0 4		
66	2.900	2.9015	69	1 1 2	90	2.9035
24	2.678	2.6792	25	2 0 0	24	2.6829
		2.6355	1	2 0 2		
22	2.437	2.4426	17	0 2 0	14	2.4429
		2.4242	4	$\bar{1}$ 1 4	4	2.4220
		2.2714	3	2 0 2	3	2.2746
5	2.249	2.2519	2	0 2 2	2	2.2517
		2.2301	1	2 1 1		
		2.2162	1	$\bar{1}$ 2 1		
16	2.188	2.1936	15	2 0 4	9	2.1924
		2.1801	1	2 1 3		
		2.1319	1	1 1 4		
		2.0996	1	0 1 5		
		1.9987	1	$\bar{1}$ 2 3		
21	1.8663	1.8700	23	0 2 4	20	1.8679
		1.8088	20	$\bar{1}$ 1 6		
43	1.8026	1.8050	23	2 2 0	29	1.8058
		1.8032	11	2 0 4		
		1.7915	1	2 2 2		
20	1.6927	1.6963	19	3 1 2	10	1.6979
		1.6775	1	3 1 0		
23	1.6264	1.6321	15	2 2 4	9	1.6309
		1.6213	16	1 1 6	11	1.6196
		1.5580	1	1 3 0		
28	1.5288	1.5388	11	3 1 2	6	1.5411
		1.5266	12	$\bar{1}$ 3 2	7	1.5265
9	1.4807	1.4841	11	1 3 2	6	1.4844
		1.4533	4	0 0 8		
8	1.4492	1.4507	10	2 2 4	7	1.4508
		1.4164	1	2 2 6		
11	1.3966	1.4010	8	2 1 6	3	1.3993
		1.3961	6	2 0 8	4	1.3927

*Kennedy (1994); only lines with intensities > 1 are listed.

However, no calibration exists for kyawthuite or a similar material for determining the hydrogen content from the IR spectrum. Using the calibrations for another high atomic weight mineral, cassiterite, and the calibration for feldspar (Rossman, 2006), hydrogen concentrations, expressed as H_2O , of 176 ppm and 294 ppm, respectively, are calculated. In either case, these

TABLE 2. Data collection and structure refinement details for kyawthuite.

Diffractometer	Rigaku R-Axis Rapid II
X-ray radiation / power	MoK α ($\lambda = 0.71075$ Å)/50 kV, 40 mA
Temperature	293(2) K
Structural formula	(B _{0.80} ³⁺ Sb _{0.20} ³⁺) _{Σ1.00} Sb _{1.00} ⁵⁺ O ₄
Space group	<i>I</i> 2/ <i>c</i>
Unit-cell dimensions	$a = 5.4624(4)$ Å $b = 4.88519(17)$ Å $c = 11.8520(8)$ Å $\beta = 101.195(7)^\circ$
<i>V</i>	310.25(3) Å ³
<i>Z</i>	4
Density (for above formula)	8.082 g cm ⁻³
Absorption coefficient	55.706 mm ⁻¹
<i>F</i> (000)	638.7
Crystal size (μm)	30 × 30 × 30
θ range	3.51 to 34.87°
Index ranges	$-8 \leq h \leq 7$, $-7 \leq k \leq 7$, $-18 \leq l \leq 19$
Refls collected / unique	3471 / 679; $R_{\text{int}} = 0.045$
Reflections with $F > 4\sigma(F)$	593
Completeness to $\theta = 34.87^\circ$	99.9%
Refinement method	Full-matrix least-squares on F^2
Parameters / restraints	32 / 0
Goof	1.083
Final <i>R</i> indices [$F_o > 4\sigma(F)$]	$R_1 = 0.0269$, $wR_2 = 0.0536$
<i>R</i> indices (all data)	$R_1 = 0.0341$, $wR_2 = 0.0577$
Extinction coefficient	0.0085(4)
Largest diff. peak / hole	+2.96 / -2.25 e/Å ³

* $R_{\text{int}} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma[F_o^2]$. Goof = $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$.
 $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$;
 $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where a is 0.0200, b is 0.8002 and P is $[2F_c^2 + \text{Max}(F_o^2, 0)]/3$.

TABLE 3. Fractional coordinates, occupancies and atom displacement parameters (Å²) for kyawthuite.

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq}		
Bi*	0	0.51246(5)	0.25	0.00894(13)		
Sb	0	0	0	0.00392(19)		
O1	0.1158(5)	-0.1576(6)	0.1541(2)	0.0096(7)		
O2	0.2383(6)	0.2965(5)	0.0610(2)	0.0095(7)		
	<i>U</i> ¹¹	<i>U</i> ²²	<i>U</i> ³³	<i>U</i> ²³	<i>U</i> ¹³	<i>U</i> ¹²
Bi	0.0098(2)	0.00876(17)	0.00801(16)	0	0.00101(11)	0
Sb	0.0041(3)	0.0044(3)	0.0030(2)	0.00001(10)	-0.00001(16)	0.00019(10)
O1	0.0107(18)	0.0121(14)	0.0056(14)	0.0028(10)	0.0006(12)	-0.0011(11)
O2	0.0092(15)	0.0086(13)	0.0108(14)	-0.0019(10)	0.0026(11)	-0.0047(11)

*Refined occupancy of the Bi site is Bi/Sb: 0.802/0.198(6).

