

A single-crystal neutron and X-ray diffraction study of a Li,Be-bearing brittle mica

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[Received 28 November 2013; Accepted 15 December 2013; Associate Editor: S. Krivovichev]

ABSTRACT

The crystal chemistry of a meso-octahedral Li,Be-bearing mica from the Harding pegmatite (Dixon, Taos County, New Mexico, USA) has been investigated by constant-wavelength single-crystal neutron diffraction at 20 K, single-crystal X-ray diffraction at 100 K and inductively coupled plasma-atomic emission spectrometry (ICP-AES). The chemical composition based on ICP-AES analysis leads to the following chemical formula (calculated on the basis of 12 oxygen atoms): $^{Ca}(\text{Na}_{0.26}\text{K}_{0.04}\text{Ca}_{0.69})_{\Sigma 0.99}^{M}(\text{Li}_{0.29}\text{Mg}_{0.03}\text{Fe}_{0.02}^{3+}\text{Al}_{1.78})_{\Sigma 2.12}^{T}(\text{Al}_{1.73}\text{Be}_{0.16}\text{Si}_{2.11})_{\Sigma 4.00}\text{O}_{12}\text{H}_{2.53}$. The apparent excess of H is probably due to the fact that the fraction of H_2O was assumed by difference to 100 wt.%, and slightly overestimated. On the basis of the previous experimental findings on Li,Be-bearing mica, X-ray (at 100 K) and neutron (at 20 K) structure refinements were performed in the space groups Cc and $C2/c$. The neutron structure refinement in the space group Cc offers a view about the (Al,Be,Si)-tetrahedral ordering: the best fit of the refinement was reached with the $T1$ and $T4$ sites occupied by (Be + Al) and $T2$ and $T3$ fully occupied by Si. This leads to a final population of $^{T}(\text{Al}_{1.88}\text{Be}_{0.12}\text{Si}_{2.00})_{\Sigma 4.00}$ p.f.u., in reasonable agreement with the chemical analysis. The neutron refinement provides unambiguous evidence of the occurrence of Li at the $M1$ site. The refined fraction of Li at the $M1$ site ranges between 0.27 and 0.29 a.p.f.u., in excellent agreement with the chemical analysis. The presence of Li, at least at a significant level, at the $M2$ (and $M3$) site can be ruled out, as a full site occupancy with the scattering length of Al was obtained. The location of the H sites and the complex hydrogen-bonding scheme are described. A comparison between the structure features of this Li,Be-mica and other brittle micas is carried out.

KEYWORDS: brittle micas, bityite, neutron diffraction, X-ray diffraction, structure refinement, ICP-AES.

Introduction

LI,BE-BEARING micas are rare in nature. Bityite, with the ideal chemical formula $\text{Ca}(\text{LiAl}_2)(\text{AlBeSi}_2)\text{O}_{10}(\text{OH})_2$, is a trioctahedral brittle mica first described by Lacroix (1908). This first occurrence was from Mt Bity, Madagascar. Later,

bityites or Li,Be-bearing micas with a composition between those of bityite and margarite (a dioctahedral brittle mica, ideally $\text{Ca}(\text{Al}_2)(\text{Al}_2\text{Si}_2)\text{O}_{10}(\text{OH})_2$) from Londonderry, Western Australia (Rowledge and Hayton, 1947), Middle Urals (Kutukova, 1959), Zimbabwe (localities: Salisbury and Bikita) and Uganda (Gallagher and Hawkes, 1966), and from Pizzo Marcio, Val Vigizzo, Piemonte, Italy (Lin and Guggenheim, 1983) were reported. Other

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DOI: 10.1180/minmag.2014.078.1.05

localities have been reported recently, though without a scientific characterization of the samples (e.g. Strickland quarry, Portland, Middlesex Co., Connecticut, USA; Harding pegmatite, Dixon, Taos Co., New Mexico; Huron claims, Point du Bois, Manitoba, Canada; Maantienvärsi pegmatite dike, Eräjärvi pegmatite area, Orivesi, Finland; Tittling, near Passau, Bavaria, Germany).

A series of studies on chemical composition, optical properties and crystal structure of Li,Be-bearing brittle micas revealed their unusual features (e.g. Strunz, 1956; Gallagher and Hawkes, 1966; Farmer and Velde, 1973; Lin and Guggenheim, 1983). Structurally, Li,Be-rich brittle micas are meso-octahedral (Ferraris and Ivaldi, 2002). On the basis of single-crystal X-ray structure refinements of a brittle mica from Pizzo Marcio, Piemonte, with composition $(\text{Ca}_{0.946}\text{Na}_{0.024}\text{K}_{0.001})_{\Sigma 0.971}(\text{Li}_{0.547}\text{Fe}_{0.007}^{3+}\text{Al}_{2.044})_{\Sigma 2.598}(\text{Al}_{1.340}\text{Be}_{0.637}\text{Si}_{2.023})_{\Sigma 4}\text{O}_{10}(\text{OH})_2$, Lin and Guggenheim (1983) showed that: Al prefers the $M2$ site; Li substitution for the vacancy at the $M1$ is coupled with the Be/Al substitution in the tetrahedral sites, without additional octahedral substitutions (or octahedral cation disordering effects). Thus, the octahedral sheet in the structure of Li,Be-bearing micas is similar to that of an Al-dioctahedral mica, but with Li that substitutes for the vacancy. As previously observed in margarite- $2M_1$ (Guggenheim and Bailey, 1975, 1978), a near-complete ordered distribution of Si and Al in the tetrahedral sheet of bityite it is highly likely, in a configuration that violates the centre of symmetry. In order to corroborate this, Lin and Guggenheim (1983) performed two structure refinements of their Li,Be-rich mica in the space groups $C2/c$ and Cc . The experimental findings suggested that the acentric space group was more likely. Accordingly, infrared spectra of Li,Be-micas reported by Farmer and Velde (1973) showed the absence of Al—O—Al bonds linking tetrahedra, suggesting an ordered Si/Al-tetrahedral distribution. Lin and Guggenheim (1983) located the H sites in their Li,Be-mica on the basis of the residuals in the difference-Fourier map of the electron density, though refinement of the H-sites coordinates was not possible.

Li,Be-bearing mica is a good candidate for a single-crystal neutron diffraction experiment. A neutron structure refinement is expected to provide: (1) a reliable location of the H sites, even with a partial site occupancy (e.g. Gatta *et al.*, 2006a,b); (2) a reliable description of the

(Si,Al,Be)-ordering at the tetrahedral sites and of the (Al,Li)-ordering at the octahedral sites due to their significantly different scattering lengths (i.e. Sears, 1986); (3) a better description of atomic displacement around the equilibrium position, as the neutron cross-section does not fall off with angle, making possible measurements at high values of $\sin\theta/\lambda$. We have selected a sample of Li,Be-rich mica from Harding Mine, Taos County, New Mexico (kindly provided by the "Museo di Storia Naturale" of Milan, n. 30772) containing large crystals suitable for neutron and X-ray diffraction (XRD) experiments. In addition, the amount of material available allowed us to perform a wet analysis of the mica by ICP-AES, which is recognized as a well established, cost-effective, multi-element technique displaying excellent sensitivity for many low atomic number elements (e.g. B, Be, Li, P, S), the alkali earths (Ba, Ca, Mg, Sr), silicon and refractories (e.g. Al, Ti, Zr), the rare-earth elements (*REEs*), Sc and Y, along with the first-row transition metals (e.g. Jarvis and Jarvis, 1992a,b and references therein). The number of elements determinable by ICP-AES varies greatly, depending on sample type and preparation procedures used. Here, ICP-AES appears to be an appropriate analytical technique which complements our neutron and XRD studies of Li,Be-rich mica.

Sample description and mineralogy

The Harding pegmatite is located in the western part of the Picuris Range about 20 miles southwest of Taos, New Mexico. In 1974, the pegmatite mine was leased by the owner to the University of New Mexico for preservation and scientific research. The mine has produced commercial quantities of beryl, lepidolite, spodumene and tantalum-niobium minerals over a period of half a century. From 1919 to 1930, lepidolite, lithian muscovite and some spodumene were mined for the production of glasses resistant to thermal shock. From 1924 to 1947, the mine started to produce microlite and tantalite-columbite (for tantalum) and spodumene (for lithium), as a response to wartime needs. From 1950 to 1958, after the mining operations ceased (Jahns and Ewing, 1976), the Harding pegmatite had produced ore beryl utilized mainly in beryllium-copper alloys, ceramics, aerospace and defence.

The Harding pegmatites lie within a complex terrane of Precambrian rocks described by

Montgomery (1953). This terrane is characterized by a thick section of arenaceous and pelitic metasedimentary rocks with inter-layered meta-volcanic rocks of basaltic to rhyolitic composition. The pegmatites include several pegmatite bodies, most are pinch-and-swell dykes that in general are 1.5 to 6 m or more thick. The main Harding dyke is highly irregular in surface plan, with an exposed length of a few hundreds of metres and thickness up to 80 m in the quarry area (Jahns and Ewing, 1976). The texture of the main pegmatite body displays a wall zone marked by quartz + albite + perthite, an intermediate zone of albite (var. cleavelandite) + albite + quartz + Li-muscovite, and a core zone distinguished by microcline + spodumene + lepidolite + albite + muscovite + quartz. Bityite was never reported in the open literature at the Harding pegmatites; it is highly likely that bityite was confused with lepidolite or muscovite. Bityite crystals from Harding mine are light brown and translucent. The cleavage is perfect micaceous on {001} and the fracture is uneven.

Brookins *et al.* (1979) found for whole rocks an age of 1.336 ± 73 m.y. and that may be taken as the average age of the pegmatite.

