Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BR1075). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Cu-Bearing Tourmaline from Paraiba, Brazil

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Abstract

Crystal structure refinement of copper-bearing tourmaline from Paraiba, Brazil, rim composition $\{Na_{0.54}Ca_{0.05}\}\{Li_{1.21}Mn_{0.04}Cu_{0.10}Al_{1.66}\}Al_6\{Si_{5.92}Al_{0.08}\}O_{18}\{BO_3\}_3\{(OH)_{3.56}F_{0.44}\}$, core composition $\{Na_{0.55}Ca_{0.01}\}\{Li_{1.16}Mn_{0.08}Cu_{0.05}Al_{1.71}\}Al_6\{Si_{5.88}Al_{0.12}\}O_{18}\{BO_3\}_3\{(OH)_{3.70}F_{0.30}\}$, shows the octahedrally coordinated Z site to be completely occupied by Al, and Li to occur only at the octahedrally coordinated

Y site. The high displacement factors at the O1 and O2 positions indicate significant positional disorder that is induced by occupancy of the X [$\simeq 0.57Na + 0.43\square$ (vacancy)] and Y [$\simeq 1.2Li + 1.8(Al + Mn^{3+})$] sites by cations of very different size and charge.

Comment

Bank, Henn, Bank, von Platen & Hofmeister (1990) reported the occurrence of Cu-rich tourmaline from the state of Paraiba, Brazil. Their samples were Mn-rich elbaite containing up to 2.1 wt% CuO and 0.11 wt% FeO, and are thus unusual in that Cu had only been reported previously in the p.p.m. range in tourmaline (Bassett, 1953; Power, 1968). Henn & Bank (1990) and Rossman, Fritsch & Shigley (1991) examined the colouration mechanisms in Cu-bearing tourmaline, and showed that Cu is solely responsible for the blue colour. Optical-absorption maxima in the 695–940 nm region were assigned to d–d transitions in Cu^{2+}, and maxima at 700 and 520 nm are due to d–d transitions in Mn^{3+}.

Two specimens were studied in the present work; a sample from the rim (T54) and a sample from the core (T55). Site occupancies were refined in the following manner. The X and Y sites contain more than two scattering species [(Na, Ca, vacancy) and (Li, Mn, Cu, Al), respectively]; hence, the chemical site occupancies cannot be refined directly. However, the total scattering at each of these sites may be derived from the refinement and then compared with the chemical species assigned to these sites from the chemical analysis and calculation of the formula unit. The scattering at the X, Y and Z sites was considered as variable and represented by a single scattering species: X = Na, Y = Mg and Z = Al. The occupancies at the Z sites refined to within one standard deviation (0.004) of unity; these values were fixed at 1.0 for the final cycles of refinement. The occupancy of the X site refined to 0.65 (2) Na for both crystals. When the scattering from the minor Ca at the X site is considered, there is reasonably good agreement between the refined scattering and the chemical species assigned to the X site from the chemical analyses. The occupancy at the Y site refined to 0.822 (6) and 0.831 (6) Mg for T54 and T55, respectively. This gives an effective Y-site scattering of 9.86 and 9.97 equivalent electrons per site for T54 and T55, respectively, and can be compared with an effective scattering of 9.70 and 9.72 equivalent electrons calculated from the site assignments from the unit formulae. Thus there is close agreement between the results of the site-occupancy refinement and the site assignments for the unit formulae calculated from the chemical analyses.

There is significant positional disorder at the O1 and O2 positions in Cu-bearing tourmaline, as indicated by the relatively high U_{eq} values at the O1 and O2 positions. This is a common feature in many tourmaline structures, and Burns, MacDonald & Hawthorne (1994)

have proposed that it is due to local positional disorder induced by occupancy of the X and Y sites by cations of very different size and charge. The occupancies derived here (Table 3), $X \simeq 0.57Na + 0.43\square$ (vacancy) and $Y \simeq 1.2Li + 1.8(Al + Mn^{3+})$, are in accord with this mechanism.

