Mn-bearing purplish-red tourmaline from the Anjanabonoina pegmatite, Madagascar

Ferdinando Bosi1, Erica Bittarello2,6 and Alessandra Marengo5,6

1Department of Earth Sciences, Sapienza University of Rome, Piazzale Aldo Moro 5, I-00185 Rome, Italy; 2Department of Geosciences, Swedish Museum of Natural History, SE-10405 Stockholm, Sweden; 3Department of Earth and Environmental Sciences, University of Bari “Aldo Moro”, via Orabona 4, I-70125 Bari, Italy; 4Associazione Micromineralogica Italiana, via San Pietro 55, I-10073 Devesi-Cirié, Italy; 5Department of Earth Sciences, University of Turin, via Tommaso Valperga Caluso 35, I-10125 Torino, Italy; and 6SpectraLab s.r.l. Academic spin-off of the University of Turin, via Tommaso Valperga Caluso 35, I-10125 Torino, Italy

Abstract

A gem-quality purplish-red tourmaline sample of alleged liddicoatitic composition from the Anjanabonoina pegmatite, Madagascar, has been fully characterised using a multi-analytical approach to define its crystal-chemical identity. Single-crystal X-ray diffraction, chemical and spectroscopic analysis resulted in the formula: \((\text{Na}_{0.41}\text{Mg}_{0.35}\text{Ca}_{0.24})_{2}^{1.00}(\text{Al}_{1.81}\text{Li}_{1.00}\text{Fe}^{3+0.04}\text{Mn}^{2+0.02}\text{Mn}^{3+0.00})_{12}\text{Ti}_{0.004}\text{O}_{37})_{2}^{1.00}\) which corresponds to the tourmaline species elbaite having the typical space group \(R3\overline{m}\) and relatively small unit-cell dimensions, \(a = 15.7935(4)\ \text{Å}, c = 7.0860(2)\ \text{Å}\) and \(V = 7.0860(2)\ \text{Å}^{3}\). Optical absorption spectroscopy showed that the purplish-red colour is caused by minor amounts of Mn\(^{3+}\) (Mn\(_2\)O\(_3\) = 0.20 wt.%). Thermal treatment in air up to 750°C strongly intensified the colour of the sample due to the oxidation of all Mn\(^{2+}\) to Mn\(^{3+}\) (Mn\(_2\)O\(_3\) up to 1.21 wt.%). Based on infrared and Raman data, a chemical-model regarding the electrostatic interaction between the X cation and W anion, and involving the Y cations as well, is proposed to explain the absence or rarity of the mineral species ‘liddicoaitie’.

Keywords: purplish-red tourmaline, crystal-structure refinement, electron microprobe, laser induced breakdown spectroscopy, Raman spectroscopy, infrared spectroscopy, optical absorption spectroscopy

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Introduction

Tourmaline is the most common and the earliest-formed boron mineral on Earth and has recently increased interest from the geoscience community (Grew et al., 2016; Dutrow and Henry, 2018; Henry and Dutrow, 2018). Tourmaline minerals are complex borosilicates that have been studied extensively in terms of their crystal structure and crystal chemistry (e.g. Foit, 1989; Grice and Ercit, 1993; Ertl et al., 2002; Novák et al., 2004; Bosi and Lucchesi, 2007; Bosi 2013, 2018; Novák et al., 2011; Henry and Dutrow, 2011; Henry et al., 2011; Cempírek et al., 2013; Ertl et al., 2018; Andreozzi et al., 2020).

The general chemical formula of tourmaline can be written as: \(X_{c}\)\(Y_{z}\)\(Z_{w}\)\(T_{x}\)\(O_{y}\)\(_{12}(BO_{3})_{3}V_{y}W_{x}\)\(\text{W}\), where \(X = \text{Na}, \text{K}, \text{Ca}\) and \(\square\) (= vacancy); \(Y = \text{Al}, \text{Cr}, \text{V}, \text{Fe}, \text{Mg}, \text{Mn}, \text{Zn}, \text{Cu}, \text{Li}\) and \(T = \text{Al}, \text{Cr}, \text{V}, \text{Fe}\) and \(\text{Mg}; T = \text{Si}, \text{Al}\) and \(B^{3+}; B = B^{3+}; V = (OH); W = (OH)\) and \(O;\) and \(W = (OH), F\) and \(O\). Note that the non-italicised letters \(X, Y, Z\) and \(B\) represent groups of cations hosted at the \([9]X\), \([6]Y\), \([6]Z\), \([3]T\) and \([3]B\) crystallographic sites (letters italicised). The letters \(V\) and \(W\) represent groups of anions accommodated at the \([10]O3\) and \([5]O1\) crystallographic sites, respectively. The \(H\) atoms occupy the \(H3\) and \(H1\) sites, which are related to \(O3\) and \(O1\), respectively. The dominance of specific ions at one or more sites of the structure gives rise to a range of distinct mineral species.

Tourmaline-supergroup minerals are currently classified into three groups, vacant, alkali and calcic, based on the \(X\)-site occupancy (Henry et al., 2011). The \(X\)-site occupancy is usually related to both paragenesis and crystallisation conditions of the host rock, and these relations may be used to reconstruct the host-rock thermal and chemical history (e.g. Henry and Dutrow, 1996; van Hinsberg et al., 2011a,b; Dutrow and Henry, 2018; Bosi et al., 2018, 2019c; Ahmadi et al., 2019). A further level of classification into subgroups is based on charge arrangements at the \(Y\) and \(Z\) sites. Tourmalines are also distinguished by the dominant anion at the \(W\) position of the general formula into hydroxy-, fluor- and oxy-species.

Tourmaline is also one of the most important gem materials on the market today, particularly renowned for its spectrum of colours: from colourless, through red, pink, yellow, orange, green, blue and violet, to brown and black (Pezzotta and Laurs, 2011). The transition elements (\(Ti, V, Cr, Fe, Mn\) and \(Cu\)) are
often invoked as colour-causing agents. Red tourmalines are commonly given the varietal name ‘rubellite’, which refers to tourmalines with colours ranging from rose, dark pink to purplish red, but do correspond to several regular mineral species: elbaite, fluoro-elbaite, rossmanite, fluoro-liddicoatite (Pezzotta and Laurs, 2011) and oxy-dravite (Bosi and Skogby, 2013).

