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STRUCTURE OF INORGANIC COMPOUNDS

Refinement of the Crystal Structure of Calcium–Lithium–Aluminum Tourmaline from the Pegmatite Vein in the Sangilen Upland (Tuva Republic)

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Abstract—The crystal structure of a natural calcium–lithium–aluminum tourmaline, which has the unique composition $(Ca_{0.62}Na_{0.32}\square_{0.06})(Al_{1.08}Li_{0.99}Fe^{2+}_{0.66}Mg_{0.24}Ti_{0.03})Al_6[Si_6O_{18}](BO_3)_3(OH_{2.28}O_{0.72}) \cdot (F_{0.84}O_{0.16})$, is refined ($R = 0.019$, $R_w = 0.022$, $S = 1.47$). It is found that the O(1)(W) site is split into two sites, O(1) and O(11), which are incompletely occupied by fluorine and oxygen anions, respectively, and that the O(3)(V) site contains bivalent oxygen anions. The solid solution studied is close in composition to the liddicoatite mineral species and differs from the latter one by the Li : Al ratio in the *Y* octahedra and the presence of bivalent oxygen anions in the O(3) site. The tourmaline studied differs from the hypothetical oxyliddicoatite by the population of the O(1)(W) site by fluorine and accommodation of additional oxygen anions in the O(3)(V) site.

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INTRODUCTION

Our studies of calcium tourmalines enriched in lithium from the pegmatite vein of the Sangilen Upland (Tuva) are continued. Earlier, the yellow lithium-containing uvite with the ideal formula $Ca(Mg_2Li)Al_6[Si_6O_{18}](BO_3)_3(OH)_3F$ was studied [1]. In the present work, the crystal structure of a green tourmaline with even larger lithium content was refined. The sample studied was found in the same rare-metal pegmatite vein, which is located in the field of development of usual spodumene pegmatites in the Solbelder River basin in the Sangilen Upland [2]. A dark green sample from a zonal tourmaline crystal was chosen for the structure refinement. The central, middle, and peripheral zones of this crystal are colored yellow, light green, and dark green, respectively.

CHEMICAL COMPOSITION OF THE ZONAL TOURMALINE

The chemical composition of the different-in-color zones of tourmaline (Table 1) was studied using X-ray spectroscopic microprobe analysis in the Institute of Precambrian Geology and Geochronology, Russian Academy of Sciences, with an ATB-55 scanning electron microscope (Japan) equipped with a LINK AN 10000/S85 microprobe attachment (analyst M.R. Pavlov).

Table 1. Chemical composition (wt %) of the zonal tourmaline from the pegmatite vein of the Sangilen Upland

Component	Color of the zone		
	yellow	light green	dark green
SiO_2	39.61	39.73	38.03
TiO_2	0.22	0.94	0.47
Al_2O_3	31.33	35.93	38.43
FeO*	0.42	4.07	5.24
MnO	0	0.06	0.07
MgO	10.24	4.16	0.84
CaO	4.74	4.12	3.80
Na_2O	0.48	0.81	0.94
F**	1.92	1.44	1.50
Li_2O	Not determined	Not determined	Not determined
Total	88.96	91.26	89.32

* FeO is the total iron.
** The fluorine content was determined on a Cameca SX50 microprobe analyzer.

Table 2. Coefficients in formulas (au) for the structures of differently colored zones of the tourmaline from the pegmatite vein of the Sangilen Upland

Element	Color of the zone		
	yellow	light green	dark green
Si	6	6	6
Ti	0.03	0.11	0.06
Al	5.59	6.40	7.15
Fe	0.05	0.51	0.69
Mn	0	0.01	0.01
Mg	2.31	0.94	0.20
Ca	0.77	0.67	0.64
Na	0.14	0.24	0.29
Li	1.02	1.04	0.90
F	0.95	0.75	0.78
OH	2.35	3.14	2.30
O		0.11	0.92

Since this method of analysis does not allow quantitative estimation of the content of light elements (Li and B) and H_2O, the results of the analysis were reduced to the formula that included six silicon atoms. The number of boron atoms per formula was taken to be three, and the lithium content was calculated on the assumption of the complete population of the *Y* site.

The results of the calculation of the crystal chemical formulas showed (Table 2) that yellow tourmaline corresponds to the lithium-containing uvite studied earlier [1]. The dark green tourmaline has a more complicated composition. The resolution of the formula into minals allowed us to assign this sample preliminarily to oxyliddicoatite, which was proposed in [3] as the hypothetical terminal member of the tourmaline group. The calculations revealed the following fractional composition of the sample studied (mol %): oxyliddicoatite minal, 64.0; schorl, 23.0; dravite, 6.7; and rossmanite, 6.0. The unaccounted residue is 0.3 mol %. The light green tourmaline from the middle zone is characterized by the following minal composition (mol %): lithium uvite, 47.0; schorl, 17.0; oxyliddicoatite, 11.0; liddicoatite, 9.0; rossmanite, 7.3; and the hypothetical $Na(Li_2Ti)Al_6[Si_6O_{18}](BO_3)_3(OH)_4$ minal, 7.0. The unaccounted residue is 1.7 mol %. By the predominant minal, the light green tourmaline should be assigned to lithium-containing uvites.

