

Synthesis and characterization of alkali-free tourmaline

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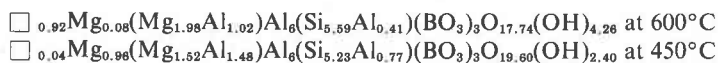
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Abstract

Alkali-free tourmalines synthesized in the system MgO-Al₂O₃-SiO₂-B₂O₃-H₂O in the presence of excess B₂O₃ and H₂O at 1 kbar have been characterized by optical and X-ray measurements, partial chemical analyses, and infrared spectra. Infrared absorption bands in the OH-stretching region are more similar to those of elbaite than dravite.

Syn. Temp. (°C)	Refractive Index		Cell Dimensions		Partial Analysis (Mole%)		
	ε	ω	a (Å)	c (Å)	SiO ₂	Al ₂ O ₃	MgO
600	1.605(1)	1.624(1)	15.884(2)	7.128(1)	49.2	32.8	18.0
450	1.607(1)	1.624(1)	15.847(5)	7.108(3)	44.2	34.9	20.9

Assuming stoichiometric boron, variables in site occupancies include numbers of (1) vacancies at alkali sites, (2) ^{IV}Al, (3) ^{VI}Al, and (4) protons. Although chemical data serve to constrain site occupancies only within broad limits, structural formulas are univariant in that determination of any one variable would fix the others. Comparison of cell parameters of alkali-free tourmaline with those of elbaite and dravite suggest approximate ^{VI}(Mg/Al) ratios which correspond to the structural formulas:



Alkali site occupancy (^{IX}Mg) and Al content are higher while the proton content is lower at 450°C than at 600°C. Alkali-free tourmaline synthesized at 600°C is an Al-rich, alkali-defective dravite.

Introduction

The synthesis of alkali-free Mg tourmaline under hydrothermal conditions was first mentioned by Frondel and Collette (1957), but few details were given and no attempt was made to characterize the products of their experiments. A decade later, Taylor and Terrell (1967) synthesized an alkali-deficient, "defect" tourmaline containing only 0.12 alkali (Na + K) atoms per formula unit [31(O,OH,F)]. A partial bulk chemical analysis was reported, but again few details were given. Thus, little is known of the conditions of synthesis, chemical composition, physical properties, or crystal chemistry of alkali-free varieties which represent a compositional end-member of the tourmaline group.

The purpose of this paper is to report on the synthesis and characterization and to discuss the crystal chemistry of alkali-free tourmaline in the system

MgO-Al₂O₃-SiO₂-B₂O₃-H₂O (Rosenberg and Foit, 1977).

Synthesis

Based on previous reports (Frondel and Collette, 1957; Taylor and Terrell, 1967), the existence of an alkali-defective dravite in the system MgO-Al₂O₃-SiO₂-B₂O₃-H₂O was anticipated. Alkali-defective tourmaline was thought to be related to dravite, NaMg₃Al₆(BO₃)₃Si₆O₁₈(OH)₄, by the substitution, Mg²⁺ + Na⁺ = Al³⁺ + □, and thus to have the structural formula □(Mg₂Al)Al₆(BO₃)₃Si₆O₁₈(OH)₄.

In order to substantiate the existence of tourmaline of this composition, a mechanical mixture with an appropriate MgO/Al₂O₃/SiO₂ ratio was prepared from reagent-grade MgO, γ-Al₂O₃ (synthesized at 700°C for 1 1/2 hours from AlCl₃·6H₂O), and quartz (Minas Gerais, Brazil). Boron in excess of the

stoichiometric amount required to form tourmaline was added as spec-pure B_2O_3 . The bulk composition of this mixture was MgO , 13.9; Al_2O_3 , 24.3; SiO_2 , 41.8; and B_2O_3 , 20.0 mole percent.

After preliminary studies in which tourmaline was synthesized in the temperature range 400–750°C at 1 kbar (Rosenberg and Foit, 1975), larger samples of this mixture were heated to 450°C and 600°C at 1 kbar for 70 days in sealed gold tubes containing excess water (solid/water ratio $\sim 2/1$), in order to obtain samples large enough for complete characterization. Although qualitative X-ray diffractometry suggested that tourmaline and H_3BO_3 were the only crystalline phases present in the air-dried products of these experiments, minor amounts of *subhedral* quartz were identified under the polarizing microscope and, in the course of later slow diffractometer scans, weak X-ray reflections corresponding to quartz were observed. Quartz appears to have crystallized during the course of the experiments, suggesting that alkali-free tourmalines do not have the same stoichiometry as alkali-defective dravite.