Specifically, fluoro-liddicoatite was redetermined and renamed in 2011 by the Subcommittee on Tourmaline Nomenclature of the International Mineralogical Association’s Commission on New Minerals, Nomenclature and Classification (IMA-CNMNC) when the nomenclature of tourmaline-supergroup minerals was reconsidered (Henry et al., 2011) and the ‘liddicoatite’ from the Antandrokomby type locality (Dunn et al., 1977; Aurisicchio et al., 1999; Webber, 2002; Dirlam et al., 2002; Ertl et al., 2006; Lussier et al., 2011; Lussier and Hawthorne, 2011) regained proper attention. Note that with the renaming of the type material as fluoro-liddicoatite, the hydroxy species ‘liddicoatite’ is no longer properly defined as a species. A new type material definition is necessary to re-establish the name. Two gem-quality samples of purplish-red prismatic crystals of alleged ‘liddicoatite’ on quartz matrix from the collection of M.E. Ciriotti (MEC) were analysed with a Jeol JSM IT300LV scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS) (University of Turin, Earth Sciences Department) to verify if they were F-dominant samples. Although B and Li were not measured, both samples were determined to be F-dominant and were classified as fluoro-liddicoatite. A small portion of a further alleged ‘liddicoatite’ sample (presented as ‘probed’ liddicoatite by its seller) in quartz–rhodizite matrix from Antandrokomby localities (the same type of purplish-red crystals are shown in the specimen in Fig. 1) was obtained by MEC, courtesy of the new owner. The sample was analysed through SEM-EDS and surprisingly showed no trace of F; in addition, its composition did not fit ‘liddicoatite’ in terms of Na and Ca.

In the present study, such a tourmaline sample from the Anjanabonoina pegmatite, central Madagascar, has been fully characterised by X-ray single-crystal diffraction, electron microprobe analysis, laser induced breakdown spectroscopy, micro-Raman, infrared and optical absorption spectroscopy, with the aim of defining its crystal-chemical identity and species.

**Occurrence**

The indexed stout prismatic purplish-red crystal was labelled (by the supplier) ‘liddicoatite’ from Anjanabonoina pegmatites, Ambohimanambola, Betafo, Vakinankaratra, Madagascar, ~55 km west-southwest of the city of Antsirabe. In addition to Anjanabonoina, ‘liddicoatite’ has been identified from several localities in central and south-central Madagascar, including Antaboaka, Jochy, Lacomisinten, Malakialina, Maroandro and the Sahatany Valley, as well as Vohitrakanga (De Vito, 2002a,b; Dirlam et al., 2002), but the present labelled locality is correct (F. Pezzotta, personal communication).

The Anjanabonoina aplite–pegmatite field is situated in the Neoproterozoic Itermbo Group, which consists of a lower unit of gneisses and an upper unit of quartzites, schists and marbles (Pezzotta and Franchi, 1997; Fernandez et al., 2001). The pegmatites were emplaced in a complex geological environment, perhaps at the contact between the lower and upper unit. The gem-bearing pegmatites postdate the main tectonic phase and, therefore, are thought to have intruded during a late phase of the magmatic cycle about 490 Ma (Paquette and Nédélec, 1998). The Li–Cs–Ta (with minor Nb–Y–F) aplite–pegmatite field extends for ~2.5 km. The veins are 2 to 12 m thick and large parts are kaolinised feldspars and/or deeply weathered (De Vito, 2002a,b).

More details about the history of the 1500s to 2000s explorations and mining of the Malagasy tourmaline gem deposits can be found in Strunz (1979), Pezzotta (1999) and Dirlam et al. (2002).

**Experimental methods and results**

**Thermal treatment**

In order to study potential dehydration and redox effects, two oriented and polished crystals were heat treated in air at 700°C (20 h) and 750°C (90 h). These thermal conditions have previously been shown to be sufficient to impose changes in Fe redox states and intracrystalline cation distribution (e.g. Filip et al., 2012; Bosi et al., 2016a,b). The 55 and 309 μm thick samples were placed in a gold container and inserted in a preheated
horizontal tube furnace equipped with a quartz-glass tube. The experiments were ended by pushing the sample container out to the cold zone of the quartz tube, which caused the sample to cool to room temperature within one minute. A distinct increase in colour intensity appeared after heat treatment, as shown in Fig. 2. Minor cracks appeared in the thicker sample after treatment at the higher temperature.

**Single-crystal structure refinement (SREF)**

A representative crystal fragment of the purplish-red tourmaline from Madagascar was selected for X-ray diffraction measurements on a Bruker KAPPA APEX-II single-crystal diffractometer (Sapienza University of Rome, Earth Sciences Department), equipped with a charge-coupled device (CCD) area detector (6.2 cm × 6.2 cm active detection area, 512 × 512 pixels) and a graphite-crystal monochromator using MoKα radiation from a fine-focus sealed X-ray tube. The sample-to-detector distance was 4 cm. A total of 3577 exposures (step = 0.2°, time/step = 20 s) covering a full reciprocal sphere with a redundancy of ~12 was collected. Final unit-cell parameters were refined using the Bruker AXS SAINT program on reflections with \( I > 10 \sigma(I) \) in the range \( 5° < \theta < 78° \). The intensity data were processed and corrected for Lorentz, polarisation and background effects using the APEX2 software program of Bruker AXS. The data were corrected for absorption using a multi-scan method (SADABS, Bruker AXS). The absorption correction led to an improvement in \( R_{int} \) (from 0.033 to 0.027). No violation of R3m symmetry was detected.

Structure refinement was done using the SHELXL-2013 program (Sheldrick, 2015). Starting coordinates were taken from Bosi et al. (2013). Variable parameters were scale factor, extinction coefficient, atom coordinates, site-scattering values (for X, Y and Z sites) and atomic-displacement factors. Attempts to refine the extinction coefficient yielded values within its standard uncertainty, thus it was not refined. Neutral scattering factors were used for the cations and oxygen atoms. As for the atomic model refinement and in accordance with the chemical analysis results (see below), the X site was modelled by setting the vacancy content to 0.32 atoms per formula unit (apfu) and allowing the remainder of the site to refine as Al = (2.81 – Li) apfu. The T site was modelled by Si versus B. The Z, B and anion sites were modelled with Al, B and O scattering factors, respectively, and with a fixed occupancy of 1 as refinement with unconstrained occupancies showed no significant deviations from this value. A final refinement was then performed by modelling the site occupancy of the O1 site with O and F fixed to the value obtained from the empirical formula (see below). Similar chemical constraints were applied to refine the H1 and H3 sites. There were no correlations greater than 0.7 between the parameters at the end of the refinement.

Table 1 lists crystal data, data-collection information and refinement details; Table 2 gives the fractional atom coordinates.