Experimental methods

Chemical analysis of the sample of Li,Be-rich mica used in this study was performed by ICP-AES using a PerkinElmer Optima 7000 DV spectrometer. In this apparatus, the sample-introduction unit includes a cyclonic spray chamber and a MEINHARD-type concentric glass nebulizer. The cyclonic spray chamber was used to provide both high sample transfer into the ICP and very fast sample rinse-in and rinse-out times. The concentric nebulizer provided excellent sensitivity and precision for aqueous solutions. A total mass of 13 mg of the Li,Be-bearing mica was used for the chemical analysis. Sample preparation, standardization and quantification of uncertainty in measurement and analytical methods were performed according to the following international protocols: EN ISO 21587 (2007) (parts 1, 2 and 3), 26845 (2008); EPA 3052 (1996), 6010c (2007); and JGCM 100 (2008). A Berghof Speedwave 4 apparatus was used as the microwave digestion system. The chemical composition of the Li,Be-mica, along with further details pertaining to the analytical methods, are given in Table 1.

Single-crystal XRD data were collected using a BRUKER-APEX II CCD diffractometer,

equipped with an Oxford Cryosystems low-temperature apparatus. Data were collected using monochromatic MoK α radiation at 100 K. A crystal of bityite (~ 0.38 mm $\times$ 0.28 mm $\times$ 0.09 mm), visibly free of defects between crossed polars, was selected for the XRD experiment. Data were measured using the ω -scan method with a counting time of 10 s per frame and a scan width of 0.5° per frame. A total number of 2884 reflections were collected up to $2\theta_{\max} = 62.35^\circ$ (Table 2). Cell parameters were retrieved using the *APEX II* software (Bruker, 2008) and refined using *SAINT* (Bruker, 2008) on all observed reflections, giving a monoclinic *C*-centred lattice with: $a = 5.0864(3)$, $b = 8.8186(5)$, $c = 19.1098(11)$ Å and $\beta = 95.445(1)^\circ$ (Table 2). Only sharp reflections populated the diffraction pattern, indicating regular stacking. The reflection conditions suggested that the space groups is *C2/c* or *Cc*. The polytypic nature of the sample is $2M_1$. Data reduction was performed using the *SAINT* software (Bruker, 2008), which corrects for Lorentz-polarization effects. Scaling and empirical absorption corrections were applied using the *SADABS* multi-scan method (Bruker, 2008).

Single-crystal neutron diffraction data were collected at 20 K on the high-resolution four-circle diffractometer D9 at ILL, with a wavelength of 0.8242(1) Å obtained using the 220 reflection of a new diamond monochromator operating in transmission geometry (Courtois *et al.*, 2013). Diamond crystal plates of high quality with dimensions of 1.5 cm $\times$ 1.5 cm $\times$ 0.17 cm have a mosaic distribution of 0.15°. We have used composite diamond crystals by stacking crystal plates on top of each other. Such a technique allows the production of sufficient thick diamond crystals with a controlled mosaic spread adapted to the instrument requirements. With an active area of 6 cm $\times$ 6 cm, it consists of four columns of four composite crystals that are ~ 0.55 cm thick with a global mosaic distribution of 0.3°. The crystals are mounted onto specific holders cut from a perfect silicon crystal in order to reduce instrumental background. The wavelength was calibrated using a germanium single crystal. D9 is equipped with a small two-dimensional area detector (Lehmann *et al.*, 1989), which allows optimal discrimination of the peak from the background. A total of 2626 reflections were collected up to $2\theta_{\max} = 79.54^\circ$ (Table 2). For all data, background corrections following Wilkinson *et al.* (1988) and Lorentz corrections were

TABLE 1. Chemical composition of the Li,Be-bearing mica from Harding pegmatite based on ICP-AES analysis. The chemical formula, calculated on the basis of 12 oxygen atoms, is: $^{Ca}(\text{Na}_{0.26}\text{K}_{0.04}\text{Ca}_{0.69})_{\Sigma 0.99}^{M}(\text{Li}_{0.29}\text{Mg}_{0.03}\text{Fe}_{0.02}^{3+}\text{Al}_{1.78})_{\Sigma 2.12}^{T}(\text{Al}_{1.73}\text{Be}_{0.16}\text{Si}_{2.11})_{\Sigma 4.00}\text{O}_{12}\text{H}_{2.53}$

Oxides	Wt.%	e.s.d.	ICP-AES (nm)	Alkaline fusion ICP-AES	Microwave assisted acid digestion ICP-AES	Wet methods
SiO ₂	32.5	± 0.5	251.611	x		(1)
Fe ₂ O ₃	0.48	± 0.05	238.204	x	x	
MnO	0.03	± 0.01	257.610	x	x	
Cr ₂ O ₃	0.01	n.d.	267.716	x	x	
TiO ₂	0.07	± 0.01	334.940	x	x	
Al ₂ O ₃	45.9	± 0.7	396.153	x	x	(2)
CaO	9.95	± 0.15	317.933	x	x	
MgO	0.29	± 0.03	285.213	x	x	
Li ₂ O	1.12	± 0.06	670.784	x	x	
BeO	1.03	± 0.06	313.107	x	x	
K ₂ O	0.47	± 0.05	766.490		x	
Na ₂ O	2.03	± 0.09	589.592		x	
SrO	0.03	± 0.01	407.771	x	x	
P ₂ O ₅	0.18	± 0.03	213.617	x	x	
H ₂ O*	5.85					
Total	100.00					
BaO	<0.01		233.527	x	x	
ZrO ₂	<0.01		343.823	x	x	
Rb ₂ O	<0.05		780.023		x	
Tl ₂ O	<0.02		190.801	x	x	
V ₂ O ₅	<0.01		292.464	x	x	
MoO ₃	<0.01		202.031	x	x	

(1) gravimetric method; (2) CyDTA-Zinc back titration method; * by difference to 100 wt.%.

applied. Least-squares matching of the observed and calculated centroids of the 896 strongest reflections gave a metrically monoclinic unit cell with: $a = 5.0590(4)$, $b = 8.7909(9)$, $c = 19.0176(18)$ Å and $\beta = 95.459(7)^\circ$, with a C -centred lattice (Table 2). Further details pertaining to the X-ray and neutron data collections are given in Table 2.

Structure refinements

The X-ray intensity data collected at 100 K were first processed with the program *E-STATISTICS* and *ASSIGN-SPACEGROUP*, implemented in the *WinGX* package (Farrugia, 1999). The statistics of distributions of the normalized structure factors (E' s) suggest that the structure is centrosymmetric (at 89.6% likelihood), as also suggested by the Sheldrick's $|E^2 - 1|$ criterion (Sheldrick, 1997) (i.e. $|E^2 - 1| = 1.014$). Two possible space groups (both

belonging to the $2/m$ Laue class) were suggested by the program: $C2/c$ and Cc . Two X-ray structure refinements, in the space groups $C2/c$ and Cc , respectively, were performed using the *SHELXL-97* software (Sheldrick, 1997, 2008), starting from the structure model of Lin and Guggenheim (1983). Neutral scattering factors of Si, Al, Be, Ca, Na, Li, O and H have been taken from the *International Tables for Crystallography Vol. C* (Wilson and Prince, 1999). The secondary isotropic extinction effect was corrected according to the Larson's formalism (1967), as implemented in *SHELXL-97*. In both the X-ray refinements, the Ca site was modelled as partially occupied by Ca and Na, and the site occupancy factors (s.o.f.) of the two cations were refined (constrained as: $\text{s.o.f.}(\text{Na}) = 1 - \text{s.o.f.}(\text{Ca})$, Table 3). The $M1$ site was modelled as partially occupied by Li, whereas $M2$ and $M3$ were modelled as fully occupied by Al (Table 3). For

TABLE 2. Details pertaining to the neutron and X-ray data collections and structure refinements.

	Neutron	X-ray
Crystal shape	Platy	Platy
Crystal size (mm)	$3.7 \times 3.1 \times 1.1$	$0.380 \times 0.280 \times 0.09$
Crystal colour	Translucent brown	Translucent brown
Unit-cell constants	$a = 5.0590(4) \text{ \AA}$ $b = 8.7909(9) \text{ \AA}$ $c = 19.0176(18) \text{ \AA}$ $\beta = 95.459(7)^\circ$ $V = 841.9(1) \text{ \AA}^3$	$a = 5.0864(3) \text{ \AA}$ $b = 8.8186(5) \text{ \AA}$ $c = 19.1098(11) \text{ \AA}$ $\beta = 95.445(1)^\circ$ $V = 853.3(2) \text{ \AA}^3$
Space Group	$Cc, C2/c$	$Cc, C2/c$
Z	4	4
T (K)	20	100
Radiation ($\text{\AA}$)	0.8242(1)	Mo- $K\alpha$
Diffractometer	D9 four circle	Bruker APEX II
Data-collection method	ω - θ scans	ω -scan, $0.5^\circ/\text{frame}$, 10 s/frame
Max. 2θ ($^\circ$)	79.54 $-7 \leq h \leq 6$ $-4 \leq k \leq 12$ $-27 \leq l \leq 28$	62.25 $-7 \leq h \leq 7$ $-9 \leq k \leq 12$ $-27 \leq l \leq 21$
Cc space group		
No. measured reflections	2626	2884
No. unique reflections	2370	1848
No. unique refl. with $F_o > 4\sigma(F_o)$	2239	1845
No. refined parameters	107	172
R_{int}	0.0187	0.0104
$R_1(F)$ with $F_o > 4\sigma(F_o)$	0.0506	0.0199
$R_1(F)$ for all the unique refl.	0.0535	0.0202
$wR_2(F^2)$	0.0950	0.0592
Weighting Scheme: a, b	0.01, 0	0.01, 0
Residuals ($e^-/\text{\AA}^3$, $\text{fm}/\text{\AA}^3$)	+1.2/-1.1	+0.5/-0.5
$C2/c$ space group		
No. measured reflections	2626	2884
No. unique reflections	1459	1243
No. unique refl. with $F_o > 4\sigma(F_o)$	1386	1240
No. refined parameters	113	95
R_{int}	0.0295	0.0113
$R_1(F)$ with $F_o > 4\sigma(F_o)$	0.0700	0.0388
$R_1(F)$ for all the unique refl.	0.0736	0.0391
$wR_2(F^2)$	0.1188	0.1310
Weighting Scheme: a, b	0.01, 0	0.01, 0
Residuals ($e^-/\text{\AA}^3$, $\text{fm}/\text{\AA}^3$)	+1.1/-1.2	+0.6/-0.7

