# Oxy-foitite, $\Box$ (Fe<sup>2+</sup>Al<sub>2</sub>)Al<sub>6</sub>(Si<sub>6</sub>O<sub>18</sub>)(BO<sub>3</sub>)<sub>3</sub>(OH)<sub>3</sub>O, a new mineral species of the tourmaline supergroup

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**Abstract:** Oxy-foitite,  $\Box$ (Fe<sup>2+</sup>Al<sub>2</sub>)Al<sub>6</sub>(Si<sub>6</sub>O<sub>18</sub>)(BO<sub>3</sub>)<sub>3</sub>(OH)<sub>3</sub>O, is a new mineral of the tourmaline supergroup. It occurs in high-grade migmatitic gneisses of pelitic composition at the Cooma metamorphic Complex (New South Wales, Australia), in association with muscovite, K-feldspar and quartz. Crystals are black with a vitreous luster, sub-conchoidal fracture and gray streak. Oxy-foitite has a Mohs hardness of ~7, and has a calculated density of 3.143 g/cm<sup>3</sup>. In plane-polarized light, oxy-foitite is pleochroic (*O* = dark brown and *E* = pale brown), uniaxial negative. Oxy-foitite belongs to the trigonal crystal system, space group *R3m*, *a* = 15.9387(3)Å, *c* = 7.1507(1)Å and *V* = 1573.20(6)Å<sup>3</sup>, *Z* = 3. The crystal structure of oxy-foitite was refined to *R*1 = 1.48% using 3247 unique reflections from single-crystal X-ray diffraction using MoK $\alpha$  radiation. Crystal-chemical analysis resulted in the empirical structural formula:

Oxy-foitite belongs to the *X*-site vacant group of the tournaline-supergroup minerals, and shows chemical relationships with foitite through the substitution  ${}^{Y}Al^{3+} + {}^{W}O^{2-} \rightarrow {}^{Y}Fe^{2+} + {}^{W}(OH)^{1-}$ .

Key-words: oxy-foitite; tourmaline; crystal structure; optical absorption spectroscopy; infrared spectroscopy; new mineral.

### 1. Introduction

The tourmaline-supergroup minerals are cyclosilicates that typically crystallize in the space group R3m. They are widespread in the Earth's crust, occurring in sedimentary rocks, granites and granitic pegmatites and in low-grade to ultrahigh-pressure metamorphic rocks (*e.g.*, Dutrow & Henry, 2011).

The general formula of tourmaline may be written as:  $XY_3Z_6T_6O_{18}(BO_3)_3V_3W$ , with  $X = Na^{1+}, K^{1+}, Ca^{2+}, \square$ (= vacancy);  $Y = Al^{3+}$ ,  $Fe^{3+}$ ,  $Cr^{3+}$ ,  $V^{3+}$ ,  $Mg^{2+}$ ,  $Fe^{2+}$ ,  $Mn^{2+}$ ,  $Li^{1+}$ ;  $Z = Al^{3+}$ ,  $Fe^{3+}$ ,  $Cr^{3+}$ ,  $V^{3+}$ ,  $Mg^{2+}$ ,  $Fe^{2+}$ ;  $T = Si^{4+}$ ,  $Al^{3+}$ ,  $B^{3+}$ ;  $B = B^{3+}$ ,  $W = OH^{1-}$ ,  $F^{1-}$ ,  $O^{2-}$ ;  $V = OH^{1-}$ ,  $O^{2-}$  being the most common occupants at each site. Note that the letters from the formula (X, Y, Z and B) are not italicized where they represent groups of cations at the <sup>[9]</sup>X, <sup>[6]</sup>Y, <sup>[6]</sup>Z, <sup>[4]</sup>T and <sup>[3]</sup>B crystallographic sites (letters italicized). As for the letters V and W, they represent groups of anions accommodated at the <sup>[3]</sup>O3 and <sup>[3]</sup>O1 crystallographic sites, respectively.

The crystal chemistry of tourmaline has been extensively studied (*e.g.*, Foit & Rosenberg, 1977; Foit, 1989; Grice & Ercit, 1993; Hawthorne *et al.*, 1993; Hawthorne, 1996, 2002, 2016; Hawthorne & Henry, 1999; Ertl *et al.*, 2002; Bosi & Lucchesi, 2007; Bosi, 2010, 2011, 2013; Lussier *et al.*, 2008, 2011a and b; Lussier & Hawthorne, 2011; Henry & Dutrow, 2011; Henry *et al.*, 2011; Bosi *et al.*, 2015a, 2016a and b). The results show that the tourmaline structure exhibit a pronounced flexibility in a chemical sense, accommodating ions of a wide range of size and charge as well as cation vacancies (commonly at the X site and rarely at the Y site). Furthermore, the structure allows extensive cation disordering between the Y and Z sites. This flexibility is reflected by the tourmaline supergroup currently consisting of 33 species approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA).