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**Table 1. Single-crystal X-ray diffraction data details for the purplish-red tourmaline from Madagascar.**

| Crystal data |  |
|--------------|---|
| Crystal sizes (mm) | 0.10 × 0.16 × 0.18 |
| Space group; \( Z \) | R3m, 3 |
| \( a (\text{Å}) \) | 15.7935(4) |
| \( c (\text{Å}) \) | 7.0860(2) |
| \( V (\text{Å}^3) \) | 1530.69(9) |

**Data collection**

| Data collection |  |
|----------------|---|
| Data collection temperature (K) | 293 |
| Range for data collection, 2θ (°) | 5–78 |
| Radiation, wavelength (Å) | MoKα, 0.71073 |
| Reciprocal space range, \( hkl \) | \(-26 \leq h \leq 25\), \(-22 \leq l \leq 24\), \(-12 \leq k \leq 12\) |
| Total number of frames | 3577 |
| Measured reflections | 12,849 |
| Unique reflections, \( R_{int} \) (%) | 2026, 3.03 |
| Redundancy | 12 |
| Absorption correction method | SADABS |

**Refinement**

| Refinement |  |
|------------|---|
| Refinement method | Full-matrix last-squares on \( F^2 \) |
| Structural refinement program | SHELXL-2013 |
| Extinction coefficient | 0.0017(3) |
| Flack parameter | 0.05(7) |
| \( wR_2 \) (%) | 3.98 |
| \( R_1 \) (%) all data | 1.89 |
| \( R_1 \) (%) for \( I > 2\sigma(I) \) | 1.80 |
| GoodF | 1.020 |
| Largest diff. peak and hole (e/Å\(^3\)) | -0.45 and 0.35 |

Notes: \( R_{int} \) = merging residual value; \( R_1 \) = discrepancy index, calculated from \( F \) data; \( wR_2 \) = weighted discrepancy index, calculated from \( F^2 \) data; GoodF = goodness of fit; Diff. Peaks = maximum and minimum residual electron density.
and equivalent isotropic displacement parameters; Table 3 shows selected bond lengths. A Supplementary Table with anisotropic displacement parameters and a Crystallographic information file have been deposited with the Principal Editor of *Mineralogical Magazine* and are available as Supplementary material (see below).

**Electron microprobe analysis (EMPA)**

Electron microprobe analysis, carried out on the same crystal that was used for the SREF, was performed using a wavelength dispersive spectrometer (WDS mode) with a Cameca SX50 instrument at the Istituto di Geologia Ambientale e Geoingegneria, CNR, Rome, Italy. The following analytical conditions were used: accelerating voltage 15 kV, beam current 15 nA and spot diameter 10 μm. 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), orthoclase (K), sphalerite (Zn), rhodonite (Mn), metallic Cr and Cu. The PAP routine was applied (Pouchou and Pichoir, 2020). The results (Table 4) represent mean values of 8 spot analyses. Vanadium, Cr, Cu, Zn and K were below detection limits (<0.03 wt.%). Chemical analysis is given in Table 4; no other elements heavier than F were detected.

**Micro-laser induced breakdown spectroscopy (μ-LIBS)**

Lithium analysis, carried out on a representative sample fragment, was performed using a double pulse Q- Switched (Nd-YAG, λ = 1064 nm) laser with a 1 μs delay between the two pulses with an energy of 110 mJ per pulse. The small spot size (7–10 μm) was obtained using a petrographic optical microscope (objective lens 10X NA 0.25 WD 14.75 mm). The LIBS spectra were acquired by an AvaSpec Fiber Optic Spectrometer (390–900 nm with 0.3 nm resolution) with a delay of 2 μs after the second pulse and an integration time of 1 ms. The main problem regarding Li quantification by LIBS concerns the self-absorption of the emission line used to extract quantitative data. In the present tourmaline, the quantitative data were obtained from linear regression using the main Li emission line intensity (λs = 670,706 nm, corresponding to the resonance transition 1s2 2s > 1s2 2p) in the range from 0.009 to 2.04 wt.% of Li2O. In this regard, we verified that the self-absorption effect of this specific line was negligible in the studied concentration range, hence, not affecting the measurements. This is consistent with previous studies on beryl (McMillan et al., 2006; Tempesta and Agrosi, 2016; Tempesta et al., 2020). Moreover, the

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**Table 2.** Fractional atom coordinates, equivalent isotropic and isotropic displacement parameters (Å²) and site occupancies for the purplish-red tourmaline from Madagascar.

| Site | x/a | y/b | z/c | Ueq | Site occupancy |
|------|-----|-----|-----|-----|----------------|
| X    | 0   | 0   | 0.2208(2) | 0.0206(6) |
| Y    | 0.12118(5) | 0.06059(2) | 0.6382(10) | 0.00809(17) |
| Z    | 0.29680(3) | 0.26032(3) | 0.6077(7) | 0.00650(8) |
| B    | 0.10901(7) | 0.21802(14) | 0.4521(2) | 0.0063(3) |
| T    | 0.19143(2) | 0.18954(2) | 0.0 | 0.00515(9) |
| O1(≡W) | 0 | 0 | 0.7750(3) | 0.0200(5) |
| O2   | 0.06014(5) | 0.12028(10) | 0.4891(2) | 0.0139(3) |
| O3(≡V) | 0.26161(11) | 0.13080(6) | 0.50677(17) | 0.0119(2) |
| O4   | 0.09391(5) | 0.18781(11) | 0.0 | 0.00771(15) |
| O5   | 0.18629(11) | 0.09314(5) | 0.90561(17) | 0.0107(2) |
| O6   | 0.19435(6) | 0.18391(6) | 0.77405(13) | 0.0109(2) |
| O7   | 0.28640(6) | 0.28591(6) | 0.07611(11) | 0.00743(15) |
| O8   | 0.20947(7) | 0.27000(7) | 0.43694(13) | 0.00766(15) |
| H1   | 0 | 0 | 0.909(4) | 0.024* |
| 4.0111 | 0.2543(19) | 0.1271(9) | 0.379(3) | 0.014* |

Table 3. Selected bond lengths (Å) for the purplish-red tourmaline from Madagascar.

| Bond | Length (Å) | Site |
|------|------------|------|
| X-O2 | 3 | 2.5145(18) |
| X-O5 | 3 | 2.6890(15) |
| X-O4 | 3 | 2.7720(16) |
| X-O8 | 3 | 2.662 |
| Y-O1 | 1.9199(14) |
| Y-O6 | 1.9503(10) |
| Y-O2 | 1.9605(10) |
| Y-O3 | 2.1349(16) |
| Ce-O | 1.37 |

*Table 4.** Chemical composition for the purplish-red tourmaline from Madagascar.

| Oxide | Weight % | Site normalised to 31 anions |
|-------|----------|-----------------------------|
| SiO2 | 35.59(35) | Si (apfu) 5.600 |
| TiO2 | 0.04(2) | Ti*(1) 0.004 |
| B2O3 | 12.51 | B 3.400 |
| Al2O3 | 42.11(50) | Al 7.810 |
| FeO | 0.31(3) | Fe*(1) 0.036 |
| MnO | 1.09(2) | Mn*(1) 0.024 |
| CaO | 1.43(5) | Ca 0.121 |
| Na2O | 1.36(4) | Na 0.241 |
| Li2O | 1.59(11|h | Li 0.414 |
| F | 0.26(8) | F 1.004 |
| H2O | 3.34* | OH 3.501 |
| O = F | -0.11 | OH 3.501 |
| MnO | 0.91 | MnO 0.20 |
| Total | 99.52 | Total 99.52 |

*Calculated by stoichiometry, (Y+Z+T+B) = 18.000 apfu.

