REVISION 1

Atomic arrangements around the O3 site in Al- and Cr-rich oxy-tourmalines: a combined EMP, SREF, FTIR and Raman study

Ferdinando Bosi^{1,2}, Henrik Skogby², Peter Lazor³ and Leonid Reznitskii⁴

¹Dipartimento di Scienze della Terra, Sapienza Università di Roma, Piazzale Aldo Moro, 5, I-00185 Rome, Italy

²Department of Geosciences, Swedish Museum of Natural History, Box 50007, SE-10405 Stockholm, Sweden

³Department of Earth Sciences, Uppsala University, SE-752 36 Uppsala, Sweden

⁴Institute of the Earth's Crust, Siberian Branch, Russian Academy of Science, Lermontova str., 128, 664033 Irkutsk, Russia

Corresponding author:

Ferdinando Bosi, e-mail: ferdinando.bosi@uniroma1.it, tel: +39 0649914901, fax: +39 064454729

Abstract A study of natural oxy-tourmalines belonging to the system oxy-dravite – chromo-alumino-povondraite – oxy-chromium-dravite from the Sludyanka crystalline complex (Southern Baikal region, Russia) was carried out to explore the characteristic vibrational bands in the principal (OH)-stretching frequency and their relations to the O3

anion site of the tourmaline structure. Relevant information was obtained using electron microprobe analysis (EMPA), structural refinement (SREF), infrared (IR) and Raman single crystal spectroscopy. The studied oxy-tourmalines are characterized by the substitution $\text{Al} \leftrightarrow \text{Cr}$ which is accompanied by redistribution of Mg over the Y and Z sites. The occurrence of strong correlations between relative peak area intensities for two IR bands at 3565 and 3519 cm^{-1} and cation site populations derived from SREF and EMP data allowed assignment of the band at 3565 cm^{-1} to the cluster $[\text{}^{\text{Y}}\text{Mg} \text{}^{\text{Z}}\text{Al} \text{}^{\text{Z}}(\text{Al,Mg})]\text{--O3}$ and the band at 3519 cm^{-1} to the cluster $[\text{}^{\text{Y}}\text{Cr} \text{}^{\text{Z}}(\text{Cr,Al}) \text{}^{\text{Z}}(\text{Cr,Al,Mg})]\text{--O3}$.

It appears that the combination of polarized IR and Raman spectra collected with the electric vector $\mathbf{E} \perp \mathbf{c}$ and $\mathbf{E} \parallel \mathbf{c}$ may provide a useful characterization of the local (OH) environments around the O3 site of the tourmaline structure.

Keywords Tourmaline, Electron microprobe, Crystal structure refinement, Infrared spectroscopy, Raman spectroscopy, Short-range arrangement

Introduction

Tourmalines are complex borosilicates and their crystal structure and crystal chemistry have been extensively studied (e.g., Foit 1989; Ertl et al. 2002; Hawthorne and Henry 1999; Bosi et al. 2010; Lussier et al. 2011; Filip et al. 2012; Cempírek et al. 2013). In accordance with Henry *et al.* (2011), the general formula of tourmaline may be written as: $\text{XY}_3\text{Z}_6\text{T}_6\text{O}_{18}(\text{BO}_3)_3\text{V}_3\text{W}$, $[\text{}^{\text{9}}\text{X} = \text{Na}^+, \text{K}^+, \text{Ca}^{2+}, \square (= \text{vacancy})$; $[\text{}^{\text{6}}\text{Y} = \text{Al}^{3+}, \text{Fe}^{3+}, \text{Cr}^{3+}, \text{V}^{3+}, \text{Mg}^{2+}, \text{Fe}^{2+}, \text{Mn}^{2+}, \text{Li}^+$; $[\text{}^{\text{6}}\text{Z} = \text{Al}^{3+}, \text{Fe}^{3+}, \text{Cr}^{3+}, \text{V}^{3+}, \text{Mg}^{2+}, \text{Fe}^{2+}$; $[\text{}^{\text{4}}\text{T} = \text{Si}^{4+}, \text{Al}^{3+}, \text{B}^{3+}$; $[\text{}^{\text{3}}\text{B} = \text{B}^{3+}$; $\text{V} (\equiv [\text{}^{\text{3}}\text{O3}) = (\text{OH})^{1-}, \text{O}^{2-}$; $\text{W} (\equiv [\text{}^{\text{3}}\text{O1}) = (\text{OH})^{1-}, \text{F}^{1-}, \text{O}^{2-}$.

Vibrational transitions in the (OH)-stretching region has been presented for tourmaline in a number of studies (e.g., Gonzalez-Carreño et al. 1988; Castañeda et al. 2000; Hoang et al. 2011; Fantini et al. 2014). For elbaite, Skogby et al. (2012) presented a unifying assignment model for observed (OH) stretching bands using a combination of

long-range information (based on diffraction techniques) and short-range information (based on spectroscopic techniques).

In this paper, we use a similar approach to explore the infrared (IR) and Raman spectra in the wavenumber region 3000-4000 cm^{-1} of six single crystals of oxy-tourmalines belonging to the solid solution system oxy-dravite – chromo-alumino-povondraite – oxy-chromium-dravite, and present a model to link the vibrational bands to stable short-range arrangements supported by bond-valence constraints.

Samples

The samples used in this study (T89104, Tmt6b, PR85v, Tm1p43e, PR107 and PR108) are macroscopically emerald green and comes from metaquartzites in the Pereval marble quarry, Sludyanka crystalline complex, Southern Baikal region, Russia. At this locality (see Bosi et al. 2012a for a more detailed description), Cr-V-bearing metamorphic rocks are associated with Cr-V-bearing diopside and tremolite, escolaitite, uvarovite, chromite, V-bearing titanite, pyrite, barite and calcite together with euhedral and subhedral crystals of tourmaline. The host-rock consists of a lens (10-15 cm thickness) of greenish-grey medium-grained quartzite within the marbles of the Pereval quarry. The crystals are euhedral, reaching up to 0.3 mm in length, and are often chemically zoned. However, homogeneous crystals also occur, and were selected for the present study.

Four of the six studied oxy-tourmalines (samples Tmt6b, PR85v, Tm1p43e and PR107) have previously been structurally and chemically characterized by means of X-ray single-crystal diffraction, electron microprobe analysis and Mössbauer spectroscopy. Moreover, samples PR85v and PR107 were also characterized by means of IR and optical absorption spectroscopy (Bosi et al. 2004; Bosi et al. 2013; Reznitskii et al. 2014). The obtained structural and chemical information revealed a chemical composition corresponding to the chromo-alumino-povondraite species with a variation predominantly in the Al and Cr contents. In order to cover the major compositional range characterized by the Cr for Al substitution, an oxy-dravite sample (PR108) and an oxy-chromium-dravite (T89104) was also structurally and chemically characterized. These samples were also characterized by IR and Raman single crystal spectroscopy (for details, see Table 1).

Experimental methods

Single-crystal structural refinement

Two representative crystals of oxy-dravite (sample PR108) and oxy-chromium-dravite (sample T89104) were selected for X-ray diffraction measurements on a Bruker KAPPA APEX-II single-crystal diffractometer, at Sapienza University of Rome (Earth Sciences Department), equipped with a CCD area detector ($6.2 \times 6.2 \text{ cm}^2$ active detection area, 512×512 pixels) and a graphite crystal monochromator, using $\text{MoK}\alpha$ radiation from a fine-focus sealed X-ray tube. The sample-to-detector distance was 4 cm. A total of 3265 (for PR108) and 1469 (for T89104) exposures (step = 0.2° , time/step = 20 s) covering the full reciprocal sphere with a redundancy of about 10 (for PR108) and 6 (for T89104). Final unit-cell parameters were refined with the Bruker AXS SAINT program using reflections with $I > 10 \sigma(I)$ in the range $5^\circ < 2\theta < 70^\circ$. 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 the multi-scan method (SADABS). The absorption correction led to a significant improvement in R_{int} . No violations of $R3m$ symmetry were noted.

Structural refinement was done with the SHELXL-2013 program (Sheldrick 2013). Starting coordinates were taken from Bosi et al. (2014). Variable parameters were: scale factor, extinction coefficient, atom coordinates, site scattering values and atom displacement factors. In detail, the *X* site was modeled by using the Na scattering factor; the *Y* site was modeled with Cr and Mg scattering factors; the occupancy of the *Z* site was modeled with Al scattering factor for sample PR108, and Cr and Mg scattering factors for sample T89104. The *T* and *B* sites were modeled, respectively, with Si and B scattering factors and with a fixed occupancy of 1, because refinement with unconstrained occupancies showed no significant deviations from this value. Three full-matrix refinement cycles with isotropic displacement parameters for all atoms were followed by anisotropic cycles until convergence was attained. No significant correlations over a value of 0.7 between the parameters were observed at the end of refinement. Table 2 lists crystal data,

data-collection information and refinement details; Table 3 gives the fractional atom coordinates and site occupancies; Table 4 gives the displacement parameters; Table 5 gives selected bond distances.

Electron microprobe analysis

Electron-microprobe analyses of the crystals used for X-ray diffraction refinement were obtained by wavelength-dispersive spectrometry (WDS mode) with a Cameca SX50 instrument at the “Istituto di Geologia Ambientale e Geoingegneria (Rome, Italy), CNR”, operating at an accelerating potential of 15 kV, a sample current of 15 nA, and a 10 μm beam diameter. Minerals and synthetic compounds were used as standards: wollastonite (Si, Ca), magnetite (Fe), rutile (Ti), corundum (Al), vanadinite (V) fluorophlogopite (F), periclase (Mg), jadeite (Na), K-feldspar (K), sphalerite (Zn), metallic Cr, Mn and Cu. Peak interferences of V $K\beta$ on Cr $K\alpha$ and Ti $K\beta$ on V $K\alpha$ were corrected and the PAP routine were applied (Pouchou and Pichoir 1991). The results (Table 6) represent mean values of 10 spot analyses. In accord with the very low concentration of Li in dravitic samples (e.g., Henry et al. 2011) and the crystallization environment of the studied sample (i.e., Cr-bearing metaquartzites), the Li_2O content was assumed to be insignificant. The elements Mn, Fe, Cu, and Zn were below the detection limits (0.03 wt%) in the studied sample.

Single crystal infrared spectroscopy

Representative crystals of the four tourmaline samples that had not previously been studied were measured by Fourier transform infrared (FTIR) spectroscopy to characterize their (OH) vibrational absorption bands. The spectrometer system consisted of a Bruker Equinox 55 spectrometer in conjunction with a Biorad infrared microscope, using a halogen lamp source, a CaF_2 beam-splitter, a wire-grid polarizer (KRS-5) and an MCT detector. The crystals were oriented by morphology and optical microscopy, mounted on glass plates in thermoplastic resin and polished on two parallel sides, including the *c*-axis direction. Polarized absorption spectra were then acquired with a resolution of 4 cm^{-1} in the wavenumber range 2000-5000 cm^{-1} parallel and perpendicular to the crystallographic *c*-axis direction, using rectangular measurement areas of ca. 50 $\times$ 50 μm on the 26-50 μm thick

crystals. Sample Tmt6b that was available in slightly larger crystal size was mounted on a 100 μm pin-hole aperture and was measured in the sample compartment of the spectrometer system using the same set-up, except for an InSb detector. As typically observed for tourmaline samples, the main (OH) absorption bands polarized parallel the **c**-axis direction were exceedingly intense, and it was not possible to thin the samples sufficiently to avoid off-scale absorption intensity for the strongest bands. Spectra obtained perpendicular to **c**-axis direction were analyzed by band-fitting using the Jandel PeakFit 4.12 software.

Single crystal Raman spectroscopy

Raman spectra were recorded on five representative single crystals using a spectroscopic system built at the Department of Earth Sciences, Uppsala University. The key system components include a high-throughput, single stage imaging spectrometer (HoloSpec f/1.8i, Kaiser Optical Systems, Inc.) equipped with a holographic transmission grating and a thermoelectrically cooled ($-60\text{ }^{\circ}\text{C}$) CCD detector (Newton, Andor Technology, 1600×400 pixels), a diode-pumped laser (Samba by Cobolt AB, 532.42 nm, 150 mW CW), and an optical imaging system (magnification 20 $\times$, spatial resolution $\sim 1\text{ }\mu\text{m}$). Two notch filters (Ondax Inc.) blocked the Rayleigh line. Polarized Raman spectra in parallel and perpendicular **c**-axis directions (n_{e} and n_{o}) were collected in the back-scattering geometry at a resolution and accuracy of about 2 cm^{-1} and 1.5 cm^{-1} , respectively. Typical acquisition time varied between 1 and 4 minutes, applying 15 mW of the laser power on the doubly-polished parallel-plate oriented single crystals.

Results

Determination of atomic proportions

In agreement with the structural-refinement results, the boron content was assumed to be stoichiometric in samples PR108 and T89104 ($\text{B}^{3+} = 3.00\text{ apfu}$). Both the site-scattering results and the bond lengths of *B* and *T* are consistent with the *B* site fully occupied by

boron and no amount of B^{3+} at the *T* site (e.g., Hawthorne 1996; Bosi and Lucchesi 2007). The (OH) content can then be calculated by charge balance with the assumption $T + Y + Z = 15.00$ (e.g., Henry and Dutrow 1996). The atomic proportions were calculated on this assumption (Table 6). The excellent match between the number of electrons per formula unit (epfu) derived from chemical and structural analysis supports this procedure, respectively: 240.6 and 240.0 epfu for sample PR108, 279.3 and 279.4 epfu for sample T89104.