After the publication of the revised tourmaline nomenclature (Henry *et al.*, 2011), 16 new tourmalines mostly belonging to the *X*-site alkali group and only two to the *X*-site calcic group have been approved by the IMA-CNMNC (Table 1). In the light of this new nomenclature scheme we realized that the chemical composition reported in Bosi & Lucchesi (2004) for sample TM84a from Cooma metamorphic Complex (New South Wales, Australia) is consistent with a new tourmaline species belonging to the *X*-site vacant group, oxy-foitite, ideally  $\Box$ (Fe<sup>2+</sup>Al<sub>2</sub>)Al<sub>6</sub>(Si<sub>6</sub>O<sub>18</sub>)(BO<sub>3</sub>)<sub>3</sub>(OH)<sub>3</sub>O. A hypothetical "oxy-foitite" end-member of the tourmaline group was proposed by Hawthorne & Henry (1999). Medaris *et al.* (2003) assessed the potential occurrence of "oxy-foitite" in a natural setting by micro-chemical analyses of zoned

890

Table 1.	Tourmalines approved	by the IMA	A since the nomenclature	revision by	y Henr	y et al.	(2011)	)."
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Name	Formula	Reference
Alkali group		
Oxy-chromium-dravite	NaCr <sub>3</sub> (Cr <sub>4</sub> Mg <sub>2</sub> )(Si <sub>6</sub> O <sub>18</sub> )(BO <sub>3</sub> ) <sub>3</sub> (OH) <sub>3</sub> O	Bosi et al. (2012a)
Tsilaisite	NaMn <sub>3</sub> Al <sub>6</sub> (Si <sub>6</sub> O <sub>18</sub> )(BO <sub>3</sub> ) <sub>3</sub> (OH) <sub>3</sub> (OH)	Bosi et al. (2012b)
Oxy-dravite	$Na(Al_2Mg)(Al_5Mg)(Si_6O_{18})(BO_3)_3(OH)_3O$	Bosi & Skogby (2013)
Oxy-schorl	$Na(Fe_2Al)Al_6(Si_6O_{18})(BO_3)_3(OH)_3O$	Bačík et al. (2013)
Oxy-vanadium-dravite <sup>b</sup>	NaV <sub>3</sub> (V <sub>4</sub> Mg <sub>2</sub> )(Si <sub>6</sub> O <sub>18</sub> )(BO <sub>3</sub> ) <sub>3</sub> (OH) <sub>3</sub> O	Bosi et al. (2013a)
Darrellhenryite	$Na(LiAl_2)Al_6(Si_6O_{18})(BO_3)_3(OH)_3O$	Novák et al. (2013)
Fluor-elbaite	Na(Li <sub>1.5</sub> Al <sub>1.5</sub> )Al <sub>6</sub> (Si <sub>6</sub> O <sub>18</sub> )(BO <sub>3</sub> ) <sub>3</sub> (OH) <sub>3</sub> F	Bosi et al. (2013b)
Vanadio-oxy-dravite	NaV <sub>3</sub> (Al <sub>4</sub> Mg <sub>2</sub> )(Si <sub>6</sub> O <sub>18</sub> )(BO <sub>3</sub> ) <sub>3</sub> (OH) <sub>3</sub> O	Bosi et al. (2014a)
Vanadio-oxy-chromium-dravite	NaV <sub>3</sub> (Cr <sub>4</sub> Mg <sub>2</sub> )(Si <sub>6</sub> O <sub>18</sub> )(BO <sub>3</sub> ) <sub>3</sub> (OH) <sub>3</sub> O	Bosi et al. (2014b)
Chromo-alumino-povondraite	NaCr <sub>3</sub> (Al <sub>4</sub> Mg <sub>2</sub> )(Si <sub>6</sub> O <sub>18</sub> )(BO <sub>3</sub> ) <sub>3</sub> (OH) <sub>3</sub> O	Reznitskii et al. (2014)
Fluor-tsilaisite	NaMn <sub>3</sub> Al <sub>6</sub> (Si <sub>6</sub> O <sub>18</sub> )(BO <sub>3</sub> ) <sub>3</sub> (OH) <sub>3</sub> F	Bosi et al. (2015b)
Maruyamaite	$K(Al_2Mg)(Al_5Mg)(Si_6O_{18})(BO_3)_3(OH)_3O$	Lussier et al. (2016)
Bosiite	$NaFe^{3+}_{3}(Al_4Mg_2)(Si_6O_{18})(BO_3)_3(OH)_3O$	Ertl et al. (2016)
Calcic group		
Adachiite	$CaFe^{2+}{}_{3}Al_{6}(Si_{5}AlO_{18})(BO_{3})_{3}(OH)_{3}(OH)$	Nishio-Hamane et al. (2014)
Lucchesiite	$CaFe^{2+}{}_{3}Al_{6}(Si_{6}O_{18})(BO_{3})_{3}(OH)_{3}O$	Bosi et al. (2017)
Vacant group		
Oxy-foitite	$\Box(Fe^{2+}Al_2)Al_6(Si_6O_{18})(BO_3)_3(OH)_3O$	This study

