

Investigations on Olenite with Excess Boron from the Koralpe, Styria, Austria

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Abstract

Chemical analyses of tourmaline crystals from a small pegmatite body, nearby the Stoffhütte, Koralpe (Styria, Austria), exhibit a pronounced excess in boron, expressed by the simplified formula $(\text{Na}_{0.43} \text{Ca}_{0.24} \square_{0.33}) (\text{Al}_{2.43} \text{Li}_{0.33} \square_{0.28}) \text{Al}_6(\text{BO}_3)_3 (\text{B}_{1.23} \text{Si}_{4.87} \text{O}_{18}) [\text{O}_{0.64}(\text{OH})_{3.36}]$. A substantial substitution of silicon by boron in the tetrahedral position is in agreement with an occupation refinement in single crystal X-ray work: the average (Si, B)-O bond length measures 1.610 Å. This is the first example for a substitution of silicon by boron in a natural tourmaline, that could be verified by crystallographic methods.

Zusammenfassung

Chemische Analysen von Turmalinkristallen aus einem geringmächtigen Pegmatitkörper, in der Nähe der Stoffhütte, Koralpe (Steiermark, Österreich), zeigen einen ausgeprägten Überschuss an Bor, der in der vereinfachten Formel $(\text{Na}_{0.43} \text{Ca}_{0.24} \square_{0.33}) (\text{Al}_{2.43} \text{Li}_{0.33} \square_{0.28}) \text{Al}_6(\text{BO}_3)_3 (\text{B}_{1.23} \text{Si}_{4.87} \text{O}_{18}) [\text{O}_{0.64}(\text{OH})_{3.36}]$ seinen Ausdruck findet. Ein substantieller Ersatz des Siliziums durch Bor in der Tetraederposition steht mit der Verfeinerung der Besetzungsdichte anhand von Röntgen-Einkristallda-

ten in Übereinstimmung: die durchschnittliche (Si, B)-O-Bindungslänge beträgt 1.610 Å. Dies ist das erste Beispiel für den Ersatz von Silizium durch Bor in einem natürlichen Turmalin, der durch kristallographische Methoden bestätigt werden konnte.

Introduction

A survey on tourmalines from Austrian localities, including lattice constants, semiquantitative EDX-analyses, as well as the compilation of morphologic and genetic aspects (ERTL, 1995) drew attention upon the lattice constants of light green, blue or even colourless tourmalines from the Koralpe, Styria, Austria (cf. MOSER and POSTL in NIEDERMAYR et al., 1986); POSTL and MOSER, 1987; POSTL, 1988). The small values of the lattice constants [$a_0 = 15.735(1)$ Å, $c_0 = 7.061(1)$ Å] and preliminary chemical analyses led to the assumption that the [9 + 1] coordinated alkaline and/or alkaline-earth-position in the structure is unoccupied. The tentative formula $Al_3Al_6(BO_3)_3Si_6O_{18}(O, OH)_4$ was proposed. But the quantitative chemical analyses of the present study show appreciable contents of sodium and calcium, hence the composition of the investigated material is close to an olenite end-member tourmaline (see Table 1). The coherency of lattice constants and chemical composition was the reason for further investigations by a detailed structure determination. The average size of these olenite crystals varies from 2 to 5 mm, some aggregates of parallel arranged crystals are up to 25 mm in length. The larger individuals are sometimes intergrown with schorl.

Experimental

The chemical composition of the present tourmaline was determined by atomic absorption spectroscopy for lithium, the Karl-Fischer titration techniques for H₂O and electron microprobe analysis for all other elements. The following standards were used for the microprobe analyses (elements and lines in parentheses): jadeite, (Na K α), K-glass (K K α), topaz (F K α), pyrore (Mg K α , Al K α , Si K α), andradite (Ca K α , Fe K α), spessartine (Mn K α), rutile (Ti K α) and dravite (B K α). The operating conditions for fluorine and boron were 6 keV accelerating voltage, 30 nA beam current, all other elements were measured with a beam of 15 keV and 15 nA. For both conditions a beam diameter of 8 μ m was used. Scans around the B K α line using a PC2 pseudo diffracting crystal proved identical line positions and shapes for boron in both the dravite and the olenite sample. The B K α -peak of our tourmaline was about 20% higher than that of dravite. The analyses were corrected by applying the Cameca

PAP procedure. Special care was taken to use identical material for the microprobe analyses, the lithium- and H₂O-determination. As the measured boron content was unusually high and the silicon content was unusually low for a tourmaline, the microprobe analyses were repeated

Table 1. Chemical composition of olenite from the Koralpe (in wt. %). E.s.d.'s in parentheses (Analyst: H.-J. Bernhardt)