Site populations

The anion site populations in the studied samples follow the general preference suggested for tourmaline (e.g., Grice and Ercit 1993; Henry et al. 2011): the O3 site (V position in the general formula) is occupied by $(OH)^{1-}$ and O^{2-} ; the O1 site (W position in the general formula) is occupied by O^{2-} , $(OH)^{1-}$ and F^{1-} . The cation distribution at the *T*, *Y* and *Z* sites was optimized by using a quadratic program to minimize the residuals between calculated and observed data (based on the chemical and structural analysis). Site-scattering values, octahedral and tetrahedral mean bond-distances (i.e., $\langle Y-O \rangle$, $\langle Z-O \rangle$ and $\langle T-O \rangle$) were calculated as the linear contribution of each cation multiplied by its ideal bond-distance. More details about the ideal distances as well as the optimization procedure may be found in Bosi et al. (2004) and Bosi and Lucchesi (2004; 2007). The robustness of this approach was confirmed by another optimization procedure (Wright et al. 2000), which led to very similar cation distributions (Table 7). The final structural formulae for samples PR108 and T89104 are reported in Table 8 along with those of the previously studied samples Tmt6b, PR85v, Tm1p43e, and PR107 for comparison reasons. In accordance with the classification of Henry et al. (2011) and the findings of Bosi and Skogby (2013) and Bosi et al. (2012a), samples PR108 and T89104 can be classified, respectively, as oxy-dravite and oxy-chromium-dravite.

Infrared and Raman spectra

The IR spectra obtained parallel to the *c*-axis direction of the tourmaline samples are characterized by a strong absorption feature in the $3450\text{-}3600\text{ cm}^{-1}$ range (Fig. 1a) which is

truncated due to exceedingly strong absorption, in line with previous studies (e.g., Bosi et al. 2012b, Skogby et al. 2012). Weak bands occur in the 3700-3800 cm^{-1} region, and are also polarized in the **c**-axis direction. Although a slight shift in position of the main absorption feature is apparent, any possible fine structures are obscured by the off-scale intensity recorded along the **c**-axis. However, spectra polarized perpendicular to the **c**-axis are much less intense and reveal two partly overlapping bands with systematic variation of their absorption intensities (Fig. 1b). This trend is associated with sample composition, where the band at higher wavenumbers increases with decreasing Cr content. In order to characterize and quantify these intensity shifts, the spectra were fitted with a model using two bands with variable absorption intensities, similar but variable band widths, and with band centres fixed at 3519 and 3565 cm^{-1} . The band centres were initially obtained by unconstrained fits of spectra of the most Al-rich sample (PR108) and the most Cr-rich sample (T89104), which are both dominated by one of these bands. Completely unconstrained fits of all spectra were also tried, but were abandoned because the low band resolution for the spectra of the intermediate compositions caused unsystematic drift of the band centres. The obtained absorption area distributions for the two bands are listed in Table 9.

For the excitation wavelength, Raman spectra in the (OH)-region are characterized by a strong red fluorescence decreasing the signal-to-noise-ratio. This precluded spectral acquisitions for sample with the highest Al-content (PR108) for which the effect was most pronounced. Raman spectra obtained for electric field (**E**) direction parallel to the **c**-axis (**E** // **c**) are shown in Fig. 2. The overall appearance of spectra as well as their evolution upon varying Al-Cr content resembles that of infrared absorption for the perpendicular configuration (**E** $\perp$ **c**) when the above-described two-band fitting model is applied. Positions of bands of the most Cr-rich sample (T89104) were used for all compositions when fitting the Raman spectra. The low quality of the spectrum for the Al-rich sample PR107 (Fig. 2) translated into a larger fitting uncertainty. The absorption area distributions for the two bands are listed in Table 9. A somewhat lower value of position of the 3556 cm^{-1} Raman band, as compared to the corresponding 3565 cm^{-1} IR band, likely originates from comparing the spectra of different polarizations, parallel Raman (**E** // **c**) versus perpendicular IR (**E** $\perp$ **c**), and from the fitting uncertainties. No Raman bands in the (OH)-region were observed for the configuration **E** $\perp$ **c**.

Discussion

Crystal chemistry

The six samples used for this study can be referred to the following ideal formulae:

- oxy-chromium-dravite, $\text{Na}^Y\text{Cr}_3^Z(\text{Cr}_4\text{Mg}_2)(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{OH})_3\text{O}$;
- chromo-alumino-povondraite, $\text{Na}^Y\text{Cr}_3^Z(\text{Al}_4\text{Mg}_2)(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{OH})_3\text{O}$;
- oxy-dravite, $\text{Na}^Y(\text{Al}_2\text{Mg})^Z(\text{Al}_5\text{Mg})(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{OH})_3\text{O}$.

They all have the *X* site dominated by Na (0.68-0.98 apfu) with minor amount of Ca, vacancies and K. The *T* site is dominated by Si (5.95-5.99 apfu) along with very minor amounts of Al. The O1 site is dominated by O^{2-} (~0.7 apfu), followed by F (0.1-0.3 apfu) and then by (OH) (up to 0.3 apfu). The main compositional variation is characterized by the substitution of Al for Cr^{3+} at both the *Y* and *Z* sites (Fig. 3). In detail, moving from oxy-chromium-dravite to chromo-alumino-povondraite and further to oxy-dravite, ^YAl increases from zero to 0.65 apfu and ^ZAl from 1.80 apfu to 4.33, whereas ^YCr decreases from 2.55 to 0.63 apfu and ^ZCr from 2.23 to 0.33 apfu. Minor amounts of V^{3+} (< 0.3 apfu) are also present, alternatively at the *Y* and *Z* site. Minor amounts of Fe^{3+} (~0.3 apfu) are present at the *Z* site only for sample PR107. The presence of Mg increases from 0.27 to 1.33 apfu at *Y*, whereas it decreases from 1.96 apfu to 1.34 apfu at *Z* in accordance with the order-disorder reaction between R^{3+} -cations and Mg at the *Y* and *Z* sites (see below). With respect to the ideal formulae, the observed octahedral site populations can chiefly be described by the ideal substitutions that follow:

oxy-chromium-dravite $\leftrightarrow$ chromo-alumino-povondraite

chromo-alumino-povondraite $\leftrightarrow$ oxy-dravite

The substitution of Al for Cr is accompanied by redistribution of Mg over the Y and Z sites, which can be summarized by the substitutions occurring along the oxy-chromium-dravite – oxy-dravite join:

Short-range arrangements around O1 and O3

Short-range bond-valence requirements around the O1 site in tourmaline (Hawthorne 1996, 2002; Bosi 2010, 2011, 2013) invoke the occurrence of the following possible and stable short-range arrangements for the studied samples:

where (OH,F) correspond to two different O1-site arrangements and $\text{R}^{3+} = \text{Al}, \text{Cr}$ and V .

As the anion at the O3 site is bonded to one Y and two Z cations, the cations occurring in the local arrangements around O1 should also be involved with the local arrangements around O3. In the studied samples, the O3 site is essentially occupied by (OH), thus practically all the Z-cations (e.g., Al, Cr, V, Mg) impact on the absorption bands of the infrared and Raman spectra around O3 because they are part of the general local arrangement $[{}^Y(\text{R})\text{--}^{\text{O3}}(\text{OH})\text{--}^Z(\text{R} + \text{R})]$, where R is a generalized cation. Moreover, in accord with bond-valence requirements (Hawthorne 1996; Bosi 2011), the high amounts of R^{3+} at the Y and Z sites may determine the occurrence of O^{2-} at the O3 site, with arrangements of the type $[{}^Y(\text{R}^{3+})\text{--}^{\text{O3}}(\text{O}^{2-})\text{--}^Z(\text{R}^{3+} + \text{R}^{3+})]$. If these arrangements occur, they will cause a disorder of $(\text{OH})^{1-}$ between the O3 and O1 sites via the mechanism ${}^{\text{O3}}(\text{OH})^{1-} + {}^{\text{O1}}(\text{O}^{2-}) \leftrightarrow {}^{\text{O3}}(\text{O}^{2-}) + {}^{\text{O1}}(\text{OH})^{1-}$. Although it is difficult to quantify ${}^{\text{O3}}(\text{O}^{2-})$ and ${}^{\text{O1}}(\text{OH})^{1-}$ associated with such a disordering mechanism, the spectra of Fig. 1 show peaks at wavenumber $> 3650 \text{ cm}^{-1}$ indicative of ${}^{\text{O1}}(\text{OH})^{1-}$ (see below) also in samples previously defined as ${}^{\text{O1}}(\text{OH})$ -free (Table 8). Therefore, it is likely that arrangements of the type $[{}^{\text{O1}}(\text{OH})^{1-}\text{--}^Y(\text{R}^{3+})\text{--}^{\text{O3}}(\text{O}^{2-})\text{--}^Z(\text{R}^{3+} + \text{R}^{3+})]$ may occur, as in sample Tmt6b: the structural formula indicates absence of ${}^{\text{O1}}(\text{OH})^{1-}$ (Table 8), whereas the IR spectrum (Fig. 1a) shows the presence of weak bands at

$\sim 3712\text{-}3762\text{ cm}^{-1}$. The amount of disorder of (OH) should, however, be very small since the peaks at wavenumber $> 3650\text{ cm}^{-1}$ are much weaker than those at wavenumber $< 3650\text{ cm}^{-1}$ and, in some samples, amounts of $^{\text{O}1}(\text{OH})$ are already predicted by stoichiometry (Table 8).

Relation between octahedral site population and vibrational peak area intensity

In line with previous studies (e.g., Gonzalez-Carreño et al. 1988; Bosi et al. 2012b) and the small $^{\text{O}1}(\text{OH})^{1-}$ contents observed in the studied samples, it can be anticipated that the weak vibrational bands above 3650 cm^{-1} are related to the O1 site and the strong bands below 3650 cm^{-1} to the O3 site (Fig. 1).

A strong positive correlation occurs between Al_{total} and the peak area intensity (PAI) in the IR (and Raman) spectra at 3565 (and 3556 in Raman) cm^{-1} ($r^2 > 0.9$) as well as between Cr_{total} and PAI at 3519 (and 3520 in Raman) cm^{-1} ($r^2 > 0.9$), indicating a distinct role of Al and Cr for the cause of these two bands. Consequently, the accommodation of cations at the Y and Z sites is expected to be related to PAI via the substitutions (1), (2) and (3), and in fact, high correlations between the amounts of Mg and Cr at the Y site and PAI are observed, whereas no reliable correlation was observed with $^{\text{Y}}\text{Al}$. Compared to the Raman spectra, the IR spectra appear to be of better quality and could also be acquired for all the six samples. Consequently, the IR data will be used to evaluate the relation between site population and vibrational peak area intensity. However, it can be noted that the Raman spectra obtained parallel to the **c**-axis essentially show the same trend as observed by FTIR spectra obtained perpendicular to the **c**-axis.

Fig. 4a displays the positive correlation between Mg at the Y site and PAI at 3565 cm^{-1} from oxy-chromium-dravite via chromo-alumino-povondraite to oxy-dravite, indicating that the occurrence of this band is strongly related to a local arrangement involving Mg at the Y site. Moreover, the deviation of the slope of the linear regression (~ 50) from the ideal value expected for oxy-dravite ($= 100$) can be ascribed to the essentially constant sum of monovalent anions $[\text{F} + (\text{OH})]$ at the O1 site (~ 0.3 apfu) which represent the dravite and fluor-dravite components. Consequently, $^{\text{Y}}\text{Mg}$ should be bonded to $^{\text{O}1}\text{O}^{2-}$ and $^{\text{O}1}(\text{OH},\text{F})$ according to the following two cluster proportions: $[\text{O}^1(\text{O}^{2-})\text{--}^{\text{Y}}(\text{Mg})\text{--}\text{O}^3(\text{OH})\text{--}^{\text{Z}}(\text{R} + \text{R})]_{0.7}$ and $[\text{O}^1(\text{OH},\text{F})\text{--}^{\text{Y}}(\text{Mg})\text{--}\text{O}^3(\text{OH})\text{--}^{\text{Z}}(\text{R} + \text{R})]_{0.3}$. The band at 3519 cm^{-1}

shows a high positive correlation with Cr at *Y* from oxy-dravite to oxy-chromium-dravite (Fig. 4b), indicating that this band is strictly related to a local arrangement involving Cr at the *Y* site. As the slope of the linear regression (~33) is in very good agreement with the substitution (3), ^YCr should be mainly bonded to ^{O1}O²⁻ rather than to ^{O1}(OH,F) according to the cluster: [^{O1}(O²⁻)–^Y(Cr)–^{O3}(OH)–^Z(R + R)].

The bands at 3565 cm⁻¹ and 3519 cm⁻¹ can therefore be assumed to be associated with ^YMg and ^YCr (respectively). However, these absorption bands also show relations with the cations at the *Z* site, which can be explained by the substitutions (1) and (2). The relation between Cr at *Z* and PAI at 3565 cm⁻¹ is displayed in Fig. 5a, indicating that this band first increases from oxy-chromium-dravite to chromo-alumino-povondraite with decreasing ^ZCr according to the substitution (1), ^ZAl → ^ZCr, and then continues to increase towards oxy-dravite but with increasing ^ZAl (and ^YMg) according to the substitution (2): ^Y(2Al + Mg) + ^Z(Al) → ^Y(3Cr) + ^Z(Mg). A corresponding explanation can be given for the relation between Cr at *Z* and PAI at 3519 cm⁻¹ (Fig. 5b). This band decreases from oxy-chromium-dravite to chromo-alumino-povondraite with decreasing ^ZCr according to substitution (1), and then continues to decrease to oxy-dravite but with decreasing ^YCr according to substitution (2). The correlation between Al at *Z* and PAI at 3565 cm⁻¹ (Fig. 5c) can be explained in a similar way. This band increases from oxy-chromium-dravite to chromo-alumino-povondraite with increasing ^ZAl according to substitution (1), and then continues to increase to oxy-dravite with increasing ^ZAl (and ^YMg) according to substitution (2). A corresponding explanation can also be given for the correlation between Al at *Z* and PAI at 3519 cm⁻¹ (Fig. 5d). This band decreases from oxy-chromium-dravite to chromo-alumino-povondraite with increasing ^ZAl according to the substitution (1), and then continues to decrease to oxy-dravite but with decreasing ^YCr according to substitution (2). The occurrence of a negative correlation between ^ZMg and the PAI at 3565 cm⁻¹ (Fig. 5e) from oxy-chromium-dravite to oxy-dravite can be explained by the substitution (3), ^Y(2Al + Mg) + ^Z(5Al) → ^Y(3Cr) + ^Z(4Cr + Mg), which decrease ^ZMg and increase ^YMg. Likewise, the positive correlation between ^ZMg and the PAI at 3519 cm⁻¹ (Fig. 5f) is linked to ^Y(3Cr) + ^Z(4Cr + Mg) → ^Y(2Al + Mg) + ^Z(5Al), which increases both ^ZMg and ^YCr.