REFINEMENT OF THE CRYSTAL STRUCTURE

The intensities of 2308 diffraction reflections ($I > 2\sigma_I$) were obtained from a sample of an irregular shape 0.24 × 0.24 × 0.30 mm in size in 1/6 of the reciprocal space on a Nicolett *R*3 automated X-ray single-crystal diffractometer ($2\vartheta_{\max} = 80°$; MoK_α radiation; graphite monochromator; ω scan mode; scan speed, 2–30 deg/min). Since tourmalines are characterized by the *R* unit cell, only the diffraction reflections that follow the $-h + k + l = 3n$ rule were collected. The integrated intensities were corrected for the *LP* factors, fluctuation of the primary beam, and absorption (the DIFABS program).

The crystal structure was refined in space group $R\,3m$, which is typical of tourmalines, with the CSD program package [4]. The least-squares refinement in the anisotropic approximation of the atomic thermal vibrations (based on 1162 reflections with $F > 4\sigma_F$) alternated with the analysis of the difference Fourier maps. The atomic coordinates in the structure of aluminum elbaite [5] were used as the starting coordinates. At the initial stage, the *X*, *Y*, and *Z* sites were populated by the Ca^{2+}, Mg^{2+}, and Al^{3+} cations, respectively, and the site occupancies were refined using the reflections with $\sin\vartheta/\lambda \le 0.5$ in order to reduce their correlation with other structural parameters, first of all, thermal parameters [6]. The detailed examination of the difference Fourier maps after the *R* factors fell to ~2% position of the hydrogen atom and the splitting of the O(1) site revealed. The coordinates and the thermal parameter of the hydrogen atom were not refined.

The final discrepancy factors are $R = 0.019$ and $R_w = 0.022$ ($W = 1/[\sigma_F^2 + 0.0002F_{\text{obs}}^2]$); $S = 1.47$. The final fractional atomic coordinates, isotropic thermal parameters,[1] and site occupancies are listed in Table 3. The bond lengths in the structure studied are given in Table 4.

RESULTS AND DISCUSSION

The results of the refinement of the crystallographic sites in the structure under study (Table 3) confirmed that a small fraction of the *X* site, which is predominantly filled with Ca^{2+} cations, remains vacant. In addition, the population of the *Z* octahedra by the Al^{3+} cations and sharing of the *Y* octahedra by Al^{3+}, Li^+, and (Fe + Mg) cations in almost equal amounts were confirmed. In order to establish the valence of the iron cations, we calculated (to a first approximation) two variants of the average distance in the *Y* octahedron using the standard distances in the octahedra based on the $(Y\text{–}O)_{\text{av}} = \Sigma(Y\text{–}O)_i c_i$ relationship, where c_i is the fraction of the *i*th cation in the *Y* site obtained by the refinement of the occupancy (Table 3). The comparison of the calculated values (2.04 and 2.01 Å for Fe^{2+} and Fe^{3+}, respectively) with the experimental value of 2.040 Å (Table 4) showed that, in the tourmaline studied, iron is virtually completely bivalent. It follows that, in the calculation of the crystal chemical formula of the sample studied, the O(1)(W) + O(3)(V) site should be assigned to the

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[1] The table of anisotropic thermal parameters is available from the authors.

Table 3. Site occupancies, fractional coordinates, and thermal parameters in the tourmaline structure (space group *R*3*m*)