<sup>a</sup> Approved tourmalines until 2011. *Alkali group*: dravite, schorl, chromium-dravite, fluor-dravite, fluor-schorl, elbaite, povondraite, fluorbuergerite, olenite, luinaite-(OH). *Calcic group*: fluor-uvite, feruvite, fluor-liddicoatite. *Vacant group*: foitite, magnesio-foitite, rossmanite. <sup>b</sup> Redefinition of the former mineral "vanadium-dravite".

tourmaline grains from quartz veins in the Baraboo Quartzite (Wisconsin, USA), and they found cores richer in "oxy-foitite". Other localities from which "oxy-foitite" compositions were reported are: Vystrčenovice, between Dačice and Telč, Moldanubian, Czech Republic (Povondra, 1981; Novák *et al.*, 2004) and Penamacor-Monsanto granite pluton, central eastern Portugal (Ribeiro da Costa *et al.*, 2014).

The new mineral and its name have been approved by the IMA-CNMNC (proposal 2016-069). The holotype specimen of oxy-foitite from the Cooma Complex is deposited in the mineralogical collections of the Museum of Earth Sciences, Department of Earth Sciences, Sapienza University of Rome, Piazzale Aldo Moro 5, 00185 Roma, Italy, catalogue number 8829/84.

# 2. Occurrence, appearance, physical and optical properties

The holotype fragment of oxy-foitite was found in granitic pegmatites in leucosomes and pegmatitic patches occurring in high-grade migmatitic gneisses of pelitic composition at the Cooma metamorphic Complex, New South Wales, Australia. Associated minerals are muscovite, K-feldspar and quartz. The oxy-foitite formation is related to the partial melting of these mentioned magmatic gneisses. Details on the Cooma metamorphic Complex can be found, for example, in Ellis & Obata (1992), and Collins (1993).

The mineral forms crystals up to  $\sim 1 \text{ cm}$  in size, subhedral prismatic and striated parallel to [0001]. They contain frequent and evenly distributed micro-fractures filled with additional phases, notably muscovite. Oxyfoitite is black with a vitreous luster and a gray streak and shows no fluorescence. It has a Mohs hardness of approximately 7, it is brittle with no observed cleavage or parting and has conchoidal fracture. The calculated density is  $3.142 \text{ g/cm}^3$ . In transmitted light, oxy-foitite is pleochroic with O = dark brown and E = pale brown. It is uniaxial negative with refractive indices, measured by the immersion method using white light from a tungsten source, of  $\omega = 1.660(5)$ ,  $\varepsilon = 1.630(5)$ . The mean index of refraction, density, and chemical composition lead to an excellent compatibility index  $(1 - K_p/K_c = 0.021)$  (Mandarino, 1981).

## 3. Experimental methods and results

Single-crystal X-ray diffraction, electron microprobe and Mössbauer spectroscopy data for oxy-foitite were reported for sample TM84a by Bosi & Lucchesi (2004). Table 2 shows chemical data for oxy-foitite reported in Bosi & Lucchesi (2004) along with new information on the compositional variation in the analyzed crystal.

#### 3.1. Single-crystal structure refinement

With regard to the structural parameters, Bosi & Lucchesi (2004) did not provide data on fractional atom coordinates, displacement parameters, hydrogen positions and the Flack parameter in the refinement of sample TM84a.