Characterization

Synthetic alkali-free tourmalines were characterized by their optical properties, X-ray powder patterns, refined unit-cell dimensions, chemistry, and infrared spectra. Optical and X-ray data for alkali-free tourmalines are compared with those for natural (Swanson *et al.*, 1964) and synthetic (Tomisaka, 1968) dravite in Table 1. Slightly different cell dimensions ($a = 15.877$, $c = 7.135A$) were obtained by refinement of Debye-Scherrer powder data for the same 600°C sample of alkali-free tourmaline by Fortier (1975); standard errors were not given.

Optical properties

Alkali-free tourmaline most commonly occurs as sheaf-like aggregates of radiating acicular crystals up to 10 μm long and 1 μm wide (Fig. 1a), similar in habit to dravite synthesized by Tomisaka (1968). Smaller, well-formed crystals (Fig. 1b) were analyzed in this study. Less commonly, tourmaline occurs as prismatic inclusions in both quartz and boric acid. The crystals, which are colorless to very pale green, display no observable pleochroism. Under crossed nicols single crystals exhibit parallel extinction and are length-fast, indicating that they are elongated in the c -axis direction. Refractive indices (Table 1) were determined using Na-light and temperature-calibrated immersion oils. Colorless and pale green crystals have the same refractive indices. The refractive

Table 1. Optical and X-ray powder diffraction data for dravite, synthetic alkali-free tourmaline, and synthetic dravite

hk.l	1.		2.			3.	
	$d_{obs.}(\text{\AA})$	I/I_0	$d_{obs.}(\text{\AA})$	$d_{calc.}(\text{\AA})$	I/I_0	$d_{obs.}(\text{\AA})$	I/I_0
10.1	6.377	28	6.339	6.330	73	6.383	14
02.1	4.981	25	4.953	4.949	28	4.997	19
30.0	4.595	17	4.589	4.585	16	4.592	19
21.1	4.221	66	4.200*	4.200	50	4.222	43
22.0	3.985	84	3.970*	3.971	100	3.978	69
01.2	3.480	62	3.449*	3.450	45	3.477	57
13.1	3.375	16	3.363	3.364	24	3.380	14
40.1	3.111	5	3.099	3.097	9	---	---
41.0	3.008	12	3.004	3.002	11	3.007	33
12.2	2.961	83	2.939*	2.940	35	2.966	60
32.1	2.897	9	2.882	2.886	< 1	2.899	17
33.0	2.656	< 1	---	---	---	---	---
31.2	2.622	7	---	---	---	---	---
05.1	2.576	100	2.568*	2.567	63	2.573	100
04.2	2.490	1	---	---	---	---	---
24.1	2.451	1	---	---	---	---	---
00.3	2.396	20	2.383	2.376	< 1	---	---
23.2	2.376	19	2.364*	2.363	17	---	---
51.1	2.342	21	2.334*	2.334	12	2.337	30
60.0	2.300	5	---	---	---	---	---
50.2	2.189	17	2.177	2.178	8	---	---
43.1	2.163	14	2.155	2.156	5	2.160	14
30.3	2.127	16	2.106	2.110	8	2.125	53
42.2	2.112	10	---	---	---	---	---
22.3	2.054	21	2.058	2.039	< 1	---	---
15.2	2.040	46	2.031*	2.030	25	2.039	51
16.1	2.019	7	---	---	---	---	---
44.0	1.991	5	---	---	---	---	---
34.2	1.920	34	1.908*	1.909	14	---	---
70.1	1.901	6	---	---	---	---	---

		600°C	450°C	
a (\AA)	15.931	15.884 (2)	15.847 (2)	15.947 (2)
c (\AA)	7.197	7.128 (1)	7.108 (3)	7.194 (2)
v (\AA^3)	1581.86	1557.46	1545.87	1584.38
ϵ	1.613	1.605 (1)	1.607 (1)	1.611 (1)
ω	1.634	1.624 (1)	1.624 (1)	1.634 (1)
sign	(-)	(-)	(-)	(-)

1. Dravite from Dobruwa, Carinthia, Austria; Swanson *et al.*, 1964.
2. Synthetic alkali-free tourmaline, 600°C, data collected using Ni-filtered Cu K α radiation; asterisk indicates reflections used in least squares refinement of lattice parameters; lattice parameters and optical data for 450°C are also given below.
3. Synthetic dravite; Tomisaka, 1968; intensity values recalculated so strongest reflection equals 100.

indices of alkali-free tourmaline are significantly lower than those of natural or synthetic dravite (Table 1).

