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Rossmanite, $\square(LiAl_2)Al_6(Si_6O_{18})(BO_3)_3(OH)_4$, a new alkali-deficient tourmaline: Description and crystal structure

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ABSTRACT

Rossmanite is a new tourmaline species from near Rožná, western Moravia, Czech Republic. It forms pale pink columnar crystals about 25 mm long and 5 mm thick, elongated along *c* with striations parallel to *c* on the prism faces. It is brittle, $H = 7$, $D_{meas} = 3.00$ g/cm^3, $D_{calc} = 3.06$ g/cm^3. In plane-polarized light, it is colorless. Rossmanite is uniaxial negative, $\omega = 1.645(1)$, $\epsilon = 1.624(1)$, trigonal, space group $R3m$, in the hexagonal setting $a = 15.770(2)$, $c = 7.085(1)$ Å, $V = 1525.8(4)$ Å^3, $Z = 3$. The strongest six X-ray diffraction lines in the powder pattern are at $d = 3.950$ Å with $I = 100\%$ for $(hkl) = (220)$; 2.552 Å, 93%, (051); 1.898 Å, 72%, (342); 4.181 Å, 58%, (211); 2.924 Å, 56%, (122); and 3.434 Å, 53%, (012). Analysis by a combination of electron microprobe, SIMS, H-line extraction, and crystal-structure refinement gave SiO_2 38.10 wt%, Al_2O_3 44.60, Na_2O 1.43, $Li_2O = 1.13$, $B_2O_3 = 10.88$, $H_2O = 3.70$, F = 0.20, O ≡ F 0.08, sum = 99.96 wt%, Fe, Mg, Ca, Mn, Ti, F, K not detected. The formula unit (31 anions) is $^X(\square_{0.57}Na_{0.43})^Y(Li_{0.71}Al_{2.17})^ZAl_6(Si_{5.92}O_{18})(B_{2.92}O_9)(OH)_{3.83}F_{0.10}O_{0.07}$, with the ideal end-member formula $\square(LiAl_2)Al_6(Si_6O_{18})(BO_3)_3(OH)_4$; thus rossmanite can be derived from elbaite $[Na(Al_{1.5}Li_{1.5})(Si_6O_{18})(BO_3)_3(OH)_4]$ by the substitution $^X\square_2 + {}^YAl \rightarrow {}^XNa_2 + {}^YLi$, where $\square$ = vacancy. The crystal structure of rossmanite was refined to an *R* index of 1.7% using 1094 observed (5σ) reflections collected with Mo*K*α X-radiation from a single crystal. The structure refinement confirmed the low occupancy of the X site and the presence of Li at the Y site. There is considerable positional disorder at the O1 and O2 sites induced by the local variations in bond-valence distribution associated with $\square$-Na disorder at X and Li-Al disorder at Y.

INTRODUCTION

The general formula of tourmaline may be written as $XY_3Z_6Si_6O_{18}(BO_3)_3W_4$ where X = Na, Ca, $\square$; Y = Mg, Fe^{2+}, Mn^{2+}, Al, Fe^{3+}, Mn^{3+}, Li; Z = Al, Fe^{3+}, Cr^{3+}, Mg; and W = OH, F, O^{2-}.

Extensive solid solution occurs among a wide variety of end-members. The X site is most commonly occupied by Na and/or Ca plus minor to accessory vacancies, although synthetic alkali-free and Ca-free tourmalines have been well-known for some time (Rosenberg and Foit 1979; Werding and Schreyer 1984). Recent work (Foit et al. 1989; MacDonald et al. 1993; Pezzotta et al. 1996; Orlandi and Pezzotta 1996; Aurisicchio and Pezzotta 1997; Lyckberg and Hawthorne 1997; Robert et al. 1997; Schreyer 1997; Selway et al. 1997; Velickov and Abs-Wurmbach 1997; Aurisicchio et al. 1997; Taylor et al. 1997; Dutrow and Henry 1997) has shown that tourmalines with dominant vacancy at the X site are relatively common. MacDonald et al. (1993) reported the first distinct X-site-vacant tourmaline species, foitite, ideally $\square(Fe^{2+}_2Al)Al_6(Si_6O_{18})(BO_3)_3(OH)_4$.

During a systematic examination of tourmalines from several Czech and Moravian pegmatites, we encountered another distinct alkali-deficient tourmaline. This has been approved as a new mineral by the International Mineralogical Association's Committee on New Minerals and Mineral Names. Rossmanite is named for George R. Rossman (born 1945), California Institute of Technology, Pasadena, California, in recognition of his work on the spectroscopy of the tourmaline minerals in particular and his wide-ranging contributions to mineralogy in general.