* Determined by μ-LIBS

* Determined by OAS.

Errors for oxides and fluorine are standard deviations (in brackets); apfu = atoms per formula unit.
Micro-Raman spectroscopy

Raman spectra of the Mn$^{3+}$-bearing red tourmaline were obtained using a micro/macro Jobin Yvon Mod. LabRam HRVIS (University of Turin, Interdepartmental Centre “G. Scansetti”), equipped with a motorised x-y stage and an Olympus microscope. The back-scattered Raman signal was collected with a 50x objective and the Raman spectrum was obtained for a 90° (perpendicular to c) oriented crystal. The 632.8 nm line of an He–Ne laser was used as excitation; laser power (20 mW) was controlled by means of a series of density filters. The minimum lateral and depth resolution was set to a few µm. The system was calibrated against Ho$_2$O$_3$-doped and Pr$_2$O$_3$/Nd$_2$O$_3$-doped standards (Hellma glass filters 666F1 and 666F7). Spectral data acquisition (5) with single counting times of 50 seconds to improve the signal-to-noise ratio. The incident excitation light was scrambled to eliminate orientation and polarisation effects. The spectrum was recorded from 100 to 4000 cm$^{-1}$ using the LabSpec 5 software package (Horiba Jobin Yvon GmbH, 2004, 2005). Band-component analysis was undertaken using a Lorentzian function (Fityk software package; Wojdyr, 2010). The intensity of the vibrational modes was proven to be very dependent on the polarisability tensor. The Raman spectrum of the present sample in the spectral region of the framework and (OH)-stretches vibrations is shown in Fig. 4.

Fourier-transform infrared (FTIR) spectroscopy

Polarised Fourier-transform infrared spectra were measured on two doubly polished single-crystal sections oriented by means of optical microscopy, and with thicknesses of 55 and 309 µm. The spectrometer system consisted of a Bruker Vertex 70 spectrometer equipped with a halogen-lamp source and a CaF$_2$ beam-splitter coupled to a Hyperion 2000 microscope with a ZnSe wire-grid polariser and an InSb detector. Spectra were measured before and after heat-treatment experiments over the wavenumber range 2000–15,000 cm$^{-1}$ with a resolution of 2 or 8 cm$^{-1}$. The measuring areas were masked by a 50–100 µm rectangular aperture to avoid cracks and inclusions. The FTIR spectra of the untreated and treated samples (e.g. Fig. 5) show typical, strongly pleochroic absorption bands in the (OH)-stretching region (3300–3800 cm$^{-1}$), including bands above ~3600 cm$^{-1}$ that demonstrate the presence of W(OH) (see below).

Optical absorption spectroscopy (OAS)

Polarised, room temperature optical absorption spectra in the range 30,000–12,500 cm$^{-1}$ (333–800 nm) were recorded at a spectral resolution of 1 nm on the same 309 µm thick section studied by FTIR spectroscopy, using an AVASPEC-ULS2048 x 16 spectrometer attached via a 400 µm ultraviolet (UV) optical fibre cable to a Zeiss Axioscope UV-microscope. A 75 W Xenon arc lamp was used as a light source, and Zeiss Ultrafluar 10× lenses served as objective and condenser. The diameter of the circular aperture was 50 µm for the untreated sample and 30 µm for the treated sample. A UV-quality Glan–Thompson prism with a working range from 40,000 to 3704 cm$^{-1}$ (250 to 2700 nm) was used as a polariser. The wavelength scale of the spectrometer was calibrated against Ho$_2$O$_3$-doped and Pr$_2$O$_3$/Nd$_2$O$_3$-doped standards (Hellma glass filters 666F1 and 666F7). Spectral data in the range 12,150–2000 cm$^{-1}$ (800–5000 nm) was taken from the FTIR measurements.

The optical absorption spectra of the untreated sample (Fig. 6) at energies below the UV-absorption edge show a set of broad absorption bands at 21,950, 19,800, ~18,000, 13,500 and ~9500 cm$^{-1}$ (corresponding to 456, 505, 556, 741 and 1053 nm). In addition, a very weak and sharp absorption band occurs at 24,330 cm$^{-1}$ (418 nm), and a set of very sharp, overlapping bands are recorded in the NIR spectral range between 6700–7200 cm$^{-1}$ (1492–1389 nm). The absorption bands recorded in spectra of the untreated sample at 24,330, 21,950 and ~18,000 cm$^{-1}$ are more intense for light polarised perpendicular to the crystallographic c-axis. Conversely, the absorption band 19800 cm$^{-1}$ is only observed as a broad shoulder in the E||c-spectrum. The set of sharp bands between 6700–7200 cm$^{-1}$ is also completely E||c-polarised.
Fig. 4. Raman spectrum of the untreated Mn-bearing purplish-red tourmaline from Madagascar.

Fig. 5. Polarised FTIR spectra ($E_{||c}$ and $E_{\perp c}$) of untreated Mn-bearing purplish-red tourmaline from Madagascar. Sample thickness 55 μm. Spectra are vertically off-set for clarity. Peak positions are indicated.

Fig. 6. Polarised OAS spectra ($E_{||c}$ and $E_{\perp c}$) of untreated and treated Mn-bearing purplish-red tourmaline from Madagascar. Sample thickness 309 μm. Spectra are vertically off-set for clarity.
The absorption spectra recorded on the heat-treated sample (Fig. 6) display comparable features to those observed in the spectra of the natural sample. However, all absorption bands at 21,950, 19,800, ~18,000, 13,500 and ~9500 cm\(^{-1}\) show pronounced intensity gains, and the set of sharp absorption bands between 6700–7200 cm\(^{-1}\) distinctly decreases in intensity.

