

1 **Revision 2**

2 **Synthesis and crystal structure of Pb-dominant tourmaline**

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5 Oleg S. Vereshchagin^{1,*}, Bernd Wunder², Sergey N. Britvin^{1,3}, Olga V. Frank-
6 Kamenetskaya¹, Franziska D.H. Wilke², Natalia S. Vlasenko⁴, Vladimir V. Shilovskikh⁴

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9 ¹Institute of Earth Sciences, Saint Petersburg State University, Universitetskaya Nab. 7/9,
10 199034 St. Petersburg, Russia

11 ²GFZ German Research Centre for Geosciences, 14473 Potsdam, Germany

12 ³Nanomaterials Research Center, Kola Science Center of Russian Academy of Sciences,
13 Fersman Str. 14, 184209 Apatity, Murmansk Region, Russia

14 ⁴Centre for Geo-Environmental Research and Modelling (Geomodel), Saint Petersburg State,
15 University, Ulyanovskaya Str. 1, 198504 St. Petersburg, Russia

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19 *E-mail: o.vereshchagin@spbu.ru

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ABSTRACT

Pb-dominant tourmaline was synthesized at 700 °C and 200 MPa in two hydrothermal experiments in the system MgO-Al₂O₃-B₂O₃-SiO₂-PbO-H₂O (run OV-4-2) and MgO-Al₂O₃-B₂O₃-SiO₂-PbO-CaO-Na₂O-H₂O (run OV-5-3), respectively. Run OV-4-2 forms needle-like (lengths up to 7 μm), lead-rich (up to 13.3 wt. % PbO) crystals that are chemically homogeneous. Run OV-5-3 forms columnar (lengths up to 400 μm) crystals that are chemically zoned (Pb-rich cores, up to 14.7 wt. % PbO, and Pb-poor rims, ~2 wt. % PbO). Additional phases that form in trace amounts are Pb-feldspar, quartz, diaspore (in OV-4-2) and talc, mullite, spinel, quartz (in OV-5-3). Single crystal structure refinement (SREF) of the central zone of Pb-rich tourmaline from the run OV-5-3 proves that Pb²⁺ cations occupy the X-site in the tourmaline structure. The unit-cell parameters of the studied tourmaline are: $a = 15.9508(10)$ Å, $c = 7.2024(6)$ Å. The formula derived from SREF results of this Pb-rich tourmaline is $X(\text{Pb}_{0.63}\square_{0.37})^Y(\text{Al}_{1.71}\text{Mg}_{1.29})^Z(\text{Al}_{5.04}\text{Mg}_{0.96})^T(\text{Si}_{6.00}\text{O}_{18})(\text{BO}_3)_3^V(\text{OH})_{3.00}^W(\text{O}_{1.00})$. Accordingly, the studied crystal is a Pb-analogue of hypothetical “oxy-uvite”, and thus referred to here as “Pb-oxy-uvite”. Similarities between (1) the paragenesis of Minh Tien tourmaline, and (2) the final experimental phase assemblages observed here, indicate comparable P, T -conditions of formation.

Key-words: tourmaline, Pb, crystal chemistry, lead end-member, synthesis

INTRODUCTION

45
46 Tourmalines are the most common borosilicates (*e.g.*, [London 2011](#)), which form in
47 rocks of different composition (*e.g.*, [Arif et al. 2010](#); [Trumbull et al. 2008](#)). Tourmaline has a
48 very accommodating crystal structure (*e.g.*, [Hawthorne et al. 2002](#); [O'Bannon III et al. 2018](#);
49 [Vereshchagin et al. 2018](#)) and is stable under a wide range of *P,T*-conditions (*e.g.*, [Ertl et al.](#)
50 [2010](#); [Bačík et al. 2011](#); [Henry and Dutrow 2012](#); [Lussier et al. 2016](#); [Berryman et al. 2019](#);
51 [Likhacheva et al. 2019](#)). There are 38 mineral species currently included in the tourmaline
52 supergroup (IMA CNMNC). The general formula for tourmaline is ${}^{\text{IX}}X {}^{\text{VI}}Y_3 {}^{\text{VI}}Z_6 ({}^{\text{IV}}T_6\text{O}_{18})$
53 $(\text{BO}_3)_3 V_3 W$ ([Henry et al. 2011](#)), where ${}^{\text{IX}}X = \text{Ca, Na, K, } \square(\text{vacancy})$; ${}^{\text{VI}}Y = \text{Li, Mg, Fe}^{2+}, \text{Fe}^{3+}$,
54 $\text{Al, Cr}^{3+}, \text{V}^{3+}$; ${}^{\text{VI}}Z = \text{Mg, Al, Fe}^{2+}, \text{Fe}^{3+}, \text{Cr}^{3+}, \text{V}^{3+}$; ${}^{\text{IV}}T = \text{Si, Al, B}$; $V = (\text{OH})^-, \text{O}^{2-}$; $W = (\text{OH})^-$,
55 $\text{F}^-, \text{O}^{2-}$. To date, for minerals of the tourmaline supergroup and tourmaline synthetic
56 analogues, there are about 25 elements that can occur as major constituents at different sites in
57 the structure (*e.g.*, [London et al. 2006](#); [Wunder et al. 2015](#); [Setkova et al. 2019](#)).