OCCURRENCE

Rossmanite was discovered in the Rožná lepidolite-subtype pegmatite in the northeastern part of the Strážek Moldanubicum, along the contact with the Svratka Unit (mica-schist zone) in the Czech Republic (Novák 1992; Černý et al. 1995; Novák and Selway 1997). The peg-

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TABLE 1. Chemical analysis and formula unit* for rossmanite

SiO_2	38.10	Si	Si	5.92
Al_2O_3	44.60	Z	Al	6.00
Na_2O	1.43	Y	Al	2.17
Li_2O	1.13		Li	0.71
B_2O_3	10.88	Sum	Y	2.88
H_2O	3.70	X	Na	0.43
F	0.20	B	B	2.92
O≡F	−0.08		OH	3.83
Sum	99.96		F	0.10
			O	0.07

* Calculated assuming 31 anions p.f.u.

matite is hosted dominantly by biotite gneiss with widespread intercalations of hornblende gneiss of the amphibolite facies. It is about 1 km long and about 35 m wide and is exposed on two hills, Hradisko and Borovina, which are separated by a fault. Rossmanite was identified from the Hradisko quarry; lepidolite was described from this locality as a new mineral species by Klaproth (1792). Rožná is a zoned pegmatite with the following textural-paragenetic units: (1) rare coarse-grained biotite-bearing wall zone; (2) abundant coarse-grained schorl-bearing intermediate zone, locally with blocks of (3) graphic unit and masses of (4) fine- to medium-grained granitic unit; (5) relatively rare blocky core-margin zone; (6) albite-lepidolite unit; (7) quartz core (Novák 1992; Černý et al. 1995; Novák and Selway 1997). The (6) albite-lepidolite unit can be divided into an outer albite sub-unit and an inner lepidolite sub-unit. Rossmanite occurs as euhedral pink columnar crystals enclosed in fine-grained purple lepidolite of the lepidolite sub-unit. In a hand sample, rossmanite is indistinguishable from the "rubellite" variety of elbaite that also occurs in the lepidolite sub-unit. The lepidolite sub-unit is dominated by lepidolite with abundant albite and pink, red, green, blue, and gray to colorless elbaite, with accessory apatite, topaz, beryl, amblygonite-montebrasite, manganocolumbite, and cassiterite.

PHYSICAL AND OPTICAL PROPERTIES

Rossmanite is pale pink, colorless in thin splinters, and has a vitreous luster; it has a white streak and shows no fluorescence under long-wave or short-wave ultraviolet light. It occurs as striated prisms up to 25 mm long and 5 mm thick, elongated along *c* with striations parallel to *c* on the prism faces. Rossmanite has a Mohs hardness of ~7, no cleavage, and is brittle. The density, measured by hydrostatic weighing in methylene iodide, is 3.00 g/cm^3, close to the calculated density of 3.06 g/cm^3.

In transmitted light, rossmanite is colorless. It is uniaxial negative with indices of refraction $\omega = 1.645(1)$, $\epsilon = 1.624(1)$ measured with gel-filtered Na light ($\lambda = 589.9$ nm).

CHEMICAL COMPOSITION

Rossmanite was analyzed by electron microprobe using a Cameca SX-50 operating in the wavelength-dispersion mode with the following conditions: excitation voltage 15 kV, beam current 20 nA, peak count time 20 s, and background count time 10 s. The following standards and crystals were used for $K\alpha$ X-ray lines: Si = diopside, PET; Al = kyanite, TAP; Mn = spessartine, LiF; Na = albite, TAP; F = fluor-riebeckite, TAP; in addition, Fe, Mg, Ca, Ti, K, were sought but not detected. Data reduction was done using the $\phi(\rho Z)$ procedure of Pouchou and Pichoir (1985). The crystal used for the collection of X-ray intensity data was analyzed by the electron microprobe at 14 different points. Lithium and B were analyzed by SIMS following the method of Ottolini and Hawthorne (unpublished manuscript). The H_2O content was analyzed by hydrogen-line extraction as described by Koehler et al. (1991). The average analysis is given in Table 1. The unit formula was calculated on the basis of 31 anions.