**Determination of atomic fractions**

For the untreated sample, manganese oxidation state was determined by OAS (see below and Table 4). All Fe was considered to be Fe\(^{3+}\) based on the OAS results and Mn and Fe redox potential arguments. Lithium was determined by μ-LIBS. Regarding the B\(^{3+}\), the SREF data indicate that it fully occupies the B site, but relatively small amounts of B\(^{3+}\) also occur at the T site: T\(-m.a.n. = 13.24(7)\) and \(<T—O> = 1.613 \pm 0.001 \text{Å}\) (Bosi et al., 2007), reflecting the presence of cations lighter and smaller than Si, such as B\(^{3+}\) (Erlt et al., 2018). As a result, the B\(_2\)O\(_3\) and (OH) content were calculated by charge balance with untreated sample is as follows:

\[
\text{(Mn}^{2+}) + (\text{OH})^- \rightarrow (\text{Mn}^{3+}) + (\text{O}^{2-}) + \frac{1}{2} \text{H}_2\text{O}(g) \quad (1)
\]

**Determination of site population and mineral formula**

The anion site populations in the samples studied follow the general preference suggested for tourmaline (e.g. Henry et al., 2011): the O3 site (V position in the general formula) can be occupied by \(\text{O}^{2-}\), \((\text{OH})^-\) and \(\text{F}^-\). The refined Z-site scattering and \(<Z—O>\) values (13 and 1.906 Å, respectively) are the typical values observed for a Z site fully occupied by Al (Bosi and Andreozzi, 2013). The resulting empirical formula for the untreated sample is as follows:

\[
\text{Na}(\text{Na}_{0.41(\text{Na}_{0.25})})\text{Al}_{2}\text{Li}_{0.00}(\text{Fe}^{2+}_{0.02}\text{Mn}^{2+}_{0.02}\text{Mn}^{3+}_{0.12}\text{Ti}_{0.004})\text{Si}_{3.00} \text{O}_{8.00} \text{F}_{0.54}(\text{OH})_{0.06} = 0.94 \text{apfu}
\]

The bond-valence analysis is consistent with the proposed site populations (Table 5). Moreover, the amount of 0.40 \(\text{T}^{3+}\) apfu is consistent with the relation of Hughes et al. (2004): \([\text{B} = [33.404–0.0346 \cdot \upsilon_{\text{cell}}]] = 0.44 \text{apfu}.

As for the treated sample, the following ordered formula is proposed:

\[
\text{Na}(\text{Na}_{0.41(\text{Na}_{0.25})})\text{Al}_{2}\text{Li}_{0.00}(\text{Fe}^{2+}_{0.02}\text{Mn}^{2+}_{0.02}\text{Mn}^{3+}_{0.12}\text{Ti}_{0.004})\text{Si}_{3.00} \text{O}_{8.00} \text{F}_{0.54}(\text{OH})_{0.06} = 0.94 \text{apfu}
\]

**Discussion**

**Tourmaline classification**

The empirical formula of the untreated sample is consistent with a tourmaline belonging to the alkali-group, subgroup 2 (Henry et al., 2011): it is Na-dominant (Na > O > Ca) at the X position of the general formula of tourmaline \(\text{XY}_3\text{Z}_4\text{X}_0\text{O}_{18}(\text{BO}_3)_3\text{V}_3\text{W}\) and hydroxy-dominant at W with \((\text{OH}+\text{F}) > \text{O}\) and \((\text{OH}) >> \text{F}\). Because Al and Si are the dominant cations at the Z and T sites (respectively), the end-member formula can be approximated as \(\text{X}(\text{Na}^+(\text{Y}^{3+})_{3/2}\text{Z}^{6+}\text{Fe}^{2+}(\text{SiO}_3)\text{V}^{3+}\text{W}^{5+}\text{OH}^-\). For formula electroneutrality reasons, the valency-imposed double site-occupancy for the Y site is required with an atomic arrangement \((\text{Li}^+_1\text{Al}^{3+}_1\text{Si}^{4+}_3\text{O}_{18}(\text{BO}_3)_3\text{OH}^-\)\). Note that, although the empirical site-total-charge at Y (= +6.986) is very close to +7, suggesting the arrangement \(\text{Al}^+_1\text{Li}^+_1\text{Si}^{4+}_3\text{O}_{18}(\text{BO}_3)_3\text{OH}^-\), the latter must be ruled out because it would lead to a charge imbalanced end-member formula: \([\text{Na}^+(\text{Al}^+_1\text{Li}^+_1\text{Si}^{4+}_3\text{O}_{18}(\text{BO}_3)_3\text{OH}^-\)\)\). Thus, only atomic arrangements consistent with \(\text{Y}^{3+}\) vibrations, such as \(\text{Al}^+_1\text{Li}^+_1\text{Si}^{4+}_3\text{O}_{18}(\text{BO}_3)_3\text{OH}^-\), can occur (Bosi et al., 2019a,b).

**Micro-Raman spectroscopy in the framework vibration region**

In accordance with the studies of Mihiailova et al. (1996), Reddy et al. (2007), McKeown (2008) and Waterphul et al. (2016b), five main ranges of framework vibrations can be identified in the Raman spectrum of the untreated sample (Fig. 4) and attributed to the following vibrating groups. (1) The range ~200–300 cm\(^{-1}\) is dominated by YO\(_6\) vibrations; in particular, the band at ~274 cm\(^{-1}\) corresponds to the Mn–O bond, previously observed in a pink-tourmaline by Reddy et al. (2007). (2) The range ~300–400 cm\(^{-1}\) (the strongest Raman peak) is generated by ZO\(_6\) vibrations, in particular the sharp peak at 377 cm\(^{-1}\) may be given by the \(\text{ZAl}^–\text{O}\) bond. (3) The range ~500–750 cm\(^{-1}\) is dominated by breathing modes of bridging oxygen atoms of TO\(_4\) rings. (4) The range ~950–1100 cm\(^{-1}\) is generated mainly from TO\(_4\) stretching vibrations. (5) The range ~1300–1400 cm\(^{-1}\) arises from B–O stretching vibrations.

With regard to the region of the (OH)-stretching vibrations (3300–3800 cm\(^{-1}\)), the Raman scattering peaks of the untreated sample show wavenumbers similar to those of the infrared absorption bands (cf. Fig. 4 with Fig. 5); thus, the (OH)-stretching modes are discussed below.

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**Table 5. Weighted bond valences (valence units) for the purplish-red tourmaline from Madagascar.**

| Site | K | Y | Z | T | B | SUM |
|------|---|---|---|---|---|-----|
| O1   | 0.42^−2\(\rightarrow\) | 1.25 |
| O2   | 0.12^+\(\rightarrow\) | 1.02 |
| O3   | 0.24 | 1.09 |
| O4   | 0.06^−\(\rightarrow\) | 2.04 |
| O5   | 0.07^−\(\rightarrow\) | 1.97 |
| O6   | 0.40^+\(\rightarrow\) | 1.96 |
| O7   | 0.54 | 2.01 |
| O8   | 0.51 | 2.03 |

Note: Weighted bond valence according to Bosi (2014). Bond valence parameters from Brown and Altermatt (1980).