In order to present a complete and more precise crystalstructure description of oxy-foitite, the single crystal used for X-ray-diffraction and electron microprobe analyses was removed from the epoxy resin and studied again with a Bruker KAPPA APEX-II single-crystal diffractometer (Sapienza University of Rome, Earth Sciences Department), equipped with a CCD area detector  $(6.2 \times 6.2 \text{ cm}^2)$ 

Sample TM84a	Average <sup>a</sup>	Min-Max range		Atomic fraction <sup>a</sup>
SiO <sub>2</sub> (wt.%)	35.67(44)	34.95-36.09	Si (apfu)	5.89
TiO <sub>2</sub>	0.22(1)	0.21-0.24	Ti <sup>4+</sup>	0.03
$B_2 \tilde{O_3}^b$	10.52		В	3.00
Al <sub>2</sub> O <sub>3</sub>	36.49(23)	36.29-36.81	Al	7.11
FeO <sub>tot</sub>	9.40(31)	9.07-9.89	Fe <sub>tot</sub>	1.30
MgO	2.48(2)	2.46-2.51	Mg	0.61
MnO	0.36(5)	0.32-0.43	Mn <sup>2+</sup>	0.05
ZnO	0.09(7)	0.00-012	Zn	0.01
CaO	0.06(7)	0.05-0.07	Ca	0.01
Na <sub>2</sub> O	1.41(4)	1.35-1.45	Na	0.45
K <sub>2</sub> Õ	0.03(1)	0.01-0.04	K	0.01
F	0.07(7)	0.00-0.15	F	0.04
H <sub>2</sub> O <sup>b</sup>	3.08		OH	3.39
Õ=F	-0.03			
Fe <sub>2</sub> O <sub>3</sub> <sup>c</sup>	1.15		Fe <sup>3+</sup>	0.14
FeOc	8.37		Fe <sup>2+</sup>	1.16
Total	99.97		X-site vacancy	0.53

Table 2. Chemical composition of oxy-foitite from electron microprobe.

*Note:* Atoms per formula unit (apfu) calculated on the basis of 31 anions (O,OH,F). Errors for oxides and fluorine (in brackets) are standard deviation of 10 point analyses.

<sup>a</sup> From Bosi & Lucchesi (2004).

<sup>b</sup> Calculated by stoichiometry.

<sup>c</sup> Determined by Mössbauer spectroscopy (Bosi & Lucchesi, 2004).

active detection area,  $512 \times 512$  pixels) and a graphitecrystal monochromator, using MoK $\alpha$  radiation from a fine-focus sealed X-ray tube. The sample-to-detector distance was 4 cm. A total of 5481 exposures (step = 0.2°, time/step = 20 s) covering a full reciprocal sphere with resolution d = 0.47 Å and redundancy of about 15 was collected. Final unit-cell parameters were refined using the Bruker AXS SAINT program on reflections with  $I > 10\sigma$ (*I*) in the range 5° < 2 $\theta$  < 97°. The intensity data were processed and corrected for Lorentz, polarization and background effects with the APEX2 software program of Bruker AXS. The data were corrected for absorption using a multi-scan method. No violations of *R*3*m* symmetry were noted.

The structure refinement (SREF) was done with the SHELXL-2013 program (Sheldrick, 2013), using neutral scattering factors. The X site was refined by setting the Ca and K occupancy to 0.01 atoms per formula unit (apfu) and allowing the remaining of the site to refine as Na =  $(0.98 - \Box)$  apfu. The Y and Z sites were modelled using Al vs. Fe. The T and B sites were refined using Si and B scattering factors, respectively, and were held fixed at full occupancy, following the observation that removing these constraints during refinement cycles resulted in no significant deviation from full occupancy at any of these sites. The H1 and H3 sites were refined by setting their occupancy to 0.39 and 1.00 (respectively), based on chemical data. The position of the H atoms bonded to the oxygen at the O1 and O3 positions in the structure was taken from the difference-Fourier map and incorporated into the refinement model; the O1-H1 and O3-H3 bond lengths were constrained to be 0.97(3) Å. The results of this new SREF provide better statistical indices and more precise structural parameters such as the

Table 3. Single-crystal X-ray diffraction data details for oxy-foitite.

Sample	TM84a
Crystal size (mm)	$0.18 \times 0.18 \times 0.20$
a (Å)	15.9387(3)
$c(\dot{A})$	7.1507(1)
$V(Å^3)$	1573.20(6)
Range for data collection, $2\theta$ (°)	5–97
Reciprocal space range h k l	-33 < h < 33
	-33 < k < 33
	$-12 \le l \le 14$
Total number of frames	5481
Measured reflections	27576
Unique reflections, $R_{int}$ (%)	3247, 1.40
Redundancy	15
Absorption correction method	SADABS
Refinement method	Full-matrix least-squares
	on $F^2$
Structural refinement program	SHELXL-97
Extinction coefficient	0.00025(19)
Flack parameter	-0.013(12)
wR2 (%)	3.80
R1 (%) all data	1.48
R1 (%) for $I > 2\sigma(I)$	1.46
GooF	1.071
Largest diff. peak and hole $(\pm e^{-1}/Å^3)$	-0.52 and 1.12