$$R_{\text{int}} = \Sigma |F_{\text{obs}}^2 - F_{\text{obs}}^2(\text{mean})| / \Sigma [F_{\text{obs}}^2]; R_1 = \Sigma (|F_{\text{obs}}| - |F_{\text{calc}}|) / \Sigma |F_{\text{obs}}|; wR_2 = [\Sigma [w(F_{\text{obs}}^2 - F_{\text{calc}}^2)^2] / \Sigma [w(F_{\text{obs}}^2)^2]]^{0.5}, \\ w = 1 / [\sigma^2(F_{\text{obs}}^2) + (a^*P)^2 + b^*P], P = (\text{Max}(F_{\text{obs}}^2, 0) + 2^*F_{\text{calc}}^2) / 3.$$

the refinement in the $C2/c$ space group, mixed (Si,Be) and (Al,Si,Be) scattering curves were used to model the tetrahedral $T1$ and $T2$ sites, respectively, with a fixed fraction of Be based on the neutron structure refinement (see below, Tables 3 and 4). For the refinement in the Cc

space group, the four independent tetrahedral sites were modelled as follows: $T1$ and $T3$ occupied by Al and Be, with $T2$ and $T3$ fully occupied by Si (Table 3). The atomic coordinates and the s.o.f. of the H sites were taken from the neutron structure refinements in $C2/c$ and Cc space groups, and not

TABLE 3. Fractional site coordinates, site occupancy factor (s.o.f) and displacement parameters ($\text{\AA}^2$) of the Li, Be-rich mica based on the X-ray structure refinements (at 100 K). The anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha^*)^2U^{11} + \dots + 2hka^*b^*U^{12}]$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Site	s.o.f.	x	y	z	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}	U_{eq}/U_{iso}
<i>Ca</i>	Ca 0.74(1), Na 0.26(1)	0	0.09233(8)	$\frac{1}{4}$	0.0078(4)	0.0090(5)	0.0064(4)	0	0.0015(2)	0	0.0077(3)
<i>M1</i>	Li 0.39(4)	$\frac{1}{4}$	$\frac{3}{4}$	0							0.027(7)
<i>M2</i>	Al 1.0	0.7466(1)	0.91560(8)	0.9998(3)	0.0048(3)	0.0052(4)	0.0047(4)	0.0002(2)	0.0008(2)	0.0002(2)	0.0049(2)
<i>T1</i>	Si 0.925(4), Be 0.02	0.4652(1)	0.92506(8)	0.14380(4)	0.0056(3)	0.0061(4)	0.0063(4)	-0.0002(2)	0.0015(2)	0.0002(2)	0.0059(2)
<i>T2</i>	Al 0.72(6), Si 0.22(6), Be 0.06	0.4552(1)	0.25546(7)	0.14383(4)	0.0035(4)	0.0045(5)	0.0024(4)	0.0005(2)	0.0004(2)	0.0004(2)	0.0034(3)
<i>O1</i>	O 1.0	0.9571(3)	0.4407(2)	0.05603(9)	0.0060(7)	0.0091(8)	0.0109(8)	0.0024(5)	0.0018(6)	-0.0003(6)	0.0086(3)
<i>O2</i>	O 1.0	0.3911(3)	0.2517(2)	0.0560(1)	0.0078(7)	0.0056(9)	0.0094(8)	0.0004(5)	0.0020(6)	0.0015(5)	0.0075(4)
<i>O3</i>	O 1.0	0.3604(3)	0.0885(2)	0.17690(9)	0.0075(7)	0.0102(9)	0.0077(8)	-0.0008(5)	0.0029(5)	0.0020(6)	0.0083(3)
<i>O4</i>	O 1.0	0.2802(3)	0.7797(2)	0.16799(9)	0.0088(7)	0.0079(7)	0.0078(7)	0.0012(6)	0.0003(5)	0.0013(6)	0.0082(3)
<i>O5</i>	O 1.0	0.2799(3)	0.3932(2)	0.17778(9)	0.0091(7)	0.0073(8)	0.0074(8)	0.0002(5)	0.0009(5)	-0.0007(6)	0.0079(3)
<i>O6</i>	O 1.0	0.4521(3)	0.5659(2)	0.05047(9)	0.0059(7)	0.0059(8)	0.0075(7)	-0.0013(5)	0.0023(5)	-0.0012(6)	0.0063(3)
<i>H1</i>	H 0.56	0.3663	0.6559	0.0618							0.07(3)
<i>H2</i>	H 0.27	0.4418	0.5943	0.0992							0.07(7)
<i>Ca</i>	Ca 0.771(4), Na 0.229(4)	-0.00033(12)	0.09233(3)	0.24941(4)	0.0079(2)	0.0087(2)	0.0070(2)	-0.0004(2)	0.0017(1)	0.0002(2)	0.0078(1)
<i>M1</i>	Li 0.413(15)	0.269(2)	0.758(1)	0.000(1)							0.018(2)
<i>M2</i>	Al 1.0	0.74815(9)	0.91652(6)	0.9922(3)	0.0030(3)	0.0040(3)	0.0051(3)	0.0009(2)	0.0008(2)	0.0003(2)	0.0040(1)
<i>M3</i>	Al 1.0	0.25504(10)	0.08566(6)	-0.00074(3)	0.0047(3)	0.0045(3)	0.0040(3)	-0.0008(2)	0.0012(2)	-0.0001(2)	0.0043(1)
<i>T1</i>	Al 0.883(3), Be 0.117(3)	0.46538(11)	0.92604(8)	0.14174(3)	0.0030(3)	0.0052(3)	0.0038(3)	-0.0007(2)	0.0013(2)	0.0009(2)	0.0039(2)
<i>T2</i>	Si 1.0	0.53493(10)	0.07566(7)	0.85430(3)	0.0052(2)	0.0037(3)	0.0044(2)	0.0004(2)	0.0011(2)	0.0001(2)	0.0044(1)
<i>T3</i>	Si 1.0	0.45659(9)	0.25580(6)	0.14413(3)	0.0041(2)	0.0053(4)	0.0038(2)	0.0005(2)	0.0009(2)	0.0002(2)	0.0044(1)
<i>T4</i>	Al 0.873(4), Be 0.127(4)	0.54537(10)	0.74504(7)	0.85661(3)	0.0043(3)	0.0030(4)	0.0040(3)	-0.0003(2)	0.0010(2)	-0.0001(3)	0.0037(2)
<i>O1</i>	O 1.0	0.9613(3)	0.4426(2)	0.0520(1)	0.0062(6)	0.0081(6)	0.0033(6)	0.0000(5)	0.0016(5)	-0.0002(5)	0.0058(3)
<i>O11</i>	O 1.0	0.0477(3)	0.5619(2)	0.9399(1)	0.0047(6)	0.0068(6)	0.0072(6)	0.0022(5)	0.0020(5)	0.0009(5)	0.0061(3)
<i>O2</i>	O 1.0	0.3981(3)	0.2531(2)	0.0588(1)	0.0105(7)	0.0057(7)	0.0044(7)	0.0013(5)	0.0003(5)	0.0006(5)	0.0069(3)
<i>O22</i>	O 1.0	0.6158(3)	0.7488(2)	0.9466(1)	0.0038(6)	0.0038(6)	0.0063(7)	-0.0011(4)	0.0010(5)	0.0004(4)	0.0046(3)
<i>O3</i>	O 1.0	0.3637(3)	0.0962(2)	0.1764(1)	0.0073(6)	0.0075(7)	0.0060(6)	0.0004(4)	0.0019(5)	0.0011(4)	0.0068(3)
<i>O33</i>	O 1.0	0.6415(3)	0.9185(2)	0.8227(1)	0.0068(6)	0.0048(7)	0.0082(7)	-0.0006(4)	0.0023(5)	-0.0004(4)	0.0065(3)
<i>O4</i>	O 1.0	0.2713(3)	0.7767(2)	0.1675(1)	0.0066(5)	0.0062(6)	0.0097(7)	-0.0007(5)	0.0008(5)	0.0004(5)	0.0075(3)
<i>O44</i>	O 1.0	0.7118(3)	0.2178(2)	0.8314(1)	0.0051(5)	0.0075(6)	0.0055(6)	0.0008(5)	0.0008(4)	0.0013(5)	0.0060(3)
<i>O5</i>	O 1.0	0.2909(3)	0.3906(2)	0.1774(1)	0.0066(6)	0.0082(6)	0.0063(7)	-0.0004(4)	-0.0003(5)	-0.0006(5)	0.0071(3)
<i>O55</i>	O 1.0	0.7316(3)	0.6034(2)	0.8216(1)	0.0052(6)	0.0060(7)	0.0071(7)	0.0026(4)	0.0008(5)	-0.0003(5)	0.0061(3)
<i>O6</i>	O 1.0	0.4544(3)	0.5674(2)	0.0499(1)							0.0061(3)
<i>O66</i>	O 1.0	0.5505(3)	0.4349(2)	0.9484(1)							0.0043(3)

<i>H1</i>	H 0.54	0.3692	0.6547	0.0617	0.10(1)*
<i>H2</i>	H 0.49	0.4423	0.5944	0.0959	0.10(1)*
<i>H3</i>	H 0.35	0.643	0.3388	0.9473	0.10(1)*
<i>H4</i>	H 0.31	0.622	0.3543	0.9239	0.10(1)*

Coordinates and s.o.f. of the H sites are from the neutron structure refinements, and not refined. For the refinement in the *C2/c* space group, the fractions of Be at the *T1* and *T2* were fixed.

refined. The refinement in the space group *C2/c* was conducted with all the atomic sites refined anisotropically, excluding *M1* (due to its low s.o.f.) and the two independent H sites (Table 3). The refinement in the space group *Cc* was conducted with all the atomic sites refined anisotropically, excluding *M1* and the hydroxyl-group sites (i.e. *O6* and *O66*, *H1*–4) (Table 3). Both the refinements converged to small R_1 values, with insignificant residuals in the difference-Fourier map of the electron density and no significant correlation among the refined parameters (Table 2). Further details pertaining to the X-ray structure refinements are given in Table 2. Site coordinates, occupancies and displacement parameters are listed in Table 3. Relevant bond distances are listed in Tables 5 and 6.