TABLE 4. Selected bond lengths (Å) in kyawthuite.

Bi–O1(×2)	2.137(3)	Sb–O1(×2)	1.970(3)
Bi–O1(×2)	2.296(3)	Sb–O2(×2)	1.988(3)
Bi–O2(×2)	2.845(3)	Sb–O2(×2)	1.989(3)
Bi–O2(×2)	2.993(3)	<Sb–O>	1.982
<Bi–O>	2.568		

amounts of hydrogen do not represent stoichiometrically significant amounts, in agreement with the X-ray structure determination.

X-ray crystallography and structure determination

Both powder and single-crystal X-ray studies were carried out using a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer, with monochromatic MoK α radiation. For the powder-diffraction study, a Gandolfi-like motion on the ϕ and ω axes was used to randomize the sample. Observed d -values and intensities were derived by profile fitting using *JADE 2010* software (Materials Data, Inc.). The powder data (in Å for MoK α) presented in Table 1 show good agreement with the pattern calculated from the structure determination and with those for synthetic BiSbO $_4$. The unit-cell parameters refined from the powder data using *JADE 2010* with whole-pattern fitting are: $a = 5.430(2)$, $b = 4.854(2)$, $c = 11.762(2)$ Å, $\beta = 101.271(7)^\circ$ and $V = 304.03(18)$ Å 3 .

The Rigaku *CrystalClear* package was used for processing of structure data, including the

TABLE 5. Bond valence sums for kyawthuite. Values are expressed in valence units.

	O1	O2	Σ
Bi	0.52 × 2→ 0.71 × 2→	0.12 × 2→ 0.17 × 2→	3.04
Sb	0.86 × 2→	0.82 × 2→ 0.82 × 2→	5.00
Σ	2.09	1.93	

Bi $^{3+}$ –O and Sb $^{3+}$ –O bond valence parameters are from Krivovichev (2012) and Sb $^{3+}$ –O are from Mills *et al.* (2009).

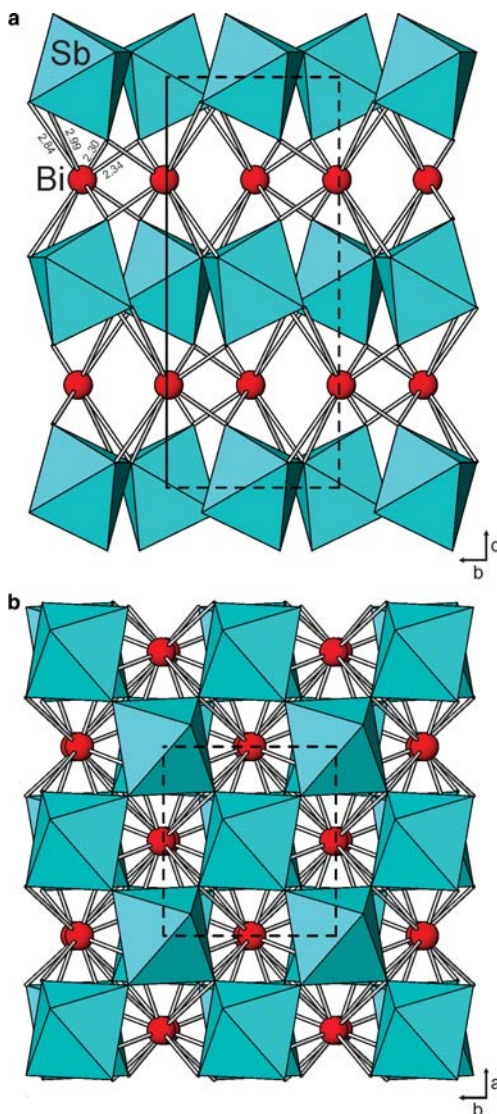


FIG. 6. Crystal structure of kyawthuite: (a) viewed along [100] (with Bi–O distances shown) and (b) viewed along [011].

application of an empirical multi-scan absorption correction using *ABSCOR* (Higashi, 2001). *SHELXL-97* software (Sheldrick, 2008) was used for the refinement of the structure. The starting atom coordinates for the structure refinement were taken from the structure determination of synthetic BiSbO $_4$ by Enjalbert *et al.* (1995). Details of data collection and structure refinement are provided in Table 2. Fractional coordinates and atom

displacement parameters are provided in Table 3, selected interatomic distances in Table 4 and bond valences in Table 5.

Description of the structure

In the structure of kyawthuite (Fig. 6), Sb^{5+}O_6 octahedra share corners to form chequerboard-like sheets parallel to $\{001\}$. Atoms of Bi^{3+} are located above and below the open squares in the sheets and form bonds to the O atoms in the sheets, thereby linking adjacent sheets into a framework. The Bi^{3+} atom is 8 coordinated with four short bonds (two at 2.137 and two at 2.296 Å) and four long bonds (two at 2.845 and two at 2.993 Å) in a lopsided configuration typical of cations with stereoactive lone electron pairs. Kyawthuite is isostructural with synthetic $\beta\text{-Sb}_2\text{O}_4$ and clinocervantite (natural $\beta\text{-Sb}_2\text{O}_4$).

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