In summary, the band at 3565 cm⁻¹ can be ascribed to the clusters [^{O1}(O²⁻)–^Y(Mg)–^{O3}(OH)–^Z(Al_{1.7}Mg_{0.3})]_{0.7} and [^{O1}(OH,F)–^Y(Mg)–^{O3}(OH)–^Z(AlAl)]_{0.3} which represent the oxy-dravite and (fluor-)dravite components (respectively), whereas the band at 3519 cm⁻¹

can be ascribed to $[\text{O}^1(\text{O}^{2-})-\text{Y}(\text{Cr})-\text{O}^3(\text{OH})-\text{Z}(\text{Al}_{1.3}\text{Mg}_{0.7})]$ and $[\text{O}^1(\text{O}^{2-})-\text{Y}(\text{Cr})-\text{O}^3(\text{OH})-\text{Z}(\text{Cr}_{1.3}\text{Mg}_{0.7})]$ which represent the chromo-alumino-povondraite and oxy-chromium-dravite components (respectively).

(OH) band assignment

Each of the more frequent local arrangements around the two types of (OH) groups, which occupy the two different crystallographic sites O1 and O3, is expected to produce an absorption band in the FTIR and Raman spectra. As above mentioned, the O1 site is surrounded by three Y cations, whereas the O3 site is surrounded by one Y and two Z cations. In addition, the occupancy of the X site may also affect the absorption band related to O1 (Gonzalez-Carreño et al. 1988).

In our band assignment model, we assume that the frequency of the (OH) stretching absorption bands is inversely related to the sum of charges of cations which are coordinated to the (OH) group (e.g., Martínez-Alonso et al. 2002; Bosi et al. 2012b). In accordance with Gatta et al. (2014), we also assume that the $\text{O}^1(\text{OH})$ group forms a very weak hydrogen bond (bond strength < 0.05 valence units), whereas the $\text{O}^3(\text{OH})$ group forms a weak hydrogen bond (bond strength ~0.11 valence units) with the closest O5 atom ($\text{O}^3\text{O}-\text{O}^3\text{H}\cdots\text{O}5$), and that the strength of the hydrogen bond will influence the frequency of the principal (OH)-stretching vibration (e.g., Libowitzky 1999). Based on these criteria, we arrive at an assignment model for the observed main IR and Raman bands to the following stable short-range arrangements:

- band 3519 cm^{-1} is assigned to $[\text{YCr}^{\text{Z}}(\text{Cr},\text{Al})^{\text{Z}}(\text{Cr},\text{Al},\text{Mg}))]-\text{O}^3(\text{OH})$
- band 3565 cm^{-1} is assigned to $[\text{YMg}^{\text{Z}}\text{Al}^{\text{Z}}(\text{Al},\text{Mg})]-\text{O}^3(\text{OH})$
- weak bands $3712\text{-}3762\text{ cm}^{-1}$ are assigned to $^{\text{Y}}[\text{Mg Mg}(\text{Mg},\text{R}^{3+})]-\text{O}^1(\text{OH})$

where R^{3+} is a group of trivalent cations at the Y sites.

Concluding remarks

The fundamental (OH)-stretching bands in IR spectra of tourmalines display pronounced pleochroism (anisotropic intensities) with very strong absorption for spectra polarized along

the **c**-axis (e.g., Gebert and Zemmann 1965) owing to the orientation of the (OH) dipoles, which is approximately parallel to the **c**-axis direction (e.g., Gatta et al. 2014). This causes severe problems for the identification of absorption bands related to the O3 site of tourmaline, as it is generally not possible to thin crystals sufficiently to avoid off-scale intensity of these bands. Raman spectra are normally not affected by this problem, but may suffer from fluorescence effects. In this study, we showed that the combination of single crystal FTIR and Raman spectra collected with $\mathbf{E} \perp \mathbf{c}$ and $\mathbf{E} \parallel \mathbf{c}$ (respectively) may provide a useful characterization of the local (OH) environments around the O3 site. Very good correlations were found between the obtained PAI at 3519 and 3565 cm^{-1} derived from short-range information and the site populations derived from long-range information (i.e., SREF and EMPA). For the system oxy-dravite – chromo-alumino-povondraite – oxy-chromium-dravite, the band at 3519 cm^{-1} was shown to be associated with $^{\text{Y}}\text{Cr}-\text{O3}-(\text{Z} + \text{Z})$, while the band at 3565 cm^{-1} was shown to be associated with $^{\text{Y}}\text{Mg}-\text{O3}-(\text{Z} + \text{Z})$.

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List of tables

- Table 1.** Methodologies used to characterize the six oxy-tourmaline samples used in this study and references.
- Table 2.** Single-crystal X-ray diffraction data details for oxy-chromium-dravite (T89104) and oxy-dravite (PR108).
- Table 3.** Fractional atom coordinates and site occupancy for oxy-chromium-dravite (T89104) and oxy-dravite (PR108).
- Table 4.** Displacement parameters ($\text{\AA}^2$) for oxy-chromium-dravite (T89104) and oxy-dravite (PR108).
- Table 5.** Selected bond distances ($\text{\AA}$) for oxy-chromium-dravite (T89104) and oxy-dravite (PR108).
- Table 6.** Chemical composition for oxy-chromium-dravite (T89104) and oxy-dravite (PR108).
- Table 7.** Cation site populations (apfu), mean atomic numbers and mean bond lengths ($\text{\AA}$) for oxy-chromium-dravite (T89104) and oxy-dravite (PR108).
- Table 8.** Structural formulae of six oxy-tourmalines used in this study.
- Table 9.** Sample thicknesses and relative peak area intensities for infrared ($\mathbf{E} \perp \mathbf{c}$) and Raman ($\mathbf{E} // \mathbf{c}$) bands.

List of figures and figure captions

- Figure 1.** FTIR spectra polarized parallel (**a**) and perpendicular (**b**) to the **c**-axis direction. From top to bottom: sample PR108, PR107, Tm1p43e, PR85v, Tmt6b and T89104. Dotted spectra indicate the two fitted bands for the T89104 spectrum. Spectra are vertically offset for clarity.
- Figure 2.** Raman spectra polarized parallel to the **c**-axis direction. From top to bottom: sample PR107, Tm1p43e, PR85v and T89104. Spectra are vertically offset for clarity.

Figure 3. Ternary diagram of the $V_{\text{total}}\text{-Cr}_{\text{total}}\text{-Al}_{\text{total}}$ subsystem for oxy-tourmaline $\text{Na}^Y(R^{3+})_3^Z(R_4^{3+}\text{Mg}_2)\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3\text{O}$. The solid black circles represent the samples used in this study. Cr_5Al_2 and $\text{Cr}_{1.5}\text{Al}_{5.5}$ indicate the borderlines between oxy-chromium-dravite and chromo-alumino-povondraite and between oxy-dravite and chromo-alumino-povondraite, respectively.

Figure 4. (a) Relative peak area intensity (PAI) for the 3565 cm^{-1} band versus Mg at Y. Dashed lines indicate expected correlation for ideal solid-solution between oxy-chromium-dravite–oxy-dravite and oxy-chromium-dravite–(fluor-)dravite. (b) PAI for the 3519 cm^{-1} band versus Cr at Y. Dashed line indicates expected correlation for ideal solid-solution between oxy-dravite and oxy-chromium-dravite. Solid lines are linear regressions for the experimental data fitted through the origin.

Figure 5. Plots of peak area distribution for the 3565 cm^{-1} and 3519 cm^{-1} bands versus cation occupancy at the Z site. Solid lines are guide for the eye, dashed lines represent a linear distribution between the end-members. (a) PAI for the 3519 cm^{-1} band versus Cr at Z. (b) PAI for the 3519 cm^{-1} band versus Cr at Z. (c) PAI for the 3565 cm^{-1} band versus Al at Z. (d) PAI for 3519 cm^{-1} band versus Al at Z. (e) PAI for the 3565 cm^{-1} band versus Mg at Z. (f) PAI for the 3519 cm^{-1} band versus Mg at Z. See text for further explanation.

Atomic arrangements around the O3 site in Al- and Cr-rich oxy-tourmalines: a combined EMP, SREF, FTIR and Raman study

Ferdinando Bosi^{1,2}, Henrik Skogby², Peter Lazor³ and Leonid Reznitskii⁴

¹Dipartimento di Scienze della Terra, Sapienza Università di Roma, Piazzale Aldo Moro, 5, I-00185 Rome, Italy

²Department of Geosciences, Swedish Museum of Natural History, Box 50007, SE-10405 Stockholm, Sweden

³Department of Earth Sciences, Uppsala University, SE-752 36 Uppsala, Sweden

⁴Institute of the Earth's Crust, Siberian Branch, Russian Academy of Science, Lermontova str., 128, 664033 Irkutsk, Russia

Corresponding author:

Ferdinando Bosi, e-mail: ferdinando.bosi@uniroma1.it, tel: +39 0649914901, fax: +39 064454729

Abstract An experimental study on oxy-tourmalines belonging to the system oxy-dravite – chromo-alumino-povondraite – oxy-chromium-dravite from the Sludyanka crystalline complex (Southern Baikal region, Russia) was carried out using electron microprobe analysis (EMPA), structural refinement (SREF), infrared (IR) and Raman single crystal spectroscopy in order to explore the characteristic vibrational bands in the principal (OH)-stretching frequency and their relations to the O3 anion site of the tourmaline structure. The studied oxy-tourmalines are characterized by the substitution $\text{Al} \leftrightarrow \text{Cr}$ which is accompanied by redistribution of Mg over the Y and Z sites. The occurrence of strong correlations between relative peak area intensities for two bands at 3565 and 3519 cm^{-1} and

cation site populations derived from SREF and EMP data allowed to ascribe the band at 3565 cm⁻¹ to the cluster [^YMg ^ZAl ^Z(Al,Mg)]–O3 and the band at 3519 cm⁻¹ to the cluster [^YCr ^Z(Cr,Al) ^Z(Cr,Al,Mg)]–O3.

Moreover, this study showed that the combination of polarized IR and Raman spectra collected with the electric vector **E** ⊥ **c** and **E** // **c** (respectively) may provide a useful characterization of the local (OH) environments around the O3 site of the tourmaline structure.

Keywords Tourmaline, Electron microprobe, Crystal structure refinement, Infrared spectroscopy, Raman spectroscopy, Short-range arrangement

Introduction

Tourmalines are complex borosilicates and their crystal structure and crystal chemistry have been extensively studied (e.g., Foit 1989; Ertl et al. 2002; Hawthorne and Henry 1999; Bosi et al. 2010; Lussier et al. 2011; Filip et al. 2012). In accordance with Henry *et al.* (2011), the general formula of tourmaline may be written as: $XY_3Z_6T_6O_{18}(BO_3)_3V_3W$, [⁹]X = Na⁺, K⁺, Ca²⁺, □ (=vacancy); [⁶]Y = Al³⁺, Fe³⁺, Cr³⁺, V³⁺, Mg²⁺, Fe²⁺, Mn²⁺, Li⁺; [⁶]Z = Al³⁺, Fe³⁺, Cr³⁺, V³⁺, Mg²⁺, Fe²⁺; [⁴]T = Si⁴⁺, Al³⁺, B³⁺; [³]B = B³⁺; V (≡ [³]O3) = OH¹⁻, O²⁻; W (≡ [³]O1) = OH¹⁻, F¹⁻, O²⁻.

Vibrational transitions in the (OH)-stretching region has been presented for tourmaline in a number of studies (e.g., Gonzalez-Carreño et al. 1988; Castañeda et al. 2000; Hoang et al. 2011; Fantini et al. 2014). For elbaite, Skogby et al. (2012) presented a unifying assignment model for observed (OH) stretching bands using a combination of long-range information (based on diffraction techniques) and short-range information (based on spectroscopic techniques).

In this paper, we use a similar approach to explore the infrared (IR) and Raman spectra in the wavenumber region 3000-4000 cm⁻¹ of six single crystals of oxy-tourmalines

belonging to the solid solution system oxy-dravite – chromo-alumino-povondraite – oxy-chromium-dravite, and present a model to link the vibrational bands to stable short-range arrangements supported by bond-valence constraints.

Samples

The samples used in this study (T89104, Tmt6b, PR85v, Tm1p43e, PR107 and PR108) are emerald green and comes from metaquartzites in the Pereval marble quarry, Sludyanka crystalline complex, Southern Baikal region, Russia. At this locality (see Bosi et al. 2012a for a more detailed description), Cr-V-bearing metamorphic rocks are associated with Cr-V-bearing diopside and tremolite, escholaite, uvarovite, chromite, V-bearing titanite, pyrite, barite and calcite together with euhedral and subhedral crystals of tourmaline. The host-rock consists of a lens (10-15 cm thickness) of greenish-grey medium-grained quartzite within the marbles of the Pereval quarry. The crystals are euhedral, reaching up to 0.3 mm in length, and are often chemically zoned, but homogeneous crystals also occur.