	1	2	3
SiO ₂	31.96 (19)	37.40	38.28
TiO ₂	0.02 (2)		
B ₂ O ₃	16.06 (31)	10.83	11.09
Al ₂ O ₃	46.71 (10)	46.71	48.71
FeO	0.05 (2)		
MnO	0.01 (2)		
MgO	0.01 (1)		
CaO	1.47 (3)		
Na ₂ O	1.46 (3)	1.46	
K ₂ O	0.02 (1)		
Li ₂ O	0.54 (-)		
F	0.11 (2)		
H ₂ O	3.25 (-)	0.93	1.91
Total	101.67	99.98	99.99

Number of ions on the basis of 31 (O, OH, F)

Si	4.871	6.000	6.000
B	<u>1.225</u> 6.096*		
B	3.000	3.000	3.000
Al	6.000	6.000	6.000
Al	2.430	3.000	3.000
Mg	0.002		
Ti	0.002		
Li	0.331		
Fe ²⁺	0.006		
Mn	<u>0.001</u> 2.772		
Na	0.431	1.000	
Ca	0.240		
K	<u>0.004</u> 0.675		
OH	3.304	1.000	2.000
F	<u>0.053</u> 3.357		

1 Mean of ten microprobe analyses (for Li and H₂O see text)

2 Theoretical olenite, NaAl₃Al₆(BO₃)₃(Si₆O₁₈)O₃(OH). (cf. SOKOLOVET al. 1986)

3 Theoretical alkali- and alkali-earth-free Al-tourmaline □Al₃Al₆(BO₃)₃(Si₆O₁₈)O₂(OH)₂

* For the excess of ions at this position (Σ Si and B) see „Experimental“, this work.

several times. No significant changes were noticed. The totals of the analyses were slightly too high (see Table 1). Microprobe analyses of boron may be inaccurate owing to several factors (BASTIN and HEIJLIGERS, 1986, MCGEE and ANOVITZ, 1996). Assuming that only for boron the obtained value was too high, its analytical value may be reduced to an amount to reach a sum of constituents of 100%. Even then the boron content is still too high for a "normal" olenite. A partial substitution of Si by B in natural tourmalines was proposed by BARTON (1969) and by SERDYUCHENKO (1980) previously, but only on the basis of chemical analyses, and not corroborated by structure determinations.

The quality of the crystal used for structure refinement was checked by film methods (Weissenberg type), using Cu-K α radiation. A detailed compilation about data collection and structure refinement is given in

Table 2. Details of crystal data, X-ray measurements, and structure determination

Crystal system	trigonal
Space group	R3m (160)
Unit - cell dimension [Å]	a = 15.7395 (2) c = 7.0656 (2)
Volume of unit - cell [Å ³]	1515.86 (5)
T (K)	295 (2)
Z	3
D _{calc} [Mg.m ⁻³]	3.057
D _{meas} [Mg.m ⁻³]	3.02 (4)
Cut crystal chip [mm ³]	0.20 × 0.50 × 0.20
Diffraktometer	Stoe AED 2
Radiation	Mo K α (λ = 0.71069 Å)
Linear absorption coefficient [mm ⁻¹]	1.34
Scan mode	ω -2 θ
Measured reflections	7630
Independent reflections	1443
R _{int}	0.026
Reflections with Fo > 4 σ (Fo)	1443
Range of hkl	\pm h, \pm k, l
Max 2 θ value [°]	80
Absorption correction	Ψ -scan data
Transmission factors	0.25 to 0.20
Refinement on F ²	
Number of variables	100
R(F), 1443 data	0.0182
Rw(F ²), 1443 data	0.0457
$w = 1/[\rho^2(\text{Fo}^2) + (0.59 \cdot \text{P})^2]$	
$\text{P} = [\max(\text{Fo}^2, 0) + 2 \cdot \text{Fc}^2]/3$	
Extinction coefficient	0.0022 (4)
Max Δ/σ	< 0.001
Final difference Fourier summation [e. Å ³]	0.43 to -0.40

Table 3. Structural parameters with e.s.d.'s in parentheses. The anisotropic displacement factors are defined as $\exp(-2\pi^2 \sum_i \Sigma_j U_{ij} h_i h_j a^* i a^* j)$; [$\text{\AA}^2 \times 10^4$]. Wyck: number of positions and Wyckoff notation. sof: occupation factors

