American Mineralogist, Volume 63, pages 332–336, 1978

The crystal structure of a 3*T* lepidolite

BRUCE E. BROWN

Department of Geological Sciences, University of Wisconsin
Milwaukee, Wisconsin 53201

Abstract

A 3*T* lepidolite with composition near $K_2(Al_{2.5}R_{0.2}Li_{3.2})(Si_7Al)O_{20}(F_3OH)$, $a = 5.200$, $c = 29.76$A, space group $P3_112$, has been refined from diffractometer data using least-squares methods. Octahedral cations are ordered on three sites: *M*1 has $(Li_{0.7}Al_{0.3})$, *M*2 has $(Li_{0.9}Al_{0.1})$, and *M*3 has $(Li_{0.1}Al_{0.9})$. *M*1 is the *trans* octahedron. Significant bond-length differences also indicate tetrahedral ordering for the two independent tetrahedra. *T*1 has $(Al_{0.2}Si_{0.8})$, and *T*2 has Si only. The σ and Δ values of 7.7° and 0.36A due to tetrahedral rotation conform to the empirical relation of McCauley and Newnham (1971).

Introduction

The lepidolite micas have proved an interesting group for structural study, embodying, as they do, a number of stacking variations and ordering arrangements. These variations have helped to clarify structural relationships which are important to the mica group as a whole. This report summarizes a crystal-structure investigation of a lepidolite having a 3*T* stacking arrangement and a composition well within the polylithionite range. Malcolm Ross of the U.S. Geological Survey kindly provided this sample, U.S. National Museum specimen R4365, which is one of Stevens' (1938) samples from Coolgardie, Australia.

Content and symmetry of the unit cell

The composition of this mica as derived from Stevens' (1938, Table 1, anal. 14) analysis is: $(K_{1.69}Na_{0.22}Rb_{0.10})$ $(Al_{2.50}Mn_{0.18}Fe_{0.03}Mg_{0.02}Ti_{0.01}Li_{3.23})$ $(Si_{6.96}Al_{1.04})O_{20}[(OH)_{0.87}F_{3.07}]$. This allocation assumes the sum of the valences of all cations except hydrogen will be 44. The composition in terms of polylithionite, trilithionite, muscovite end members (Foster, 1960, p. 116) places this lepidolite closest to the polylithionite end member, with a relative ratio PL 84.8, TL 12.7, MS 2.5.

Symmetry and cell dimensions were determined on 0.5mm squares cut with a wire saw from the high-quality 0.1mm thick mica sheet. This mica is uniaxial, which suggests that the symmetry is trigonal or hexagonal. Zero and first-level *c*-axis precession photographs are identical at intervals of 120° around the dial axis and show the trigonal nature of the mica. Precession photographs of levels perpendicular to the trigonal (*c*) axis (a^*a^*) show sixfold symmetry on the zero level and threefold symmetry on upper levels. The *a* axes are chosen to be the 5.2A axes, consistent with the practice of Güven and Burnham (1967) in 3*T* muscovite. The a^*a^* zero and upper-level precession photographs show $2/m$ symmetry to be associated with the ⟨21.0⟩ directions. Reflections of type $00l$ with $l \neq 3n$ are systematically absent and indicate the presence of a threefold screw axis parallel to *c*. The above observations lead to a diffraction symbol of $\bar{3}mP3_1$ with the twofold axes normal to *a*, giving possible space groups $P3_112$ and $P3_212$. The existence of reflections with indices simultaneously following the rules $(h - k) = 0$ and $(k + l) \neq 0$ plus the agreement between calculated and observed structure factors along the $(10l)$ row indicates that the crystals are not twinned (Güven and Burnham, 1967).

The cell dimensions as measured from precession photographs are $a = 5.205$, $c = 29.77$A. Cell dimensions determined on the single-crystal diffractometer by least-squares methods are $a = 5.200\text{A} \pm 0.005$ and $c = 29.76\text{A} \pm 0.01$.

Experimental

Data for the refinement were recorded using monochromatized Mo$K\alpha$ radiation on a Picker single-crystal diffractometer. The data set consisted initially of 3400 observed and unobserved reflections. This triply and doubly redundant set was reduced to 705 nonequivalent reflections through the symmetry relationships in Laue group $\bar{3}$ ($\bar{3}$ was used rather than $\bar{3}m$) and

0003-004X/78/0304-0332$02.00

Table 1. Positional parameters, isotropic thermal parameters, and multiplier parameters for 3*T* lepidolite. The space group is $P3_112$, and the origin is on 3_112. Potassium is the fixed atom in this acentric structure. Standard deviations derived from the last refinement cycle are in parenthesis and refer to the last decimal place. The Wyckoff notation is in the parenthesis following each atom identifying symbol.