Four of the six studied oxy-tourmalines (samples Tmt6b, PR85v, Tm1p43e and PR107) have previously been structurally and chemically characterized by means of X-ray single-crystal diffraction, electron microprobe analysis and Mössbauer spectroscopy. Moreover, samples PR85v and PR107 were also characterized by means of IR and optical absorption spectroscopy (Bosi et al. 2004; Bosi et al. 2013; Reznitskii et al. 2014). The obtained structural and chemical information revealed a chemical composition corresponding to the chromo-alumino-povondraite species with a variation predominantly in the Al and Cr contents. In order to cover the major compositional range characterized by the Cr for Al substitution, an oxy-dravite sample (PR108) and an oxy-chromium-dravite (T89104) was also structurally and chemically characterized. These samples were also characterized by IR and Raman single crystal spectroscopy (for details, see Table 1).

Experimental methods

Single-crystal structural refinement

Two representative crystals of oxy-dravite (sample PR108) and oxy-chromium-dravite (sample T89104) were selected for X-ray diffraction measurements on a Bruker KAPPA APEX-II single-crystal diffractometer, at Sapienza University of Rome (Earth Sciences Department), equipped with a CCD area detector ($6.2 \times 6.2 \text{ cm}^2$ active detection area, 512×512 pixels) and a graphite crystal monochromator, using $\text{MoK}\alpha$ radiation from a fine-focus sealed X-ray tube. The sample-to-detector distance was 4 cm. A total of 3265 (for PR108) and 1469 (for T89104) exposures (step = 0.2° , time/step = 20 s) covering the full reciprocal sphere with a redundancy of about 10 (for PR108) and 6 (for T89104). Final unit-cell parameters were refined with the Bruker AXS SAINT program using reflections with $I > 10 \sigma(I)$ in the range $5^\circ < 2\theta < 70^\circ$. 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 the multi-scan method (SADABS). The absorption correction led to a significant improvement in R_{int} . No violations of $R3m$ symmetry were noted.

Structural refinement was done with the SHELXL-2013 program (Sheldrick 2013). Starting coordinates were taken from Bosi et al. (2014). Variable parameters were: scale factor, extinction coefficient, atom coordinates, site scattering values and atom displacement factors. In detail, the *X* site was modeled by using the Na scattering factor; the *Y* site was modeled considering the presence of Cr and Mg; the occupancy of the *Z* site was modeled considering Al for sample PR108, and Cr and Mg for sample T89104. The *T* and *B* sites were modeled, respectively, with Si and B scattering factors and with a fixed occupancy of 1, because refinement with unconstrained occupancies showed no significant deviations from this value. Three full-matrix refinement cycles with isotropic displacement parameters for all atoms were followed by anisotropic cycles until convergence was attained. No significant correlations over a value of 0.7 between the parameters were observed at the end of refinement. Table 2 lists crystal data, data-collection information and refinement details; Table 3 gives the fractional atom coordinates and site occupancies; Table 4 gives the displacement parameters; Table 5 gives selected bond distances.

Electron microprobe analysis

Electron-microprobe analyses of the crystals used for X-ray diffraction refinement were obtained by wavelength-dispersive spectrometry (WDS mode) with a Cameca SX50 instrument at the “Istituto di Geologia Ambientale e Geoingegneria (Rome, Italy), CNR”, operating at an accelerating potential of 15 kV and a sample current of 15 nA, 10 μm beam diameter. Minerals and synthetic compounds were used as standards: wollastonite (Si, Ca), magnetite (Fe), rutile (Ti), corundum (Al), vanadinite (V), fluorophlogopite (F), periclase (Mg), jadeite (Na), K-feldspar (K), sphalerite (Zn), metallic Cr, Mn and Cu. The overlap corrections and the PAP routine were applied (Pouchou and Pichoir 1991). The results (Table 6) represent mean values of 10 spot analyses. In accord with the very low concentration of Li in dravitic samples (e.g., Henry et al. 2011) and the crystallization environment of the studied sample (i.e., Cr-bearing metaquartzites), the Li_2O content was assumed to be insignificant. The elements Mn, Fe, Cu, and Zn were below the detection limits (0.03 wt%) in the studied sample.

Single crystal infrared spectroscopy

Representative crystals of the four tourmaline samples that had not previously been studied were measured by Fourier transform infrared (FTIR) spectroscopy to characterize their (OH) vibrational absorption bands. The spectrometer system consisted of a Bruker Equinox 55 spectrometer in conjunction with a Biorad infrared microscope, using a halogen lamp source, a CaF_2 beam-splitter, a wire-grid polarizer (KRS-5) and an MCT detector. The crystals were oriented by morphology and optical microscopy, mounted on glass plates in thermoplastic resin and polished on two parallel sides, including the *c*-axis direction. Polarized absorption spectra were then acquired with a resolution of 4 cm^{-1} in the wavenumber range 2000-5000 cm^{-1} parallel and perpendicular to the crystallographic *c*-axis direction, using rectangular measurement areas of ca. 50 $\times$ 50 μm on the 26-50 μm thick crystals. Sample Tmt6b that was available in slightly larger crystal size was mounted on a 100 μm pin-hole aperture and was measured in the sample compartment of the spectrometer system using the same set-up, except for an InSb detector. As typically observed for tourmaline samples, the main (OH) absorption bands polarized parallel the *c*-axis direction were exceedingly intense, and it was not possible to thin the samples sufficiently to avoid off-scale absorption intensity for the strongest bands. Spectra obtained

perpendicular to **c**-axis direction were analyzed by band-fitting using the Jandel PeakFit 4.12 software.

Single crystal Raman spectroscopy

Raman spectra were recorded on five representative single crystals using a spectroscopic system built at the Department of Earth Sciences, Uppsala University. The key system components include a high-throughput, single stage imaging spectrometer (HoloSpec f/1.8i, Kaiser Optical Systems, Inc.) equipped with a holographic transmission grating and a thermoelectrically cooled (−60 °C) CCD detector (Newton, Andor Technology, 1600 × 400 pixels), a diode-pumped laser (Samba by Cobolt AB, 532.42 nm, 150 mW CW), and an optical imaging system (magnification 20×, spatial resolution ~1 μm). Two notch filters (Ondax Inc.) blocked the Rayleigh line. Polarized Raman spectra in parallel and perpendicular **c**-axis directions (n_e and n_o) were collected in the back-scattering geometry at a resolution and accuracy of about 2 cm^{−1} and 1.5 cm^{−1}, respectively. Typical acquisition time varied between 1 and 4 minutes, applying 15 mW of the laser power on a doubly-polished parallel-plate oriented single crystal, roughly 0.5 mm thick.

Results

Determination of atomic proportions

In agreement with the structural-refinement results, the boron content was assumed to be stoichiometric in samples PR108 and T89104 ($B^{3+} = 3.00$ apfu). Both the site-scattering results and the bond lengths of *B* and *T* are consistent with the *B* site fully occupied by boron and no amount of B^{3+} at the *T* site (e.g., Hawthorne 1996; Bosi and Lucchesi 2007). The (OH) content can then be calculated by charge balance with the assumption $T + Y + Z = 15.00$. The atomic proportions were calculated on this assumption (Table 6). The excellent match between the number of electrons per formula unit (epfu) derived from chemical and structural analysis supports this procedure, respectively: 240.6 and 239.9 epfu for sample PR108, 279.3 and 279.5 epfu for sample T89104.

Site populations

The anion site populations in the studied sample follow the general preference suggested for tourmaline (e.g., Grice and Ercit 1993; Henry et al. 2011): the O3 site (V position in the general formula) is occupied by (OH), and the O1 site (W position in the general formula) is occupied by O^{2-} , $(OH)^{1-}$ and F^{1-} . The cation distribution at the *T*, *Y* and *Z* sites was optimized by using a quadratic program to minimize the residuals between calculated and observed data (based on the chemical and structural analysis). Site-scattering values, octahedral and tetrahedral mean bond-distances (i.e., $\langle Y-O \rangle$, $\langle Z-O \rangle$ and $\langle T-O \rangle$) were calculated as the linear contribution of each cation multiplied by its ideal bond-distance. More details about the ideal distances as well as the optimization procedure may be found in Bosi et al. (2004) and Bosi and Lucchesi (2004; 2007). The robustness of this approach was confirmed by another optimization procedure (Wright et al. 2000), which led to very similar cation distributions (Table 7). The final structural formulae for samples PR108 and T89104 are reported in Table 8 along with those of the previously studied samples Tmt6b, PR85v, Tm1p43e, and PR107 for comparison reasons. In accordance with the classification of Henry *et al.* (2011) and the findings of Bosi and Skogby (2013) and Bosi et al. (2012a), samples PR108 and T89104 can be classified, respectively, as oxy-dravite and oxy-chromium-dravite.

Infrared and Raman spectra

The IR spectra obtained parallel to the *c*-axis direction of the tourmaline samples are characterized by a strong absorption feature in the 3450-3600 cm^{-1} range (Fig. 1a) which is truncated due to exceedingly strong absorption, in line with previous studies (e.g., Bosi et al. 2012b, Skogby et al. 2012). Weak bands occur in the 3700-3800 cm^{-1} region, and are also polarized in the *c*-axis direction. Although a slight shift in position of the main absorption feature is apparent, any possible fine structures are obscured by the off-scale intensity recorded along the *c*-axis. However, spectra polarized perpendicular to the *c*-axis are much less intense and reveal two partly overlapping bands with systematic variation of their absorption intensities (Fig. 1b). This trend is associated with sample composition,

where the band at higher wavenumbers increases with decreasing Cr content. In order to characterize and quantify these intensity shifts, the spectra were fitted with a model using two bands with fixed positions (3519 and 3565 cm^{-1}), but varying absorption areas. The band positions were initially obtained by an unconstrained fit of spectra of the most Al-rich sample (PR108) and the most Cr-rich sample (T89104), which are both dominated by one of these bands. The obtained absorption area distributions for the two bands are listed in Table 9.

For the used excitation wavelength, Raman spectra in the (OH)-region are characterized by a strong red fluorescence decreasing the signal-to-noise-ratio. This precluded spectral acquisitions for sample with the highest Al-content (PR108) for which the effect was the most pronounced. Raman spectra obtained for electric field (**E**) direction parallel to the **c**-axis (**E** // **c**) are shown in Fig. 2. The overall appearance of spectra as well as their evolution upon varying Al-Cr content resembles that of infrared absorption for the perpendicular configuration (**E** $\perp$ **c**) when the above-described two-band fitting model is applied. Positions of bands of the most Cr-rich sample (T89104) were used for all compositions when fitting the Raman spectra. The low quality of the spectrum for the Al-rich sample PR107 (Fig. 2) translated into a larger fitting uncertainty. The obtained absorption area distributions for the two bands are listed in Table 9. A somewhat lower value of position of the 3556 cm^{-1} Raman band, as compared to the corresponding 3565 cm^{-1} IR band, originates likely from comparing the spectra of different polarizations, parallel Raman (**E** // **c**) versus perpendicular IR (**E** $\perp$ **c**), and from the fitting uncertainties. No Raman bands in the (OH)-region were observed for the configuration **E** $\perp$ **c**.

Discussion

Crystal chemistry

The six samples used for this study can be referred to the following ideal formulae:

- oxy-chromium-dravite, $\text{Na}^Y\text{Cr}_3^Z(\text{Cr}_4\text{Mg}_2)(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{OH})_3\text{O}$;
- chromo-alumino-povondraite, $\text{Na}^Y\text{Cr}_3^Z(\text{Al}_4\text{Mg}_2)(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{OH})_3\text{O}$;
- oxy-dravite, $\text{Na}^Y(\text{Al}_2\text{Mg})^Z(\text{Al}_5\text{Mg})(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{OH})_3\text{O}$.

They all have the *X* site dominated by Na (0.68-0.98 apfu) with minor amount of Ca, vacancies and K. The *T* site is dominated by Si (5.95-5.99 apfu) along with very minor amounts of Al. The O1 site is dominated by O²⁻ (~0.7 apfu), followed by F (0.1-0.3 apfu) and then by (OH) (up to 0.3 apfu). The main compositional variation is characterized by the substitution of Al for Cr³⁺ at both the *Y* and *Z* sites (Fig. 3). In detail, moving from oxy-chromium-dravite to chromo-alumino-povondraite and further to oxy-dravite, ^YAl increases from zero to 0.65 apfu and ^ZAl from 1.80 apfu to 4.33, whereas ^YCr decreases from 2.55 to 0.63 apfu and ^ZCr from 2.23 to 0.33 apfu. Minor amounts of V³⁺ (< 0.3 apfu) are also present, alternatively at the *Y* and *Z* site. Minor amounts of Fe³⁺ (~0.3 apfu) are present at the *Z* site only for sample PR107. The presence of Mg increases from 0.27 to 1.33 apfu at *Y*, whereas it decreases from 1.96 apfu to 1.34 apfu at *Z* according to an order-disorder reaction between R³⁺-cations and Mg at the *Y* and *Z* sites (see below). With respect to the ideal formulae, the observed octahedral site populations can chiefly be described by the ideal substitutions that follow:

oxy-chromium-dravite ↔ chromo-alumino-povondraite

chromo-alumino-povondraite ↔ oxy-dravite

The substitution of Al for Cr is accompanied by redistribution of Mg over the *Y* and *Z* sites, which can be summarized by the substitutions occurring along the oxy-chromium-dravite – oxy-dravite join:

Short-range arrangements around O1 and O3

Short-range bond-valence requirements around the O1 site in of tourmaline (Hawthorne 1996, 2002; Bosi 2010, 2011, 2013) invoke the occurrence of the following possible and stable short-range arrangements for the studied samples:

where (OH,F) correspond to two different O1-site arrangements and $R^{3+} = \text{Al}, \text{Cr}$ and V .

As the anion at the O3 site is bonded to one Y and two Z cations, the cations occurring in the local arrangements around O1 should also be involved with the local arrangements around O3. In the studied sample, the O3 site is practically fully occupied by (OH), thus all the Z -cations (e.g., Al, Cr, V, Mg) impact on the absorption bands of the infrared and Raman spectra around O3 because they are part of the general local arrangement $[{}^Y(R)\text{--}^{\text{O3}}(\text{OH})\text{--}^Z(R + R)]$, where R is a generic cation.