Atom	Wyck	x	y	z	sof	U_{11}/U_{iso}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Na	3a	0.0	0.0	0.7863 (2)	0.07 (2)	240 (10)	U_{11}	205 (11)	0	0	1/2 U_{11}
Ca	3a	0.0	0.0	0.7863 (2)	0.05 (1)	240 (10)	U_{11}	205 (11)	0	0	1/2 U_{11}
Al (1)	9b	0.72742 (2)	0.45484 (3)	0.69377 (8)	0.399 (1)	90 (1)	98 (2)	127 (2)	20 (1)	1/2 U_{23}	1/2 U_{22}
Li (1)	9b	0.72742 (2)	0.45484 (3)	0.69377 (8)	0.101 (1)	90 (1)	98 (2)	127 (2)	20 (1)	1/2 U_{23}	1/2 U_{22}
Al (2)	18c	0.70336 (2)	0.73949 (2)	0.39367 (4)	0.978 (3)	100 (1)	112 (1)	87 (1)	6 (1)	-8 (1)	54 (1)
Li (2)	18c	0.70336 (2)	0.73949 (2)	0.39367 (4)	0.022 (3)	100 (1)	112 (1)	87 (1)	6 (1)	-8 (1)	54 (1)
Si	18c	0.80884 (2)	0.81074 (2)	0.00000 (4)	0.873 (3)	96 (1)	89 (1)	86 (1)	-7 (1)	1 (1)	37 (1)
B (1)	18c	0.80884 (2)	0.81074 (2)	0.00000 (4)	0.127 (3)	96 (1)	89 (1)	86 (1)	-7 (1)	1 (1)	37 (1)
O (1)	9b	0.94018 (3)	0.88036 (7)	0.50990 (17)	0.5	183 (3)	92 (3)	165 (4)	13 (3)	1/2 U_{23}	1/2 U_{22}
O (2)	9b	0.90602 (4)	0.81204 (8)	0.92518 (16)	0.5	151 (2)	197 (4)	136 (4)	-23 (3)	1/2 U_{23}	1/2 U_{22}
O (3)	9b	0.79598 (4)	0.59197 (8)	0.82810 (14)	0.5	133 (2)	233 (4)	99 (3)	11 (3)	1/2 U_{23}	1/2 U_{22}
O (4)	9b	0.42632 (4)	0.85264 (9)	0.57106 (16)	0.5	157 (2)	227 (4)	128 (4)	-5 (3)	1/2 U_{23}	1/2 U_{22}
O (5)	18c	0.80684 (4)	0.81726 (4)	0.22691 (10)	1.0	107 (2)	111 (2)	101 (2)	-2 (2)	4 (2)	43 (2)
O (6)	18c	0.71337 (4)	0.71409 (4)	0.92579 (9)	1.0	110 (2)	110 (2)	106 (2)	-8 (2)	12 (2)	42 (2)
O (7)	18c	0.79067 (4)	0.73015 (5)	0.56501 (10)	1.0	90 (2)	126 (2)	116 (2)	32 (2)	10 (2)	53 (2)
O,F	3a	0.0	0.0	0.2293 (3)	0.16667	172 (4)	U_{11}	147 (2)	0	0	1/2 U_{11}
B	9b	0.89097 (4)	0.78193 (9)	0.54964 (19)	0.5	97 (3)	94 (4)	103 (4)	6 (3)	1/2 U_{23}	1/2 U_{22}
H	9b	0.794 (1)	0.589 (3)	0.956 (8)	0.5	517 (11)					

Table 4. Selected interatomic distances and some mean values $\langle \rangle$ [Å] as well as bond angles [°]. E.s.d.'s in parentheses

Na	-	O(1)	=	2.544 (2);	3x	Al(1)	-	O,F	=	1.898 (1);	1x		
	-	O(4)	=	2.669 (1);	3x		-	O(5)	=	1.919 (1);	2x		
	-	O(2)	=	2.743 (1);	3x			O(1)	=	1.954 (1);	2x		
	-	O,F	=	3.130 (2);	1x			O(3)	=	2.096 (1);	1x		
		Al(2)	-	O(7)	=	1.878 (1)							
			-	O(6)	=	1.880 (1)							
			-	O(5)	=	1.883 (1)							
			-	O(7')	=	1.892 (1)							
			-	O(6')	=	1.923 (1)							
			-	O(3)	=	1.974 (1)							
Si	-	O(6)	=	1.600 (1)		O(6)	-	Si	-	O(5)	=	110.38 (3)	
	-	O(5)	=	1.608 (1)					-	O(2)	=	109.83 (5)	
	-	O(2)	=	1.609 (1)					-	O(4)	=	109.64 (5)	
	-	O(4)	=	1.623 (1)		O(5)	-	Si	-	O(2)	=	112.06 (5)	
									-	O(4)	=	110.41 (5)	
				$\langle 1.610 \rangle$		O(2)	-	Si	-	O(4)	=	104.34 (6)	
B	-	O(1)	=	1.371 (2);	1x	O(1)	-	B	-	O(7)	=	121.33 (5);	2x
	-	O(7)	=	1.372 (1);	2x	O(7)	-	B	-	O(7)	=	117.25 (10);	1x
				$\langle 1.372 \rangle$									

Table 2. In all calculations complex neutral scattering functions were used and the Lorentz and polarization effects were corrected in usual ways. ($|Fo| - |Fc|$) lists are deposited at the „Institut für Mineralogie und Kristallographie der Universität Wien“. The refined atomic parameters and anisotropic displacement factors are given in Table 3, selected interatomic distances and bond angles in Table 4. The sum of occupation factors for positions Al(1)/Li(1), Al(2)/Li(2), and Si/B(1) are constrained constant with multiplicity 0.5, 1.0 and 1.0 respectively, for position Na/Ca they are unconditionally free variables.

