

CU-BEARING ELBAITE FROM PARAIBA, BRAZIL

(DATA FROM ERTL ET AL. 2002: POLYHEDRON DISTORTIONS IN TOURMALINE. CAN. MINERAL., 40, 153-163)

EXPERIMENTAL

A bright blue single crystal of copper-bearing tourmaline from Paraíba, Brazil, was ground to a sphere of approximately 180 μm diameter. The crystal was mounted on an Enraf-Nonius CAD4 single-crystal diffractometer, and the unit cell (Table 1) was determined from least-squares refinement of the setting angles of 25 reflections, each measured in four positions. Intensity data were collected using the parameters in Table 1, and absorption was corrected using ψ -scans measured on six reflections.

The structure was refined using the SHELXTL (v. 6.10) package of programs, with parameters listed in Table 1. The H atom associated with O3 (H3) was easily located in the difference map, and subsequently refined. No H atom was found near O1. To obviate any effects of refining too large a portion of the total scattering at one time, a two-step refinement procedure was undertaken. Initially, Al_Z, B_B, O1-O8 and H3 were constrained to fully occupy their respective sites; the X site was modeled with Na scattering factors and the Y site was modeled with Al scattering factors, both with unconstrained multiplicity. Occupancy of the T site was modeled with Si and B scattering factors, with the assumption that (Si + B) = 1. Using these initial occupancy values, optimization of occupancies by the method of Wright et al. (2000) was undertaken. In subsequent refinements, X, Y, and Z multiplicities were fixed at the optimized values while the T site multiplicity was allowed to refine as above. Such a procedure honors the total chemistry, site-valence and site-scattering in determination of multiplicity values of the constrained sites. In retrospect, such a cautious approach was not necessary as changes in the refined values were insignificant.

Table 2 contains the atom coordinates and equivalent-isotropic displacement parameters for the atoms, and Table 3 gives selected bond-lengths. Observed and calculated structure factors (Table 4) may be obtained from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

Chemical analysis

The crystal used for the structure refinement was analyzed with a wavelength-dispersive ARL SEMQ electron microprobe (EMP) at the Naturhistorisches Museum Wien, Austria (Table 5).

Accelerating voltage was 15 kV, beam current 20 nA, and spot size 2 μm . Natural silicates, oxides, and elements (native copper) were used as standards, and data were corrected with the method of Bence & Albee (1968). Fluorine was determined by F-ion sensitive electrodes on a bulk sample from which the structure crystal was obtained.

B_2O_3 was calculated as $\text{B} + \text{Si} = 9$ by assuming that there is no $^{[4]}\text{Al}$ in the crystal structure; this assumption is supported by the structure refinement (Table 3), and also the $\langle T\text{-O} \rangle$ distance of 1.6187 Å (Table 3) which is permissive of the presence of $^{[4]}\text{B}$. MacDonald & Hawthorne (1995a) observed similar or even smaller $\langle T\text{-O} \rangle$ bond lengths of 1.617 Å and 1.616 Å in elbaïtes with 0.81 and 0.38 wt.% CuO from the same locality. The ideal $\langle T\text{-O} \rangle$ bond length (T site fully occupied with Si) has been determined to be *ca.* 1.620 Å by different structure studies (MacDonald & Hawthorne 1995b, Bloodaxe *et al.* 1999, Ertl *et al.* 2001). H_2O was calculated as $(\text{OH}) + \text{F} = 4$ [although Dyar *et al.* (1998) showed that it is possible to have a maximum of *ca.* 0.4 O^{2-} instead of OH^- at the W site in Al- and Li-rich tourmalines]. Li_2O was calculated as difference to 100% (instead of $\text{Li} = 3 - \sum Y$) because Ertl *et al.* (1997) and Hughes *et al.* (2000) showed vacancies > 0.2 *pfu* to occur at the Y site of Al-rich, Li-bearing tourmaline (olenite); all calculations were iterated to self-consistency. MacDonald & Hawthorne (1995a) reported totals of 98.14 and 98.77 wt.% on two Cu-bearing tourmalines; the main difference is due to the calculation of B_2O_3 . All Mn was assumed to be trivalent, and all Cu was assumed to be divalent on the basis of spectroscopic data (Henn & Bank 1990, Rossman *et al.* 1991).

TABLE 1. CRYSTAL DATA AND RESULTS OF STRUCTURE REFINEMENT FOR
COPPER-BEARING TOURMALINE

Unit cell			
Least squares (space group: $R3m$)			
a (Å)	15.8308(32)	c	7.0957(8)
θ limit	1.0 - 30.0°	Scan type	$\omega/2\theta$
Scan time(s)	≤ 65 s		
Orientation stds.	3/300 reflections	Intensity stds.	3 per 4 hrs
Data collected	3091, $+h, \pm k, \pm l$	R_{merge}	0.014
Unique data	1099	Variables	93
Data $> 4\sigma_I$	869		
Goodness-of-fit:	1.131		
$R1$	0.016	$wR2$	0.041
Largest peaks on difference map ($e/\text{Å}^3$)			
(+)	0.63	(-)	0.26

Note: Numbers in parentheses denote one ESD of least units cited.

