

The structure of vanadium-bearing tourmaline and its implications regarding tourmaline solid solutions

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Abstract

The structure of an alkali cation-deficient, vanadium tourmaline has been refined ($R = 0.041$ for 2727 intensity data) in order to evaluate the effects of tourmaline composition on structural distortion. V-tourmaline, $(\text{Na}_{0.44}\text{Ca}_{0.36}\text{Mg}_{0.18}\text{K}_{0.02})(\text{Mg}_{1.87}\text{V}_{0.76}\text{Cr}_{0.19}\text{Fe}_{0.18}^{2+})\text{Al}_{5.56}\text{V}_{0.38}\text{Ti}_{0.06}^{4+}(\text{Si}_{5.63}\text{Al}_{0.37})(\text{B}_{2.98}\square_{0.02})\text{O}_{27}(\text{O}_{1.10}\text{OH}_{2.58}\text{F}_{0.32})$, is rhombohedral with $a = 15.967(2)$ and $c = 7.191(1)\text{Å}$; space group $R3m$. Despite compositional differences the structure is very similar to those of other members of the tourmaline group, most notably a recently refined aluminous dravite. Analysis of tourmaline-group structural data reveals (1) a negative correlation between tetrahedral bond angle variance and mean "alkali"(3a)-oxygen bond length; (2) negative correlations between both 9b and 18c octahedral angle variances and mean 9b-O bond length; (3) a negative correlation between ditrigonality and 9b octahedral angle variance; (4) a positive correlation between weighted mean octahedral bond length and cell volume; and (5) a positive correlation between Na occupancy in the 3a site and mean 3a-O bond length. These observations demonstrate a systematic flexibility of the structure in response to diverse cation substitution.

The lack of a distinct coupling between the sizes of the 9b and 18c octahedra in refined tourmaline structures and the extensive and possibly complete substitution of Al^{3+} in the 9b site in tourmalines suggest that the presence of cations that can vary in size (e.g., $\text{Fe}^{2+}, \text{Fe}^{3+}$) in order to create a compatible edge may not be a prerequisite for dravite-elbaite solid solution. In view of the structural flexibility of tourmaline and the ease of proton exchange to maintain charge balance, the apparent immiscibility of dravite and elbaite is thought to reflect extreme fractionation of Mg and Li during petrogenesis and by the tourmaline structure, due to the large difference in the field strengths of these cations. Other major features of tourmaline substitutional chemistry are also rationalized on the basis of cation field strength.

Introduction

The crystal chemistry of the tourmaline group is exceedingly complex. In addition to solid-solution series extending from schorl to dravite and from schorl to elbaite, Foit and Rosenberg (1974, 1975, 1977) reported the existence of two additional substitutions (1) $\text{R}^+ + \text{R}^{2+} = \text{R}^{3+} + \square$ and (2) $\text{H}^+ + \text{R}^{2+} = \text{R}^{3+}$ in natural tourmalines of the schorl-dravite series, which together result in solid solution toward an alkali cation-deficient series, $\text{R}_{1-x}^+\text{R}_x^{3+}\text{R}_6^{3+}(\text{BO}_3)_3\text{Si}_6\text{O}_{18}\text{O}_{3-x}(\text{OH})_{1+x}$.

The extent of substitution in any structure is determined not only by the coordination and dimensions of the sites available for substitution and the tolerance of the structure to distortion, but also by the characteristics of the ions themselves (e.g., field

strength). While a large amount of structural data on members of the tourmaline group (dravite, Buerger *et al.*, 1962; buergerite, Barton, 1969; elbaite, Donnay and Barton, 1972; schorl, Fortier and Donnay, 1975; uvite and an aluminous dravite, Schmetzer, 1978) has accumulated over the past 15 years, systematic structural changes produced by these substitutions have not been deciphered. The structure of a significantly alkali cation-deficient, vanadium-rich tourmaline has been examined and analyzed in conjunction with all available tourmaline structural data in an attempt to evaluate the structural significance of cation substitution. It was anticipated that this study would lead to a better understanding of the role of structural distortion and cation field strength (Weyl and Marboe, 1962) in limiting tourmaline composition.

Table with multiple columns and rows of numerical data, including various values and some labels like 'L = 6' or 'L = 12'. The data is organized in a grid-like structure.