*Notes*:  $R_{int}$  = merging residual value; R1 = discrepancy index, calculated from *F*-data; wR2 = weighted discrepancy index, calculated from  $F^2$ -data; GooF = goodness of fit; diff. peak = maximum and minimum residual electron density. Radiation, Mo $K\alpha$  = 0.71073 Å. Data collection temperature = 293 K. Space group R3m; Z = 3.

bond distances, with respect to the data reported by Bosi & Lucchesi (2004). Table 3 shows selected X-ray diffraction details, while Table 4 reports fractional atom coordinates, equivalent displacement parameters and site

Site	x	У	Ζ	$U_{ m eq}$	Occupancy
X	0	0	0.2252(4)	0.0199(6)	$Na_{0.458(7)}Ca_{0.01}K_{0.01}$
Y	0.12365(2)	0.06182(2)	0.62928(5)	0.00727(6)	$Al_{0.592(3)}Fe_{0.408(3)}$
Ζ	0.29792(2)	0.26128(2)	0.60960(4)	0.00477(6)	$Al_{0.982(2)}Fe_{0.018(2)}$
В	0.11004(3)	0.22009(7)	0.45435(15)	0.00567(12)	$B_{1,00}$
Т	0.19175(2)	0.18973(2)	Ó	0.00403(3)	Si <sub>1.00</sub>
O1(≡W)	Ó	Ó	0.7741(3)	0.0254(4)	$O_{1.00}$
02	0.06151(3)	0.12302(6)	0.48961(14)	0.01398(15)	O <sub>1.00</sub>
O3(≡V)	0.26499(8)	0.13249(4)	0.50862(13)	0.01306(13)	O <sub>1.00</sub>
04	0.09380(3)	0.18761(6)	0.06941(12)	0.00880(10)	$O_{1.00}$
05	0.18739(6)	0.09370(3)	0.09204(12)	0.00885(10)	O1 00
06	0.19665(4)	0.18603(4)	0.77549(8)	0.00779(7)	$O_{1.00}$
07	0.28532(3)	0.28576(3)	0.07791(8)	0.00671(7)	O1 00
08	0.20968(4)	0.27057(4)	0.43943(9)	0.00815(7)	O1.00
H1	0	0	0.907(4)	$0.03^{a}$	Ho 20
H3	0.255(2)	0.1276(10)	0.379(3)	0.016 <sup>a</sup>	$H_{1.00}$

Table 4. Fractional atom coordinates, equivalent displacement parameters (Å<sup>2</sup>) and site occupancy for oxy-foitite.

<sup>a</sup> Isotropic displacement parameters ( $U_{iso}$ ) for H1 and H3 constrained to have a  $U_{iso}$  1.2 times the  $U_{eq}$  value of the O1 and O3 oxygen atoms.

Table 5. Selected bond distances (Å) in oxy-foitite.

Sample TM84a	Bond distance
X-O2 (×3)	2.541(2)
X-O5 (×3)	2.7565(13)
X-O4 (×3)	2.8192(14)
<x-0></x-0>	2.706
Y-O2 (×2)	1.9738(6)
<i>Y</i> –O1	1.9963(11)
Y-O6 (×2)	2.0156(6)
<i>Y</i> –O3	2.1333(11)
<y-0></y-0>	2.018
Z-06	1.8749(6)
Z-07	1.8853(5)
Z-08	1.8877(6)
Z–O8′	1.9206(6)
Z-07'	1.9561(5)
Z-O3	1.9832(5)
<z-0></z-0>	1.918
<i>B</i> -O2	1.3633(12)
<i>B</i> –O8 (×2)	1.3795(7)
< <i>B</i> -O>	1.374
<i>T</i> –O6	1.6099(6)
<i>T</i> –O7	1.6108(5)
<i>T</i> –O4	1.6222(3)
<i>T</i> –O5	1.6355(4)
<7-0>	1.620
H1–O1	0.95(3)
H3–O3	0.93(2)

occupancies. Table 5 reports selected bond distances. Anisotropic displacement parameters and a CIF file are provided as Supplementary Material linked to this article and freely available on the GSW website of the journal: http://eurjmin.geoscienceworld.org.