Relation between octahedral site population and vibrational peak area intensity

In line with previous studies (e.g., Gonzalez-Carreño et al. 1988; Bosi et al. 2012b) and the very small $^{\text{O1}}(\text{OH})$ contents observed in the structural formulae, it can be anticipated that the weak vibrational bands above 3650 cm^{-1} are related to the O1 site and the strong bands below 3650 cm^{-1} to the O3 site (Fig. 1).

A strong positive correlation occurs between Al_{total} and the peak area intensity (PAI) in the IR (and Raman) spectra at 3565 (and 3556 in Raman) cm^{-1} ($r^2 > 0.9$) as well as between Cr_{total} and PAI at 3519 (and 3520 in Raman) cm^{-1} ($r^2 > 0.9$), indicating a distinct role of Al and Cr for the cause of these two bands. Consequently, the accommodation of cations at the Y and Z sites is expected to be related to PAI via the substitutions (1), (2) and (3), and in fact, high correlations between the amounts of Mg and Cr at the Y site and PAI are observed, whereas no relevant correlation was observed with ^YAl . With respect to the Raman spectra, the IR spectra appear to be of better quality and could also be acquired for all the six samples. Consequently, we will use the IR data to evaluate the relation between site population and vibrational peak area intensity. However, it can be noted that the Raman spectra obtained parallel to the c -axis essentially show the same trend as observed by FTIR spectra obtained perpendicular to the c -axis.

Fig. 4a displays the positive correlation between and Mg at the Y site and PAI at 3565 cm^{-1} from oxy-chromium-dravite via chromo-alumino-povondraite to oxy-dravite, indicating that the occurrence of this band is strongly related to a local arrangement

involving Mg at the *Y* site. Moreover, the deviation of the angular coefficient of the linear regression (~50) from the ideal value expected for oxy-dravite (= 100) can be ascribed to the practically constant sum of monovalent anions [F + (OH)] at the O1 site (~0.3 apfu) which represent the dravite and fluor-dravite components. Consequently, ^YMg should be bonded to ^{O1}O²⁻ and ^{O1}(OH,F) according to the following two cluster proportions: [^{O1}(O²⁻)–^Y(Mg)–^{O3}(OH)–^Z(R + R)]_{0.7} and [^{O1}(OH,F)–^Y(Mg)–^{O3}(OH)–^Z(R + R)]_{0.3}. The band at 3519 cm⁻¹ shows a high positive correlation with Cr at *Y* from oxy-dravite to oxy-chromium-dravite (Fig. 4b), indicating that this band is strictly related to a local arrangement involving Cr at the *Y* site. As the angular coefficient of the linear regression (~33) is in very good agreement with the substitution (3), ^YCr should be mainly bonded to ^{O1}O²⁻ rather than to ^{O1}(OH,F) according to the cluster: [^{O1}(O²⁻)–^Y(Cr)–^{O3}(OH)–^Z(R + R)].

The bands at 3565 cm⁻¹ and 3519 cm⁻¹ can therefore be assumed to be associated with ^YMg and ^YCr (respectively). However, these absorption bands also show relations with the cations at the *Z* site, which can be explained by the substitutions (1) and (2). The relation between Cr at *Z* and PAI at 3565 cm⁻¹ is displayed in Fig. 5a, indicating that this band first increases from oxy-chromium-dravite to chromo-alumino-povondraite with decreasing ^ZCr according to the substitution (1), ^ZAl → ^ZCr, and then continues to increase towards oxy-dravite but with increasing ^ZAl (and ^YMg) according to the substitution (2): ^Y(2Al + Mg) + ^Z(Al) → ^Y(3Cr) + ^Z(Mg). A corresponding specular explanation can be given for the relation between Cr at *Z* and PAI at 3519 cm⁻¹ (Fig. 5b). This band decreases from oxy-chromium-dravite to chromo-alumino-povondraite with decreasing ^ZCr according to substitution (1), and then continues to decrease to oxy-dravite but with decreasing ^YCr according to substitution (2). The correlation between Al at *Z* and PAI at 3565 cm⁻¹ (Fig. 5c) can be explained in a similar way. This band increases from oxy-chromium-dravite to chromo-alumino-povondraite with increasing ^ZAl according to substitution (1), and then continues to increase to oxy-dravite with increasing ^ZAl (and ^YMg) according to substitution (2). A specular explanation can also be given for the correlation between Al at *Z* and PAI at 3519 cm⁻¹ (Fig. 5d). This band decreases from oxy-chromium-dravite to chromo-alumino-povondraite with increasing ^ZAl according to the substitution (1), and then it continues to decrease to oxy-dravite but with decreasing ^YCr according to substitution (2). The occurrence of a negative correlation between ^ZMg and the PAI at 3565 cm⁻¹ (Fig. 5e) from oxy-chromium-dravite to oxy-dravite can be explained by the substitution (3),

${}^Y(2\text{Al} + \text{Mg}) + {}^Z(5\text{Al}) \rightarrow {}^Y(3\text{Cr}) + {}^Z(4\text{Cr} + \text{Mg})$, which decrease ${}^Z\text{Mg}$ and increase ${}^Y\text{Mg}$. Likewise, the positive correlation between ${}^Z\text{Mg}$ and the PAI at 3519 cm^{-1} (Fig. 5f) is linked to ${}^Y(3\text{Cr}) + {}^Z(4\text{Cr} + \text{Mg}) \rightarrow {}^Y(2\text{Al} + \text{Mg}) + {}^Z(5\text{Al})$, which increases both ${}^Z\text{Mg}$ and ${}^Y\text{Cr}$.

In summary, the band at 3565 cm^{-1} can be ascribed to the clusters $[{}^{O1}(\text{O}^{2-})-{}^Y(\text{Mg})-{}^{O3}(\text{OH})-{}^Z(\text{Al}_{1.7}\text{Mg}_{0.3})]_{0.7}$ and $[{}^{O1}(\text{OH},\text{F})-{}^Y(\text{Mg})-{}^{O3}(\text{OH})-{}^Z(\text{AlAl})]_{0.3}$ which represent the oxy-dravite and (fluor-)dravite components (respectively), whereas the band at 3519 cm^{-1} can be ascribed to $[{}^{O1}(\text{O}^{2-})-{}^Y(\text{Cr})-{}^{O3}(\text{OH})-{}^Z(\text{Al}_{1.3}\text{Mg}_{0.7})_{\Sigma 2.0}]$ and $[{}^{O1}(\text{O}^{2-})-{}^Y(\text{Cr})-{}^{O3}(\text{OH})-{}^Z(\text{Cr}_{1.3}\text{Mg}_{0.7})]$ which represent the chromo-alumino-povondraite and oxy-chromium-dravite components (respectively).

(OH) band assignment

Each of the more frequent local arrangements around the two types of (OH) groups, which occupy the two different crystallographic sites O1 and O3, is expected to produce an absorption band in the FTIR and Raman spectra. As above mentioned, The O1 site is surrounded by three Y cations, whereas the O3 site is surrounded by one Y and two Z cations. In addition, the occupancy of the X site may also affect the absorption band related to O1 (Gonzalez-Carreño et al. 1988).

In our band assignment model, we assume that the frequency of the (OH) stretching absorption bands is inversely related to the sum of charges of cations which are coordinated to the (OH) group (e.g., Martínez-Alonso et al. 2002; Bosi et al. 2012b). In accordance with Gatta et al. (2014), we also assume that: the ${}^{O1}(\text{OH})$ group forms a very weak hydrogen bond (bond strength < 0.05 valence units), whereas the ${}^{O3}(\text{OH})$ group forms a weak hydrogen bond (bond strength ~ 0.11 valence units) with the closest O5 atom (${}^{O3}\text{O}-{}^{O3}\text{H}\cdots\text{O5}$), and that the strength of the hydrogen bond will impact on the frequency of the principal (OH)-stretching vibration (e.g., Libowitzky 1999). Based on these criteria, we arrive at an assignment model for the observed main IR and Raman bands to stable short-range arrangements as follows:

- the band at 3519 cm^{-1} is assigned to $[{}^Y\text{Cr } {}^Z(\text{Cr},\text{Al}) {}^Z(\text{Cr},\text{Al},\text{Mg})] - {}^{O3}(\text{OH})$
- the band at 3565 cm^{-1} is assigned to $[{}^Y\text{Mg } {}^Z\text{Al } {}^Z(\text{Al},\text{Mg})] - {}^{O3}(\text{OH})$
- the weak bands at $3712\text{--}3762\text{ cm}^{-1}$ are assigned to ${}^Y[\text{Mg Mg (Mg}, R^{3+})] - {}^{O1}(\text{OH})$

where R^{3+} is a group of trivalent cations at the Y sites.

Concluding remarks

The fundamental (OH)-stretching bands in IR spectra of tourmalines display pronounced pleochroism (anisotropic intensities) with very strong absorption for spectra polarized along the **c**-axis (e.g., Gebert and Zemmann 1965) owing to the orientation of the (OH) dipoles, which is approximately parallel to the **c**-axis direction (e.g., Gatta et al. 2014). This causes severe experimental problems for the identification of absorption bands related to the O3 site of tourmaline, as it is generally not possible to thin crystals sufficiently to avoid off-scale intensity of these bands. Raman spectra are normally not affected by this problem, but may suffer from fluorescence effects. In this study, we showed that the combination of single crystal FTIR and Raman spectra collected with **E** // **c** and **E** $\perp$ **c** (respectively) may provide a useful characterization of the local (OH) environments around the O3 site. Very good correlations were found between the obtained PAI at 3519 and 3565 cm⁻¹ derived from short-range information and the site populations derived from long-range information (i.e., SREF and EMPA). For the system oxy-dravite – chromo-alumino-povondraite – oxy-chromium-dravite, the band at 3519 cm⁻¹ was shown to be associated with ^YCr–O3–(Z + Z), while the band at 3565 cm⁻¹ was shown to be associated with ^YMg–O3–(Z + Z).

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List of tables

- Table 1.** Methodologies used to characterize the six oxy-tourmaline samples used in this study and references.
- Table 2.** Single-crystal X-ray diffraction data details for oxy-chromium-dravite (T89104) and oxy-dravite (PR108).
- Table 3.** Fractional atom coordinates and site occupancy for oxy-chromium-dravite (T89104) and oxy-dravite (PR108).
- Table 4.** Displacement parameters ($\text{\AA}^2$) for oxy-chromium-dravite (T89104) and oxy-dravite (PR108).
- Table 5.** Selected bond distances ($\text{\AA}$) for oxy-chromium-dravite (T89104) and oxy-dravite (PR108).
- Table 6.** Chemical composition for oxy-chromium-dravite (T89104) and oxy-dravite (PR108).
- Table 7.** Cation site populations (apfu), mean atomic numbers and mean bond lengths ($\text{\AA}$) for oxy-chromium-dravite (T89104) and oxy-dravite (PR108).
- Table 8.** Structural formulae of six oxy-tourmalines used in this study.
- Table 9.** Sample thicknesses and relative peak area intensities for infrared- and Raman-bands

List of figures and figure captions

- Figure 1.** FTIR spectra polarized parallel (**a**) and perpendicular (**b**) to the **c**-axis direction. From top to bottom: sample PR108, PR107, Tm1p43e, PR85v, Tmt6b and T89104. Dotted spectra indicate the two fitted bands for the T89104 spectrum. Spectra are vertically offset for clarity.
- Figure 2.** Raman spectra polarized parallel to the **c**-axis direction. From top to bottom: sample PR107, Tm1p43e, PR85v and T89104. Spectra are vertically offset for clarity.

Figure 3. Ternary diagram of the $V_{\text{total}}\text{-Cr}_{\text{total}}\text{-Al}_{\text{total}}$ subsystem for oxy-tourmaline $\text{Na}^Y(R^{3+})_3^Z(R_4^{3+}\text{Mg}_2)\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3\text{O}$. The solid black circles represent the samples used in this study. Cr_5Al_2 and $\text{Cr}_{1.5}\text{Al}_{5.5}$ indicate the borderlines between oxy-chromium-dravite and chromo-alumino-povondraite and between oxy-dravite and chromo-alumino-povondraite, respectively.

Figure 4. (a) PAI for the 3565 cm^{-1} band versus Mg at Y. Dashed lines indicate expected correlation for ideal solid-solution between oxy-chromium-dravite–oxy-dravite and oxy-chromium-dravite–(fluor-)dravite. (b) PAI for the 3519 cm^{-1} band versus Cr at Y. Dashed line indicates expected correlation for ideal solid-solution between oxy-dravite and oxy-chromium-dravite. Solid lines are linear regressions for the experimental data fitted through the origin.

Figure 5. Plots of peak area distribution for the 3565 cm^{-1} and 3519 cm^{-1} bands versus cation occupancy at the Z site. Solid lines are guide for the eye, dashed lines represent a linear distribution between the end-members. (a) PAI for the 3519 cm^{-1} band versus Cr at Z. (b) PAI for the 3519 cm^{-1} band versus Cr at Z. (c) PAI for the 3565 cm^{-1} band versus Al at Z. (d) PAI for 3519 cm^{-1} band versus Al at Z. (e) PAI for the 3565 cm^{-1} band versus Mg at Z. (f) PAI for the 3519 cm^{-1} band versus Mg at Z. See text for further explanation.