X-ray data

Although the X-ray powder diffraction data for the three tourmalines compared in Table 1 are sufficiently similar to suggest that they have the same basic structural configuration, significant differences are apparent. The relative order of the four strongest reflections of synthetic dravite is very similar to that of natural dravite, whereas the ordering in alkali-free tourmaline is much different. Furthermore, the refined unit-cell parameters of alkali-free tourmalines are markedly smaller than those of either synthetic or

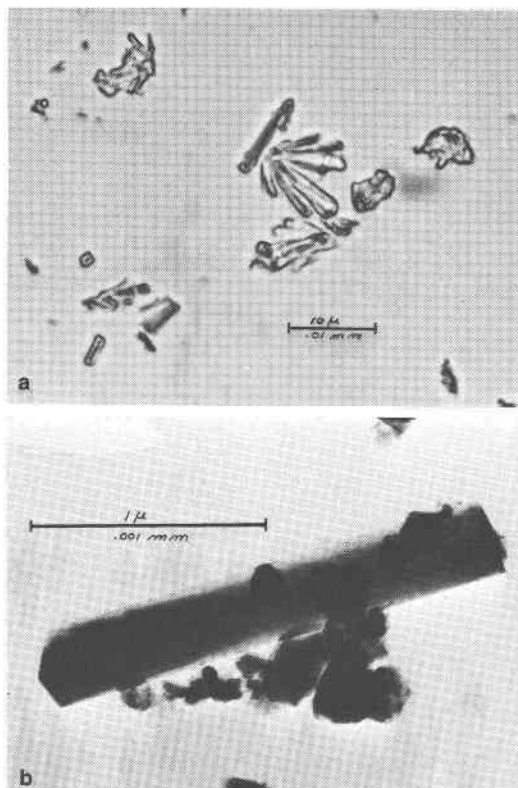


Fig. 1. (a) Photomicrograph of alkali-free tourmaline in plane polarized light. (b) Electron micrograph of alkali-free tourmaline.

natural dravite. While a unique structural configuration cannot be ruled out without single-crystal studies, the fact that the unit-cell dimensions of elbaite (e.g., Donnay and Barton, 1972) are smaller than those of alkali-free tourmaline suggests that these differences could be accounted for by substitutional chemistry.

Chemistry

Electron microprobe analysis of alkali-free tourmaline was not feasible due to the small size of the synthetic crystals. However, partial chemical analyses were obtained by means of an AEI electron microscope microprobe analyzer (EMMA-4) equipped with KEVEX energy-dispersive analysis system which permits quantitative determination of elemental ratios (Cliff and Lorimer, 1975; Lorimer and Cliff, 1976). Twelve random point analyses of well-formed crystals (Fig. 1b) were averaged to obtain count-rate data for MgO, Al₂O₃, and SiO₂. Relative percentages of MgO, Al₂O₃, and SiO₂ were calculated using natural dravite (Dobruwa, Carinthia, Austria, NMNH 103791; Swanson *et al.*, 1964) as a standard and

assuming direct proportionality of the ratio, percent oxide/average counts per unit time, between sample and standard (Table 2). Chemical data for Dobruwa dravite were obtained by electron microprobe analysis. Because the thickness of crystals in the sample and standard was not known, only relative percentages of these oxides in the sample could be obtained. This limitation is inherent in EMMA analyses.

Alkali-free tourmalines synthesized in this study are poorer in silica and richer in alumina and magnesia than the starting material. This is in accord with the observation of small amounts of quartz in the samples. In fact, the compositions of synthetic tourmalines projected into the system MgO–Al₂O₃–SiO₂ lie on an extension of the line drawn between the starting composition and SiO₂ (Fig. 2).

By assuming that boron is present in stoichiometric quantities¹ and by varying the numbers of protons, a series of structural formulas was calculated for each alkali-free tourmaline based on 31(O,OH). Variation in the number of protons results in concomitant changes in the numbers of Mg, Al, and Si atoms in calculated formulas. Cation-site assignments followed procedures commonly used in tourmaline structural studies (e.g. Buerger *et al.*, 1962; Donnay and Barton, 1972).