TABLE 2. Indexed powder pattern for rossmanite

I	d_{meas} Å	d_{calc} Å	*hkl*
28	7.925	7.900	110
33	6.314	6.294	101
29	4.931	4.921	021
58	4.181	4.176	211
100	3.950	3.947	220
52	3.434	3.431	012
24	3.345	3.344	131
11	3.080	3.079	401
22	2.985	2.984	410
56	2.924	2.923	122
14	2.589	2.590	312
93	2.552	2.551	051
10	2.362	2.363	003
29	2.321	2.321	511
10	2.164	2.165	502
12	2.141	2.142	431
12	2.097	2.098	303
13	2.026	2.028	223
34	2.019	2.019	152
9	2.000	2.000	161
72	1.898	1.898	342
9	1.852	1.853	413
9	1.832	1.832	621
9	1.758	1.758	104
25	1.641	1.64	063
16	1.626	1.626	271
12	1.487	1.488	054
17	1.437	1.437	514
10	1.405	1.405	651
16	1.392	1.392	633
12	1.343	1.342	1001
6	1.330	1.330	562
8	1.313	1.312	1001
14	1.298	1.298	1010
10	1.259	1.259	505
5	1.115	1.115	933
18	1.018	1.018	773

Note: a = 15.788(2) Å, c = 7.089(1) Å; V = 1530.5(2) Å^3.

TABLE 3. Unit-cell dimensions and data pertaining to crystal-structure refinement of rossmanite

a (Å)	15.770(2)	radiation	Mo$K\alpha$
c (Å)	7.085(1)	scan mode	ω-2θ
V (Å^3)	1525.9(4)	θ range	2-30°
Space group	*R*3*m*	Total |*F*|	1135
R (obs)	1.70%	|F_{obs}|	1094
R (all)	1.91%	*R*(az)	0.93%

TABLE 4. Final parameters for the crystal structure of rossmanite

Atom	x	y	z	U_{eq}*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
X	0	0	0.8408	222(13)	237(17)	237(17)	193(22)	0	0	$U_{11}/2$
Y	0.06084(3)	0.93916(3)	0.4373(6)	65(3)	51(3)	51(3)	79(4)	−12(1)	12(1)	14(3)
Z	0.25942(3)	0.29637(3)	0.4656(6)	54(2)	69(2)	46(2)	45(2)	−1(1)	−10(1)	29(2)
Si	0.18965(3)	0.19163(2)	0.0721(6)	46(1)	41(2)	45(2)	50(2)	2(1)	5(1)	21(1)
B	0.89078(8)	0.10922(8)	0.6198(7)	55(5)	53(4)	53(4)	51(7)	0(3)	0(3)	21(7)
O(1)	0	0	0.3015(7)	171(7)	216(8)	216(8)	82(10)	0	0	$U_{11}/2$
O(2)	0.93952(5)	0.06048(5)	0.5809(6)	109(4)	138(5)	138(5)	108(7)	1(2)	−1(2)	112(5)
O(3)	0.12998(6)	0.87002(6)	0.5647(6)	111(4)	95(4)	95(4)	65(6)	−11(3)	11(3)	−12(5)
O(4)	0.90516(5)	0.09484(5)	−0.0017(6)	87(4)	66(4)	66(4)	83(6)	3(2)	−3(2)	−1(5)
O(5)	0.09386(7)	0.90614(6)	−0.0229(6)	92(4)	75(4)	75(4)	77(6)	10(2)	−10(2)	−1(5)
O(6)	0.18346(7)	0.19363(7)	0.2988(6)	73(3)	81(4)	79(4)	51(4)	0(3)	3(3)	34(3)
O(7)	0.28630(6)	0.28694(7)	−0.0034(6)	64(3)	54(4)	62(4)	61(4)	−3(3)	14(3)	17(3)
O(8)	0.27035(7)	0.20965(7)	0.6359(6)	71(3)	87(4)	49(4)	79(4)	−9(3)	−31(3)	35(3)

* $U_{ij} = U_{ij} \times 10^4$.