*Expected mean atomic valence (or formal charge) from the empirical formula.
FTIR spectra in the (OH)-stretching region and band assignment

Infrared spectra of the untreated and treated samples recorded in polarised mode parallel to the c-axis direction display a very intense absorption feature in the 3400–3600 cm$^{-1}$ region, which is truncated due to excessive absorption (Fig. 5). This problem is commonly encountered in polarised transmission spectra of tourmaline single crystals, and it is normally not possible to thin samples sufficiently to get this main band ‘on scale’. Bands of lower intensity occur on both the low-energy (ca. 3340 cm$^{-1}$) and high-energy (3650, 3665 and 3703 cm$^{-1}$) sides of the major absorption band. Spectra polarised perpendicular to the c-axis direction ($E_\perp c$) show a set of bands with substantially lower intensities (Fig. 5). The spectral range that is obscured by excessive absorption in the $E||c$ direction displays here the presence of three bands at wavenumbers 3464, 3540 and 3597 cm$^{-1}$, indicating (OH)-dipoles aligned close to, but with a small inclination to the c-axis (Gatta et al., 2014).

After thermal treatment, a number of changes can be observed in the FTIR spectra: the sharp band at 3665 cm$^{-1}$ progressively decreases in intensity and almost disappears in the $E||c$ direction (Fig. 7), whereas a new band appears at 3395 cm$^{-1}$, visible in the $E_\perp c$ direction (Fig. 8). The (OH) bands in the overtone region (Fig. 9) show a distinct decrease in absorption intensity, amounting to 17±3% as estimated from spectral fitting. However, a general decrease in absorption band intensity is not observed in the principal (OH)-region in spectra of the heat-treated samples polarised in the $E_\perp c$ direction. Instead, we observe a weak increase in intensity, probably related to a decrease in polarisation efficiency due to microcracks and other crystal imperfections formed during heat treatment, leading to minor contributions from the extremely intense absorbance in the $E||c$ direction.

In the tourmaline structure, the O1 site (≡ W) is surrounded by three Y cations, whereas the O3 site (≡ V) is surrounded by one Y and two Z cations. In accord with Gatta et al. (2014), we assume that: the O1(OH) group forms a very weak hydrogen bond (bond strength < 0.05 valence units, vu) with O4 and O5, whereas the O3(OH) group forms a weak hydrogen bond (bond strength ~0.11 vu) with the closest O5 atom (O3–H3⋅⋅⋅O5); the strength of the hydrogen bond will cause a frequency shift of
the principal (OH)-stretching vibration (e.g. Libowitzky, 1999). Therefore, the relative weak vibrational bands above ~3600 cm
<sup>-1</sup> may be assigned to the O1 site, whereas the strong bands below ~3600 cm
<sup>-1</sup> may be assigned to the O3 site (e.g. Gonzalez-Carreño et al., 1988; Bosi et al., 2015). Based on the studies of Skogby et al. (2012), Bosi et al. (2012, 2016b), Watenphul et al. (2016a) and Kutzschbach et al. (2016) as well as on the observed site populations, the FTIR bands of the present purplish-red tourmaline may be related to the following atomic arrangements:

~3350 cm
<sup>-1</sup> is assigned to hydrogen bond O3O–H3⋯O5, which may reflect both the presence of B
<sup>III</sup> and the X-site occupancy; ~3395 cm
<sup>-1</sup> is assigned to 3[Li.Ma2+Al]2Al2–O3(OH); ~3464, 3540 and 3597 cm
<sup>-1</sup> to 3[Li,Mn2+Al]2Al2–O3(OH); ~3650 cm
<sup>-1</sup> is assigned to 3(LiAlAl)–O3(OH); ~3665 cm
<sup>-1</sup> is assigned to 3(LiMn2+Al)–O3(OH); and ~3703 cm
<sup>-1</sup> is assigned to 3(LiAlAl)–O3(OH)–X(Na).

The main difference between the FTIR spectra of the untreated and treated sample occurs in gradual decrease in the intensity of the band at 3665 cm
<sup>-1</sup> and the appearance of the band at 3395 cm
<sup>-1</sup> with the increase in temperature up to 750°C. As a result, these bands, in particular that at 3665 cm
<sup>-1</sup>, may be correlated directly with the decreased Mn
<sup>2+</sup> and increased Mn
<sup>3+</sup> content, according to the redox reaction (1), reported in the section ‘Determination of atomic fractions’. However, it appears that (OH) is also lost by mechanisms other than the redox reaction. Only a partial loss of 0.12 (OH) apfu can be coupled to the oxidation of Mn
<sup>2+</sup>, whereas the total (OH) loss as estimated from the decrease of (OH) overtone intensities (17 ± 3%) corresponds to ca. 0.6 (OH) apfu. The reason for this additional dehydration is unknown, but may be related to initial breakdown processes of the crystal structure.

Of particular interest is also the association of the O1(OH) stretching modes with the X-site constituents: the bands between ~3600–3700 cm
<sup>-1</sup> are considered associated with □, whereas those above 3700 cm
<sup>-1</sup> are considered associated with Na
<sup>+</sup>. This distinction is related to the repulsive electrostatic interaction between the X
<sup>III</sup> cation and H
<sup>+</sup> of the O1(OH) group, which reinforces the strength of the O1O–H bond, shifting the (OH)-stretching mode towards higher wavenumbers (e.g. Gonzalez-Carreño et al., 1988; Berryman et al., 2016; Watenphul et al., 2016a). Consequently, the presence of Na
<sup>+</sup> determines an electrostatic repulsion with H1H
<sup>+</sup> along the crystallographic c-axis, whereas the substitution XNa+ removes such a repulsion (Fig. 10).

From the energetic-stability viewpoint, the rossmanite type arrangements (YYY)–O1(OH)–X□ should hence be more likely to occur than the elbaite type arrangement (YYY)–O1(OH)–X(Na). The X
<sup>III</sup>–H
<sup>+</sup> repulsion effect will be stronger with the substitution XCa2+ → 2Na+. On the other hand, this cation–cation repulsion can be removed by the chemical substitution O1F → D2(OH) or the deprotonation process O1(OH) → ½ O2(g) → O1O2+ + ½ H2O(g), both of which would favour the occurrence of fluor-liddicoatite and darrellhenryite type arrangements (YYY)–O1(O,F)–X(Na,Ca).