(1) Si⁴⁺ was supplemented by enough Al³⁺ to fill the tetrahedral site.

(2) The smaller octahedral site (18c) was assumed to be occupied exclusively by the Al³⁺; the remaining Al³⁺ was assigned to the larger octahedral site (9b) along with enough Mg²⁺ for full occupancy².

¹ The very small amounts of B which may substitute for Si in tourmaline, inferred mainly from the slight shortening of Si–O bond lengths (e.g. elbaite, Donnay and Barton, 1972), are neglected in this study.

² Since our data bear only on overall octahedral occupancy, the actual distribution of Mg²⁺ and Al³⁺ between the 18c and 9b octahedral sites is neglected. The assumed distribution of cations between octahedral sites is a formality based on the overwhelming predominance of Al³⁺ in the smaller (18c) site in natural tourmaline (e.g., elbaite, Donnay and Barton, 1972).

Table 2. Chemical data (mole percent): partial compositions recalculated to 100 percent

	Starting Composition	Alkali-free tourmaline 600°C	EMMA 450°C	Dobruwa Dravite Electron Microprobe
SiO ₂	52.25	49.18	44.21	50.46
Al ₂ O ₃	30.38	32.80	34.86	26.21
MgO	17.38	18.02	20.94	23.21

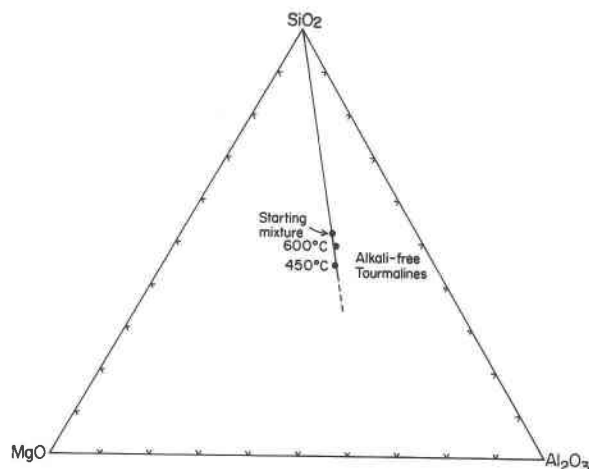


Fig. 2. Ternary diagram showing compositions (mole percent) of the starting mixture and alkali-free tourmalines projected into the system $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$.

(3) Excess Mg^{2+} was assumed to occupy the 9-coordinated alkali site. If the total Mg^{2+} available was less than unity, the remaining portion of the site was assumed to be vacant.

(4) Formulas with excess cations or octahedral vacancies were considered unlikely³.

Numbers of protons producing acceptable formulas vary from 1.25 to 5.4. The corresponding range of site occupancies for both alkali-free tourmalines is shown in Figure 3. If we assume that boron is present in stoichiometric quantities, variables in the structural chemistry of alkali-free tourmaline are numbers of (1) protons, (2) vacancies in the alkali site, (3) Al^{3+} in tetrahedral coordination, and (4) Al^{3+} in octahedral coordination. The structural formulas are univariant in that if one of these variables were known then the others would be fixed.

Chemical data for alkali-free tourmaline serve to constrain site occupancies within broad limits (Fig. 3). For example, in tourmaline synthesized at 600°C the alkali defect may range from 1 to 100 percent; proton numbers from 1.25 to 4.5; tetrahedral Al^{3+} from 0.45 to 0.08 and octahedral Al^{3+} from 6.96 to 7.82 per formula unit. The thermal behavior of second harmonic generator signals for this sample is consistent with a nearly vacant alkali site (Fortier, 1975). However, structural refinement based on single-crystal X-ray data would be necessary to obtain accurate estimates of actual site occupancies.

³ The possible presence of a small proportion of octahedral vacancies which has been inferred for some natural elbaite (Foit and Rosenberg, 1977) has been neglected.

Unfortunately, suitable crystals are not currently available.

Infrared spectra

Infrared spectra of synthetic and natural tourmalines were obtained, using a Perkin-Elmer 467 spectrophotometer and conventional KBr pellet techniques (Lyon, 1967). Few spectra of tourmaline have been reported in the literature and detailed band assignments have not been attempted. While the basic features of the spectra of both alkali-free tourmalines are quite similar to those reported in the literature (Plyusnina *et al.*, 1969, 1974; Moenke, 1974), some differences do appear in the OH-stretching region.