TABLE 6. Selected interatomic distances (Å) and angles (°) in rossmanite

Si-O(4)a	1.614(2)	O(4)a-Si-O(5)b	105.6(2)
Si-O(5)b	1.627(3)	O(4)a-Si-O(6)	111.8(2)
Si-O(6)	1.610(6)	O(4)a-Si-O(7)c	109.2(2)
Si-O(7)c	1.605(2)	O(5)b-Si-O(6)	110.4(2)
⟨Si-O⟩	1.614	O(5)b-Si-O(7)c	109.0(2)
		O(6)-Si-O(7)c	110.6(2)
		⟨O-Si-O⟩	109.4
B-O(2)	1.359(1)	O(2)-B-O(8)d ×2	121.4(1)
B-O(8)a,d	1.377(2)	O(8)d-B-O(8)e	117.1(1)
⟨B-O⟩	1.371	⟨O-B-O⟩	120.0
Z-O(3)e	1.954(2)	O(3)e-Z-O(6)	81.4(1)
Z-O(6)	1.875(4)	O(3)e-Z-O(7)g	97.6(2)
Z-O(7)f	1.940(3)	O(3)e-Z-O(8)	91.0(2)
Z-O(7)g	1.882(4)	O(3)e-Z-O(8)g	97.4(1)
Z-O(8)	1.895(4)	O(6)-Z-O(7)f	92.9(2)
Z-O(8)g	1.880(4)	O(6)-Z-O(8)	91.5(1)
⟨Z-O⟩	1.904	O(6)-Z-O(8)g	95.3(2)
		O(7)f-Z-O(7)g	89.2(1)
		O(7)f-Z-O(8)	95.7(1)
		O(7)f-Z-O(8)g	76.5(1)
		O(7)g-Z-O(8)	77.5(2)
		O(7)g-Z-O(8)g	95.7(1)
		⟨O-Z-O⟩	90.2
Y-O(1)h	1.920(3)	O(1)h-Y-O(2)i,j	83.7(1)
Y-O(2)i,j	1.944(3)	O(1)-Y-O(6)e,k	100.6(2)
Y-O(3)	2.093(3)	O(2)i-Y-O(2)j	94.8(2)
Y-O(6)e,k	1.948(3)	O(2)i,j-Y-O(6)e,k	88.0(1)
⟨Y-O⟩	1.966	O(3)-Y-O(2)i,j	99.3(2)
		O(3)-Y-O(6)e,k	76.2(1)
		O(6)e-Y-O(6)k	89.1(2)
		⟨O-Y-O⟩	90
X-O(2)a,h,l	2.474(3)	O(2)a-X-O(2)h ×3	70.7(1)
X-O(4)m,n,o	2.820(2)	O(2)a-X-O(4)m ×6	126.9(1)
X-O(5)e,p,q	2.740(2)	O(2)a-X-O(4)o ×3	71.4(1)
⟨X-O⟩	2.678	O(2)a-X-O(5)e ×6	87.1(1)
		O(4)m-X-O(4)n ×3	105.4(1)
		O(4)m-X-O(5)e ×6	55.3(1)
		O(4)n-X-O(5)p ×3	136.1(1)
		O(5)e-X-O(5)p ×3	108.3(1)

Note: Equivalent positions are a: $-x + y, y, z$; b: $x, x - y, 1 + z$; c: $x, y, 1 + z$; d: $1 - y, 1 + x - y, z$; e: $x, x - y, z$; f: $\frac{1}{3} - y, \frac{2}{3} + x - y, \frac{2}{3} + z$; g: $\frac{2}{3} - x + y, 1 + \frac{1}{3} - x, \frac{1}{3} + z$; h: $1 - x + y, 1 - x, z$; i: $1 + x, 1 + x - y, z$; j: $-x + y, -x, z$; k: $1 - x + y, 1 - x, z$; l: $1 + x, 2 + x - y, z$; m: $1 + x, y, -1 + z$; n: $1 + x, 2 + x - y, -1 + z$; o: $-x + y, y, -1 + z$; p: $x, 1 + y, z$; q: $2 - x + y, 1 + y, z$.

X-RAY CRYSTALLOGRAPHY

The powder-diffraction pattern for a bulk sample was recorded on a Philips PW 1710 diffractometer with graphite-monochromatized Cu$K\alpha$ X-radiation. Peak positions were measured by fitting a five-point parabolic curve to the top of the diffraction peaks, followed by correction for α_1–α_2 splitting; NBS Si was used as a standard. Cell dimensions were refined from the corrected *d*-values using the program CELREF (Appleman and Evans 1973); the indexed powder-pattern and refined cell-dimensions are given in Table 2.

CRYSTAL STRUCTURE

A fragment of rossmanite was ground to a sphere and mounted on a Nicolet R3m four-circle diffractometer. Cell dimensions and intensity data were collected according to the experimental procedure of Hawthorne et al. (1993). Refined unit-cell dimensions and selected data pertaining to crystal-structure refinement are given in Table 3.