The neutron intensity data collected at 20 K were processed first following the same protocol as already described for the X-ray data. The statistics of distributions of E 's and the Sheldrick's $|E^2 - 1|$ criterion suggest that the structure is centrosymmetric (at 84.6% likelihood, $|E^2 - 1| = 0.980$). Also in this case, two structure refinements have been performed in the space group *C2/c* and *Cc*, respectively, using the *SHELXL-97* software (Sheldrick, 1997, 2008), starting from the structure models of Lin and Guggenheim (1983). The secondary isotropic extinction effect was corrected following Larson (1967). The neutron scattering lengths of Si, Al, Be, Ca, Na, Li, O and H have been used according to Sears (1986). The sites population was modelled as described previously for the X-ray refinements: (1) a mixed (Ca,Na) neutron scattering length was used to model the *Ca* site; (2) the length of Li was used at *M1* and that of Al at *M2* and *M3*, respectively; (3) for the refinement in the *Cc* space group, *T1* and *T3* were modelled as occupied by Al and Be, whereas *T2* and *T3* as fully occupied by Si (Table 4); for the refinement in the *C2/c* space group, mixed (Si,Be) and (Al,Si,Be) scattering lengths were used to model the tetrahedral *T1* and *T2* sites, respectively, with a fixed fraction of Be based on the acentric structure refinement (i.e. Be fraction at *T2*) and chemical analysis (i.e. Be fraction at *T1*) (Tables 1 and 4). Such a sites population provides the best figures of merit of both refinements (i.e. irrespective of adoption of an acentric or centrosymmetric structural model). The first cycles of both refinements were conducted without any H site, leaving intense negative residual peaks in the difference-Fourier map of

TABLE 4. Fractional site coordinates, site occupancy factor (s.o.f.) and displacement parameters ($\text{\AA}^2$) of the Li,Be-rich mica based on the neutron structure refinements (at 20 K). The anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha^*)^2U^{11} + \dots + 2hka^*b^*U^{12}]$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Site	s.o.f.	x	y	z	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}	$U_{eq}U_{iso}$
<i>Ca</i>	Ca 0.81(3), Na 0.19(3)	0	0.0924(2)	$\frac{1}{4}$	0.0064(6)	0.0084(7)	0.0081(7)	0	0.0012(4)	0	0.0076(3)
<i>M1</i>	Li 0.291(15)	$\frac{1}{4}$	$\frac{3}{4}$	0							0.003(2)
<i>M2</i>	Al 1.0	0.7465(3)	0.9154(2)	0.9997(1)	0.0025(4)	0.0027(5)	0.0042(5)	-0.0003(5)	0.0002(3)	0.0013(5)	0.0031(2)
<i>T1</i>	Al 0.48(3), Si 0.50(3), Be 0.02	0.4654(2)	0.9251(2)	0.1440(1)	0.0020(4)	0.0028(5)	0.0050(5)	-0.0003(3)	0.0002(3)	-0.0002(4)	0.0033(3)
<i>T2</i>	Al 0.452(3), Si 0.452(3), Be 0.06	0.4554(2)	0.2551(2)	0.1440(1)	0.0018(4)	0.0028(5)	0.0027(5)	0.0003(3)	-0.0002(3)	-0.0005(4)	0.0024(2)
<i>O1</i>	O 1.0	0.95655(16)	0.44037(10)	0.05592(5)	0.0042(3)	0.0057(4)	0.0083(4)	0.0014(2)	0.0000(2)	-0.0012(3)	0.0061(2)
<i>O2</i>	O 1.0	0.39055(16)	0.25211(11)	0.05585(5)	0.0061(3)	0.0045(3)	0.0071(4)	0.0010(3)	0.0008(2)	0.0004(3)	0.0059(2)
<i>O3</i>	O 1.0	0.36028(17)	0.08880(12)	0.17679(5)	0.0068(3)	0.0086(3)	0.0063(3)	-0.0001(3)	0.0020(2)	0.0007(3)	0.0071(2)
<i>O4</i>	O 1.0	0.28033(17)	0.77942(10)	0.16820(5)	0.0077(3)	0.0054(4)	0.0065(3)	0.0009(2)	0.0002(3)	0.0002(3)	0.0066(2)
<i>O5</i>	O 1.0	0.28007(17)	0.39346(11)	0.17817(5)	0.0077(3)	0.0052(4)	0.0058(3)	-0.0004(3)	-0.0002(2)	-0.0012(3)	0.0063(2)
<i>O6</i>	O 1.0	0.45186(16)	0.56632(10)	0.05081(5)	0.0055(3)	0.0040(4)	0.0074(4)	-0.0008(2)	0.0020(2)	-0.0003(3)	0.0056(2)
<i>H1</i>	H 0.562(9)	0.3663(7)	0.6559(4)	0.0618(3)	0.017(1)	0.016(2)	0.051(2)	0.001(1)	0.012(1)	-0.013(2)	0.028(1)
<i>H2</i>	H 0.274(10)	0.4418(18)	0.5943(13)	0.0992(3)	0.035(4)	0.051(5)	0.019(3)	-0.011(4)	0.013(3)	-0.014(4)	0.034(2)
<i>Ca</i>	Ca 0.79(4), Na 0.21(4)	0.0009(10)	0.0920(2)	0.2491(3)	0.0073(6)	0.0078(7)	0.0074(7)	0.0015(12)	0.0011(4)	0.0002(13)	0.0075(4)
<i>M1</i>	Li 0.2665(6)	0.253(6)	0.759(3)	0.0020(14)							0.003(2)
<i>M2</i>	Al 1.0	0.7479(7)	0.9160(4)	0.9991(2)							0.0031(6)
<i>M3</i>	Al 1.0	0.2547(7)	0.0853(4)	-0.0003(2)							0.0036(6)
<i>T1</i>	Al 0.95(1), Be 0.05(1)	0.4666(6)	0.9255(4)	0.14181(17)							0.0027(2)*
<i>T2</i>	Si 1.0	0.5355(5)	0.0756(4)	0.85432(16)							0.0027(2)*
<i>T3</i>	Si 1.0	0.4569(5)	0.2551(3)	0.14414(13)							0.0027(2)*
<i>T4</i>	Al 0.94(1), Be 0.06(1)	0.5454(6)	0.7449(4)	0.85629(15)							0.0027(2)*
<i>O1</i>	O 1.0	0.9596(3)	0.4435(2)	0.05228(10)							0.0043(3)
<i>O11</i>	O 1.0	0.0471(3)	0.5632(3)	0.94042(10)							0.0044(4)
<i>O2</i>	O 1.0	0.3956(4)	0.2536(3)	0.05835(11)							0.0063(4)
<i>O22</i>	O 1.0	0.6142(3)	0.7494(2)	0.94649(10)							0.0036(3)
<i>O3</i>	O 1.0	0.3610(4)	0.0956(2)	0.17611(12)							0.0058(4)
<i>O33</i>	O 1.0	0.6403(4)	0.9180(2)	0.82243(12)							0.0057(4)
<i>O4</i>	O 1.0	0.2729(4)	0.7769(2)	0.16767(11)							0.0052(3)
<i>O44</i>	O 1.0	0.7122(4)	0.2183(3)	0.83131(11)							0.0057(4)
<i>O5</i>	O 1.0	0.2896(4)	0.3915(3)	0.17727(11)							0.0053(4)
<i>O55</i>	O 1.0	0.7305(4)	0.6038(3)	0.82119(12)							0.0059(4)
<i>O6</i>	O 1.0	0.4524(4)	0.5676(3)	0.05010(11)							0.0053(4)
<i>O66</i>	O 1.0	0.5499(4)	0.4348(3)	0.94822(10)							0.0052(4)

H1	H 0.54(3)	0.369(2)	0.6547(12)	0.0617(6)	0.025(3)
H2	H 0.49(2)	0.442(2)	0.5944(11)	0.0959(5)	0.029(3)
H3	H 0.35(3)	0.643(2)	0.3388(12)	0.9473(7)	0.010(3)
H4'	H 0.31(3)	0.622(2)	0.3543(14)	0.9239(8)	0.011(3)
H4''	H	0.547	0.418	0.900	

The coordinates of the H4'' site were deduced on the basis of the difference-Fourier map of the nuclear density and not involved in the refinement. * Restrained to the same value.

the nuclear density. Further refinement cycles were then performed to assign H to the negative residual peaks (as hydrogen has a negative neutron scattering length; Sears, 1986). The refinement in the space group *C2/c* was finalized with anisotropic displacement parameters for all atomic sites, excluding the sparsely occupied *M1*. In contrast, the refinement in the acentric space group *Cc* was finalized with isotropic displacement parameters; only the *Ca* site was modelled anisotropically (Table 4). Both the refinements converged with insignificant residuals, mean-square atomic displacement tensors positive definite and no significant correlation among the refined parameters. Further details pertaining to the neutron structure refinements are given in Table 2. Refined atomic coordinates, occupancies and isotropic/equivalent displacement parameters are listed in Table 4. Relevant bond distances are listed in Tables 7 and 8.