Absorption bands in the OH-stretching region of alkali-free tourmaline (Fig. 4) can be accounted for by structural OH. A weak band at approximately 1640 cm^{-1} , assigned to water, disappeared after the sample was heated to 190°C in vacuum. The remaining bands in the OH-stretching region are probably due to the presence of OH at several structural sites (Donnay and Barton, 1972), and to variations in cation-site occupancies. A comparison of the infrared spectrum of alkali-free tourmaline, synthesized at 600°C , with those of elbaite (Brown Derby Pegmatite, Gunnison Co., Colorado) and dravite (Dobruwa, Carinthia, Austria) is shown in Figure 4.

Despite its broader bands in the OH-stretching

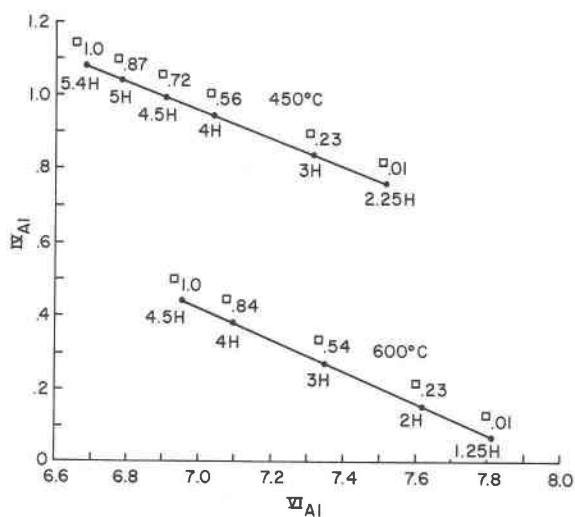


Fig. 3. Diagram showing the ranges of probable site occupancies in alkali-free tourmalines: VI Al , aluminum in octahedral coordination; IV Al , aluminum in tetrahedral coordination; \square , vacancies in alkali sites; H, protons.

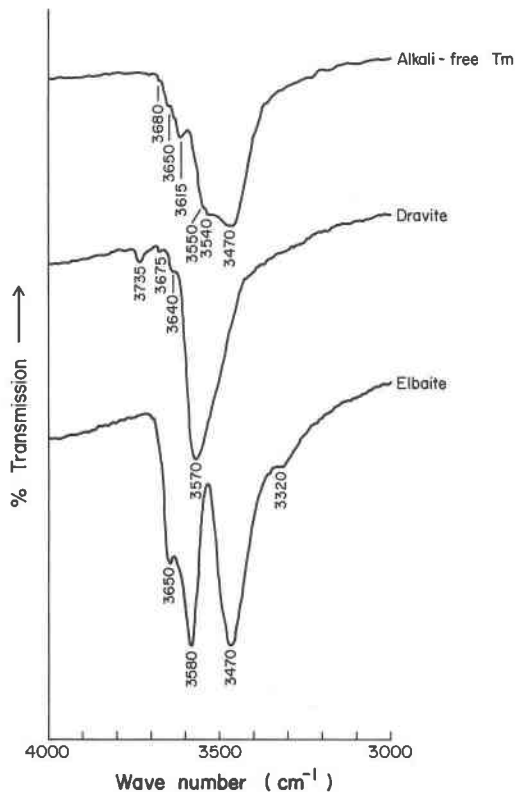


Fig. 4. Infrared spectra of alkali-free tourmaline 600°C, dravite (Dobruwa, Austria, NMNH 103791), and elbaite (Brown Derby Pegmatite, Gunnison Co., Colorado) in the OH-stretching region.

region, alkali-free tourmaline is more similar to elbaite than to dravite. Three strong bands in elbaite at 3470, 3580, and 3650 cm^{-1} probably correspond to bands at 3470, 3540, and 3650 cm^{-1} in alkali-free tourmaline, whereas the spectrum of dravite shows only one strong band at 3570 cm^{-1} . This similarity is probably due to the presence of significant amounts of Al^{3+} in addition to Li^+ and Mg^{2+} in the 9b octahedral sites of elbaite and alkali-free tourmaline respectively. Mg^{2+} is by far the predominant cation in this site in dravite. While the weak band in alkali-free tourmaline at 3680 cm^{-1} may correspond to a similar band in dravite at 3675 cm^{-1} , the bands at 3615 cm^{-1} and 3550 cm^{-1} appear to be unique and may be related to alkali deficiency. Spectra of alkali-free tourmalines synthesized at 600°C (Fig. 4) and 450°C are very similar and may be considered identical for purposes of this discussion.