Table with multiple columns and rows, containing numerical data and some text labels like 'L = -13', 'L = 10', and 'L = -8'.

-16	-11	598	608	-4	-3	1040	1032	-1	-8	284	279	20	7	287	307	9	5	798	808	9	2	503	510	4			
-17	0	175	184	-4	-6	824	862	-1	-11	226	219	20	10	198	217	9	8	173	173	9	5	251	280	0			L = -14
-17	-3	67	111	-4	-9	799	813	-2	0	638	615	21	2	607	604	9	11	365	352	9	8	292	283	0			
-17	-6	303	306	-4	-12	1016	1035	-2	-3	364	341	21	5	199	223	9	14	521	512	9	11	254	225	0			
-17	-9	452	449	-4	-15	437	421	-2	-6	449	439	21	8	165	158	9	17	490	476	9	14	377	373	0			
-18	-1	552	546	-4	-18	461	476	-2	-9	150	147	22	0	309	322	9	20	77	125	10	0	361	351	1			
-18	-4	621	637	-5	-1	583	595	-2	-12	242	244	22	3	118	117	10	0	1293	1284	10	3	343	322	1			
-18	-7	364	328	-5	-4	566	549	-3	-1	155	135	22	6	156	113	10	3	969	958	10	6	506	499	2			
-19	-2	348	371	-5	-7	911	924	-3	-4	210	160	23	1	314	311	10	6	637	614	10	9	295	308	2			
-19	-5	0	61	-5	-10	1580	1623	-3	-7	264	249	23	4	522	533	10	9	130	98	10	12	623	644	3			
-20	0	836	836	-5	-13	196	182	-3	-10	166	183	23	7	208	216	10	12	524	516	10	15	267	244	4			

TABLE COMPLETE

Table 4. Magnitude and orientation of the principal axes of the thermal ellipsoids (standard deviations in parentheses)

Atom	Axis r_i	rms amplitude, \AA	Angle ($^\circ$) with respect to:		
			+a ₁	+a ₂	+c
Na,Ca,Mg	1	0.133(2)	90	90	0
	2	0.138(1)	150	30	90
	3	0.138(1)	60	60	90
Mg,V,Cr,Fe	1	0.060(1)	120	0	90
	2	0.065(1)	137(6)	90	122(1)
	3	0.097(1)	63(1)	90	148(1)
Al,V,Ti	1	0.065(1)	27(44)	93(45)	90(58)
	2	0.066(1)	75(66)	126(6)	36(6)
	3	0.075(1)	111(7)	36(6)	54(6)
B	1	0.063(5)	90	30(33)	88(10)
	2	0.068(5)	180	60	90
	3	0.085(4)	90	92(12)	2(10)
Si,Al	1	0.060(1)	79(18)	44(16)	74(4)
	2	0.063(2)	167(16)	52(17)	80(8)
	3	0.072(1)	83(7)	108(6)	19(5)
O(1)	1	0.094(5)	90	90	0
	2	0.105(4)	150	30	90
	3	0.105(4)	60	60	90
O(2)	1	0.068(4)	90	31(2)	97(3)
	2	0.106(3)	180	60	90
	3	0.120(3)	90	84(5)	7(3)
O(3)	1	0.080(3)	92(10)	90	3(3)
	2	0.086(3)	60	180	90
	3	0.135(3)	30(2)	90	87(2)
O(4)	1	0.068(4)	0	120	90
	2	0.100(3)	90	103(3)	164(5)
	3	0.125(3)	90	33(3)	106(5)
O(5)	1	0.057(4)	120	0	90
	2	0.105(3)	88(3)	90	178(5)
	3	0.132(3)	30(2)	90	88(5)
O(6)	1	0.073(3)	95(8)	68(8)	23(6)
	2	0.089(4)	39(29)	150(22)	73(10)
	3	0.093(2)	51(29)	71(27)	104(9)
O(7)	1	0.069(2)	65(3)	60(4)	67(4)
	2	0.089(2)	83(8)	118(8)	30(6)
	3	0.104(3)	26(4)	136(6)	108(8)
O(8)	1	0.057(4)	20(5)	101(5)	94(2)
	2	0.086(3)	71(5)	158(4)	70(3)
	3	0.116(2)	93(3)	71(3)	21(3)