Discussion

The chemical composition of the Li,Be-bearing mica from Harding Mine, Taos County, New Mexico, based on ICP-AES analysis (Table 1), leads to the following chemical formula (calculated on the basis of 12 oxygen atoms): $Ca(Na_{0.26}K_{0.04}Ca_{0.69})_{\Sigma 0.99}M(Li_{0.29}Mg_{0.03}Fe_{0.02}^{3+}Al_{1.78})_{\Sigma 2.12}T(Al_{1.73}Be_{0.16}Si_{2.11})_{\Sigma 4.00}O_{12}H_{2.53}$. There is a virtual excess of H, due to the fact that the fraction of H₂O was assumed by difference to 100%, and was probably slightly overestimated. The Be and Li contents are modest (i.e. 0.16 and 0.29 a.p.f.u., respectively) if compared to those of the bityite from Piemonte reported by Lin and Guggenheim (1983) [i.e. $(Ca_{0.946}Na_{0.024}K_{0.001})_{\Sigma 0.971}(Li_{0.547}Fe_{0.007}^{3+}Al_{2.044})_{\Sigma 2.598}(Al_{1.340}Be_{0.637}Si_{2.023})_{\Sigma 4}O_{10}(OH)_2$]. In our mica, the interlayer site (i.e. *Ca*) is occupied mainly by Ca, but a significant fraction of Na occurs, along with minor K.

The neutron (at 20 K) and X-ray (at 100 K) single-crystal intensity data show that the 'average' symmetry of the Li,Be-bearing brittle mica of this study is monoclinic *C2/c*. The statistics of distributions of the normalized structure factors suggest that the structure is centrosymmetric (at ~90% likelihood). However, the structure refinements make the scenario less obvious: (1) a highly ordered distribution of the site population among the tetrahedral sites suggest that the acentric structure model is more realistic, (2) the statistic parameters of the refinements

TABLE 5. Relevant bond distances (Å) and angles (°) based on the X-ray structure refinement in the space group $C2/c$.

$Ca-O3 \times 2$	2.4082(17)	$O6-H1$	0.941(2)
$Ca-O4 \times 2$	2.4705(17)	$O6 \cdots O4$	3.120(2)
$Ca-O5 \times 2$	2.4390(17)	$H1 \cdots O4$	2.381(2)
		$O6-H \cdots O4$	135.3(1)
$M1-O1 \times 2$	2.2066(17)	$O6-H1$	0.941(2)
$M1-O2 \times 2$	2.2016(17)	$O6 \cdots O1$	3.307(2)
$M1-O6 \times 2$	2.1060(16)	$H1 \cdots O1$	2.558(2)
		$O6-H1 \cdots O1$	136.8(1)
$M2-O1$	1.9013(18)	$O6-H1$	0.941(2)
$M2-O1'$	1.9144(17)	$O6 \cdots O2$	3.301(2)
$M2-O2$	1.9037(18)	$H1 \cdots O2$	2.553(2)
$M2-O2'$	1.9156(18)	$O6-H1 \cdots O2$	136.6(1)
$M2-O6$	1.8934(17)		
$M2-O6'$	1.8942(17)		
$T1-O1$	1.6793(19)	$O6-H2$	0.971(2)
$T1-O3$	1.6810(17)	$O6 \cdots O4$	3.120(2)
$T1-O4$	1.6807(18)	$H2 \cdots O4$	2.298(2)
$T1-O5$	1.6929(18)	$O6-H \cdots O4$	141.9(1)
$T2-O2$	1.6800(20)		
$T2-O3$	1.6903(17)		
$T2-O4$	1.6873(17)		
$T2-O5$	1.6737(18)		
α	21.3(5)		

The e.s.d. of the O–H, O $\cdots$ O, H $\cdots$ O and O–H $\cdots$ O values are probably underestimated due to the fixed H sites coordinates (see text for details); α is the tetrahedral rotation angle (Brigatti and Guggenheim, 2002).

quality (e.g. R_1 , wR_2 , observation/parameters ratio, residuals) do not provide clear evidence about the ‘actual’ space group, though the acentric structure model appears to be more likely; (3) the location of the proton sites deduced on the basis of the centrosymmetric model appears to be more realistic, and less affected by positional site disorder (see below), than that based on the acentric structure model.

Our structure refinements confirm a mixed (Ca+Na) population at the Ca site (Table 3). If we consider all four refinements in this study (i.e. Cc : X-ray, neutron; $C2/c$: X-ray, neutron), the refined Ca and Na fraction at the Ca site are 77 ± 4 and $23 \pm 4\%$, respectively. As the site population was modelled with (Na + Ca) only, the agreement with the chemical analysis is good (i.e. $(Na_{0.26}K_{0.04}Ca_{0.69})_{\Sigma 0.99}$, Table 1). Neutron and X-ray structure refinements in centrosymmetric and acentric space groups show a significantly distorted Ca -polyhedron, with $\Delta(Ca-O)_{\max}$ (i.e.

the difference between the longest and the shortest $Ca-O$ bond distances) ranging between 0.05 and 0.07 Å (Tables 5, 6, 7 and 8).

Li has a negative neutron scattering length (Sears, 1986), and our neutron refinement provides unambiguous evidence of the occurrence of Li at the $M1$ site. The presence of Li, at least at a significant level, at the $M2$ (and $M3$) site can be ruled out, as a full site occupancy with the scattering length of Al was obtained (Table 4). The refined fraction of Li at the $M1$ site ranges between 0.27 and 0.29 a.p.f.u. (neutron data, Table 4), in excellent agreement with the chemical analysis (i.e. 0.29 a.p.f.u., Table 1). X-ray data tend to overestimate the fraction of Li at the $M1$ site (to ~ 0.4 a.p.f.u., Table 3). X-ray and neutron structure refinements consistently show a pronounced distortion of the $M1$ polyhedron with $\Delta(M1-O)_{\max}$ (i.e. the difference between the longest and the shortest $M1-O$ bond distances) ranging between 0.1 and 0.2 Å (Tables 5, 6, 7 and 8); as expected, the

TABLE 6. Relevant bond distances (Å) and angles (°) based on the X-ray structure refinement in the space group *Cc*.

<i>Ca</i> – <i>O3</i>	2.422(2)	<i>M1</i> – <i>O1</i>	2.105(13)	<i>O6</i> – <i>H1</i>	0.922(2)	<i>O6</i> – <i>H2</i>	0.919(2)
<i>Ca</i> – <i>O4</i>	2.470(2)	<i>M1</i> – <i>O2</i>	2.289(14)	<i>O6</i> ... <i>O1</i>	3.309(2)	<i>O6</i> ... <i>O3</i>	3.048(2)
<i>Ca</i> – <i>O5</i>	2.431(2)	<i>M1</i> – <i>O6</i>	2.111(13)	<i>H1</i> ... <i>O1</i>	2.591(2)	<i>H2</i> ... <i>O3</i>	2.517(2)
<i>Ca</i> – <i>O33</i>	2.402(2)	<i>M1</i> – <i>O11</i>	2.304(12)	<i>O6</i> – <i>H1</i> ... <i>O1</i>	135.1(1)	<i>O6</i> – <i>H</i> ... <i>O3</i>	117.1(1)
<i>Ca</i> – <i>O44</i>	2.470(2)	<i>M1</i> – <i>O22</i>	2.118(14)				
<i>Ca</i> – <i>O55</i>	2.442(2)	<i>M1</i> – <i>O66</i>	2.103(13)	<i>O6</i> – <i>H1</i>	0.922(2)	<i>O6</i> – <i>H2</i>	0.919(2)
				<i>O6</i> ... <i>O2</i>	3.288(2)	<i>O6</i> ... <i>O4</i>	3.118(2)
<i>M2</i> – <i>O1</i>	1.865(2)	<i>M3</i> – <i>O1</i>	1.873(2)	<i>H1</i> ... <i>O2</i>	2.545(1)	<i>H2</i> ... <i>O4</i>	2.332(2)
<i>M2</i> – <i>O2</i>	1.946(2)	<i>M3</i> – <i>O2</i>	1.961(2)	<i>O6</i> – <i>H1</i> ... <i>O2</i>	137.9(1)	<i>O6</i> – <i>H</i> ... <i>O4</i>	143.4(1)
<i>M2</i> – <i>O6</i>	1.901(2)	<i>M3</i> – <i>O6</i>	1.892(2)				
<i>M2</i> – <i>O11</i>	1.936(2)	<i>M3</i> – <i>O11</i>	1.967(2)	<i>O6</i> – <i>H1</i>	0.922(2)	<i>O6</i> – <i>H2</i>	0.919(2)
<i>M2</i> – <i>O22</i>	1.877(2)	<i>M3</i> – <i>O22</i>	1.857(2)	<i>O6</i> ... <i>O4</i>	3.118(2)	<i>O6</i> ... <i>O5</i>	3.073(2)
<i>M2</i> – <i>O66</i>	1.902(2)	<i>M3</i> – <i>O66</i>	1.898(2)	<i>H1</i> ... <i>O4</i>	2.384(2)	<i>H2</i> ... <i>O5</i>	2.545(2)
				<i>O6</i> – <i>H</i> ... <i>O4</i>	136.6(1)	<i>O6</i> – <i>H</i> ... <i>O5</i>	117.0(1)
<i>T1</i> – <i>O1</i>	1.719(2)	<i>T2</i> – <i>O11</i>	1.636(2)				
<i>T1</i> – <i>O3</i>	1.739(2)	<i>T2</i> – <i>O33</i>	1.626(2)	<i>O66</i> – <i>H3</i>	0.970(2)	<i>O66</i> – <i>H4</i>	0.943(2)
<i>T1</i> – <i>O4</i>	1.744(2)	<i>T2</i> – <i>O44</i>	1.627(2)	<i>O66</i> ... <i>O11</i>	3.293(2)	<i>O66</i> ... <i>O11</i>	3.293(2)
<i>T1</i> – <i>O5</i>	1.757(2)	<i>T2</i> – <i>O55</i>	1.627(2)	<i>H3</i> ... <i>O11</i>	2.491(2)	<i>H4</i> ... <i>O11</i>	2.628(2)
				<i>O66</i> – <i>H</i> ... <i>O11</i>	140.0(1)	<i>O66</i> – <i>H</i> ... <i>O11</i>	128.0(1)
<i>T3</i> – <i>O2</i>	1.630(2)	<i>T4</i> – <i>O22</i>	1.724(2)				
<i>T3</i> – <i>O3</i>	1.625(2)	<i>T4</i> – <i>O33</i>	1.749(2)	<i>O66</i> – <i>H3</i>	0.970(2)	<i>O66</i> – <i>H4</i>	0.943(2)
<i>T3</i> – <i>O4</i>	1.631(2)	<i>T4</i> – <i>O44</i>	1.736(2)	<i>O66</i> ... <i>O22</i>	3.314(2)	<i>O66</i> ... <i>O22</i>	3.314(2)
<i>T3</i> – <i>O5</i>	1.622(2)	<i>T4</i> – <i>O55</i>	1.740(2)	<i>H3</i> ... <i>O22</i>	2.534(2)	<i>H4</i> ... <i>O22</i>	2.676(2)
				<i>O66</i> – <i>H</i> ... <i>O22</i>	137.4(1)	<i>O66</i> – <i>H</i> ... <i>O22</i>	125.5(1)
α_1	21.3(5)			<i>O66</i> – <i>H3</i>	0.970(2)	<i>O66</i> – <i>H4</i>	0.943(2)
α_2	21.5(5)			<i>O66</i> ... <i>O44</i>	3.113(2)	<i>O66</i> ... <i>O44</i>	3.113(2)
				<i>H3</i> ... <i>O44</i>	2.513(2)	<i>H4</i> ... <i>O44</i>	2.222(2)
				<i>O66</i> – <i>H</i> ... <i>O44</i>	120.0(1)	<i>O66</i> – <i>H</i> ... <i>O44</i>	157.3(1)