TABLE 2. POSITIONAL PARAMETERS AND EQUIVALENT ISOTROPIC U VALUES
FOR ATOMS IN COPPER-BEARING TOURMALINE

Atom	x	y	z	<i>Occ</i>	<i>U_{eq}</i>
X	0	0	$\frac{1}{4}$	Na _{0.733}	0.0229(4)
T	0.19196(2)	0.18983(2)	0.0157(3)	Si _{0.958(4)} B _{0.042}	0.0050(1)
B	0.10908(7)	$2x$	0.4702(4)	B _{1.00}	0.0077(3)
Y	0.12346(5)	$1/2x$	-0.3510(3)	Al _{0.777}	0.0092(1)
Z	0.29691(3)	0.26008(3)	-0.3748(3)	Al _{0.989}	0.00683(9)
O1	0	0	-0.2036(5)	O _{1.00}	0.0322(7)
O2	0.06024(5)	$2x$	0.5052(4)	O _{1.00}	0.0158(3)
O3	0.26533(12)	$1/2x$	-0.4770(4)	O _{1.00}	0.0141(3)
O4	0.09375(5)	$2x$	0.0884(4)	O _{1.00}	0.0105(3)
O5	0.18718(11)	$1/2x$	0.1116(4)	O _{1.00}	0.0110(3)
O6	0.19557(6)	0.18483(7)	-0.2102(3)	O _{1.00}	0.0092(2)
O7	0.28659(7)	0.28620(6)	0.0939(3)	O _{1.00}	0.0082(2)
O8	0.20944(7)	0.26984(7)	0.4544(3)	O _{1.00}	0.0092(2)
H3*	0.263(2)	$1/2x$	-0.589(5)	O _{1.00}	0.025(8)

*H3 was refined isotropically.

The column labeled *Occ* (occupancy) denotes the element whose scattering factors were used to determine the electron occupancy of the site.

TABLE 3. SELECTED INTERATOMIC DISTANCES IN COPPER-BEARING TOURMALINE

Site		Distance	Site		Distance
X-	O2(x3)	2.4513(22)	T-	O6	1.6078(11)
	O5(x3)	2.7476(17)		O7	1.6105(9)
	O4(x3)	2.8148(17)		O4	1.6208(6)
Mean		2.6712	O5	1.6355(7)	
			Mean		1.6187
B-	O2	1.3621(24)	Y-	O2(x2)	1.9590(11)
	O8(x2)	1.3806(14)		O6(x2)	1.9683(11)
Mean		1.3744	O1	1.9897(18)	
			O3	2.1405(18)	
			Mean		1.9975
Z-	O6	1.8562(10)			
	O7	1.8814(10)			
	O8	1.8845(10)			
	O8	1.9037(10)			
	O7	1.9424(10)			
	O3	1.9585(8)			
Mean		1.9045			

TABLE 5. CHEMICAL COMPOSITION AND UNIT FORMULA OF BLUE CU-BEARING
TOURMALINE FROM PARAÍBA, BRAZIL.

	Cu-tourmaline ¹	Cu-tourmaline ²
SiO ₂ wt. %	37.16(36)	36.54
TiO ₂	0.01(1)	---
B ₂ O ₃	12.15 ³	12.03
Al ₂ O ₃	41.34(40)	40.97
Cr ₂ O ₃	0.00(0)	---
FeO	0.01(1)	---
Mn ₂ O ₃	0.40(7)	0.52
CuO	0.94(8)	1.09
MgO	0.01(1)	---
CaO	0.40(8)	0.63
Li ₂ O	1.85 ⁴	1.88
Na ₂ O	1.72(8)	1.77
K ₂ O	0.04(1)	---
F	0.90(7) ⁵	0.79
H ₂ O	3.45 ⁶	3.45
O=F	-0.38	-0.33
Sum	100.00	100.00
	31	31
n		
Si <i>apfu</i>	5.753	5.739
^[4] B	0.246	0.261
Sum T site	5.999	6.000
^[3] B	3.000	3.000
Al	7.542	7.582
Mg	0.002	---
Mn ³⁺	0.047	0.062
Ti	0.001	---
Fe ²⁺	0.001	---
Cu ²⁺	0.110	0.130
Li	1.151	1.190
Sum Y, Z sites	8.854	8.964
Ca	0.066	0.106
Na	0.516	0.540
K	0.007	---
Sum X site	0.589	0.646
Sum cations	18.442	18.610
H	3.562	3.61
F	0.441	0.39
Sum OH + F	4.003	4.00

Note: ¹ Average of 10 EMP analyses (estimated standard deviation in parentheses). ² Wt. percent calculated from optimal site occupancies and normalized to 100%. A component is not considered significant unless its value exceeds the uncertainty. ³ B₂O₃ calculated as B + Si = 9. ⁴ Li₂O calculated by difference to 100%. ⁵ Fluorine was determined by F-ion sensitive electrodes. ⁶ H₂O calculated as (OH) + F = 4. All calculations were iterated to self-consistency.