Figure 1
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TABLE 2. Single-crystal X-ray diffraction data details for oxy-chromium-dravite (T89104) and oxy-dravite (PR108)

Sample	T89104	PR108
Crystal size (mm)	$0.11 \times 0.18 \times 0.20$	$0.15 \times 0.17 \times 0.25$
a (Å)	16.0572(3)	15.9710(2)
c (Å)	7.33280(10)	7.22710(10)
V (Å ³)	1637.34(5)	1596.46(5)
Range for data collection, 2θ (°)	5 - 73	5 - 65
Reciprocal space range hkl	$-26 \leq h \leq 24$ $-23 \leq k \leq 26$ $-6 \leq l \leq 12$	$-24 \leq h \leq 22$ $-24 \leq k \leq 20$ $-9 \leq l \leq 10$
Total number of frames	1469	3265
Set of measured reflections	5024	6874
Unique reflections, R_{int} (%)	1416, 1.46	1354, 1.86
Redundancy	5	10
Absorption correction method	SADABS	SADABS
Refinement method	Full-matrix last-squares on F^2	Full-matrix last-squares on F^2
Structural refinement program	SHELXL-2013	SHELXL-2013
Extinction coefficient	0.00062(8)	0.0003(2)
Flack parameter	0.07(2)	0.07(4)
$wR2$ (%)	2.79	3.99
$R1$ (%) all data	1.29	1.63
$R1$ (%) for $I > 2\sigma(I)$	1.28	1.60
GooF	1.096	1.073
Largest diff. peak and hole ($\pm e^{-}/\text{\AA}^3$)	0.42 and -0.26	0.34 and -0.28

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. Peaks = maximum and minimum residual electron density. Radiation, $\text{MoK}\alpha = 0.71073$ Å. Data collection temperature = 293 K. Space group $R3m$; $Z = 3$.

Table 3

TABLE 3. Fractional atom coordinates and site occupancy for oxy-chromium-dravite (T89104) and oxy-dravite (PR108)

Sample					PR108			
T89104								
Site	<i>x</i>	<i>y</i>	<i>z</i>	Site occupancy	<i>x</i>	<i>y</i>	<i>z</i>	Site occupancy
<i>X</i>	0	0	0.22571(18)	Na _{1.029(7)}	0	0	0.2285(2)	Na _{1.132(10)}
<i>Y</i>	0.123327(16)	0.061663(8)	0.63791(6)	Cr _{0.906(4)} Mg _{0.094(4)}	0.12370(4)	0.06185(2)	0.63654(10)	Cr _{0.341(6)} Mg _{0.659(2)}
<i>Z</i>	0.297699(16)	0.261729(17)	0.60850(5)	Cr _{0.396(3)} Mg _{0.604(3)}	0.29807(4)	0.26190(4)	0.61116(10)	Al _{1.028(4)}
<i>B</i>	0.10971(6)	0.21943(12)	0.4543(2)	B _{1.00}	0.10995(10)	0.21989(19)	0.4538(4)	B _{1.00}
<i>T</i>	0.189916(18)	0.18822(2)	0	Si _{1.00}	0.19128(3)	0.18954(3)	0	Si _{1.00}
O1	0	0	0.7652(2)	O _{1.00}	0	0	0.7690(4)	O _{1.00}
O2	0.06026(4)	0.12052(7)	0.48998(14)	O _{1.00}	0.06067(6)	0.12135(13)	0.4848(3)	O _{1.00}
O3	0.25583(8)	0.12792(4)	0.50932(15)	O _{1.00}	0.26107(14)	0.13053(7)	0.5117(3)	O _{1.00}
O4	0.09254(4)	0.18509(9)	0.07194(15)	O _{1.00}	0.09264(7)	0.18529(15)	0.0717(3)	O _{1.00}
O5	0.18281(8)	0.09141(4)	0.09112(14)	O _{1.00}	0.18263(14)	0.09131(7)	0.0918(3)	O _{1.00}
O6	0.19125(5)	0.18199(5)	0.78034(11)	O _{1.00}	0.19406(9)	0.18448(9)	0.7787(2)	O _{1.00}
O7	0.28301(5)	0.28266(5)	0.07273(11)	O _{1.00}	0.28446(9)	0.28403(8)	0.07746(19)	O _{1.00}
O8	0.20717(6)	0.26765(6)	0.43740(12)	O _{1.00}	0.20886(9)	0.26956(9)	0.4401(2)	O _{1.00}
H3	0.2554(16)	0.1277(8)	0.393(3)	H _{1.00}	0.257(3)	0.1287(13)	0.402(5)	H _{1.00}

Table 4

TABLE 4. Displacement parameters ($\text{\AA}^2$) for oxy-chromium-dravite (T89104) and oxy-dravite (PR108)

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}	$U_{\text{eq}}/U_{\text{iso}}^*$
Site	T89104						
<i>X</i>	0.0236(5)	0.0236(5)	0.0199(6)	0	0	0.0118(3)	0.0223(4)
<i>Y</i>	0.00441(10)	0.00434(8)	0.00661(9)	-0.00017(3)	-0.00034(7)	0.00221(5)	0.00511(6)
<i>Z</i>	0.00439(11)	0.00480(11)	0.00581(9)	0.00044(7)	-0.00004(7)	0.00233(8)	0.00498(6)
<i>B</i>	0.0061(4)	0.0071(6)	0.0092(5)	0.0010(4)	0.0005(2)	0.0035(3)	0.0074(2)
<i>T</i>	0.00503(12)	0.00458(11)	0.00662(11)	-0.00037(8)	-0.00031(9)	0.00229(9)	0.00546(6)
O1	0.0059(4)	0.0059(4)	0.0076(6)	0	0	0.0029(2)	0.0064(3)
O2	0.0054(3)	0.0051(4)	0.0080(4)	0.0011(3)	0.00055(15)	0.0026(2)	0.00620(18)
O3	0.0102(5)	0.0107(4)	0.0070(4)	0.00038(17)	0.0008(3)	0.0051(2)	0.00937(19)
O4	0.0079(3)	0.0166(5)	0.0093(4)	-0.0008(4)	-0.00039(18)	0.0083(3)	0.01029(19)
O5	0.0144(5)	0.0069(3)	0.0085(4)	0.00064(18)	0.0013(4)	0.0072(3)	0.00911(18)
O6	0.0091(3)	0.0064(3)	0.0059(3)	-0.0008(2)	-0.0003(2)	0.0038(3)	0.00717(13)
O7	0.0077(3)	0.0060(3)	0.0100(3)	-0.0013(2)	-0.0023(2)	0.0007(3)	0.00910(13)
O8	0.0048(3)	0.0084(3)	0.0171(3)	0.0030(3)	0.0011(3)	0.0029(3)	0.01028(14)
H3							0.014*
	PR108						
<i>X</i>	0.0136(6)	0.0136(6)	0.0147(9)	0	0	0.0068(3)	0.0140(5)
<i>Y</i>	0.0059(3)	0.0046(2)	0.0079(3)	-0.00104(9)	-0.00209(18)	0.00293(14)	0.00598(19)
<i>Z</i>	0.0061(2)	0.0064(2)	0.0066(2)	0.00035(17)	-0.00021(16)	0.00297(17)	0.00641(14)
<i>B</i>	0.0075(8)	0.0081(10)	0.0075(10)	-0.0001(8)	0.0000(4)	0.0040(5)	0.0076(4)
<i>T</i>	0.0059(2)	0.00550(19)	0.0070(2)	-0.00074(15)	-0.00070(16)	0.00264(15)	0.00621(12)
O1	0.0114(8)	0.0114(8)	0.0100(14)	0	0	0.0057(4)	0.0110(5)
O2	0.0107(6)	0.0066(7)	0.0141(9)	0.0010(6)	0.0005(3)	0.0033(4)	0.0109(4)
O3	0.0210(9)	0.0151(6)	0.0062(8)	0.0004(3)	0.0008(6)	0.0105(5)	0.0135(4)
O4	0.0092(5)	0.0188(9)	0.0114(8)	-0.0009(7)	-0.0004(3)	0.0094(5)	0.0121(3)
O5	0.0164(9)	0.0084(5)	0.0121(8)	0.0012(3)	0.0025(6)	0.0082(4)	0.0114(3)
O6	0.0120(6)	0.0105(5)	0.0073(5)	-0.0018(4)	-0.0014(4)	0.0061(4)	0.0097(2)
O7	0.0096(5)	0.0081(5)	0.0112(6)	-0.0009(4)	-0.0028(4)	0.0019(4)	0.0107(2)
O8	0.0065(5)	0.0100(6)	0.0183(6)	0.0024(4)	0.0008(5)	0.0039(5)	0.0117(3)
H3							0.02*

Notes: Equivalent (U_{eq}) and isotropic (U_{iso}) displacement parameters; H-atom was constrained to have a U_{iso} 1.5 times the U_{eq} value of the O3 oxygen.

TABLE 5. Selected bond distances (Å) for oxy-chromium-dravite (T89104) and oxy-dravite (PR108)

Sample	T89104	PR108
$X-O2^{B,F} (\times 3)$	2.5620(14)	2.500(2)
$X-O5^{B,F} (\times 3)$	2.7271(12)	2.712(2)
$X-O4^{B,F} (\times 3)$	2.8099(13)	2.802(2)
$\langle X-O \rangle$	2.700	2.673
$Y-O1$	1.9524(8)	1.9607(16)
$Y-O6^C (\times 2)$	1.9764(8)	1.9882(13)
$Y-O2^B (\times 2)$	2.0130(7)	2.0186(13)
$Y-O3$	2.0699(11)	2.103(2)
$\langle Y-O \rangle$	2.000	2.014
$Z-O8^E$	1.9502(8)	1.9066(13)
$Z-O7^E$	1.9641(8)	1.9205(14)
$Z-O8$	1.9583(8)	1.9358(14)
$Z-O6$	1.9901(8)	1.9236(14)
$Z-O7^D$	1.9915(8)	1.9637(13)
$Z-O3$	2.0379(5)	2.0068(10)
$\langle Z-O \rangle$	1.982	1.945
$B-O8^A (\times 2)$	1.3609(11)	1.3717(19)
$B-O2$	1.400(2)	1.381(3)
$\langle B-O \rangle$	1.374	1.375
$T-O7$	1.5974(7)	1.5998(12)
T^*-O6	1.6147(8)	1.6032(15)
$T-O4$	1.6269(4)	1.6272(8)
$T-O5$	1.6427(5)	1.6443(9)
$\langle T-O \rangle$	1.620	1.620
$H3-O3$	0.85(2)	0.80(4)

Notes: Standard uncertainty in parentheses. Superscript letters: A = ($y - x, y, z$); B = ($y - x, -x, z$); C = ($x, x - y, z$); D = ($y - x + 1/3, -x + 2/3, z + 2/3$); E = ($-y + 2/3, x - y + 1/3, z + 1/3$); F = ($-y, x - y, z$). Transformations relate coordinates to those of Table 3.

* Positioned in adjacent unit cell.

TABLE 7. Cation site populations (apfu), mean atomic numbers and mean bond lengths (Å) for oxy-chromium-dravite (T89104) and oxy-dravite (PR108)

Site	Site population	Mean atomic number		Mean bond length	
		refined	calculated	refined	calculated*
Sample T89104					
X	0.98 Na + 0.02 K	11.3(1)	11.20		
Y	2.55 Cr ³⁺ + 0.27 Mg + 0.14 V ³⁺ + 0.04 Ti ⁴⁺ (2.58 Cr ³⁺ + 0.27 Mg + 0.15 V ³⁺) [†]	22.9(1)	22.9	2.000	1.988
Z	2.23 Cr ³⁺ + 1.80 Al + 1.96 Mg (2.20 Cr ³⁺ + 1.81 Al + 1.96 Mg + 0.03 Ti ⁴⁺) [†]	16.8(1)	16.8	1.982	1.984
T	5.95 Si + 0.05 Al	14 [‡]	14.0	1.620	1.620
B	3 B	5 [‡]	5		
Sample PR108					
X	0.68 Na + 0.25 Ca + 0.06 □ + 0.01 K	12.5(1)	12.7		
Y	1.33 Mg + 0.65 Al + 0.63 Cr ³⁺ + 0.27 V ³⁺ + 0.12 Ti ⁴⁺ (1.38 Mg + 0.60 Al + 0.63 Cr ³⁺ + 0.26 V ³⁺ + 0.12 Ti ⁴⁺) [†]	16.1(1)	16.1	2.014	2.014
Z	4.33 Al + 1.34 Mg + 0.33 Cr ³⁺ (4.39 Al + 1.29 Mg + 0.32 Cr ³⁺) [†]	13.36(5)	13.38	1.945	1.943
T	5.99 Si + 0.01 Al	14 [‡]	14	1.620	1.619
B	3 B	5 [‡]	5		

Notes: apfu = atoms per formula unit;
* Calculated using the ionic radii of Bosi and Lucchesi (2007).
[†] Site populations optimized by the procedure of Wright et al. (2000).
[‡] Fixed in the final stages of refinement