Atoms	Distance (Å)	Atoms	Distance (Å)	Angles (°)
Si-O(4)	1.630(1)	0(4) - 0(5)	2.567(2)	103.19(7)
Si-O(5)	1.646(1)	0(4) - 0(7)	2.663(1)	110.31(7)
Si [*] -O(6)	1.613(1)	0(5) - 0(7)	2.674(1)	110.45(6)
Si-O(7)	1.612(1)	0(6) - 0(4)*	2.683(2)	111.64(7)
		0(6) - 0(5)*	2.679(2)	110.56(7)
Mean	1.625	0(6) - 0(7)	2.650(1)	110.49(5)
		Mean	2.653	
B-O(2)	1.369(1)	0(8) ¹ - 0(2) 2x	2.385(1)	120.7(1)
B-O(8) ¹ 2x	1.376(1)	0(8) - 0(8) ¹	2.367(3)	118.6(1)
Mean	1.374	Mean	2.379	
Mg-O(1)	1.971(2)	0(1) - 0(2) ² 2x	2.673(3)	84.15(6)
Mg-O(2) ² 2x	2.018(1)	0(1) - 0(6) ³ 2x	3.047(1)	100.10(6)
Mg-O(3)	2.137(2)	0(2) - 0(2) ²	2.915(1)	92.45(6)
Mg-O(6) ³	2.004(1)	0(2) ⁷ - 0(6) ³ 2x	2.822(2)	89.09(5)
		0(3) - 0(2) ² 2x	3.169(2)	99.37(6)
Mean	2.026	0(3) - 0(6) ³ 2x	2.560(2)	76.31(4)
		0(6) - 0(6) ³	2.811(3)	89.07(8)
		Mean	2.856	
Al-O(3)	1.995(1)	0(3) - 0(6)	2.560(2)	82.33(6)
Al-O(6)	1.893(1)	0(3) - 0(7) ⁵	2.888(2)	95.67(6)
Al-O(7) ⁴	1.955(1)	0(3) - 0(8)	2.793(2)	90.64(6)
Al-O(7) ⁵	1.900(1)	0(3) - 0(8) ⁵	2.891(2)	95.80(7)
Al-O(8)	1.932(1)	0(6) - 0(8)	2.729(2)	91.00(5)
Al-O(8) ⁵	1.900(1)	0(6) - 0(8) ⁵	2.793(2)	94.86(6)
		0(7) ⁴ - 0(6)	2.784(2)	92.69(6)
Mean	1.929	0(7) ⁴ - 0(7) ⁵	2.738(1)	90.50(2)
		0(7) ⁴ - 0(8)	2.898(2)	77.64(6)
		0(7) ⁵ - 0(8)	2.417(1)	96.41(6)
		0(7) ⁵ - 0(8) ⁵	2.825(2)	78.20(5)
		0(7) ⁴ - 0(8) ⁵	2.417(1)	96.08(5)
		Mean	2.728	
Na-O(2) ^{2,6} 3x	2.536(2)	0(2) ^{2,6} - 0(2) ^{2,6} 3x	2.9149(3)	70.17(6)
Na-O(4) ^{2,6} 3x	2.780(1)	0(2) ^{2,6} - 0(4) ^{2,6} 3x	3.0784(23)	70.61(4)
Na-O(5) ^{2,6} 3x	2.704(2)	0(2) ^{2,6} - 0(5) ^{2,6} 6x	3.5865(23)	86.32(4)
		0(4) ^{2,6} - 0(4) ^{2,6} 3x	4.4576(6)	106.61(5)
Mean	2.673	0(4) ^{2,6} - 0(5) ^{2,6} 6x	2.5665(9)	55.79(4)
		Mean	3.251	
H-O(3)	0.86(4)	0(3) - 0(5)	3.191(2)	154.(2)
H-O(5)	2.39(4)			

1 = y-x,y,z; 2 = y-x,-x,z; 3 = x,x-y,z; 4 = y-x+1/3,-x+2/3,z+2/3;
5 = -y+2/3,x-y+1/3,z+1/3; 6 = -y,x-y,z transformations relating
coordinates to those of Table 4.

* = positioned in an adjacent unit cell.