The structure refinement was initiated with the atomic coordinates of foitite (MacDonald et al. 1993) using the SHELXTL system of programs, and rapidly converged to an R index of ~1.8% for an anisotropic displacement model. The crystal used in the collection of the X-ray intensity data was subsequently analyzed by electron microprobe techniques (see above), and the most appropriate X-ray scattering factors were used at the final stages of refinement, which converged to an R index of 1.7% for 1094 observed (5σ) reflections. Final atomic parameters are given in Table 4, observed and calculated struc-

TABLE 7. Site-scattering values and site populations in rossmanite

Site	X-ray scattering (epfu)	EMPA (epfu)	Site-population (apfu)	Site-scattering (epfu)
X	5.0(1)	4.7	0.57 □ + 0.43 Na	4.7
Y	30.9(2)	30.3	2.17 Al + 0.83 Li	30.7
Z	78	78.0	6.00 Al	78

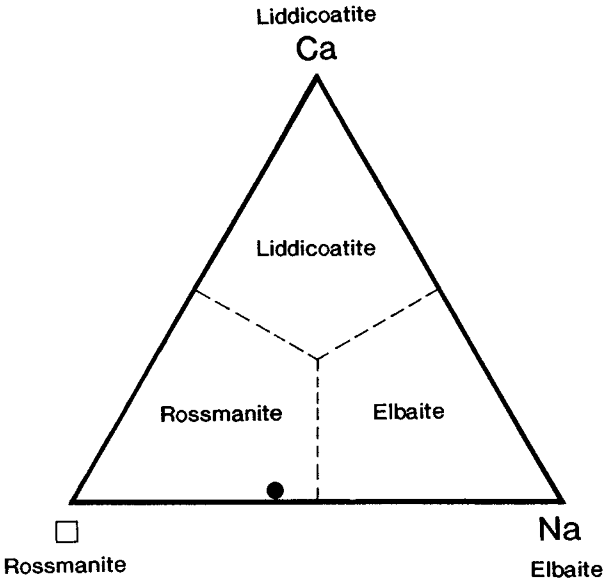

FIGURE 1. Lithium-aluminum tourmalines with different X-site compositions; the composition of rossmanite from Rožná is shown by a filled circle.

ture factors are listed in Table 5[1], selected interatomic distances and angles are given in Table 6, and the refined site-scattering values are given in Table 7.

DISCUSSION

Site-scattering refinement

The refined site-scattering value for the X-site cations (Table 7) closely agrees with that expected for the site contents indicated by the formula unit calculated from the chemical analysis (Table 1). This agreement confirms the low occupancy of the X site by Na, showing that a vacancy (□) is the dominant ''component'' at that site. The refined site-scattering values at the Y and Z sites (Table 7) also closely agree with the site populations assigned from the chemical analysis.

Anion disorder

The equivalent isotropic-displacement factor at the O1 site is much larger than those at the other anion positions (Table 4). This has been discussed in some detail by Burns et al. (1994), who attributed this feature in elbaitic tourmalines to perturbations associated with different local arrangements of cations coordinating this anion. A similar argument may be invoked here. The O1 anion is bonded to 3 Y cations and the O2 anion is bonded to 1 Y and 1 X cations; the Y cations may be Al or Li, and the X cations may be Na or □. The wide diversity of bond-valence arrangements induces significant positional disorder at these two positions as each anion locally adopts a position that satisfies its bond-valence requirements according to the specific local cation configuration to which it is coordinated.

Ideal formula of rossmanite

End-member rossmanite has the ideal formula $\square(LiAl_2)Al_6(Si_6O_{18})(BO_3)_3(OH)_4$, with the most novel characteristic being the vacant X-site. Rossmanite can be derived from elbaite $[Na(Al_{1.5}Li_{1.5})Al_6Si_6O_{18}(BO_3)_3(OH)_4]$, by the substitution ${}^X\square_2 + {}^YAl \rightarrow {}^XNa_2 + {}^YLi$, represented by the exchange vector ${}^X\square_2\,{}^YAl({}^XNa_2\,{}^YFe^{2+})_{-1}$. It is the X-site-vacant member of a family of Li-Al tourmalines (Fig. 1). As is apparent from Table 1 and Figure 1, rossmanite shows solid solution toward elbaite.

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[1] For a copy of Table 5, Document AM-98-014, contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. Deposit items may also be available on the American Mineralogist web site at http://www.minsocam.org.

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