TABLE 8. Structural formulae of six oxy-tourmalines used in this study

Sample	Structural formula	Reference
PR108 (oxy-dravite)	$^X(\text{Na}_{0.68}\text{Ca}_{0.25}\square_{0.06}\text{K}_{0.01})_{\Sigma 1.00} \text{ } ^Y(\text{Mg}_{1.33}\text{Al}_{0.65}\text{Cr}^{3+}_{0.63}\text{V}^{3+}_{0.27})_{\Sigma 3.00} \text{ } ^Z(\text{Al}_{4.33}\text{Mg}_{1.34}\text{Cr}^{3+}_{0.33})_{\Sigma 6.00}$ $[\text{T}(\text{Si}_{5.99}\text{Al}_{0.01})_{\Sigma 6.00} \text{O}_{18}] (\text{ } ^\text{B}\text{BO}_3)_3 \text{ } ^\text{V}(\text{OH})_3 \text{ } ^\text{W}[\text{O}_{0.65}\text{F}_{0.10}(\text{OH})_{0.26}]_{\Sigma 1.00}$	[1]
PR107 (chromo-alumino-povondraite)	$^X(\text{Na}_{0.76}\text{Ca}_{0.19}\square_{0.03}\text{K}_{0.02})_{\Sigma 1.00} \text{ } ^Y(\text{Cr}^{3+}_{1.94}\text{Mg}_{0.93}\text{Al}_{0.07}\text{Ti}^{4+}_{0.06})_{\Sigma 3.00} \text{ } ^Z(\text{Al}_{3.74}\text{Mg}_{1.43}\text{Fe}^{3+}_{0.32}\text{V}^{3+}_{0.19}\text{Cr}^{3+}_{0.16}\text{Fe}^{2+}_{0.15})_{\Sigma 6.00}$ $[\text{T}(\text{Si}_{5.99}\text{Al}_{0.01})_{\Sigma 6.00} \text{O}_{18}] (\text{ } ^\text{B}\text{BO}_3)_3 \text{ } ^\text{V}(\text{OH})_3 \text{ } ^\text{W}[\text{O}_{0.69}\text{F}_{0.23}(\text{OH})_{0.08}]_{\Sigma 1.00}$	[2]
Tm1p43e (chromo-alumino-povondraite)	$^X(\text{Na}_{0.89}\text{Ca}_{0.03}\square_{0.06}\text{K}_{0.02})_{\Sigma 1.00} \text{ } ^Y(\text{Cr}^{3+}_{2.17}\text{Mg}_{0.65}\text{Al}_{0.10}\text{V}^{3+}_{0.06}\text{Zn}_{0.02})_{\Sigma 3.00} \text{ } ^Z(\text{Al}_{3.25}\text{Mg}_{1.52}\text{Cr}^{3+}_{0.97}\text{V}^{3+}_{0.22}\text{Fe}^{2+}_{0.04})_{\Sigma 6.00}$ $[\text{T}(\text{Si}_{5.99}\text{Al}_{0.01})_{\Sigma 6.00} \text{O}_{18}] (\text{ } ^\text{B}\text{BO}_3)_3 \text{ } ^\text{V}(\text{OH})_3 \text{ } ^\text{W}[\text{O}_{0.71}\text{F}_{0.26}(\text{OH})_{0.03}]_{\Sigma 1.00}$	[4]
PR85v (chromo-alumino-povondraite)	$^X(\text{Na}_{0.87}\text{Ca}_{0.07}\square_{0.04}\text{K}_{0.02})_{\Sigma 1.00} \text{ } ^Y(\text{Cr}^{3+}_{2.29}\text{Mg}_{0.71})_{\Sigma 3.00} \text{ } ^Z(\text{Al}_{3.04}\text{Mg}_{1.54}\text{Cr}^{3+}_{1.18}\text{V}^{3+}_{0.22}\text{Fe}^{3+}_{0.01})_{\Sigma 6.00}$ $[\text{T}(\text{Si}_{5.96}\text{Al}_{0.04})_{\Sigma 6.00} \text{O}_{18}] (\text{ } ^\text{B}\text{BO}_3)_3 \text{ } ^\text{V}(\text{OH})_3 \text{ } ^\text{W}[\text{O}_{0.73}\text{F}_{0.25}(\text{OH})_{0.02}]_{\Sigma 1.00}$	[3]
Tmt6b (chromo-alumino-povondraite)	$^X(\text{Na}_{0.89}\text{Ca}_{0.07}\square_{0.02}\text{K}_{0.02})_{\Sigma 1.00} \text{ } ^Y(\text{Cr}^{3+}_{2.23}\text{Mg}_{0.46}\text{V}^{3+}_{0.24}\text{Fe}^{2+}_{0.04}\text{Ti}^{4+}_{0.03})_{\Sigma 3.00} \text{ } ^Z(\text{Al}_{2.34}\text{Mg}_{1.86}\text{Cr}^{3+}_{1.80})_{\Sigma 6.00}$ $[\text{T}(\text{Si}_{5.98}\text{Al}_{0.02})_{\Sigma 6.00} \text{O}_{18}] (\text{ } ^\text{B}\text{BO}_3)_3 \text{ } ^\text{V}[(\text{OH})_{2.98}\text{O}_{0.02}]_{\Sigma 3.00} \text{ } ^\text{W}(\text{O}_{0.67}\text{F}_{0.33})_{\Sigma 1.00}$	[4]
T89104 (oxy-chromium-dravite)	$^X(\text{Na}_{0.98}\text{K}_{0.02})_{\Sigma 1.00} \text{ } ^Y(\text{Cr}^{3+}_{2.55}\text{V}^{3+}_{0.14}\text{Mg}_{0.27}\text{Ti}^{4+}_{0.04})_{\Sigma 3.00} \text{ } ^Z(\text{Cr}^{3+}_{2.23}\text{Al}_{1.80}\text{Mg}_{1.96})_{\Sigma 6.00}$ $[\text{T}(\text{Si}_{5.95}\text{Al}_{0.05})_{\Sigma 6.00} \text{O}_{18}] (\text{ } ^\text{B}\text{BO}_3)_3 \text{ } ^\text{V}[(\text{OH})_{2.92}\text{O}_{0.08}]_{\Sigma 3.00} \text{ } ^\text{W}(\text{O}_{0.68}\text{F}_{0.32})_{\Sigma 1.00}$	[1]

[1] = present study, [2] = Bosi et al. (2013), [3] = Reznitskii et al. (2014), [4] = Bosi et al. (2004)

Table 9 Sample thicknesses and peak area intensities for infrared- and Raman-bands

Sample	PR108	PR107	PR85v	Tm1p43e	Tmt6b	T89104
Thickness (μm)	48	47	26	45	50	41
Infrared-bands						
PAI (%) 3519	29	56	73	71	79	90
PAI (%) 3565	71	44	27	29	21	10
Raman-bands						
PAI (%) 3520	-	60 ^a	62	60	-	82
PAI (%) 3556	-	40 ^a	38	40	-	18

PAI = Fitted relative peak area intensity for the vibrational-bands

^a Large fitting error (~15%)

TABLE 1. Methodologies used to characterized the six oxy-tourmaline samples used in this study and references

Sample	EMP	SREF	MS	OAS	IR	RAMAN
PR108	This study	This study	-	-	This study	-
PR107	Bosi et al. (2013)	Bosi et al. (2013)	Bosi et al. (2013)	Bosi et al. (2013)	Bosi et al. (2013)	This study
PR85v	Reznitskii et al. (2014)	Reznitskii et al. (2014)	-	Reznitskii et al. (2014)	Reznitskii et al. (2014)	This study
Tm1p43e	Bosi et al. (2004)	Bosi et al. (2004)	-	-	This study	This study
Tmt6b	Bosi et al. (2004)	Bosi et al. (2004)	-	-	This study	-
T89104	This study	This study	-	-	This study	This study

EMP = electron microprobe; SREF = structural refinement; MS = Mössbauer spectroscopy; OAS = optical absorption spectroscopy; IR = infrared spectroscopy; RAMAN = Raman spectroscopy

TABLE 2. Single-crystal X-ray diffraction data details for oxy-chromium-dravite (T89104) and oxy-dravite (PR108)

Sample	T89104	PR108
Crystal size (mm)	0.11 × 0.18 × 0.20	0.15 × 0.17 × 0.25
<i>a</i> (Å)	16.0572(3)	15.9710(2)
<i>c</i> (Å)	7.3328(1)	7.2471(1)
<i>V</i> (Å ³)	1637.34(5)	1600.88(5)
Range for data collection, 2θ (°)	5 - 73	5 - 65
Reciprocal space range <i>hkl</i>	$-26 \leq h \leq 24$ $-23 \leq k \leq 26$ $-6 \leq l \leq 12$	$-24 \leq h \leq 22$ $-24 \leq k \leq 20$ $-9 \leq l \leq 10$
Total number of frames	1469	3265
Set of measured reflections	5024	6874
Unique reflections, <i>R</i> _{int} (%)	1416, 1.46	1354, 1.86
Redundancy	5	10
Absorption correction method	SADABS	SADABS
Refinement method	Full-matrix last-squares on <i>F</i> ²	Full-matrix last-squares on <i>F</i> ²
Structural refinement program	SHELXL-2013	SHELXL-2013
Extinction coefficient	0.00060(9)	0.0003(2)
Flack parameter	0.073(19)	0.07(4)
<i>wR</i> 2 (%)	2.80	4.02
<i>R</i> 1 (%) all data	1.29	1.65
<i>R</i> 1 (%) for <i>I</i> > 2σ(<i>I</i>)	1.28	1.61
GooF	1.099	1.083
Largest diff. peak and hole (±e ⁻ /Å ³)	0.42 and -0.29	0.34 and -0.30

Notes: *R*_{int} = merging residual value; *R*1 = discrepancy index, calculated from *F*-data; *wR*2 = weighted discrepancy index, calculated from *F*²-data; GooF = goodness of fit; Diff. Peaks = maximum and minimum residual electron density. Radiation, MoKα = 0.71073 Å. Data collection temperature = 293 K. Space group *R*3*m*; *Z* = 3.

TABLE 6. Chemical composition for oxy-chromium-dravite (T89104) and oxy-dravite (PR108)

Sample	T89104	PR108
SiO ₂ wt%	32.61(9)	36.25(33)
TiO ₂	0.28(5)	0.95(1)
B ₂ O ₃	9.53*	10.51*
Al ₂ O ₃	8.62(33)	25.51(55)
Cr ₂ O ₃	33.16(58)	7.42(52)
V ₂ O ₃	0.98(15)	2.09(3)
MgO	8.20(12)	10.83(15)
CaO	bdl	1.43(11)
Na ₂ O	2.76(6)	2.11(4)
K ₂ O	0.10(2)	0.05(1)
F	0.56(5)	0.20(9)
H ₂ O	2.40*	2.95*
–O ≡ F	–0.24	–0.08
Total	99.96	100.62

Atomic proportions normalized to 31 anions

Si apfu	5.95	5.99
Ti ⁴⁺	0.04	0.12
B	3.00	3.00
Al	1.85	4.97
Cr ³⁺	4.78	0.97
V ³⁺	0.14	0.28
Mg	2.23	2.67
Ca	-	0.25
Na	0.98	0.68
K	0.02	0.01
F	0.32	0.10
OH	2.92	3.26

* Calculated by stoichiometry.

Notes: Errors for oxides are standard deviations (in brackets) of 7 spot analyses; apfu = atoms per formula unit.

Table 3

TABLE 3. Fractional atom coordinates and site occupancy for oxy-chromium-dravite (T89104) and oxy-dravite (PR108)

Sample					PR108			
T89104								
Site	<i>x</i>	<i>y</i>	<i>z</i>	Site occupancy	<i>x</i>	<i>y</i>	<i>z</i>	Site occupancy
<i>X</i>	0	0	0.22571(23)	Na _{1.030(8)}	0	0	0.22857(24)	Na _{1.131(10)}
<i>Y</i>	0.12333(2)	0.06166(2)	0.63792(7)	Cr _{0.905(5)} Mg _{0.095(5)}	0.12371(4)	0.06185(2)	0.63655(10)	Cr _{0.340(6)} Mg _{0.660(6)}
<i>Z</i>	0.29770(2)	0.26173(2)	0.60851(6)	Cr _{0.396(3)} Mg _{0.604(3)}	0.29807(4)	0.26189(4)	0.61118(10)	Al _{1.029(4)}
<i>B</i>	0.10971(7)	0.21941(15)	0.45434(26)	B _{1.00}	0.10994(10)	0.21987(20)	0.45380(38)	B _{1.00}
<i>T</i>	0.18992(2)	0.18822(2)	0	Si _{1.00}	0.19129(3)	0.18953(3)	0	Si _{1.00}
O1	0	0	0.76520(29)	O _{1.00}	0	0	0.76915(44)	O _{1.00}
O2	0.06026(5)	0.12052(9)	0.48998(18)	O _{1.00}	0.06066(7)	0.12133(13)	0.48483(28)	O _{1.00}
O3	0.25584(10)	0.12792(5)	0.50928(19)	O _{1.00}	0.26110(14)	0.13055(7)	0.51161(28)	O _{1.00}
O4	0.09255(5)	0.18509(11)	0.07200(18)	O _{1.00}	0.09265(7)	0.18530(15)	0.07174(28)	O _{1.00}
O5	0.18281(8)	0.09141(4)	0.09112(14)	O _{1.00}	0.18259(14)	0.09130(7)	0.09175(27)	O _{1.00}
O6	0.19124(7)	0.18200(7)	0.78035(13)	O _{1.00}	0.19404(9)	0.18448(9)	0.77871(20)	O _{1.00}
O7	0.28300(7)	0.28267(6)	0.07274(13)	O _{1.00}	0.28445(9)	0.28404(8)	0.07748(19)	O _{1.00}
O8	0.20715(7)	0.26764(7)	0.43738(15)	O _{1.00}	0.20886(9)	0.26956(9)	0.44006(21)	O _{1.00}
H3	0.2555(19)	0.1278(9)	0.393(3)	H _{1.00}	0.2546(25)	0.1273(12)	0.386(3)	H _{1.00}

TABLE 4. Displacement parameters ($\text{\AA}^2$) for oxy-chromium-dravite (T89104) and oxy-dravite (PR108)