### 3.2. Site populations

The combination of the chemical and structural data resulted in the empirical structural formula:

 $\begin{array}{l} \overset{X}{(\bigsqcup_{0.53} Na_{0.45} Ca_{0.01} K_{0.01})_{\Sigma 1.00}} \overset{Y}{(Al_{1.53} Fe^{2+}_{1.16} Mg_{0.22} Mn^{2+}_{0.05} Zn_{0.01} Ti^{4+}_{0.03})_{\Sigma 3.00} \overset{Z}{(Al_{5.47} Fe^{3+}_{0.14} Mg_{0.39})_{\Sigma 6.00}} \\ [(Si_{5.89} Al_{0.11})_{\Sigma 6.00} O_{18}] (BO_3)_3 \overset{V}{(OH)_3} \overset{W}{[O_{0.57} F_{0.04} (OH)_{0.39}]_{\Sigma 1.00}}. \end{array}$ 

This formula is similar to that optimized by Bosi & Lucchesi (2004). The robustness of this site population was confirmed by another optimization procedure (Wright *et al.*, 2000), which led to very similar results.

The bond valence analysis is fully consistent with the mean formal valence derived from the site populations (Table 6). Bond valence sums at the respective sites are calculated using the formula and bond valence parameters from Brown & Altermatt (1985).

### 3.3. X-ray powder diffraction

The X-ray powder-diffraction pattern for oxy-foitite was collected using a Panalytical X'pert powder diffractometer equipped with an X'celerator silicon-strip detector. The range 5–80° (2 $\theta$ ) was scanned with a step-size of 0.017° using a sample spinner with the sample mounted on a background-free holder. The diffraction data (for CuK $\alpha$  = 1.54059 Å), corrected using Si as an internal standard, are listed in Table 7.

The program UnitCell (Holland & Redfern, 1997) was used to refine unit-cell parameters in the trigonal system: a=15.9640(4) Å, c=7.1598(3) Å and V=1580.2(1) Å<sup>3</sup>.

### 3.4. Optical absorption spectroscopy

Room-temperature polarized optical absorption spectra were recorded on the polished single-crystal fragment that also was used for FTIR spectroscopy (see below) in the range 300–1100 nm with an AVASPEC-ULS2048  $\times$  16 spectrometer attached via a 400  $\mu$ m UV optic fiber cable to a Zeiss Axiotron UV-microscope. A 75 W Xenon

Site	Х	Y	Ζ	Т	В	BVS
O1(W)		$0.44^{\times 3} \rightarrow$				1.31
02	$0.07^{\times 3}\downarrow$	$0.47^{\times 2} \downarrow \rightarrow$			1.02	2.02
O3(V)		0.30	$0.41^{\times 2} \rightarrow$			1.13
04	0.03 <sup>×3</sup> ↓			$1.00^{\times 2} \rightarrow$		2.03
05	$0.04^{\times 3}\downarrow$			$0.96^{\times 2} \rightarrow$		1.97
O6	•	$0.42^{\times 2}\downarrow$	0.55	1.03		2.01
07			0.54	1.03		2.02
			0.45			
08			0.49		$0.98^{\times 2}$	2.00
			0.54		·	
BVS	0.40	2.51	2.98	4.03	2.98	
MFV	0.48	2.53	2.94	3.98	3.00	

Table 6. Bond valence calculations (valence units) for oxy-foitite.

MFV=mean formal valence from site populations.

Table 7. Powder X-ray data (I > 5%) for oxy-foitite.

Ι	$d_{\rm meas}$ (Å)	$d_{\text{calc}}$ (Å)	h k l
51	6.357	6.358	101
18	4.973	4.973	021
8	4.608	4.608	300
47	4.220	4.221	2 1 1
49	3.990	3.991	220
100	3.466	3.466	012
6	3.380	3.380	131
6	3.017	3.017	140
87	2.953	2.953	122
6	2.900	2.900	321
98	2.579	2.579	051
17	2.387	2.387	003
18	2.374	2.374	232
13	2.346	2.346	511
15	2.188	2.188	502
11	2.166	2.166	431
17	2.119	2.119	303
30	2.048	2.048	223
50	2.041	2.040	152
8	2.023	2.022	161
12	1.872	1.872	143
9	1.852	1.852	621
7	1.776	1.777	3 3 3
25	1.658	1.658	063
12	1.644	1.644	271
14	1.596	1.596	550
7	1.590	1.589	404
22	1.503	1.503	054
23	1.452	1.452	514

Notes: I = measured intensity,  $d_{\text{meas}} =$  measured interplanar spacing;  $d_{\text{calc}} =$  calculated interplanar spacing; hkl = reflection indices.

arc lamp was used as a light source and Zeiss Ultrafluar  $10 \times$  lenses served as objective and condenser. The size of the circular measure aperture was 34  $\mu$ m in diameter. A UV-quality Glan-Thompson prism with a working range from 250 to 2700 nm (40000 to 3704 cm<sup>-1</sup>) was used as polarizer. The spectra in the range 1100–2000 nm were recorded with the FTIR microscope-spectrometer described below.