**Optical spectra**

With the exception of the broad absorption band at ~9500 cm
<sup>-1</sup>, the characteristics (band energy, band width and polarisation) of all observed bands in the spectra of the present sample are in very good agreement with those recorded for Mn
<sup>3+</sup>-bearing tourmaline specimens (Reinitz and Rossman, 1988; Ertl et al., 2005; Novák et al., 2013; Bosi et al., 2017a). In agreement with these previously published studies we assign bands at 21,950, 19,800, ~18,000, 13,500 cm
<sup>-1</sup> to electronic transitions in octahedrally coordinated Mn
<sup>3+</sup> and the very weak and sharp band at 24,330 cm
<sup>-1</sup> to an electronic transition in octahedrally coordinated Mn
<sup>2+</sup>. The set of strongly E∥-polarised, sharp bands in the
NIR region between 6700–7200 cm\(^{-1}\) are due to overtones of the fundamental (OH)-stretching modes.

Based on the intensity of the Mn\(^{3+}\) band at \(\sim 18,000\) cm\(^{-1}\) in the spectrum perpendicular to the c-axes (Fig. 6) in combination with the published molar absorption coefficient for that absorption band (Reinitz and Rossman, 1988), we calculate an Mn\(_2\)O\(_3\) content of \(\sim 1\) wt.%. However, the strong intensity increase by a factor of \(\sim 4\times\) for this band in spectra of our heat-treated sample, in combination with the analysed MnO\(_{tot}\) content, strongly suggests that the absorption coefficient for the band is somewhat higher than that indicated by Reinitz and Rossman (1988). Assuming that all Mn\(^{2+}\) was oxidised to Mn\(^{3+}\) during the heat treatment of our sample we determine an absorption coefficient of \(\sim 30\) l mole\(^{-1}\) cm\(^{-1}\), compared to the value of \(\sim 7.5\) suggested by Reinitz and Rossman (1988). Based on this revised absorption coefficient we calculate a Mn\(_2\)O\(_3\) content of \(\sim 0.2\) wt.% for the untreated sample.

In view of the limited set of transition metals (Mn, Fe and Ti) in the present tourmaline, the number of potential origins for the broad absorption band recorded at \(\sim 9500\) cm\(^{-1}\) is very limited as well. The broadness of this band and its relatively high intensity exclude that it is caused by electron transitions in Mn\(^{2+}\) or Fe\(^{3+}\), which all give rise to much weaker and also sharper spin-forbidden absorption bands. Furthermore, redox potential arguments exclude the presence of Fe\(^{2+}\) in a Mn\(^{3+}\)-bearing substance. Finally, Ti\(^{4+}\) is not a chromophore and Ti\(^{3+}\) is also excluded on the basis of redox potential considerations. Consequently, there remain only transitions in Mn\(^{3+}\) as a cause for the \(\sim 9500\) cm\(^{-1}\) band. This assignment is in agreement with observations of a broad Mn\(^{3+}\)-related absorption band at \(\sim 1040\) nm (corresponding to \(\sim 9615\) cm\(^{-1}\)) in optical spectra of oxidised Mn\(^{3+}\)-rich elbaite (Ertl et al., 2012). It is also in agreement with the observed increase in band intensity on heat treatment (oxidation) of the present sample. The relatively low energy of this band offers two main alternative assignment schemes. Firstly, low-energy bands caused by transitions in Mn\(^{3+}\) are frequently observed in spectra of substances, in which the cation is at the centre of octahedra that are characterised by one or two metal–ligand bonds deviating strongly from the remaining ones, either by being considerably shorter or longer (Burns, 1993). Secondly, transitions in tetrahedrally coordinated \(^{14}\)Mn\(^{3+}\) may also give rise to spectral bands of relatively low energy, as shown by a broad absorption band at \(10,800\) cm\(^{-1}\) in spectra of \(^{14}\)Mn\(^{3+}\)-doped spinel (Bosi et al., 2007). The observed intensity increase for the \(\sim 9500\) cm\(^{-1}\) band in response to heat treatment, i.e. oxidation, represents a strong argument against this second suggestion, as this would require Mn\(^{2+}\) to be located initially at the tetrahedrally coordinated sites of tourmaline, which is highly unlikely (Bačík and Fridrichová, 2020). Furthermore, the SREF results provide no indications for \(^{14}\)Mn\(^{3+}\) and consequently we prefer the suggestion that the band is caused by a transition in Mn\(^{3+}\) cations at octahedrally coordinated sites, where the local electronic field around the cation is strongly distorted from the \(O_h\) symmetry.

**Conclusions**

The comprehensive multi-analytical approach of the present study shows that the gem-quality purplish-red colour of the hand specimen of elbaite from the Anjanabonoina pegmatite (Madagascar) is caused by Mn\(^{3+}\), which occurs as a minor element (Mn\(_2\)O\(_3\) = 0.20 wt.%), corresponding to 0.02 apfu). The colour intensity strongly increases with increasing Mn\(^{3+}\) concentrations (Mn\(_2\)O\(_3\) up to 1.21 wt.%, corresponding to 0.15 apfu).

Although the bulk chemical composition of the present sample corresponds to elbaite, based on the electrostatic H\(^{+}\)–Na\(^{+}\) repulsion, the more intense FTIR bands related to O1 could be ascribed to the rossmanite-type arrangements \((Y\)YY\(\)–\(O\)\(1\))\(–\)(OH)\(–\)\(X\)\(\)\(\square\) rather than elbaite-type ones \((Y\)YY\(\)–\(O\)\(1\))\(–\)(OH)\(–\)\(X\)\(\)\(Na\).

Following this model of the electrostatic interaction between the X cation and W anions, the substitution F \(\rightarrow\) (OH) as well as the removal of H from the W(OH) group would favour the occurrence of fluor-liddicoatie- and darrellhenryite-type clusters. On the other hand, the presence of H in the W(OH) group could explain the absence or rarity of tourmalines such as ‘liddicoatie’, ideally Ca(Li\(_2\)Al)Si\(_6\)O\(_{16}\)(BO\(_3\))\(_3\)(OH)\(_3\). The latter is still, in fact, a missing mineral species. Similar arguments might be applied to uvite, CaMg\(_3\)Al\(_2\)Si\(_6\)O\(_{18}\)(BO\(_3\))\(_3\)(OH)\(_3\) (Bosi et al., 2020), but in this case we have to consider the increased total charge at the Y site of uvite (\(+6\) compared to ‘liddicoatie’ \(+5\)), which may accommodate composition with a strong H\(^{+}\)–Ca\(^{2+}\) repulsive effect. In this regard, Ertl and Bačík (2020) described the correlations between the F content and the X-site charge, whereas Henry and Dutrow (2011) showed: (1) that interaction among the X, Y and O1 sites can accommodate unfavourable compositions; (2) the latter may also be influenced by the petrological environment, which may yield deviation from the limitations imposed by the tourmaline crystal chemistry. Bosi et al. (2017b) showed that direct correlation between F and Cr observed in Cr tourmalines from the Sludyanka complex, Lake Baikal, Russia, requires the occurrence of the local arrangements \(Y(CrCrCr)^{1+}\)(F), which should be unstable from a short-range bond-valence perspective (e.g. Bosi, 2013, 2018).