Atom	x	y	z	B	Mult.*
K(b)	0.1111	0.8889	5/6	1.92(4)	0.481(3)**
M1(a)	0.421(4)	0.579(4)	1/3	1.7(3)	0.28(1)**
M2(a)	0.779(3)	0.221(3)	1/3	0.03(20)	0.23(1)**
M3(a)	0.121(2)	0.879(2)	1/3	0.52(5)	0.571(5)**
T1(c)	0.7867(8)	0.2127(7)	0.0890(1)	0.23(5)	0.94(1)
T2(c)	0.4572(8)	0.5555(8)	0.0903(1)	1.59(8)	0.98(1)
Oa(c)	0.777(2)	0.172(2)	0.0349(3)	0.6(1)	1
Ob(c)	0.446(2)	0.571(2)	0.0356(3)	0.9(2)	1
OH(c)	0.090(2)	0.864(2)	0.0333(3)	0.43(9)	1
Oc(c)	0.654(2)	0.874(2)	0.1116(2)	1.4(1)	1
Od(c)	0.120(3)	0.426(2)	0.1076(2)	1.7(1)	1
Oe(c)	0.583(2)	0.350(2)	0.1121(3)	2.2(2)	1

*Mult. = multiplier refers to the scaling of the scattering factor. For the M atoms a composite factor $Li_{1/3}Al_{2/3}$ was used. Non composite factors for K, Si, and O were used for the other atoms.
**The interlayer cation and the octahedral cation are special positions and "half atoms" were used to compensate for the symmetry multiplication by ORFLS.

by omission of unobserved reflections. All indices were transformed to either *hkl* or *hkl* and a card deck printed. Most reflections were represented by three data cards, some by two. From this card deck the following data were calculated: (1) *Fo* values using Lorentz polarization corrections; no absorption corrections were included, (2) an average *Fo* for each reflection, (3) a standard deviation for each *Fo*, derived from the multiple observations of each reflection.[1] This standard deviation was used in the weighting of the least-squares data.

Preliminary coordinates were derived from the refined structure of lithian fluorphlogopite (Takeda and Donnay, 1966), using a transformation matrix to convert the monoclinic lithian fluorphlogopite coordinates to the trigonal lepidolite coordinates. After transformation the origin was translated to 3_112. The atom designation for the Coolgardie 3*T* lepidolite follows that used by Güven and Burnham (1967) in their refinement of a 3*T* muscovite, except that the octahedral cations are designated by *M* and renumbered so that *M*(1) is the *trans* octahedron and *M*(2) and *M*(3) are *cis* octahedra.

The scattering factors were derived from Berghuis *et al.* (1955). A "mixed atom" factor consisting of 1/3 Li and 2/3 Al was used in the octahedral position. During the refinement the octahedral, tetrahedral, and interlayer cation scattering factors were scaled by a modified ORFLS least-squares program to fit the actual atom population in a given site more precisely.

During the first five cycles of refinement the structure was refined in space group $P3_1$. The *R* value converged at 0.103, and it was apparent from the correlation matrix that atoms that would be related by the twofold axis in $P3_112$ were not behaving independently. Hence refinement was continued in space group $P3_112$, and the *R* value reached 0.106 within a few cycles. A large improvement in *R* came as the result of the introduction of the weighting factors based on the standard deviations computed during the reduction of symmetry-equivalent data. (Note that we could have reduced the number of data further than was done, since the refinement was completed in space group $P3_112$ instead of $P3_1$. However, the doubly redundant data consisting of 705 reflections were used for the complete refinement.)

The *R* value reduced to 0.047 after 16 cycles. The final parameters from this cycle are in Table 1. Bond distances and errors were computed from these data using ORFFE, and are listed in Tables 2 and 3. The computer programs used in this study were from the library of the crystallographic programs used by the crystallographic group of the Department of Chemistry at the University of Wisconsin, Madison, under the supervision of L. F. Dahl.

Discussion

Octahedral ordering

The average octahedral cation-to-oxygen bond lengths are significantly different for each of the three

[1] To obtain a copy of these data, order Document AM-78-068 from the Business Office, Mineralogical Society of America, 1909 K Street, NW, Washington, DC 20006. Please remit $1.00 in advance for the microfiche.

Table 2. Octahedral bond lengths and angles.