58 Tourmalines containing significant amounts of lead (up to 17.5 wt. % PbO) from the
59 Minh Tien granitic pegmatite, Vietnam were first reported by [Sokolov and Martin \(2009\)](#).
60 Recently, their geological settings and paragenesis were reported in detail ([Kubernátová 2019](#);
61 [Kubernátová and Cempírek 2019](#)). Additionally, Pb-bearing tourmalines also have been found
62 in Momeik, Myanmar (up to 1640 ppm Pb; [Ertl et al. 2007](#)), Eastern Alps, Austria (up to 0.5
63 wt. % PbO₂; [Ertl et al. 2019](#)), Madagascar (up to 0.5 wt. % PbO; [Lussier et al. 2011](#)) and Alto
64 Ligonha area, Mozambique (up to 15.4 wt.% PbO; [Sokolov and Martin 2009](#)). Even though
65 Pb-rich tourmaline has been known for more than a dozen years, lead distribution over
66 different sites in tourmaline crystal structure has not been studied yet. The aim of this study is
67 to synthesize a Pb-rich tourmaline, determine its crystal structure and characterize its crystal-
68 chemical features.

MATERIALS AND METHODS

69

70 **Synthesis**

71 Pb-bearing tourmaline was synthesized at a temperature of 700 °C and a pressure 200
72 MPa using hydrothermal pressure equipment. Two experiments were conducted, having
73 runtimes of 10 days (OV-4-2) and 14 days (OV-5-3). A mixture of solid MgO, γ -Al₂O₃, SiO₂,
74 and H₃BO₃ in the atomic proportions of end-member magnesio-foitite
75 ($\square(\text{Mg}_2\text{Al})\text{Al}_6(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{OH})_4$) was prepared following a procedure modified after
76 [Berryman et al. \(2015\)](#). Lead was added as PbO. In the experiment OV-4-2, the
77 PbO/magnesio-foitite ratio was 1/5. In the experiment OV-5-3, solid CaO and Na₂O were also
78 added to the oxide mixture to study possible Na-Ca-Pb substitution. The
79 CaO/Na₂O/PbO/magnesio-foitite ratio in this experiment was 1/1/2/20. To produce large
80 tourmaline crystals suitable for X-ray single crystal studies, the two-chamber method of [von](#)
81 [Goerne et al. \(1999\)](#) was applied to experiment the OV-5-3. Fifty milligrams of the oxide
82 mixture was loaded in gold capsules along with deionized water (1 μl of fluid for every 3 mg
83 of solid). The capsules were placed in standard, cold-seal hydrothermal pressure vessels, with
84 the pressure maintained within 10 MPa of the target pressure. Temperature was measured
85 with a Ni–CrNi thermocouple placed within the wall of the autoclave, with an estimated error
86 of ± 10 °C. The samples were quenched by cooling the autoclave with compressed air to less
87 than 100 °C in 5 min. Finally, the sample material was removed and prepared for analysis by
88 optical microscopy, X-ray diffraction, scanning electron microscopy and electron microprobe
89 analysis.

90 **Analytical techniques**

91 Powder X-ray diffraction (PXRD) patterns of newly formed phases were recorded on a
92 STOE Stadi P diffractometer (CuK α_1 radiation, 40 kV accelerating voltage, a 40 mA beam
93 current, 2 Θ range 5–125°, 0.01° step). Relative phase proportions were determined by
94 Rietveld refinement using Bruker TOPAS v. 5.0 software.