Experimental
Compound T54
Crystal data

$\{Na_{0.54}Ca_{0.05}\}\{Li_{1.21}Mn_{0.04}-$
$Cu_{0.10}Al_{1.66}\}Al_6\{Si_{5.92}-$
$Al_{0.08}\}O_{18}\{BO_3\}_3-$
$\{(OH)_{3.56}F_{0.44}\}$
$M_r = 940.16$
Rhombohedral
$R3m$
$a = 15.818$ (2)
$c = 7.087$ (1)
$V = 1535.8$ (4) $Å^3$
$Z = 3$
$D_x = 3.070$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 40 reflections
$\theta = 3-14°$
$\mu = 1.07$ mm^{-1}
$T = 297$ K
Trigonal prism
0.24 mm (radius)
Bright blue
Crystal source:
Paraiba, Brazil

Data collection

Nicolet $R3m$ diffractometer
$\theta-2\theta$ scans
Absorption correction:
spherical
$T_{min} = 0.711$, $T_{max} = 0.727$
1122 measured reflections
1122 independent reflections
1114 observed reflections
$[I > 2.5\sigma(I)]$

$\theta_{max} = 30°$
$h = 0 \rightarrow 19$
$k = 0 \rightarrow 19$
$l = -11 \rightarrow 11$
2 standard reflections
monitored every 48 reflections
intensity decay: 1.5%

Refinement

Refinement on F
$R = 0.022$
$wR = 0.025$
$S = 1.2$
1114 reflections
92 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.00061F^2]$
$(\Delta/\sigma)_{max} = 0.04$

$\Delta\rho_{max} = 0.18$ e $Å^{-3}$
$\Delta\rho_{min} = -0.20$ e $Å^{-3}$
Extinction correction:
isotropic (empirical)
Extinction coefficient:
0.0015 (2) [form given in *SHELXTL/PC User's Manual* (Sheldrick, 1990)]
Atomic scattering factors from Cromer & Mann (1968)

Compound T55
Crystal data

$\{Na_{0.55}Ca_{0.01}\}\{Li_{1.16}Mn_{0.08}-$
$Cu_{0.05}Al_{1.71}\}Al_6\{Si_{5.88}-$
$Al_{0.12}\}O_{18}\{BO_3\}_3-$
$\{(OH)_{3.70}F_{0.30}\}$
$M_r = 938.15$
Rhombohedral
$R3m$
$a = 15.805$ (2)
$c = 7.084$ (1)

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 40 reflections
$\theta = 3-15°$
$\mu = 1.04$ mm^{-1}
$T = 297$ K
Trigonal prism
0.22 mm (radius)

$V = 1532.6$ (5) $Å^3$
$Z = 3$
$D_x = 3.064$ Mg m^{-3}

Pale blue
Crystal source:
Paraiba, Brazil

Data collection

Nicolet $R3m$ diffractometer
$\theta-2\theta$ scans
Absorption correction:
spherical
$T_{min} = 0.716$, $T_{max} = 0.767$
1122 measured reflections
1122 independent reflections
1122 observed reflections
$[I > 2.5\sigma(I)]$

$\theta_{max} = 30°$
$h = 0 \rightarrow 19$
$k = 0 \rightarrow 19$
$l = -11 \rightarrow 11$
2 standard reflections
monitored every 48 reflections
intensity decay: 1.5%

Refinement

Refinement on F
$R = 0.020$
$wR = 0.023$
$S = 1.4$
1112 reflections
92 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.00058F^2]$
$(\Delta/\sigma)_{max} = 0.04$

$\Delta\rho_{max} = 0.18$ e $Å^{-3}$
$\Delta\rho_{min} = -0.18$ e $Å^{-3}$
Extinction correction:
isotropic (empirical)
Extinction coefficient:
0.0006 (2) [form given in *SHELXTL/PC User's Manual* (Sheldrick, 1990)]
Atomic scattering factors from Cromer & Mann (1968)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* ($Å^2$)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	Site	x	y	z	U_{eq}
T54					
X†	3(a)	0	0	0.8408	0.0274 (9)
Y‡	9(b)	0.06155 (4)	0.93845 (4)	0.4396 (4)	0.0060 (3)
Z§	18(c)	0.26003 (4)	0.29690 (3)	0.4643 (4)	0.0052 (2)
Si	18(c)	0.18989 (3)	0.19191 (3)	0.0736 (4)	0.0056 (2)
B	9(b)	0.89061 (9)	0.10939 (9)	0.6187 (5)	0.0068 (7)
O1	3(a)	0	0	0.2946 (7)	0.0288 (1)
O2	9(b)	0.93945 (7)	0.06055 (7)	0.5838 (5)	0.0136 (5)
O3	9(b)	0.13203 (8)	0.86797 (8)	0.5666 (5)	0.0135 (5)
O4	9(b)	0.90603 (7)	0.09397 (7)	0.0009 (5)	0.0097 (5)
O5	9(b)	0.09363 (7)	0.90637 (7)	−0.0231 (5)	0.0103 (5)
O6	18(c)	0.1846 (1)	0.1954 (1)	0.2993 (5)	0.0088 (4)
O7	18(c)	0.28637 (8)	0.2865 (1)	−0.0045 (4)	0.0072 (4)
O8	18(c)	0.2699 (1)	0.2094 (1)	0.6348 (4)	0.0082 (4)
T55					
X†	3(a)	0	0	0.8408	0.0272 (10)
Y‡	9(b)	0.06106 (4)	0.93894 (4)	0.4393 (5)	0.0058 (3)
Z§	18(c)	0.25994 (4)	0.29674 (3)	0.4650 (4)	0.0056 (2)
Si	18(c)	0.18977 (3)	0.19175 (3)	0.0737 (5)	0.0055 (2)
B	9(b)	0.89073 (9)	0.10927 (9)	0.6197 (6)	0.0069 (7)
O1	3(a)	0	0	0.2965 (7)	0.0255 (9)
O2	9(b)	0.93938 (7)	0.06062 (7)	0.5833 (5)	0.0139 (6)
O3	9(b)	0.13148 (8)	0.86852 (8)	0.5670 (6)	0.0131 (5)
O4	9(b)	0.90567 (7)	0.09433 (7)	0.0008 (5)	0.0089 (5)
O5	9(b)	0.09369 (7)	0.90631 (7)	−0.0228 (5)	0.0097 (5)
O6	18(c)	0.1847 (1)	0.1950 (1)	0.2996 (5)	0.0088 (4)
O7	18(c)	0.28641 (8)	0.2865 (1)	−0.0040 (5)	0.0078 (4)
O8	18(c)	0.2703 (1)	0.2095 (1)	0.6355 (5)	0.0082 (4)