Atom	Distance	Angle(°) at metal atom(s)	Atom	Distance	Angle(°) at metal atom(s)	Atom	Distance	Angle(°) at metal atom(s)
				METAL-OXYGEN				
M1-Oa	2.300(8)		M2-Oa	2.150(9)		M3-Oa	1.805(8)	
-Ob	1.852(9)		-Ob	2.097(11)		-Ob	1.929(8)	
-OH	1.956(8)		-OH	2.093(9)		-OH	2.026(9)	
Mean	2.036(5)		Mean	2.113(6)		Mean	1.920(5)	
				OXYGEN-OXYGEN				
				Unshared Edges				
		M1			M2			M3
Oa-Ob(2x)	3.031(12)	93.1(6)	Oa-Ob(2x)	3.292(12)	101.5(6)	Oa-Ob(2x)	2.711(10)	93.2(6)
Oa-OH(2x)	3.121(12)	94.0(6)	Oa-OH(2x)	3.100(12)	93.9(6)	Oa-OH(2x)	2.797(12)	93.6(6)
Ob-OH(2x)	2.928(15)	100.4(6)	Ob-OH(2x)	3.185(12)	98.9(6)	Ob-OH(2x)	2.905	94.5(6)
Mean	3.027	95.8	Mean	3.192	98.1	Mean	2.804	93.8
				Shared Edges				
		M1 M2			M2 M3			M1 M3
Oa-Oa	3.063(8)	83.5(5), 90.9(5)	Oa-Obx2	2.663(8)	77.7(6), 91.0(6)	Oa-OHx2	2.528(11)	72.4(6), 82.4(6)
Ob-OHx2	2.744(12)	92.1(6), 81.8(6)	OH-OH	2.733(14)	81.5(6), 84.8(6)	Ob-Ob	2.644(9)	91.1(5), 86.5(5)
Mean	2.851	89.2 84.8	Mean	2.686	79.0 88.9	Mean	2.567	78.6 83.8

crystallographically independent octahedra in this structure: $M(1) = 2.037(5)$, $M(2) = 2.099(6)$, $M(3) = 1.919(5)$. The octahedral composition is from Stevens' (1938) analysis: $(Al_{2.50}Li_{3.23}Mn_{0.18}Fe_{0.03}Mg_{0.02}Ti_{0.01})$ or hereafter $(Al_{2.50}Li_{3.23}R_{0.24})$.

The bond lengths for Li–(O,F), Al–(O,F), and R–(O,F) with O/F of 0.74/0.26, as calculated from Shannon and Prewitt (1969), are 2.100, 1.887, and 2.18A. The ordering pattern derived from these bond lengths (Table 3) can be compared with the ordering pattern derived from the scattering-factor refinements done on each octahedra by the least-squares program. The scattering factor data and the bond-length data agree reasonably well. Octahedral $M1$ and $M3$ bond-length populations are within two standard deviations of the same populations as determined by scattering-factor refinement. The $M2$ population differs by more than this but may be rationalized by including R (mainly Mn) cations in this site. The distributions derived from bond lengths are: $M(1) = Li_{0.70}Al_{0.30}$, $M(2) = Li_{1.0}Al_0$, $M(3) = Li_{0.15}Al_{0.85}$, and from scattering factors are: $M(1) = Li_{0.73}Al_{0.27}$, $M(2) = Li_{0.92}R_{0.08}$, and $M(3) = Li_{0.21}Al_{0.79}$. The three octahedra can be considered as having two lithium-rich positions ($M1$ and $M2$) and one aluminum-rich position, $M3$.

Table 3. Bond lengths and angles for the tetrahedral layer and the interlayer.

Atoms	Distance	Atoms	Distance	Angle at atom	α (°)
T1-Oa	1.62(1)	Oa-Oc	2.65(1)	106.9(4)	
-Oc	1.68(1)	-Od	2.69(1)	112.5(3)	
-Od	1.62(1)	-Oe	2.84(2)	118.2(5)	
-Oe	1.69(1)	Oc-Od	2.68(2)	108.7(2)	
Mean	1.652(8)	-Oe	2.68(2)	105.3(4)	
		Od-Oe	2.62(2)	104.8(5)	
		Mean	2.694(9)	109.4	
T2-Ob	1.63(1)	Ob-Oc	2.66(1)	111.7(6)	
-Oc	1.58(1)	-Od	2.60(2)	106.3(6)	
-Od	1.62(1)	-Oe	2.80(1)	117.5(6)	
-Oe	1.64(1)	Oc-Od	2.58(2)	108.0(5)	
Mean	1.617(8)	-Oe	2.56(2)	105.3(4)	
		Od-Oe	2.63(2)	107.8(5)	
		Mean	2.638(9)	109.4	
K-Oc(2x)	3.300(8)	K-Oc(2x)	2.856(7)		
-Od(2x)	3.281(8)	-Od(2x)	3.001(8)		
-Oe(2x)	3.215(10)	-Oe(2x)	2.920(9)		
Mean	3.265(5)	Mean	2.926(5)		
Od-Oc-Oe				104.5(3)	7.75
Oe-Oc-Od				135.5(3)	7.75
Mean					7.75
Oe-Od-Oc				104.0(3)	8.00
Oc-Od-Oe				135.8(3)	7.90
Mean					7.93
Oc-Oe-Od				134.3(4)	7.15
Od-Oe-Oc				105.3(3)	7.35
Mean					7.25
Overall Mean					7.65