The recorded spectra (Fig. 1) show three broad absorption bands at 22730 (440 nm), 13990 (715 nm) and 9090 (1110 nm) cm<sup>-1</sup>. The bands are strongly polarized in  $\mathbf{E} || O(\mathbf{E} \perp \mathbf{c})$ . They are assigned in accordance with Taran *et al.* (1993) to Fe<sup>2+</sup>-Ti<sup>4+</sup> intervalence charge transfer (440 nm) and enhanced spin-allowed *d*–*d* transitions in octahedrally coordinated Fe<sup>2+</sup> (715 and 1110 nm). In addition to these strong absorption bands caused by electronic 3*d*-transitions, a number of relatively sharp and weak bands are observed in the  $\mathbf{E} || E(\mathbf{E} || \mathbf{c})$  spectra at 7112 (1406 nm), 7092 (1410 nm) and 6959 (1437 nm) cm<sup>-1</sup>. These bands represent overtones of the fundamental (OH)-stretching bands observed at ~3500 cm<sup>-1</sup>.

#### 3.5. Fourier transform infrared (FTIR) spectroscopy

Polarized FTIR absorption spectra in the wavenumber range 2000–5000 cm<sup>-1</sup>, typical for (OH)-vibrational bands, were measured on an 42  $\mu$ m thick single-crystal section cut parallel to the **c** axis using a Bruker Vertex spectrometer equipped with a Hyperion II microscope, a NIR source, a CaF<sub>2</sub> beam-splitter, a ZnSe wire-grid polarizer and an InSb detector.

Spectra recorded parallel to the **c**-axis direction  $(\mathbf{E} \| \mathbf{c})$ contain a major absorption feature in the 3450-3600 cm<sup>-</sup> range which is truncated due to exceedingly strong absorption (Fig. 2). Bands in this range can be related to the local arrangement 3[Y(Fe<sup>2+</sup>,Al) ZA1 ZA1]-V(OH)<sub>3</sub> (Watenphul et al., 2016), i.e., to the occurrence of (OH) at the V position (O3 site) of the tourmaline general formula. At lower wavenumbers, a band occurs around  $3375 \text{ cm}^{-1}$ being related to the hydrogen bond <sup>V</sup>O-H...O5 (Bosi et al., 2012b; Skogby et al., 2012). At higher wavenumbers, two sharp bands occur at 3632 and  $3726 \text{ cm}^{-1}$ , which are also strongly polarized in the **c**-axis direction. The occurrence of relatively weak bands in this range are consistent with the minor concentrations of <sup>W</sup>(OH)<sub>0.39</sub> reported in the empirical formula, and can be respectively related to the local arrangements  ${}^{X}(\Box)$ - ${}^{Y}(Fe^{2+}Fe^{2+}Al)$ - ${}^{W}(OH)$  and  ${}^{X}(Na)$ - ${}^{Y}(Fe^{2+}Fe^{2+}Al)$ - ${}^{W}(OH)$  detected in the foitite vibrational spectrum (Watenphul et al., 2016). The (OH) content was



Fig. 1. Polarized optical absorption spectra of oxy-foitite (sample thickness  $42 \ \mu m$ ) in the UV-VIS-NIR region.

Table 8. Selected properties of oxy-foitite and foitite.

	Oxy-foitite <sup>a</sup>	Foitite <sup>b</sup>
a (Å)	15.9387(3)	15.967(2)
c(Å)	7.1507(1)	7.126(1)
$V(Å^3)$	1573.20(6)	1573.3(4)
Space group	R3m	R3m
Optic sign	Uniaxial (-)	Uniaxial (–)
ω	1.660(5)	1.664(1)
3	1.640(5)	1.642(1)
Color	Black	Bluish black
Pleochroism	O = dark brown	O = pale lavender
	E = pale brown	$\hat{E} = \text{dark blue}$
Ref.	This work	MacDonald et al. (1993)

*Note*: The pleochroism reported in MacDonald *et al.* (1993) is anomalous. All other tournalines reported so far in literature display a reverse pleochroic scheme with O > E.

<sup>a</sup>  $\Box$ (Fe<sup>2+</sup>Al<sub>2</sub>)Al<sub>6</sub>(Si<sub>6</sub>O<sub>18</sub>)(BO<sub>3</sub>)<sub>3</sub>(OH)<sub>3</sub>O.