† Site occupancy = 0.57 Na.
‡ Site occupancy = 0.4 Li + 0.6 (Al + Mn).
§ Site occupancy = 1.0 Al.

Table 2. Selected geometric parameters (Å, °)

		T54	T55
X—O2	× 3	2.464 (3)	2.466 (3)
X—O4	× 3	2.814 (2)	2.820 (1)
X—O5	× 3	2.741 (1)	2.741 (1)
<X—O>		2.673	2.675
Y—O3		2.131 (2)	2.130 (2)
Y—O1		1.975 (3)	1.954 (3)
Y—O2	× 2	1.960 (3)	1.953 (3)
Y—O6	× 2	1.964 (3)	1.965 (3)
<Y—O>		1.992	1.987
Z—O6		1.858 (3)	1.861 (3)
Z—O8		1.902 (3)	1.901 (3)
Z—O3		1.960 (2)	1.961 (2)
Z—O7		1.943 (2)	1.942 (3)
Z—O7		1.877 (3)	1.876 (4)
Z—O8		1.884 (3)	1.880 (3)
<Z—O>		1.904	1.903
Si—O6		1.604 (4)	1.605 (5)
Si—O7		1.609 (2)	1.610 (2)
Si—O4		1.618 (2)	1.616 (2)
Si—O5		1.638 (2)	1.635 (3)
<Si—O>		1.617	1.616
B—O2		1.361 (1)	1.357 (1)
B—O8	× 2	1.374 (2)	1.377 (2)
<B—O>		1.370	1.370

Table 3. Electron-microprobe analysis (wt%) and unit formulae of Cu-bearing tourmalines

Li_2O, B_2O_3, H_2O were estimated by stoichiometry; Ti, V, Cr, Fe, Zn, Mg and K were not detected.

	T54	T55
SiO_2	37.15	37.20
Al_2O_3	41.20	41.97
B_2O_3	10.91	10.99
Mn_2O_3	0.30	0.69
CaO	0.28	0.08
CuO	0.81	0.38
Li_2O	1.88	1.83
Na_2O	1.75	1.78
F	0.88	0.60
H_2O	3.35	3.51
O=F	−0.37	−0.25
Total	98.14	98.77
Na	0.541	0.546
Ca	0.048	0.014
ΣX	0.589	0.560
Li	1.211	1.164
Mn	0.036	0.083
Cu	0.097	0.045
Al	1.656	1.708
ΣY	3.000	3.000

Al	6.000	6.000
ΣZ	6.000	6.000
Si	5.919	5.884
Al	0.081	0.116
ΣSi	6.000	6.000
OH	3.557	3.700
F	0.443	0.300
ΣOH	4.000	4.000

The crystals used for the collection of the X-ray intensity data were analyzed on a CAMECA SX-50 electron microprobe in wavelength-dispersion mode according to the method of Burns *et al.* (1994). Analytical data are given in Table 3; structural formulae were calculated on the basis of 31 anions, assuming stoichiometric amounts of H_2O (as OH), B_2O_3 (as BO_3) and Li_2O (as Li). The amount of Li assigned to the Y site was equal to the ideal sum of the Y site minus the amount of other cations occupying the site (Li = 3 − ΣY) and the calculation was iterated to self-consistency. 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). Observed bond lengths are consistent with these assumptions.

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