The three octahedra in $3T$ muscovite (Güven and Burnham, 1967) are likewise all different (Al-rich, Al–R, and vacant). This may imply that similar mica structures in which the symmetry allows only two independent octahedra [*i.e.*, $2M_2$ lepidolite, (Sartori *et al.*, 1973), fluor-polylithionite (Takeda and Burnham, 1969)] are in fact showing pseudosymmetry. The mirror planes in these and other structures may be relating octahedra which are not in fact identical. Pseudosymmetry is well known in layer-silicate structures (Bailey, 1975).

Table 4. Comparison of the octahedral distributions of 3*T* lepidolite and muscovite, $2M_2$ lepidolite, and fluorpolylithionite.

Octahedron	3T Lepidolite	3T Muscovite**	Fluorpoly-lithionite†	2M2 Lepidolite Elba††	2M2 Lepidolite Rozna§
M1	$Li_{70}Al_{30}$	--	$Li_{89}Al_{11}$	$Li_{95}Al_{05}$	$Li_{35}Al_{10}$
M2	$Li_{89}R_{11}$	$Al_{83}R_{17}$	$Li_{55}Al_{45}$*	$Li_{37}Al_{63}$*	$Li_{35}Al_{65}$*
M3	$Li_{14}Al_{86}$	Al_{100}	$Li_{55}Al_{45}$	$Li_{37}Al_{63}$	$Li_{35}Al_{65}$

*Symmetrically equivalent as refined
**Data of Guven and Burnham (1967)
†Data of Takeda and Burnham (1969)
††Data of Sartori et al. (1973)
§Data of Takeda et al. (1971)

The ordering pattern may be, in part, charge-controlled. The aluminum-rich $M(3)$ cation averages 3.67A from the tetrahedral cations, the lithium-rich $M(2)$ cation averages 3.2A from the tetrahedral cations, and the intermediate $M(1)$ cation averages 3.48A from the tetrahedral cations. As noted by Bailey (1975), in most octahedral ordering patterns in micas with monoclinic symmetry, the *trans* octahedral cation (on the symmetry plane of the layer) is generally larger than the *cis* octahedral cation (related by the symmetry plane of the layer). In this 3*T* lepidolite the smaller of the two larger octahedra is in the *trans* position. The largest and smallest octahedra $M(2)$ and $M(3)$ are in *cis* arrangement.

A comparison of octahedral distributions for several micas is found in Table 4. Octahedral ordering patterns are distinctly different between the 3*T* and $2M_2$ varieties of lepidolite.

Ordering and distortions in the tetrahedral sheet and interlayer sites

The $P3_112$ space group symmetry of 3*T* lepidolite allows two independent tetrahedra. The average *T*–O bond lengths are significantly different in the two tetrahedra, and aluminum–silicon ordering is indicated. The tetrahedral bond lengths suggested for layer silicates by Smith and Bailey (1963) of Si–O = 1.62 and Al–O = 1.77A lead to cation contents of $(Al_{0.22}Si_{0.78})$ for $T(1)$ and $(Si_{1.0})$ for $T(2)$. The tetrahedral bond length relation determined by Hazen and Burnham (1973) for layer silicates leads to cation contents somewhat higher in aluminum; $(Al_{0.27}Si_{0.73})$ for $T(1)$ and $(Al_{0.06}Si_{0.94})$ for $T(2)$. These populations are in reasonable agreement with the allocation from the chemical analysis, which suggests a tetrahedral population of $(AlSi_7)$. As with other layer silicates in which tetrahedral ordering has been observed, these tetrahedra alternate around the pseudohexagonal ring. This observation of Si/Al tetrahedral ordering contrasts with the results from the Rozna (Takeda *et al.*, 1971) and Elba (Sartori *et al.*, 1973) $2M_2$ lepidolites, where very little tetrahedral ordering is indicated from the bond-length data.