95 Single-crystal X-ray diffraction (SREF) data were collected by means of Bruker
96 Kappa APEX II diffractometer equipped with flat APEX II CCD detector, using MoK α
97 radiation generated by the microfocus tube. Data collection and processing routines were
98 carried out using Bruker APEX2 and Bruker SAINT programs. The crystal structure of Pb-
99 tourmaline was solved by the dual space method and refined using *SHELX*-2018 set of
100 programs (Scheldrick 2015) via Olex2 v.1.2.8 graphical user interface (Dolomanov et al.
101 2009). The occupancy of partially vacant X-site was freely refined assuming scattering factor
102 of Pb⁰. The distribution of Mg and Al between fully occupied octahedral Y- and Z- sites was
103 fixed according to (1) bond-valence considerations (the exact values reported derived from
104 the manual minimization of difference between the average ionic charge of atoms occupying
105 the site (Y/Z) and sum of bond valences) and (2) the electron microprobe data. It is
106 noteworthy that the attempted free refinement of Al/Mg ratios at the octahedral sites gave
107 almost the same results as the process of determining occupancies manually based on bond
108 valence calculations. The average bond length at the T-site, 1.625 Å, suggests that the T-
109 tetrahedron is occupied solely by Si, hence the occupancy was fixed at Si = 1.

110 Composition and morphology of synthesized crystals were analyzed on the epoxy-
111 mounted, polished, and carbon-coated samples by means of a JEOL Hyperprobe JXA-8500F
112 equipped with a thermal field-emission cathode and five wavelength-dispersive
113 spectrometers (WDS) and an Hitachi S-3400N scanning electron microscope (SEM) equipped
114 with AzTec Energy X-Max 20 energy dispersive spectrometer (EDX), using the following
115 analytical standards: schorl for Si (K α), and Al (K α), wollastonite for Ca (K α), albite for Na
116 (K α), diopside for Mg (K α) and vanadinite for Pb (M β). WDS raw data were processed
117 applying a $\phi(\rho Z)$ correction scheme (CITZAF; Armstrong 1995). To monitor possible peak
118 shifts during the course of the measurements, the calibration material was analyzed before,
119 during and after the analysis. EDX maps were obtained under 20 kV accelerating voltage, 1.5

120 nA beam current, 60 sec dwell time. All the calculations and corrections were conducted
121 automatically with Oxford AzTec software. Tourmaline empirical was calculated on the basis
122 of 15 ($T + Y + Z$) atoms per formula unit (*apfu*) considering that: (1) vacancies may occur at
123 the X -site, (2) lead occurs at the X -site, (3) no excess of boron ($B = 3$ *apfu*). H_2O was
124 calculated on the basis of an electroneutral formula as: $V_{OH}=3$ and ${}^W O/OH$ ratio, based on
125 $Y+Z+T=15$.

126 RESULTS AND DISCUSSION

127 Morphology and composition of the run products

128 Solid run products from synthesis OV-4-2 and OV-5-3 differ significantly (Table S1).
129 The main solid product in both syntheses is tourmaline (~72 and ~52 vol.%, respectively).
130 Additional phases in the run OV-4-2 are lead feldspar (~12 vol.%; Table S1; Figure 1a),
131 diaspore (~3 vol.%) and quartz (~8 vol.%), whereas the synthesis OV-5-3 contains talc (~20
132 vol.%; Figure 1b), mullite (~12 vol.%), spinel (~9 vol.%) and quartz (~4 vol.%).

133 In both experiments, tourmaline forms euhedral elongated crystals (Figure 1c, 1d). The
134 forms of the resultant crystals are dominated by (1) trigonal pyramids and trigonal prisms
135 (OV-4-2); and (2) trigonal pyramids and hexagonal prisms (OV-5-3). Tourmalines from the
136 synthesis OV-4-2 form rosette-like, acicular aggregates of small, thin crystals (up to 1×7 μm ;
137 Figure 1c). Tourmalines from the synthesis OV-5-3 are much larger (up to 40×400 μm ;
138 Figure 1d) and are observed both as single crystals and as intergrowth of crystals.

139 Tourmaline crystals from the synthesis OV-4-2 do not show significant chemical
140 zoning, while tourmalines from the synthesis OV-5-3 demonstrate strong chemical zonation
141 (Figure 2; Table 1). Tourmalines from the synthesis OV-5-3 show compositional rim-core
142 variation: an increase in PbO and MgO content and a decrease in Al_2O_3 content. There is also
143 an inverse correlation between Pb and Na content in the tourmaline ($r^2=0.99$; Table 1); the
144 Na/Pb zonation is shown in Figure 2. The X -site of the Pb-rich core region of the synthesized

145 tourmaline is dominated by lead (0.51-0.71 *apfu*, Table 1). Thus, according to the current
146 classification (Henry et al. 2011), this tourmaline belongs to Ca-group and could be classified
147 as a member of the hypothetical “Pb-oxy-uvite” – “Pb-uvite” – oxy-foitite series.