Detailed band assignments would be premature at this time. A study of the OH-stretching region in natural and synthetic tourmaline is underway in this laboratory.

Discussion and conclusions

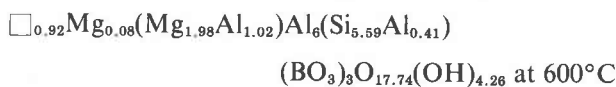
Although it has not been possible to specify site occupancies in alkali-free tourmaline using the EMMA chemical data alone, an estimate of any one of the previously mentioned structural-chemical variables based on physical properties would provide values for the others, and thus an approximate structural formula.

The unit-cell dimensions of tourmaline are largely dependent on the contents of the octahedral sites. Compositional end-members of the tourmaline group (dravite, schorl, and elbaite), which differ mainly in their octahedral site occupancies, can be unambiguously distinguished by their cell dimensions. Intermediates between these end-members lie close to well-defined linear trends on unit-cell dimension diagrams (*e.g.*, *a* vs. *c*, Donnay and Barton, 1972), despite variable occupancies at alkali sites or the presence of small amounts of tetrahedral Al in some samples. Uvites, $\text{CaMg}_3(\text{Al}_5\text{Mg})(\text{BO}_3)_3\text{Si}_6\text{O}_{18}(\text{OH})_4$, or dravites containing large amounts of Ca in their alkali sites, for example, lie on the dravite-schorl trend, and thus cannot be distinguished on the basis of cell dimensions from dravite-schorls with no appreciable Ca^{2+} in their alkali sites (Dunn *et al.*, 1977b). Thus, to a first approximation, alkali-site occupancy appears to have little effect on cell dimensions. Comparison of cell dimensions of elbaites with and without tetrahedral Al, as implied from the numbers of Si atoms in their structural formulas, suggests that small amounts of tetrahedral Al likewise have little effect on the cell parameters (*e.g.*, Chaudhry and Howie, 1976).

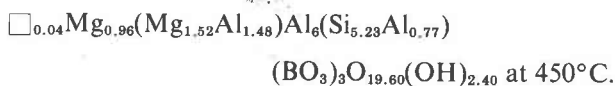
Although cell parameters of a natural tourmaline with a low octahedral Mg/Al ratio are not available for comparison with its alkali-free analog, elbaite can serve in its place, because the ionic radius of ${}^{\text{VI}}\text{Li}^+$ (0.76Å, Shannon, 1976) is close to that of ${}^{\text{VI}}\text{Mg}^{2+}$ (0.72Å, *ibid.*). Dravite from the Hirose Mine, Japan (Kitahara, 1966; Tomisaka, 1968) and elbaite from San Diego County, California (Donnay and Barton, 1972) have been chosen on the basis of chemical analyses and refined cell parameters as representatives of their respective end-member compositions for purposes of comparison. Octahedral-site occupancies in the Hirose dravite ($\text{R}^{2+}/\text{R}^{3+} = 0.49$) and in the San Diego elbaite [$(\text{Li}^+ + \text{R}^{2+})/\text{R}^{3+} = 0.19$] are very close to those in the ideal end-members (dravite = 0.50; elbaite = 0.20); both are also low in iron.

The cell dimensions of alkali-free tourmalines (Fig. 5, 600°C, A; 450°C) lie close to a line drawn between the cell parameters of the natural representatives of

end-member composition, while cell dimensions determined by Fortier (1975) for the tourmaline synthesized at 600°C (Fig. 5, 600°C, B) lie on this line. The number of octahedral Al atoms in alkali-free tourmaline may be estimated by interpolation between those of the natural compositions, assuming a linear dependence of cell dimensions on the Mg(Li)/Al ratio. Interpolation yields octahedral Mg/Al ratios which imply structural formulas approximating



and



These synthetic tourmalines appear to be close to end-members with respect to alkali-site occupancy.