<sup>b</sup>  $\Box$ (Fe<sup>2+</sup><sub>2</sub>Al)Al<sub>6</sub>(Si<sub>6</sub>O<sub>18</sub>)(BO<sub>3</sub>)<sub>3</sub>(OH)<sub>3</sub>(OH).

also estimated from the absorbance of the overtone bands in the 6700–7200 cm<sup>-1</sup> range (Ertl *et al.*, 2010), indicating 3.0 wt.% H<sub>2</sub>O in agreement with the chemical data (Table 2).

# 4. End-member formula, name and relation to other species

The empirical structural formula of the present sample is consistent with a tourmaline belonging to the vacant group, oxy-subgroup 3 (Henry *et al.*, 2011, 2013): vacancy-dominant at the X position of the general formula of tourmaline  $XY_3Z_6T_6O_{18}(BO_3)_3V_3W$  and oxygen-dominant at W with  $O^{2-} > OH + F$ . As  $AI^{3+}$  is the dominant cation at Y and Z, and overall site valence of *Y* is 7.60+ (closer to 8+ than to 7+) and of *Z* is 17.59+ (closer to 18+ than to 17+), the unique possible valence-



Fig. 2. Polarized FTIR absorption spectra in the (OH) stretching frequency region of oxy-foitite, vertically offset for clarity. The main band around  $3500 \text{ cm}^{-1}$  is truncated in the **E**||**c** direction due to excessive absorption. Sample thickness  $42 \,\mu\text{m}$ .

arrangements are  ${}^{\rm Y}(R^{2+}R^{3+}_{2})^{\Sigma 8+}$  and  ${}^{\rm Z}(R^{3+}_{6})^{\Sigma 18+}$ . The combination of these arrangements with the sitepopulation information results in  ${}^{\rm Y}({\rm Fe}^{2+}{\rm Al}_2)^{\Sigma 8+}$  and  $(A1_6)^{\Sigma 18+}$ . Note that the occurrence of a dominant cation arrangement such as  ${}^{Y}(Fe^{2+}_{2}Al)^{\Sigma7+}$  is in stark contrast to the crystal-chemical information. Therefore, in accordance with the valency-imposed double-site occupancy and the dominant-valency rule (Hatert & Burke, 2008), the present tourmaline composition leads to formula  $\Box$ (Fe<sup>2+</sup>Al<sub>2</sub>)Al<sub>6</sub>(Si<sub>6</sub>O<sub>18</sub>) the end-member  $(BO_3)_3(OH)_3O.$ 

Since no tourmalines have been yet documented with this composition, it can be classified as a new species. The closest end-member composition of a valid tourmaline species is that of foitite, ideally  $\Box$ (Fe<sup>2+</sup><sub>2</sub>Al)Al<sub>6</sub>(Si<sub>6</sub>O<sub>18</sub>) (BO<sub>3</sub>)<sub>3</sub>(OH)<sub>3</sub>(OH). In parallel with the naming of a number of other tourmaline-supergroup species, *e.g.*, oxyschorl and oxy-dravite, we have chosen to name the present tourmaline oxy-foitite rather than to introduce a new rootname. This emphasizes its relations to the species foitite rather than obscuring them. Ideally, oxy-foitite is related to foitite by the substitution  ${}^{Y}Al^{3+} + {}^{W}O^{2-} \rightarrow$  ${}^{Y}Fe^{2+} + {}^{W}(OH)^{1-}$ . The properties of these two tourmaline species are compared in Table 8.

In general, tourmalines display a very complex chemical composition associated with an only intermediate structural complexity, and are the most common and the earliest boron minerals formed on Earth (Grew *et al.*, 2016). The discovery of new tourmaline species enlarges our understanding of this amazing compositional flexibility. Similar to the oxy-schorl formation (Bačík *et al.*, 2013), the occurrence of oxy-foitite seems to be a result of fluid composition characterized by high A1 and low Na contents rather than temperature/pressure variations. The deprotonization (*i.e.*,  $O^{2-}$  at the O1 site) is most likely not a direct reflection of prevailing oxygen fugacities, but is driven by the reaction  $\Box + 2Al^{3+} + O^{2-} \rightarrow Na^{1+} + 2Fe^{2+} + (OH)^{1-}$ , *i.e.*, it is a result of local charge-balance requirements imposed by tournaline formation from fluids. These conclusions indicate that crystallographic constraints are at least as important as petrological factors in tournaline forming processes.

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