148 **Crystal structure of synthetic tourmaline**

149 The results of single crystal X-ray structure refinement on Pb-rich material taken from
150 the central region of a crystal from experiment OV-5-3 (No 1; Table 1; Figure 2) are
151 summarized in Tables S2-S4. Comparison of our synthetic Pb-rich tourmaline with published
152 data on Al-Mg tourmalines, having X-site vacant (synthetic magnesio-foitite; [Berryman et al.](#)
153 [2016](#)), X-site occupied by Ca (synthetic oxy-uvite; [Berryman et al. 2016](#)) and X-site occupied
154 by Na (natural dravite; [Pertlik et al. 2003](#)) shows its crystal-chemical features. The unit-cell
155 parameters of the studied tourmaline ($a = 15.9508(10)$, $c = 7.2024(6)$ Å; Table S2)
156 significantly exceed those of the magnesio-foitite ($a = 15.910(1)$, $c = 7.131(1)$ Å; [Berryman et](#)
157 [al. 2016](#)), oxy-uvite ($a = 15.907(1)$, $c = 7.179(1)$ Å; [Berryman et al. 2016](#)) and are slightly
158 larger than those of dravite ($a = 15.946(1)$, $c = 7.172(1)$ Å; [Pertlik et al. 2003](#)). The site
159 scattering (*epfu*; electrons per formula unit) of the X-site indicates presence of lead cation at
160 this site (51.74(1) *epfu*; Table S3). Further evidence for Pb at the X-site comes from the
161 average bond length in XO_9 polyhedron ($\langle X-O \rangle = 2.696$ Å; Table S5) and XO_9 volume
162 ($V(XO_9) = 32.36$ Å³; Table S5). These are significantly larger than those of oxy-uvite ($\langle X-O \rangle$
163 $= 2.656$ Å, $V(XO_9) = 30.98$ Å³; [Berryman et al. 2016](#)) or dravite ($\langle X-O \rangle = 2.663$ Å, $V(XO_9)$
164 $= 31.25$ Å³; [Pertlik et al. 2003](#)) and attributed to the larger ionic radius of Pb^{2+} relative to Ca^{2+}
165 and Na^+ ($r^{IX}Ca^{2+} = 1.18 < r^{IX}Na^+ = 1.24$ Å $< r^{IX}Pb^{2+} = 1.35$ Å; [Shannon 1976](#)). The synthesis of
166 our Pb-tourmaline was carried out under acid conditions (boric acid solution). It is known
167 from inorganic chemistry that Pb^{4+} can not exist in acidic aqueous solutions. In fact, Pb^{2+} can
168 only be oxidized to Pb^{4+} under acid conditions *via* electrochemical pathway – a process
169 occurring in lead accumulators. Because of that, there are no compounds of Pb^{4+} (neither

170 mineral nor synthetic) known to precipitate in acidic aqueous media. Therefore, there is no
171 reason to expect Pb^{4+} in synthetic Pb-tourmaline. Bond valence calculations also prove the
172 presence of Pb^{2+} at the X-site (Table S6). Disordering of Al/Mg over both Y- and Z-sites is
173 supported by (1) WDS data, which consistently show $\text{Al} > 6 \text{ apfu}$; and (2) a observed $\langle \text{Z-O} \rangle$
174 value of 1.934 Å, which is significantly greater than that known to correspond to full $^{\text{Z}}\text{Al}$
175 occupancy in tourmaline (1.904-1.910 Å; Hawthorne et al. 1993; Lussier et al. 2011;
176 Kutzschbach et al. 2016). This latter point is in accord with the size difference between
177 $r^{\text{VI}}\text{Al}=0.54$ and $r^{\text{VI}}\text{Mg}=0.72$ Å (Shannon 1976). Complete occupancy of the T-site by Si is
178 shown by both WDS results and the observed $\langle \text{T-O} \rangle$ distance. The final formula of the
179 studied synthetic Pb-rich tourmaline is $^{\text{X}}(\text{Pb}_{0.63}\square_{0.37})^{\text{Y}}(\text{Al}_{1.71}\text{Mg}_{1.29})^{\text{Z}}(\text{Al}_{5.04}\text{Mg}_{0.96})^{\text{T}}(\text{Si}_{6.00}\text{O}_{18})$
180 $(\text{BO}_3)_3^{\text{V}}(\text{OH})_{3.00}^{\text{W}}(\text{O}_{1.00})$. The small difference between chemical composition of core of the
181 crystal from OV-5-3 (No 1; Table 1) and SREF formula could be resulted from the zonation
182 “in deep” of the crystal, which can’t be seen on SEM.