The observed tetrahedral rotation angle, α, is 7.7° (Table 3), and this fits well with the empirical relation derived by McCauley and Newnham (1971), $\alpha(°) = 218.0\ (b_t/b_o) - 1.5$ (field strength) $- 221.5$, relating the α angle to the chemical analytical data. An α of 8.3° is calculated from the chemical formula by the McCauley and Newnham relationship. Similarly the Δ value obtained from observed K–O distances fits the McCauley and Newnham relationship of $\Delta = (0.47\text{A/degree}) \times \alpha$. The observed Δ of $3.268 - 2.927 = 0.34$A can be related to a calculated Δ of $(0.47) \times 7.7° = 0.36$A.

This mica, as in other fluorine-rich micas, has a low (layer thickness)/*b* ratio, or it is "flattened." For instance, the $d(003)/b$ ratio in 3*T* muscovite is 1.11, whereas this ratio in 3*T* lepidolite is 1.100. The Elba (Takeda *et al.*, 1971) and Rozna (Sartori *et al.*, 1973) lepidolites are similar to 3*T* lepidolite with $d(002)/b$ ratios of 1.102 and 1.099 respectively.

The basal oxygen sheet is slightly corrugated. The average level of this sheet is at $Z/c = -0.1104$. Oc and Oe are below this level (toward the potassium atom) by 0.0012(0.036A) and 0.0017(0.051A) respectively. Od is above this level by 0.0028(0.083A). Three standard deviations of the Z/c coordinates equal between 0.0006 and 0.0009, or from 0.02A–0.03A, suggesting that this departure from a plane is real. The Od atoms at $Z/c = -0.1076$ are arranged in rows parallel to [010]. Oc and Oe atoms form somewhat zig-zag lines also parallel to [010]. Since the Od row is "high" by 0.08A and the Oc, Oe row is "low" by 0.04A, we can look upon the effect as a corrugation. Corrugation of this sort is also found in lepidolite $2M_2$ (Sartori *et al.*, 1973) and also in all dioctahedral micas.

Acknowledgments

The author is indebted to A. A. Khan, University of Illinois, Chicago Circle, for help in collecting the diffractometer data; to W.

Baur of that institution for graciously providing time on the diffractometer; to L. F. Dahl and research associates of the Chemistry Department of the University of Wisconsin, Madison, for use of and help with computer programs; and to S. W. Bailey, Department of Geology and Geophysics, University of Wisconsin-Madison, for critical review of the manuscript. This work was supported by NSF grant GA-432.

References

Bailey, S. W. (1975) Cation ordering and pseudosymmetry in layer silicates. *Am. Mineral., 60,* 175–187.

Berghuis, J., I. J. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry and A. L. Veenendaal (1955) New calculations of atomic scattering factors. *Acta Crystallogr., 8,* 478–483.

Foster, M. D. (1960) Interpretation of the composition of lithium micas. *U.S. Geol. Prof. Paper, 354-E,* 115.

Güven, N. and C. W. Burnham (1967) The crystal structure of 3*T* muscovite. *Z. Kristallogr., 125,* 163–183.

Hazen, R. M. and C. W. Burnham (1973) The crystal structures of one-layer phlogopite and annite. *Am. Mineral., 58,* 889–900.

McCauley, J. W. and R. E. Newnham (1971) Origin and prediction of ditrigonal distortions in micas. *Am. Mineral., 56,* 1626–1637.

Sartori, F., M. Franzini and S. Merlino (1973) Crystal structure of a $2M_2$ lepidolite. *Acta Crystallogr., B29,* 573–578.

Shannon, R. D. and C. T. Prewitt (1969) Effective ionic radii in oxides and fluorides. *Acta Crystallogr., B25,* 925–946.

Smith, J. V. and S. W. Bailey (1963) Second review of Al–O and Si–O tetrahedral distances. *Acta Crystallogr., 16,* 801–810.

Stevens, R. E. (1938) New analyses of lepidolites and their interpretation. *Am. Mineral., 23,* 607–628.

Takeda, H. and C. W. Burnham (1969) Fluor-polylithionite: a lithium mica with nearly hexagonal $(Si_2O_5)^{2-}$ ring. *Mineral. J., 6,* 102–109.

——— and J. D. H. Donnay (1966) Trioctahedral one-layer micas. III. Crystal structure of a synthetic lithium fluormica. *Acta Crystallogr., 20,* 638–646.

———, N. Haga and R. Sadanaga (1977) Structural investigation of polymorphic transition between $2M_2$, 1*M*-lepidolite + $2M_1$-muscovite. *Mineral. J., 6,* 203–215.

Manuscript received April 25, 1977; accepted for publication October 14, 1977.