The e.s.d. of the O–H, O...O, H...O and O–H...O values are probably underestimated due to the fixed H sites coordinates (see text for details); α is the tetrahedral rotation angle (Brigatti and Guggenheim, 2002).

distortion appears to be more pronounced in the acentric refined structures. X-ray and neutron refinements in the *C2/c* space group provide a modest distortion of the *M2* octahedron, both with $\Delta(M2-O)_{\max} \approx 0.02$ Å (Tables 5 and 7). The refinements performed in the *Cc* space group lead to $\Delta(M2-O)_{\max} \approx 0.07$ and 0.08 Å and $\Delta(M3-O)_{\max} \approx 0.10$ and 0.11 Å (Tables 6 and 8).

The neutron structure refinement in the space group *Cc* offers a picture about the (Al,Be,Si)-tetrahedral ordering. The best fit of the refinement was reached with the *T1* and *T4* sites occupied by (Be + Al) and *T2* and *T3* fully occupied by Si. This leads to a final population of ${}^T(\text{Al}_{1.88}\text{Be}_{0.12}\text{Si}_{2.00})_{\Sigma 4.00}$ p.f.u., in a reasonable agreement with the chemical analysis (i.e. $(\text{Al}_{1.73}\text{Be}_{0.16}\text{Si}_{2.11})_{\Sigma 4.00}$, Table 1). The tetrahedral bond distances based on the neutron and X-ray structure refinements in the *Cc* space group support the aforementioned

ordering scheme (Tables 6 and 8). The X-ray and neutron structure refinements show a high value of the tetrahedral rotation angle (defined as: $\alpha = 1/6 \cdot \sum_{i=1}^6 |120^\circ - \varphi_i|/2$, where φ_i is the angle between basal edges of neighbouring tetrahedra articulated in the six-membered ring; Brigatti and Guggenheim, 2002, and references therein) in our Li,Be-rich mica (Tables 5, 6, 7 and 8). The large value of α reflects the difference in dimension between the tetrahedral and octahedral sheets. Our results are consistent with the previous experimental findings on brittle micas (e.g. margarite, Joswig *et al.*, 1983; clintonite, Gatta *et al.*, 2012; bityite, Lin and Guggenheim, 1983). There is no significant difference between the tetrahedral rotation angles in the acentric and centrosymmetric structure models based on X-ray and neutron diffraction data, as shown in Tables 5, 6, 7 and 8. The X-ray and neutron refinements performed in

TABLE 7. Relevant bond distances (Å) and angles (°) based on the neutron structure refinement in the space group $C2/c$.

$Ca-O3 \times 2$	2.397(1)	$O6-H1$	0.932(4)
$Ca-O4 \times 2$	2.455(2)	$O6-H1^*$	0.9647
$Ca-O5 \times 2$	2.424(2)	$O6 \cdots O4$	3.101(1)
		$H1 \cdots O4$	2.372(5)
$M1-O1 \times 2$	2.194(1)	$O6-H \cdots O4$	134.9(3)
$M1-O2 \times 2$	2.192(1)		
$M1-O6 \times 2$	2.097(1)	$O6-H1$	0.932(4)
		$O6-H1^*$	0.9647
$M2-O1$	1.891(2)	$O6 \cdots O1$	3.290(1)
$M2-O1'$	1.908(2)	$H1 \cdots O1$	2.547(4)
$M2-O2$	1.892(2)	$O6-H \cdots O1$	136.9(3)
$M2-O2'$	1.904(2)		
$M2-O6$	1.886(2)	$O6-H1$	0.932(4)
$M2-O6'$	1.895(2)	$O6-H1^*$	0.9647
		$O6 \cdots O2$	3.285(1)
$T1-O1$	1.676(2)	$H1 \cdots O2$	2.544(4)
$T1-O3$	1.675(2)	$O6-H \cdots O2$	136.8(3)
$T1-O4$	1.677(2)		
$T1-O5$	1.685(2)	$O6-H2$	0.959(7)
		$O6-H2^*$	1.0014
$T2-O2$	1.678(2)	$O6 \cdots O3$	3.018(1)
$T2-O3$	1.677(2)	$H2 \cdots O3$	2.463(8)
$T2-O4$	1.678(2)	$O6-H \cdots O3$	116.7(5)
$T2-O5$	1.673(2)		
		$O6-H2$	0.959(7)
α	21.4(3)	$O6-H2^*$	1.0014
		$O6 \cdots O4$	3.101(1)
		$H2 \cdots O4$	2.289(10)
		$O6-H \cdots O4$	141.9(6)
		$O6-H2$	0.959(7)
		$O6-H2^*$	1.0014
		$O6 \cdots O5$	3.055(1)
		$H2 \cdots O5$	2.505(10)
		$O6-H \cdots O5$	116.4(5)
		$M1-H1$	1.510(6)
		$M1-H2$	2.46(1)
		$H1-H2$	0.95(1)
		$H1 \angle (001)$	15.6(3)
		$H2 \angle (001)$	74.8(4)

α is the tetrahedral rotation angle (Brigatti and Guggenheim, 2002).

*Bond distances corrected for “riding motion” effect (Busing and Levy, 1964).

the Cc space group show essentially the same value for the α angle for the two independent tetrahedral sheets (i.e. $\alpha_1 = 21.4(6)^\circ$, $\alpha_2 = 21.5(6)^\circ$, neutron data, Table 8). Similar evidence was reported for the structure of margarite (20.9 and 20.6° ; Joswig *et al.*, 1983) and in bityite (21.6 and

21.7° ; Lin and Guggenheim, 1983) refined in the space group Cc .

The neutron refinement adopting the centrosymmetric structure model provided two independent H sites (i.e. $H1$ and $H2$, Table 4). The occupancy factors of the $H1$ and $H2$ sites were refined without any restraint. The s.o.f. of $H1$ is 56.2(9)%, whereas that of $H2$ is 27.4(10)%. The sum s.o.f.($H1$) + s.o.f.($H2$) is $\sim 84\%$. We cannot exclude a modest presence of F, replacing the OH-groups; F content was not analysed (Table 1). Due to the similar neutron scattering length of O and F (Sears, 1986), and the expected small amount of F (Table 1), no attempt to refine the fraction of F at the $O6$ site was possible. The $H1$ and $M1$ sites are mutually exclusive, as their distance is ~ 1.51 Å. As a matter of fact, the refined occupancy factor of the $M1$ site is 29(2)% (neutron data, Table 4). The thermal displacement of the H sites is described here anisotropically. The geometry of the two hydroxyl groups and their hydrogen bonding at 20 K is well defined: the $O6-H1$ and $O6-H2$ bond distances corrected for “riding motion” (Busing and Levy, 1964) are ~ 0.965 and ~ 1.001 Å, respectively (Table 7). The $O6-H1$ vector points toward the $M1$ site at an angle of $15.6(3)^\circ$ above the (001) plane (Table 7). This configuration is similar to those observed in pure di-octahedral micas (e.g. Brigatti and Guggenheim, 2002; Ferraris and Ivaldi, 2002; Gatta *et al.*, 2011a and references therein), though with a more pronounced value of the $H1 \angle (001)$ angle. In contrast, the $O6-H2$ vector describes an angle of $74.8(4)^\circ$ above the (001) plane (Table 7), with a configuration similar to that observed in pure tri-octahedral micas (i.e. with the orientation of the O–H vector nearly perpendicular to (001); Brigatti and Guggenheim, 2002; Ferraris and Ivaldi, 2002; Gatta *et al.*, 2011b and references therein), though with a less pronounced value of the $H2 \angle (001)$ angle (Table 7). The $O6-H1$ group forms three significantly weak hydrogen bonds (*sensu* Gilli and Gilli, 2009) to the oxygens $O1$, $O2$ and $O4$ (with $H1 \cdots O1 = 2.547(4)$, $H1 \cdots O2 = 2.544(4)$ and $H1 \cdots O4 = 2.372(5)$ Å, Table 7). The $O6-H1 \cdots O$ angles are all similar in value ($\sim 136^\circ$, Table 7). The configuration of the tri-furcated hydrogen-bonding scheme is shown in Fig. 1. The H-bonding scheme of the $O6-H2$ group appears to be less obvious. The $O6-H2 \cdots O$ angles suggest one energetically favourable H-bond, with $O4$ as acceptor (with $H2 \cdots O4 = 2.289(10)$ Å, $O6-H2 \cdots O4 = 141.9(6)^\circ$). However, two further H-bonds are possible with $O3$ and $O5$ as acceptors

CRYSTAL CHEMISTRY OF $\text{Li}_x\text{Be-MICA}$ TABLE 8. Relevant bond distances ($\text{\AA}$) and angles ($^\circ$) based on the neutron structure refinement in the space group Cc .