183 IMPLICATIONS

184 Henry et al. (2011) classifies tourmalines into primary groups on the basis of X-site
185 occupancy. Natural tourmalines commonly contain at the X-site, Na^+ , Ca^{2+} , \square , and, more
186 rarely, K^+ (e.g., Lussier et al. 2016; Berryman et al. 2014), whereas synthetic tourmaline could
187 also contain NH_4^+ (Wunder et al. 2015), Li^+ (Kutzschbach et al. 2017) and Ag^+ (London et al.
188 2006). Our data show that tourmaline can incorporate significant amounts of Pb^{2+} (up to 0.71
189 apfu) at the X-site. Natural Pb-rich tourmalines (e.g., Sokolov and Martin 2009) thus (1)
190 belong to the Ca-group (based on dominant-valence rule) and (2) be new members of the
191 tourmaline supergroup (where $^{\text{X}}\text{Pb} > 0.5 \text{ apfu}$). Interestingly, Pb-bearing tourmalines reported
192 by Sokolov and Martin (2009) and Kubernátová (2019) are also Li-rich and could be
193 classified as “Pb-liddicoatite” and “Pb-elbaite”. The synthetic Pb-dominant tourmaline from

194 this study can be used as an anthropotype for further investigations into the parageneses of
195 natural, Pb-rich tourmalines, as these tend to be very small and show strong chemical zoning.

196 Natural Pb-tourmalines from the Minh Tien granitic pegmatite are strongly zoned
197 concerning its Pb-contents (from 1.11 to 15.31 wt. % PbO; [Martin 2018, personal](#)
198 [communications](#)) and were found in association with Pb-bearing feldspar (up to 0.7 wt. %
199 PbO; [Sokolov and Martin 2009](#)), quartz and albite ([Sokolov and Martin, 2009](#); [Kubernátová,](#)
200 [2019](#)). Pb-rich synthetic tourmaline from our experiment OV-4-2 at 200 MPa, 700 °C
201 precipitates with a very similar phase assemblage (lead feldspar, quartz and diaspore), which
202 might indicate similar *P,T*-conditions of their formation.

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Table 1. Chemical composition of Pb-bearing tourmalines (WDS)

Component, wt.%	OV-4-2	OV-5-3 (1*)	OV-5-3 (2*)	OV-5-3 (3*)	
SiO ₂	32.39	31.69	33.37	36.85	
Al ₂ O ₃	32.52	30.64	33.59	36.83	
MgO	9.25	10.55	8.88	7.96	
PbO	13.34	14.69	10.79	2.40	
Na ₂ O	0.00	0.00	0.39	1.11	
CaO	0.00	0.25	0.21	0.19	
H ₂ O (calc)	2.89	3.02	2.82	3.04	
B ₂ O ₃ ** (calc)	9.79	9.68	9.99	10.67	
Total	100.18	100.52	100.04	99.05	
Calculated on the basis of 15 (<i>T</i> + <i>Y</i> + <i>Z</i>) atoms per formula unit					
<i>X</i>	Pb	0.64	0.71	0.51	0.11
	Na	0.00	0.00	0.13	0.35
	Ca	0.00	0.05	0.04	0.03
	□	0.36	0.24	0.32	0.51
<i>Y+Z</i>	Al	6.55	6.18	6.70	7.07
	Mg	2.45	2.82	2.30	1.93
	Sum	9	9	9	9
<i>T</i>	Si	5.75	5.69	5.81	6.00
	Al	0.25	0.31	0.19	0.00
	Sum	6	6	6	6
<i>V+W</i>	O	0.58	0.38	0.72	0.70
	OH	3.42	3.62	3.28	3.30
	Sum	4	4	4	4

Note: * Note: *numbers are those from Figure 2. **B₂O₃ fixed at 3 *apfu*.

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FIGURE CAPTIONS

314 Figure 1. SEM images of Pb-bearing tourmaline and associated phases: (a) tourmaline needles

315 in massive Pb-feldspar (BSE-image; OV-4-2), (b) elongated columnar tourmaline crystals

316 with talc (plate crystals) and mullite (SE-image; OV-5-3), (c) sun-like tourmaline crystals

317 (SE-image; OV-4-2), (d) intergrowth of columnar tourmaline crystals (BSE-image; OV-5-3).

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319 Figure 2. SEM image of zoned Pb-tourmaline crystal (OV-5-3): (a) SE-image, (b) elemental

320 map in NaK α , CaK α and PbM α of studied crystal, (c) sodium distribution in the crystal, (d)

321 lead distribution in the crystal.

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