Discussion

The combined results of chemical analyses and X-ray investigations of the tourmaline under discussion with the formula $(\text{Na}_{0.43} \text{Ca}_{0.24} \square_{0.33})(\text{Al}_{2.43} \text{Li}_{0.33} \square_{0.28})\text{Al}_6(\text{BO}_3)_3(\text{B}_{1.23} \text{Si}_{4.87} \text{O}_{18})[\text{O}_{0.64}(\text{OH})_{3.36}]$ convincingly show (contrary to the preliminary note by ERTL 1995).

- a) that the X position is partly occupied by Na and Ca (and by traces of K) atoms, and
- b) that the Si position contains appreciable amounts of B.

The ratio B/Si calculated from chemical analyses with ≈ 0.25 differs considerably from the ratio determined by the X-ray work with ≈ 0.15 . The reason for this discrepancy might be an analytical error in the B determination (too high values) by microprobe analyses already mentioned above. Further it seems to be worth mentioning that from diagrams where the $\langle \text{Si-O} \rangle$ bond length [\AA] is plotted against the Si content [apfu = atoms per formula unit] (HAWTHORNE 1996, 1997) for our experimental $\langle (\text{Si}, \text{B})\text{-O} \rangle = 1.610 \text{\AA}$ a value of ≈ 5.70 Si [apfu] is deducible. Our chemical analyses as well as the least squares refinement of the occupancy (Table 3) indicate for Si [apfu] a value < 5.25 . The reasons for this discrepancy between $\langle \text{Si-O} \rangle$ [\AA] and Si [apfu] are not clear, but our experimental values for Si [apfu] 5.25 and $\langle \text{Si-O} \rangle = 1.610 \text{\AA}$ seem to be well established. Vacancies and partial Al substitution of Si-position cannot be excluded by the X-ray work.

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References

- BARTON R. JR., 1969: Refinement of the crystal structure of buergerite and the absolute orientation of tourmalines. – *Acta Cryst. B* 25, 1524–1533.
- BASTIN, G. F., and HEIJLIGERS, H. J. M., 1986: Quantitative electron probe microanalyses of boron in binary borides. – University of Technology, publ. of the Lab. for Phys. Chem. 115p.
- ERTL A., 1995: Elbait, Olenit, Dravit-Buergerit-Mischkristalle, Dravit, Uvit und ein neuer Al-Turmalin(?) von österreichischen Fundstellen. *Mitt. Österr. Miner. Ges* 140, 55–72.
- HAWTHORNE, F. C., 1996: Structural mechanisms for light-element variations in tourmaline. *Canad. Mineral.* Vol. 34, 123–132.
- HAWTHORNE, F. C., 1997: The crystal chemistry of tourmaline: current status. „Tourmaline 1997“ International Symposium on Tourmaline. Abstracts, 34–35.
- MCGEE, J. J. and ANOVITZ, L. M., 1996: Microprobe Analysis of geological Materials. In: GREW, E. S. and ANOVITZ L. M., (1996): Boron Mineralogy, Petrology and Geochemistry, *Rev. in Mineralogy*, 33, 771–786.
- NIEDERMAYR, G., MOSER, B., POSTL, W., and WALTER, F., 1986: Neue Mineralfunde aus Österreich XXXV. *Carinthia II*, 176./96., 521–547.
- POSTL, W., 1988: Neue Mineralfunde in der Steiermark. *Mitt. Österr. Miner. Ges.* 133, 7–11.
- POSTL, W., and MOSER, B., 1987: Ein Turmalinpegmatit östlich der Stoffhütte, Koralpe, Steiermark. *Mitt. Abt. Miner. Landesmuseum Joanneum*, 55, 13–20.
- SERDYUCHENKO, D. P., 1980: Different positions of boron in tourmaline lattices. *Dokl. Akad. Sci. USSR* 254, 177–179 (in Russian).
- SOKOLOV, P. B., GORSKAYA, M. G., GORDIENKO, V. V., PETROV, M. G., KRETSER, YU. L., FRANK-KAMENSKII, V. A., 1986: Olenit $\text{Na}_{1-x}\text{Al}_3\text{Al}_6\text{B}_3\text{Si}_6\text{O}_{27}(\text{O}, \text{OH})_4$ a new high-aluminous mineral of the tourmaline group. *Zapiski Vses. Mineralog. Obshch* 115, 119–123 (in Russian).

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