<i>Ca-O3</i>	2.393(6)	<i>M1-O1</i>	2.11(3)	<i>O6-H1</i>	0.911(11)	<i>O6-H2</i>	0.908(10)
<i>Ca-O4</i>	2.456(5)	<i>M1-O2</i>	2.19(3)	<i>O6-H1*</i>	0.9423	<i>O6-H2*</i>	0.9511
<i>Ca-O5</i>	2.416(5)	<i>M1-O6</i>	2.12(3)	<i>O6...O1</i>	3.305(3)	<i>O6...O3</i>	3.022(3)
<i>Ca-O33</i>	2.401(6)	<i>M1-O11</i>	2.27(3)	<i>H1...O1</i>	2.589(11)	<i>H2...O3</i>	2.490(9)
<i>Ca-O44</i>	2.460(5)	<i>M1-O22</i>	2.20(3)	<i>O6-H1...O1</i>	136.0(9)	<i>O6-H...O3</i>	117.8(7)
<i>Ca-O55</i>	2.426(5)	<i>M1-O66</i>	2.07(3)				
				<i>O6-H1</i>	0.911(11)	<i>O6-H2</i>	0.908(10)
<i>M2-O1</i>	1.868(4)	<i>M3-O1</i>	1.852(5)	<i>O6-H1*</i>	0.9423	<i>O6-H2*</i>	0.9511
<i>M2-O2</i>	1.925(5)	<i>M3-O2</i>	1.947(5)	<i>O6...O2</i>	3.273(3)	<i>O6...O4</i>	3.098(3)
<i>M2-O6</i>	1.896(5)	<i>M3-O6</i>	1.888(5)	<i>H1...O2</i>	2.544(11)	<i>H2...O4</i>	2.322(10)
<i>M2-O11</i>	1.933(5)	<i>M3-O11</i>	1.952(5)	<i>O6-H1...O2</i>	137.4(9)	<i>O6-H...O4</i>	143.2(8)
<i>M2-O22</i>	1.865(5)	<i>M3-O22</i>	1.863(5)				
<i>M2-O66</i>	1.892(5)	<i>M3-O66</i>	1.895(5)	<i>O6-H1</i>	0.911(11)	<i>O6-H2</i>	0.908(10)
				<i>O6-H1*</i>	0.9423	<i>O6-H2*</i>	0.9511
<i>T1-O1</i>	1.707(4)	<i>T2-O11</i>	1.637(4)	<i>O6...O4</i>	3.098(3)	<i>O6...O5</i>	3.050(3)
<i>T1-O3</i>	1.736(4)	<i>T2-O33</i>	1.622(4)	<i>H1...O4</i>	2.375(11)	<i>H2...O5</i>	2.530(10)
<i>T1-O4</i>	1.732(4)	<i>T2-O44</i>	1.624(4)	<i>O6-H...O4</i>	136.3(9)	<i>O6-H...O5</i>	116.8(7)
<i>T1-O5</i>	1.734(4)	<i>T2-O55</i>	1.629(4)				
				<i>O66-H3</i>	0.967(11)	<i>O66-H4'</i>	0.938(14)
<i>T3-O2</i>	1.632(4)	<i>T4-O22</i>	1.718(4)	<i>O66-H3*</i>	0.9882	<i>O66-H4'*</i>	0.9591
<i>T3-O3</i>	1.621(4)	<i>T4-O33</i>	1.738(4)	<i>O66...O11</i>	3.270(4)	<i>O66...O11</i>	3.270(4)
<i>T3-O4</i>	1.630(4)	<i>T4-O44</i>	1.723(4)	<i>H3...O11</i>	2.472(11)	<i>H4'...O11</i>	2.611(13)
<i>T3-O5</i>	1.629(4)	<i>T4-O55</i>	1.726(4)	<i>O66-H...O11</i>	139.7(8)	<i>O66-H4...O11</i>	127.8(9)
α_1	21.4(6)	<i>M1-H1</i>	1.53(3)				
α_2	21.5(6)	<i>M1-H2</i>	2.42(3)	<i>O66-H3</i>	0.967(11)	<i>O66-H4'</i>	0.938(14)
		<i>M1-H3</i>	1.33(3)	<i>O66-H3*</i>	0.9882	<i>O66-H4'*</i>	0.9591
		<i>M1-H4</i>	1.78(3)	<i>O66...O22</i>	3.290(3)	<i>O66...O22</i>	3.290(3)
		<i>H1-H2</i>	0.89(1)	<i>H3...O22</i>	2.512(11)	<i>H4'...O22</i>	2.653(11)
		<i>H3-H4'</i>	0.47(2)	<i>O66-H...O22</i>	137.5(8)	<i>O66-H4'...O22</i>	125.8(9)
		<i>H1</i> $\angle$ (001)	8.0(7)	<i>O66-H3</i>	0.967(11)	<i>O66-H4'</i>	0.938(14)
		<i>H2</i> $\angle$ (001)	74.6(6)	<i>O66-H3*</i>	0.9882	<i>O66-H4'*</i>	0.9591
		<i>H3</i> $\angle$ (001)	3.7(8)	<i>O66...O44</i>	3.096(3)	<i>O66...O44</i>	3.096(3)
		<i>H4'</i> $\angle$ (001)	32.0(5)	<i>H3...O44</i>	2.501(13)	<i>H4'...O44</i>	2.211(15)
				<i>O66-H...O44</i>	119.7(8)	<i>O66-H4...O44</i>	157(1)
		<i>H4''</i> $\angle$ (001)	~ 89.8			<i>O66-H4''</i>	~ 0.95
						<i>O66...O33</i>	~ 3.02
						<i>H4''...O33</i>	~ 2.41
						<i>O66-H4''...O33</i>	~ 122
						<i>O66...O44</i>	~ 3.10
						<i>H4''...O44</i>	~ 2.38
						<i>O66-H4''...O44</i>	~ 133
						<i>O66...O55</i>	~ 3.05
						<i>H4''...O55</i>	~ 2.45
						<i>O66-H4''...O55</i>	~ 121

 α is the tetrahedral rotation angle (Brigatti and Guggenheim, 2002).

* Bond distances corrected for "riding motion" effect (Busing and Levy, 1964).