Site		Occupancy, au	*x*/*a*	*y*/*b*	*z*/*c*	$U^*_{eq/iso}$ × 100, Å^{-2}
X	3*a*	$Ca_{0.62}Na_{0.32}\square_{0.06}$	0	0	0.2289(3)	1.30(3)
Y	9*b*	$Al_{0.36}Li_{0.33}Fe_{0.22}Mg_{0.08}Ti_{0.01}$	0.12379(8)	0.06190	0.6319(2)	0.44(3)
Z	18*c*	$Al_{1.00}$	0.29735(5)	0.26050(5)	0.6113(1)	0.52(2)
B	9*b*	$B_{1.00}$	0.1094(1)	0.2188	0.4533(5)	0.58(7)
Si	18*c*	$Si_{1.00}$	0.19223(4)	0.19026(4)	0	0.44(2)
O(1)	3*a*	$F_{0.84}$	0	0	0.7861(13)	3.30(3)
O(11)	9*b*	$OH_{0.05}$	0.0329(12)	0.0165	0.797(2)	1.00(3)
O(2)	9*b*	$O_{1.00}$	0.0600(1)	0.1200	0.4784(4)	1.51(7)
O(3)	9*b*	$OH_{0.76}O_{0.24}$	0.2702(2)	0.1351	0.5097(3)	0.84(6)
O(4)	9*b*	$O_{1.00}$	0.0921(1)	0.1842	0.0727(3)	0.87(6)
O(5)	9*b*	$O_{1.00}$	0.1840(2)	0.0920	0.0947(3)	0.87(6)
O(6)	18*c*	$O_{1.00}$	0.1968(1)	0.1868(1)	0.7754(2)	0.67(5)
O(7)	18*c*	$O_{1.00}$	0.2859(1)	0.2857(1)	0.0813(2)	0.60(4)
O(8)	18*c*	$O_{1.00}$	0.2097(1)	0.2702(1)	0.4408(3)	0.69(5)
H	9*b*	$H_{1.00}$	0.252	0.126	0.415	4.00

* $U_{eq} = 1/3[U_{11}(a^*)^2a^2 + \ldots 2U_{23}b^*c^*bc\cos\alpha]$.

Table 4. Bond lengths (Å) in the structure of the sample under investigation

Y octahedron		*Z* octahedron		Si tetrahedron	
Y–O(1)	2.027(6)	*Z*–O(3)	1.955(4)	Si–O(4)	1.630(4)
Y–O(11)	1.720(2)	*Z*–O(6)	1.849(4)	Si–O(5)	1.645(4)
Y–O(2) × 2	2.003(4)	*Z*–O(7)	1.959(4)	Si–O(6)	1.602(4)
Y–O(3)	2.195(5)	*Z*–O(7)	1.859(4)	Si–O(7)	1.610(4)
Y–O(6) × 2	2.006(4)	*Z*–O(8)	1.911(4)	Si–O_{av}	1.622
Y–O_{av}	2.040; 1.989	*Z*–O(8)	1.885(4)	*X* polyhedron	
B triangle		*Z*–O_{av}	1.906	*X*–O(2) × 3	2.426(4)
B–O(2)	1.370(4)			*X*–O(4) × 3	2.768(4)
B–O(8) × 2	1.383(5)			*X*–O(5) × 3	2.707(5)
B–O_{av}	1.379			*X*–O_{av}	2.634

$(OH, F)^-_{3.28}O^{2-}_{0.72})$ composition in order to compensate for the charge.

In the structure studied, similar to that of the lithium-containing uvite [1], the O(1)(W) site is split into two sites, namely, O(1) and O(11) (Table 3). The O(1) site is located in the threefold symmetry axis, whereas the O(11) site is shifted from this axis to the plane of symmetry. The O(1)–O(11) distance is 0.46 Å. The *Y*–O(1) bond is significantly longer than the *Y*–O(11) bond (~2.03 and 1.72 Å, respectively; Table 4). The refinement of the occupancy of the O(1) site showed that, on the assumption of its population with fluorine anions only (by analogy with the previous studies [1]), their fraction is ~0.8 au, which agrees with the data of chemical analyses (Table 2). The fraction of oxygen anions (or OH groups) in the O(11) site (according to the results of the refinement) is ~0.2 au. The total occupancy of the O(1) and O(11) sites (with consideration for their multiplicities) is equal to unity, which indi-

Table 5. Unit cell parameters of liddicoatites (space group *R*3*m*)

a, Å	*c*, Å	References
15.894(4)	7.115(2)	Our data
15.875(3)	7.126(2)	[7]
15.880(1)	7.115(1)	[8]
15.882(1)	7.118(1)	[8]

Table 6. Site occupancies (au) and bond lengths (Å) in the crystal structures of liddicoatites

X polyhedron		*Y* octahedron			*Z* octahedron		References
Occupancy	X–O$_{av}$	occupancy	Y–O$_{av}$	Y–O(1) Y–O(3)	occupancy	Z–O$_{av}$	
$Ca_{0.62}Na_{0.32}\square_{0.06}$	2.634	$Al_{0.36}Li_{0.33}Fe_{0.22}$ $Mg_{0.08}Ti_{0.01}$	2.040	2.027 2.195	$Al_{1.00}$	1.906	Our data
$Ca_{0.65}Na_{0.35}$	2.646	$Al_{0.53}Li_{0.47}$	2.044	2.027 2.186	$Al_{1.00}$	1.908	[7]
$Ca_{0.45}Na_{0.44}\square_{0.11}$	2.645	$Li_{0.41}Al_{0.40}Mn_{0.18}$ $Mg_{0.01}$	2.066	2.183 2.184	$Al_{1.00}$	1.907	[8]
$Ca_{0.45}Na_{0.44}$ $K_{0.04}\square_{0.07}$	2.644	$Li_{0.40}Al_{0.40}Mn_{0.18}$ $Mg_{0.01}(Fe + Ti)_{0.01}$	2.063	2.178 2.185	$Al_{1.00}$	1.907	[8]

cates that the resultant occupancies are reliable. It follows from the refined value of the occupancy that all the bivalent oxygen anions (0.72 au per the refined formula) cannot be accommodated in the O(11) site and, therefore, a part of them populate the O(3)(V) site, which is usually filled mainly by OH groups.