The unit-cell dimensions of liddicoatite (Fig. 5, L), the Ca-analog of elbaite (Dunn *et al.*, 1977a), are close to those of alkali-free tourmaline synthesized at 600°C (Fig. 5, A and B), implying similar octahedral-site occupancies. The octahedral-site occupancy of liddicoatite calculated from its chemical analysis, $(\text{Li}^+ + \text{R}^{2+})/\text{R}^{3+} = 0.25$, is in close accord with the value (0.28) obtained from interpolation of its cell parameters between those of the Hirose dravite and the San Diego elbaite (Fig. 5), despite the predominance of Ca^{2+} rather than Na in the alkali site. This confirms the relative insignificance of alkali-site occupancy in determining cell dimensions, and verifies the method of estimating octahedral-site occupancy based on cell dimensions.

Estimated site occupancies differ from those of the alkali-defective tourmaline anticipated at the outset in the presence and variability of ^{IV}Al and ^{IX}Mg as well as the range of proton numbers. These unexpected site occupancies are not unique. The number of Si atoms in natural tourmaline with no excess B is often found to be less than 6 [based on $31(\text{O},\text{OH})$], implying the presence of some tetrahedral Al (*e.g.*, Deer *et al.*, 1966). Furthermore, infrared spectra of tourmalines, particularly elbaite, suggest the presence of some ^{IV}Al (Plyusnina *et al.*, 1969). Mg^{2+} cations have been frequently assigned to alkali sites in studies of natural materials. In the unusual Mg-rich tourmaline described by Wang and Hsu (1966), Mg^{2+} occupies 1/2 the alkali sites, and 10 percent of the tetrahedral sites are occupied by Al. Similar but smaller ^{IX}Mg and ^{IV}Al occupancies may be implied from other chemical analyses in the literature. The

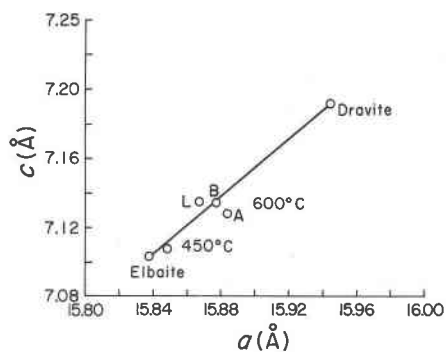


Fig. 5. Diagram showing the relationship between the unit-cell dimensions of synthetic alkali-free tourmalines [600°C, A (this study), B (Fortier, 1975); 450°C (this study)], and those of dravite (Hirose Mine, Tottori Prefecture, Japan; Kitahara, 1966) and elbaite (San Diego Co., Calif.; Donnay and Barton, 1972). L, liddicoatite (Dunn *et al.*, 1977a).

numbers of protons in dravite and especially in elbaite frequently exceed four (Foit and Rosenberg, 1977); hydroxyl groups may occupy as many as four structural sites in dravite (Donnay and Barton, 1972). Proton deficiency is common in natural aluminous tourmalines (Foit and Rosenberg, 1977). Structural formulas have also included alkali-defects (*e.g.* $\square_{0.18}$; Donnay and Barton, 1972) although the percent defect in natural tourmaline is relatively small (Foit and Rosenberg, 1977) compared with synthetic alkali-free tourmaline. Partial chemical analysis suggests that 88 percent of the alkali sites are vacant in the alkali-deficient tourmaline synthesized by Taylor and Terrell (1967).

Alkali-free tourmaline synthesized at 600°C may be regarded as an Al-rich, alkali-defective dravite; ^{IV}Al is compensated for by the presence of excess protons. Because Mg^{2+} occupies the alkali sites at lower temperatures, additional Al^{3+} is required to fill the 9b octahedral site. Charge balance is maintained by the further substitution of Al^{3+} for Si^{4+} and by the loss of protons. As a result the SiO_2 content of alkali-free tourmaline decreases with temperature (Fig. 2). In the tourmaline synthesized at 450°C, the alkali site is almost fully occupied, and the $\text{Mg}^{2+}/\text{Al}^{3+}$ ratio in the 9b octahedral site approaches unity. Thus, neglecting proton numbers, alkali-free tourmaline more similar to elbaite has been synthesized at 450°C than at 600°C.

In natural tourmalines Mg^{2+} and defects are present at alkali sites, Al replaces Mg in octahedral coordination, and the number of protons is variable (Foit and Rosenberg, 1977). Thus alkali-free tourmalines are end-members of the tourmaline group, although

end-member compositions are not closely approached in nature.

Acknowledgments

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