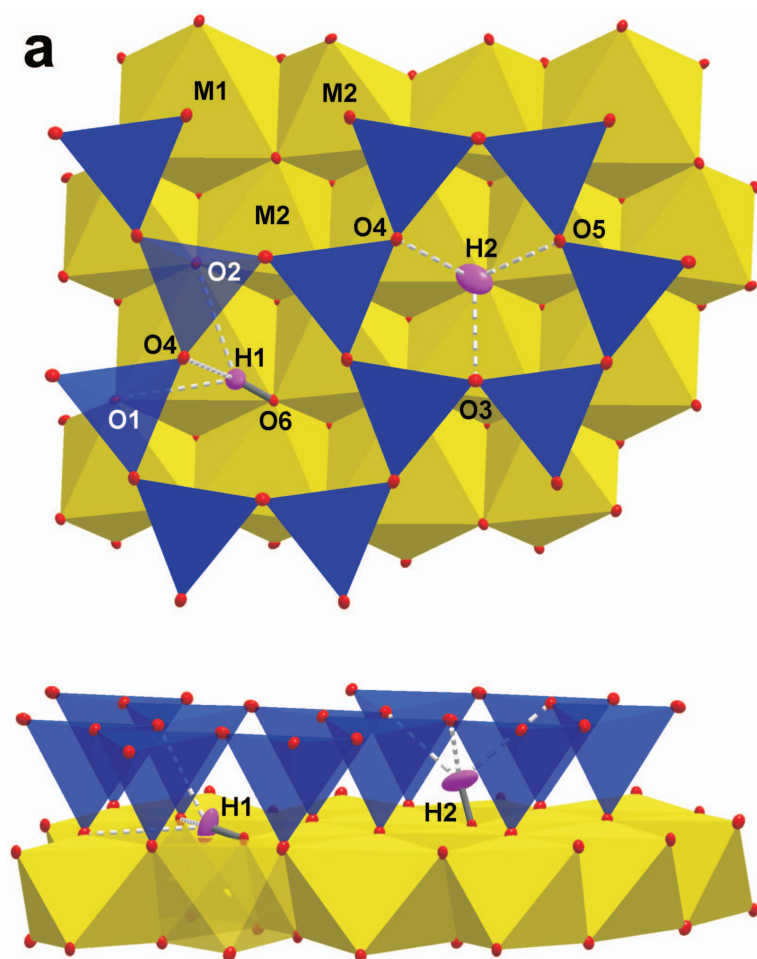
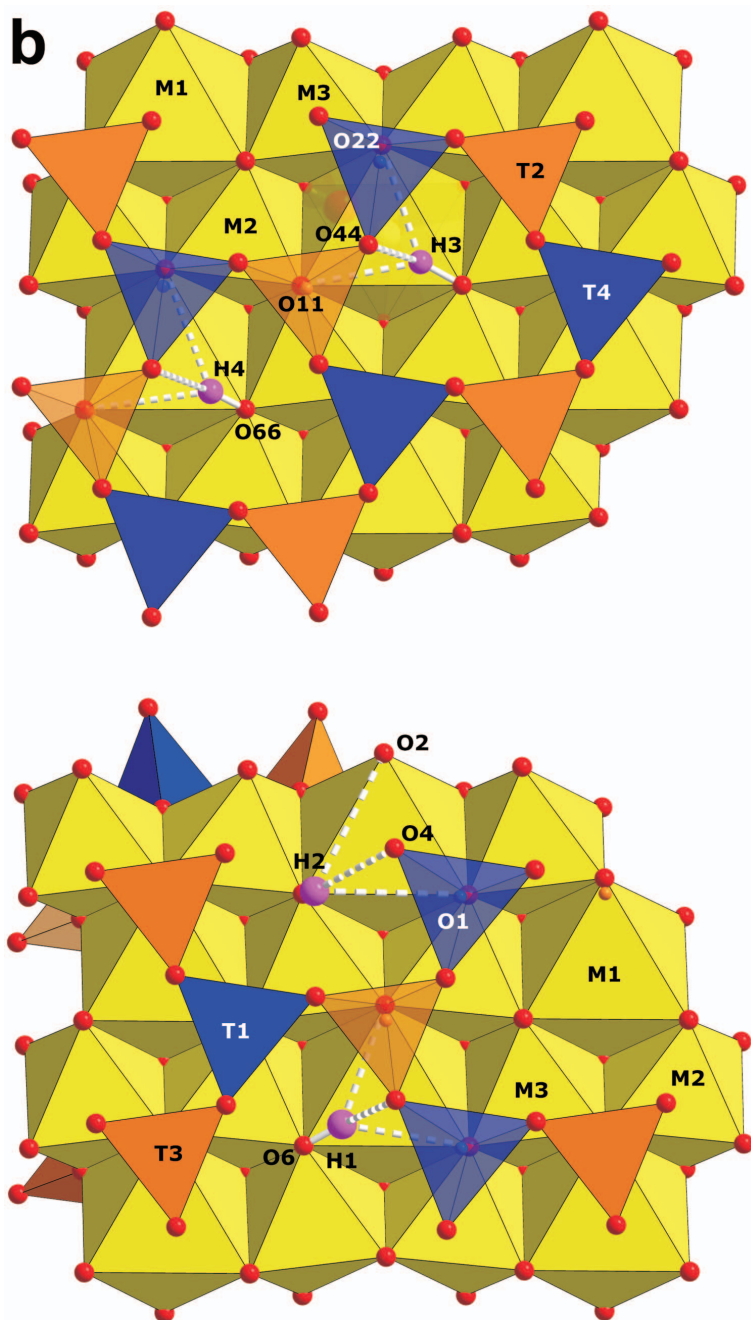


FIG. 1. Views of the structure of the Li,Be-bearing mica based on the neutron structure refinement (at 20 K): (a) in the $C2/c$ space group; and (b (facing page)) in the Cc space group. The hydrogen bonding scheme of the mutually exclusive H sites (i.e. $H1$ and $H2$, $H3$ and $H4$) is shown.

(with $H2 \cdots O3 = 2.463(8) \text{ \AA}$, $O6-H2 \cdots O3 = 116.7(5)^\circ$, $H2 \cdots O5 = 2.505(10) \text{ \AA}$, $O6-H2 \cdots O5 = 116.4(5)^\circ$, Table 7). The tri-furcated configuration of the hydrogen-bonding scheme of $H2$ is shown in Fig. 1.

More complex is the configuration of the hydroxyl groups deduced on the basis of the neutron structure refinement in the space group Cc . The difference-Fourier map of the nuclear density map (phased without the H sites) showed evidence of a partially disordered distribution of the proton sites, leading to a more complex scenario than that expected with only four independent H sites. However, the refinement

converges with four independent H sites with partial site occupancy (here labelled $H1$, $H2$, $H3$ and $H4'$, Tables 2 and 4). In this case, the couple $H1$ and $H2$ (both bound to $O6$) resembles a configuration similar to that described for the refinement in the centrosymmetric space group: the $O6-H1$ vector points toward the $M1$ site at an angle of $8.0(7)^\circ$ above the (001) plane, whereas the $O6-H2$ vector forms an angle of $74.6(6)^\circ$ with (001) (Table 8, Fig. 1). In contrast, the couple $H3$ and $H4'$ (both bound to $O66$) shows a different configuration: the $O66-H3$ vector points toward the $M1$ site at an angle of $3.7(8)^\circ$ above the (001) plane and the $O66-H4'$ vector describe an angle



of $32.0(5)^\circ$ with (001) (Table 8, Fig. 1). The orientation of the $O66-H4'$ vector appears to be unusual if we consider the known configurations in dioctahedral or trioctahedral micas. Apparently, there is no reason to expect a

different orientation of the OH-groups. Locally, the different nature of the cation at the Ca site can play a different role in the proton-cation repulsion. We tend to consider the unusual configuration of the $O66-H4'$ vector as the

result of a positional disorder, which hinders the actual, and unambiguous, location of the $H4'$ site. In fact, an inspection of the difference-Fourier map shows a broad distribution of the nuclear density around the coordinates of $H4'$, along with a further minimum close to $H4'$, here labelled as $H4''$ (its coordinates are listed in Table 4). The co-presence of $H4'$ and $H4''$ made the refinement unstable, and so the $H4''$ site (with a weaker intensity in the nuclear density map) was not considered.

Each of the four independent proton sites (i.e. $H1$, $H2$, $H3$ and $H4'$) forms tri-furcated hydrogen-bonds as described in Table 8 and shown in Fig. 1. Briefly: $O1$, $O2$ and $O4$ act as acceptors of the bonds promoted by $H1$; $O3$, $O4$ and $O5$ act as acceptors of the bonds promoted by $H2$; $O11$, $O22$ and $O44$ are bonded to the mutually exclusive $H3$ and $H4'$ sites (Table 8, Fig. 1). Even though the refinement does not converge with both the $H4'$ and $H4''$, we have calculated the orientation of the $O66-H4''$ vector and its potential H-bonding scheme (Table 8). Its orientation resembles that usually found in trioctahedral micas (i.e. with $H4'' \angle (001) \sim 89.8^\circ$), along with a tri-furcated H-bonding scheme (Table 8).

Li,Be-mica: centric or acentric structure?

In the previous studies on brittle micas, the choice of space group was driven mainly by the ordering of the tetrahedral sites. Margarite- $2M_1$ structure, for example, was first refined in the space group $C2/c$ with a disordered (Si,Al)-distribution (Takéuchi, 1965), and later in the space group Cc with an almost fully ordered (Si,Al)-tetrahedral population (Joswig *et al.*, 1983). The clintonite- $1M$ structure was conventionally refined in space group $C2/m$ due to its excess Al (with a resulting violation of Loewenstein's avoidance rule; Joswig *et al.*, 1986; Gatta *et al.*, 2012). For their Li,Be-rich brittle mica (bityite), Lin and Guggenheim (1983) performed two comparative refinements in the acentric and centrosymmetric space groups. The authors reported the results of both the refinements, and this reflects the difficulty to provide a unique answer about the presence of the inversion centre. However, Lin and Guggenheim (1983) were inclined to consider the Cc space group as more likely, and the statistic parameters of the refinements support their conclusions.

The chemical composition of the Li,Be-mica from Piemonte used by Lin and Guggenheim

(1983) differs significantly from that of the mica used in this study. In particular, the Li content (0.55 a.p.f.u., located entirely at the $M1$ site) suggests that the nature of the Li,Be-mica from Piemonte is closer to trioctahedral than that of our mica (in which 0.29 a.p.f.u. of Li occurs entirely at the $M1$ site, Table 1). As a consequence, the Be content is also significantly different (0.16 a.p.f.u. in our mica, 0.64 a.p.f.u. in the mica from Piemonte). If the ordering of Be at the tetrahedral sites governs the space group (i.e. centric vs. acentric), it is even more difficult to assign the actual space group to our Li,Be-mica from the Harding pegmatite. However, if we consider the statistic parameters of the structure refinements and the reasonable agreement between the refined population at the tetrahedral sites and that obtained by the chemical analysis [i.e. neutron refinement in space group Cc : ${}^T(\text{Al}_{1.88}\text{Be}_{0.12}\text{Si}_{2.00})_{\Sigma 4.00}$ p.f.u., Table 4; ICP-AES analysis: $(\text{Al}_{1.73}\text{Be}_{0.16}\text{Si}_{2.11})_{\Sigma 4.00}$, Table 1], we are inclined to consider the acentric space group as more likely. The main contradictory evidence to the Cc space group is the statistical distribution of the normalized structure factors, which suggests an average centric structure, and the partial disordering at the H sites in the acentric structure. They both tend to suggest the $C2/c$ space group as more likely.

Acknowledgements

The authors thank the Institute Laue-Langevin, Grenoble (France), for the allocation of beam time. This project was funded by the Italian MIUR grant n. 2008SPZ743. The sample of bityite used in this study was kindly provided by F. Pezzotta – Museo di Storia Naturale, Milano. P. Williams, S. Krivovichev and two anonymous reviewers are thanked.

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