Thus, based on the X-ray structure analysis, the refined crystal chemical formula of the tourmaline studied is $Ca_{0.62}Na_{0.32}\square_{0.06})(Al_{1.08}Li_{0.99}Fe_{0.66}Mg_{0.24}Ti_{0.03})Al_6 \cdot [Si_6O_{18}](BO_3)_3(OH_{2.28}O_{0.72})(F_{0.84}O_{0.16})$.

The unit cell parameters of the tourmaline studied and the mean bond lengths in the main polyhedra of its structure are close to those observed in the liddicoatite structures (Tables 5, 6). The almost identical dimensions of the *Y* octahedra in the structure studied and that of the iron-free liddicoatite [7] (~2.04 Å) are due to close sizes of the Li^+ and Fe^{2+} cations (the mean cation-to-oxygen distances in the octahedra are ~2.16 and 2.14 Å, respectively [6]). The increased dimensions of the *Y* octahedra in the liddicoatite structures reported in [8] (2.06–2.07 Å) are due to the accommodation of larger sized Mn^{2+} cations ($(Mn–O)_{av}$ = 2.24 Å [6]).

In the structure of tourmaline studied and that of liddicoatite described in [7], the O(1)(W) and O(3)(V) sites are populated mainly by fluorine and hydroxyl ions, respectively. In both structures, the *Y*–O(1) and *Y*–O(3) bond lengths differ significantly (2.03 and 2.19 Å, respectively; Table 6). In the structures of manganese-containing liddicoatites [8], where the content of fluorine anions is much less (only 0.3 au per formula), these distances are actually equal (~2.18 Å). This observation confirms the accommodation of fluorine in the O(1) site of the tourmaline studied.

The parameters of the O(3)–H...O(5) hydrogen bond in the structure studied [H–O(3), 0.720 Å; H···O(5), 2.463 Å; O(3)···O(5), 3.182 Å; and the O(3)–H···O(5) angle, 177.6°] are close to the values observed in other tourmaline structures [1].

CONCLUSIONS

The results of our studies show that calcium tourmalines from the pegmatite vein of the Sangilen Upland, which are enriched in lithium, vary in composition. Along with yellow lithium-containing uvites with the ideal formula $Ca(Mg_2Li)Al_6(Si_6O_{18})(BO_3)_3(OH)_3F$, this vein contains dark green tourmalines, whose composition can be described according to the results of the structural study by the following four-component system:

$$Ca(Li_{1.5}Al_{1.5})Al_6[Si_6O_{18}](BO_3)_3((OH)_2O)F$$

$$(62 \text{ mol } \%),$$

$$NaFe_3Al_6[Si_6O_{18}](BO_3)_3(OH)_3F \ (23 \text{ mol } \%),$$

$$NaMg_3Al_6[Si_6O_{18}](BO_3)_3(OH)_3OH \ (9 \text{ mol } \%),$$

$$\square(Al_2Li)Al_6[Si_6O_{18}](BO_3)_3(OH)_3OH \ (6 \text{ mol } \%).$$

The main component of such solid solutions corresponds to the mineral species which is close in composition to liddicoatite with the ideal formula $Ca(Li_2Al)Al_6[Si_6O_{18}](BO_3)_3(OH)_3F$, but differs from the latter one by the Li : Al ratio in the *Y* octahedra and the presence of bivalent oxygen anions in the O(3)(V) site. The Li : Al ratio in the tourmaline studied corresponds to that in the hypothetical oxyliddicoatite with the ideal formula $Ca(Li_{1.5}Al_{1.5})Al_6[Si_6O_{18}](BO_3)_3(OH)_3O$. An essential difference of the tourmaline studied from the hypothetical oxyliddicoatite consists in the population of the O(1)(W) site by fluorine and accommodation of additional oxygen anions in the O(3)(V) site.

Thus, the zonal tourmalines from the pegmatite vein of the Sangilen Upland are unique in chemical composition. The presence of zones which are different in color and essentially different in mineral composition in the same crystal sample indicates that the sample was formed under specific conditions characterized by abrupt changes. The dark green tourmaline reported in this paper, as well as the yellow one described in [1], can be considered as a new mineral species.

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