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}	$U_{\text{eq}}/U_{\text{iso}}^*$
Site	T89104						
<i>X</i>	0.0236(6)	0.0236(6)	0.0198(8)	0	0	0.0118(3)	0.0223(5)
<i>Y</i>	0.00439(13)	0.00433(10)	0.00659(11)	-0.00017(4)	-0.00035(8)	0.00220(6)	0.00510(8)
<i>Z</i>	0.00439(13)	0.00479(13)	0.00581(11)	0.00044(8)	-0.00004(8)	0.00232(10)	0.00498(8)
<i>B</i>	0.0062(5)	0.0071(7)	0.0092(7)	0.0010(6)	0.0005(3)	0.0035(4)	0.0074(3)
<i>T</i>	0.00502(15)	0.00459(14)	0.00661(13)	-0.00037(10)	-0.00031(11)	0.00229(11)	0.00546(8)
O1	0.0058(5)	0.0058(5)	0.0077(8)	0	0	0.0029(3)	0.0064(4)
O2	0.0054(4)	0.0051(5)	0.0081(5)	0.0011(4)	0.00053(19)	0.0025(2)	0.0062(2)
O3	0.0102(6)	0.0106(4)	0.0071(5)	0.0004(2)	0.0008(4)	0.0051(3)	0.0093(2)
O4	0.0079(4)	0.0166(7)	0.0094(5)	-0.0008(4)	-0.0004(2)	0.0083(3)	0.0103(2)
O5	0.0144(6)	0.0069(4)	0.0085(5)	0.0006(2)	0.0013(4)	0.0072(3)	0.0091(2)
O6	0.0091(4)	0.0064(4)	0.0059(3)	-0.0007(3)	-0.0003(3)	0.0038(3)	0.00717(16)
O7	0.0077(4)	0.0061(4)	0.0099(3)	-0.0013(3)	-0.0023(3)	0.0007(3)	0.00910(16)
O8	0.0048(4)	0.0084(4)	0.0171(4)	0.0030(3)	0.0011(3)	0.0029(3)	0.01030(17)
H3							0.011*
	PR108						
<i>X</i>	0.0135(6)	0.0135(6)	0.0148(9)	0	0	0.0067(3)	0.0139(5)
<i>Y</i>	0.0058(3)	0.0045(2)	0.0080(3)	-0.00106(9)	-0.00212(18)	0.00288(14)	0.00596(19)
<i>Z</i>	0.0062(2)	0.0064(2)	0.0067(2)	0.00037(17)	-0.00018(17)	0.00298(18)	0.00649(14)
<i>B</i>	0.0074(8)	0.0080(10)	0.0077(11)	0.0000(8)	0.0000(4)	0.0040(5)	0.0077(4)
<i>T</i>	0.0058(2)	0.0055(2)	0.0071(2)	-0.00073(15)	-0.00072(16)	0.00264(16)	0.00622(12)
O1	0.0114(8)	0.0114(8)	0.0102(14)	0	0	0.0057(4)	0.0110(6)
O2	0.0107(6)	0.0065(7)	0.0144(9)	0.0010(6)	0.0005(3)	0.0033(4)	0.0110(4)
O3	0.0206(9)	0.0148(6)	0.0066(8)	0.0005(3)	0.0010(7)	0.0103(5)	0.0134(4)
O4	0.0092(5)	0.0187(9)	0.0118(8)	-0.0009(7)	-0.0004(3)	0.0094(5)	0.0122(3)
O5	0.0163(9)	0.0083(5)	0.0122(8)	0.0012(3)	0.0024(7)	0.0082(4)	0.0114(3)
O6	0.0120(6)	0.0104(5)	0.0074(5)	-0.0018(4)	-0.0014(4)	0.0061(4)	0.0097(2)
O7	0.0095(5)	0.0080(5)	0.0113(6)	-0.0009(4)	-0.0028(4)	0.0019(4)	0.0107(3)
O8	0.0064(5)	0.0099(6)	0.0188(6)	0.0023(4)	0.0008(5)	0.0039(5)	0.0118(3)
H3							0.016*

Notes: Equivalent (U_{eq}) and isotropic (U_{iso}) displacement parameters; H-atom was constrained to have a U_{iso} 1.2 times the U_{eq} value of the O3 oxygen.

TABLE 5. Selected bond distances (Å) for oxy-chromium-dravite (T89104) and oxy-dravite (PR108)

Sample	T89104	PR108
$X-O2^{B,F} (\times 3)$	2.562(2)	2.503(2)
$X-O5^{B,F} (\times 3)$	2.727(2)	2.713(2)
$X-O4^{B,F} (\times 3)$	2.810(2)	2.804(2)
$\langle X-O \rangle$	2.700	2.673
$Y-O1$	1.953(1)	1.962(2)
$Y-O6^C (\times 2)$	1.977(1)	1.990(1)
$Y-O2^B (\times 2)$	2.0131(9)	2.020(1)
$Y-O3$	2.070(1)	2.105(2)
$\langle Y-O \rangle$	2.000	2.015
$Z-O8^E$	1.950(1)	1.909(1)
$Z-O7^E$	1.964(1)	1.923(1)
$Z-O8$	1.959(1)	1.938(1)
$Z-O6$	1.990(1)	1.926(1)
$Z-O7^D$	1.992(1)	1.965(1)
$Z-O3$	2.0380(7)	2.008(1)
$\langle Z-O \rangle$	1.982	1.945
$B-O8^A (\times 2)$	1.361(1)	1.372(2)
$B-O2$	1.400(2)	1.381(3)
$\langle B-O \rangle$	1.374	1.375
$T-O7$	1.5974(9)	1.601(1)
T^*-O6	1.615(1)	1.608(2)
$T-O4$	1.6271(5)	1.6279(8)
$T-O5$	1.6426(6)	1.6447(9)
$\langle T-O \rangle$	1.621	1.620
$H3-O3$	0.93(2)	0.92(2)
$O3-O5$	3.230	3.231

Notes: Standard uncertainty in parentheses. Superscript letters: A = (y – x, y, z); B = (y – x, – x, z); C = (x, x – y, z); D = (y – x + 1/3, – x + 2/3, z + 2/3); E = (–y + 2/3, x – y + 1/3, z + 1/3); F = (–y, x – y, z). Transformations relate coordinates to those of Table 3.

* Positioned in adjacent unit cell.

TABLE 7. Cation site populations (apfu), mean atomic numbers and mean bond lengths (Å) for oxy-chromium-dravite (T89104) and oxy-dravite (PR108)

Site	Site population	Mean atomic number		Mean bond length	
		refined	calculated	refined	calculated*
Sample T89104					
X	0.98 Na + 0.02 K	11.3(1)	11.20		
Y	2.55 Cr ³⁺ + 0.27 Mg + 0.14 V ³⁺ + 0.04 Ti ⁴⁺ (2.58 Cr ³⁺ + 0.27 Mg + 0.15 V ³⁺) [†]	22.9(1)	22.9	2.000	1.988
Z	2.24 Cr ³⁺ + 1.80 Al + 1.96 Mg (2.20 Cr ³⁺ + 1.81 Al + 1.96 Mg + 0.03 Ti ⁴⁺) [†]	16.8(1)	16.8	1.982	1.984
T	5.95 Si + 0.05 Al	14 [‡]	14.0	1.621	1.620
B	3 B	5 [‡]	5		
Sample PR108					
X	0.68 Na + 0.25 Ca + 0.06 □ + 0.01 K	12.4(1)	12.7		
Y	1.34 Mg + 0.65 Al + 0.62 Cr ³⁺ + 0.27 V ³⁺ + 0.12 Ti ⁴⁺ (1.38 Mg + 0.60 Al + 0.63 Cr ³⁺ + 0.26 V ³⁺ + 0.12 Ti ⁴⁺) [†]	16.1(1)	16.1	2.015	2.014
Z	4.33 Al + 1.33 Mg + 0.34 Cr ³⁺ (4.39 Al + 1.29 Mg + 0.32 Cr ³⁺) [†]	13.38(5)	13.38	1.945	1.943
T	5.99 Si + 0.01 Al	14 [‡]	14	1.620	1.619
B	3 B	5 [‡]	5		

Notes: apfu = atoms per formula unit;
* Calculated using the ionic radii of Bosi and Lucchesi (2007).
[†] Site populations optimized by the procedure of Wright et al. (2000).
[‡] Fixed in the final stages of refinement

TABLE 8. Structural formulae of six oxy-tourmalines used in this study

Sample	Structural formula	Reference
PR108 (oxy-dravite)	$^X(\text{Na}_{0.68}\text{Ca}_{0.25}\square_{0.06}\text{K}_{0.01})_{\Sigma 1.00} ^Y(\text{Mg}_{1.34}\text{Al}_{0.65}\text{Cr}^{3+}_{0.62}\text{V}^{3+}_{0.27}\text{Ti}^{4+}_{0.12})_{\Sigma 3.00} ^Z(\text{Al}_{4.33}\text{Mg}_{1.33}\text{Cr}^{3+}_{0.34})_{\Sigma 6.00}$ $[^T(\text{Si}_{5.99}\text{Al}_{0.01})_{\Sigma 6.00} \text{O}_{18}] (^B\text{BO}_3)_3 ^V(\text{OH})_3 ^W[\text{O}_{0.65}\text{F}_{0.10}(\text{OH})_{0.26}]_{\Sigma 1.00}$	[1]
PR107 (chromo-alumino-povondraite)	$^X(\text{Na}_{0.76}\text{Ca}_{0.19}\square_{0.03}\text{K}_{0.02})_{\Sigma 1.00} ^Y(\text{Cr}^{3+}_{1.94}\text{Mg}_{0.93}\text{Al}_{0.07}\text{Ti}^{4+}_{0.06})_{\Sigma 3.00} ^Z(\text{Al}_{3.74}\text{Mg}_{1.43}\text{Fe}^{3+}_{0.32}\text{V}^{3+}_{0.19}\text{Cr}^{3+}_{0.16}\text{Fe}^{2+}_{0.15})_{\Sigma 6.00}$ $[^T(\text{Si}_{5.99}\text{Al}_{0.01})_{\Sigma 6.00} \text{O}_{18}] (^B\text{BO}_3)_3 ^V(\text{OH})_3 ^W[\text{O}_{0.69}\text{F}_{0.23}(\text{OH})_{0.08}]_{\Sigma 1.00}$	[2]
Tm1p43e (chromo-alumino-povondraite)	$^X(\text{Na}_{0.89}\text{Ca}_{0.03}\square_{0.06}\text{K}_{0.02})_{\Sigma 1.00} ^Y(\text{Cr}^{3+}_{2.17}\text{Mg}_{0.65}\text{Al}_{0.10}\text{V}^{3+}_{0.06}\text{Zn}_{0.02})_{\Sigma 3.00} ^Z(\text{Al}_{3.25}\text{Mg}_{1.52}\text{Cr}^{3+}_{0.97}\text{V}^{3+}_{0.22}\text{Fe}^{2+}_{0.04})_{\Sigma 6.00}$ $[^T(\text{Si}_{5.99}\text{Al}_{0.01})_{\Sigma 6.00} \text{O}_{18}] (^B\text{BO}_3)_3 ^V(\text{OH})_3 ^W[\text{O}_{0.71}\text{F}_{0.26}(\text{OH})_{0.03}]_{\Sigma 1.00}$	[4]
PR85v (chromo-alumino-povondraite)	$^X(\text{Na}_{0.87}\text{Ca}_{0.07}\square_{0.04}\text{K}_{0.02})_{\Sigma 1.00} ^Y(\text{Cr}^{3+}_{2.29}\text{Mg}_{0.71})_{\Sigma 3.00} ^Z(\text{Al}_{3.04}\text{Mg}_{1.54}\text{Cr}^{3+}_{1.18}\text{V}^{3+}_{0.22}\text{Fe}^{3+}_{0.01})_{\Sigma 6.00}$ $[^T(\text{Si}_{5.96}\text{Al}_{0.04})_{\Sigma 6.00} \text{O}_{18}] (^B\text{BO}_3)_3 ^V(\text{OH})_3 ^W[\text{O}_{0.73}\text{F}_{0.25}(\text{OH})_{0.02}]_{\Sigma 1.00}$	[3]
Tmt6b (chromo-alumino-povondraite)	$^X(\text{Na}_{0.89}\text{Ca}_{0.07}\square_{0.02}\text{K}_{0.02})_{\Sigma 1.00} ^Y(\text{Cr}^{3+}_{2.23}\text{Mg}_{0.46}\text{V}^{3+}_{0.24}\text{Fe}^{2+}_{0.04}\text{Ti}^{4+}_{0.03})_{\Sigma 3.00} ^Z(\text{Al}_{2.34}\text{Mg}_{1.86}\text{Cr}^{3+}_{1.80})_{\Sigma 6.00}$ $[^T(\text{Si}_{5.98}\text{Al}_{0.02})_{\Sigma 6.00} \text{O}_{18}] (^B\text{BO}_3)_3 ^V[(\text{OH})_{2.98}\text{O}_{0.02}]_{\Sigma 3.00} ^W(\text{O}_{0.67}\text{F}_{0.33})_{\Sigma 1.00}$	[4]
T89104 (oxy-chromium-dravite)	$^X(\text{Na}_{0.98}\text{K}_{0.02})_{\Sigma 1.00} ^Y(\text{Cr}^{3+}_{2.55}\text{V}^{3+}_{0.14}\text{Mg}_{0.27}\text{Ti}^{4+}_{0.04})_{\Sigma 3.00} ^Z(\text{Cr}^{3+}_{2.24}\text{Al}_{1.80}\text{Mg}_{1.96})_{\Sigma 6.00}$ $[^T(\text{Si}_{5.95}\text{Al}_{0.05})_{\Sigma 6.00} \text{O}_{18}] (^B\text{BO}_3)_3 ^V[(\text{OH})_{2.92}\text{O}_{0.08}]_{\Sigma 3.00} ^W(\text{O}_{0.68}\text{F}_{0.32})_{\Sigma 1.00}$	[1]

Note: Minor deviations in the amounts of O and OH at the *V* and *W* positions may occur due to disordering effects (see text).

[1] = present study, [2] = Bosi et al. (2013), [3] = Reznitskii et al. (2014), [4] = Bosi et al. (2004)

Table 9 Sample thicknesses and relative peak area intensities for infrared (**E** ⊥ **c**) and Raman (**E** // **c**) bands.

Sample	PR108	PR107	PR85v	Tm1p43e	Tmt6b	T89104
Thickness (μm)	48	47	26	45	50	41
Infrared-bands						
PAI (%) 3519	29	56	73	71	79	90
PAI (%) 3565	71	44	27	29	21	10
Raman-bands						
PAI (%) 3520	-	60 ^a	62	60	-	82
PAI (%) 3556	-	40 ^a	38	40	-	18

PAI = Fitted relative peak area intensity for the vibrational-bands

^a Large fitting error (~15%)