**Supplementary material.** To view supplementary material for this article, please visit [https://doi.org/10.1180/mgm.2021.2021.2001.2002](https://doi.org/10.1180/mgm.2021.2021.2001.2002)

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**References**

Ahmadi S., Tahmasbi Z., Khalaji A.A. and Zaf F. (2019) Chemical variations and origin of tourmalines in Ielah zar granite of Kerman (Soutestan Iran). *Periodico de Mineralogia*, 88, 117–129.

Andreozzi G.B., Bosi F., Celata B., Capizzi L.S., Stagno V. and Beckett-Brown et al. (1999) Homogeneous association of M. Serracino, to whom the authors express their gratitude. Funding by Sapienza University of Rome (Prog. Università 2018 to F. Bosi) is gratefully acknowledged. We thank F. Pezzotta for providing the photo of the sample analysed in this study. Comments and suggestions by the Associate Editor Ian T. Graham, A. Ertl and two anonymous reviewers were much appreciated.

Andreezzi G.B., Bosi F., Celata B., Capizzi L.S., Stagno V. and Beckett-Brown A. Ertl and two anonymous reviewers were much appreciated.

Aurisicchio C., Demartin F., Ottolini L. and Pezzotta F. (1999) Homogeneous chemical behavior of Fe\(^{3+}\) in tourmaline dictated by structural stability: insights from a school with formula Na\(^+(Fe^{3+}Al)^{4+}(AlFe^{3+})\)(Si\(_8\)O\(_{22}\))(BO\(_3\))\(_3\)(OH)\(_3\) OH\(_2\) from Seagull batholith (Yukon Territory, Canada). *Physics and Chemistry of Minerals*, 47, 25.

Bačík C., Demartin F., Ottolini L. and Pezzotta F. (1999) Homogeneous liddicoatie from Madagascar: a possible reference material? First EMPA, SIMS and SREF data. *European Journal of Mineralogy*, 11, 237–242.

Bosi P. and Fridrichová G. (2020) Cation partitioning among crystallographic sites based on bond-length constraints in tourmaline-supergroup minerals. *American Mineralogist*, [https://doi.org/10.2138/am-2021-7804](https://doi.org/10.2138/am-2021-7804)

Berrymo J.E., Wunder B., Ertl A., Koch-Müller M., Rheude D., Scheidl K., Giester G. and Heinrich W. (2016) Influence of the X-site composition on tourmaline’s crystal structure: Investigation of synthetic K-dravite, dravit, oxy-uvite, and magnesio-foitite using SREF and Raman spectroscopy. *Physics and Chemistry of Minerals*, 43, 83–102.
Grew E.S., Bosi F., Gunter M., Hálenius U., Trumbull R.B. and Yates M.G. (2018) Fluor-elitebaite, epidoteilite and Ta-Nb oxides from a pegmatite of the 3000 MA Sencini pluton, Swaziland: Evidence for lithium-cesium-tantalum (LCT) pegmatites in the Mesoarchean. European Journal of Mineralogy, 30, 205–218.

Grice J.D. and Ercit T.S. (1993) Ordering of Fe and Mg in the tourmaline crystal structure: the correct formula. Neues Jahrbuch für Mineralogie, Abhandlungen, 165, 245–266.

Henry D.J. and Dutrow B.L. (1996) Metamorphic tourmaline and its petrologic applications. Pp. 503–557 in: Boron: Mineralogy, Petrology and Geochemistry (E.S. Grewe and L.M. Anwitz, editors). Reviews in Mineralogy and Geochemistry, vol. 33. Mineralogical Society of America, Chantilly, Virginia, USA.

Henry D.J. and Dutrow B.L. (2011) The incorporation of fluorine in tourmaline: Internal crystallographic controls or external environmental influences? The Canadian Mineralogist, 49, 41–56.

Henry D.J. and Dutrow B.L. (2018) Tourmaline studies through time: contributions to scientific advancements. Journal of Geosciences, 63, 77–98.

Henry D.J., Novák M., Hawthorne F.C., Ertl A., Dutrow B., Uher P. and Pezzotta F. (2011) Nomenclature of the tourmaline-supergroup minerals. American Mineralogist, 96, 895–913.

Horiba Jobin Yvon GmbH (2004, 2005) LabSpec software for Raman spectroscopic data analysis, acquisition and manipulation. Version 5.64.15. HORIBA Jobin Yvon SAS, Villeneuve d’Ascq, France.

Hughes J.M., Ertl A., Dyar M.D., Grewe E.S., Wieder beck M. and Brandstätter F. (2018) Tourmaline studies through time: contributions to scientific advancements. The Canadian Mineralogist, 97, 822–825.

Libowitzky E. (1999) Correlation of O-H stretching frequencies and O vibrations in complex silicates. The Canadian Mineralogist, 37, 101–104.

Lubowitzky E. (1999) Correlation of O-H stretching frequencies and O–H⋯O hydrogen bond lengths in minerals. Monatshfte für Chemie, 130, 1047–1059.

Lussier A.J. and Hawthorne F. (2011) Oscillatory zoned lithium-rich tourmaline from Anjanabono, central Madagascar. II. Compositional variation and mechanism of substitution. The Canadian Mineralogist, 49, 89–103.

Lussier A.J., Abdu Y., Hawthorne F.C., Michaelis V.K., Aguiar P.M. and Kroeker S. (2011) Oscillatory zoned lithium-rich tourmaline from Anjanabono, central Madagascar. I. Crystal chemistry and structure by SREF and 27Al MAS NMR spectroscopy. The Canadian Mineralogist, 49, 63–88.

McKenow D.A. (2008) Raman spectroscopy, vibrational analysis, and heating of bauergerite tourmaline. Physics and Chemistry of Minerals, 35, 259–270.

McMillan N.J., McManus C.E., Harmon R.S., De Lucia Jr., F.C. and Miziolk A.W. (2006) Laser induced breakdown spectroscopy analysis of complex silicate minerals – beryl. Analytical and Bioanalytical Chemistry, 385, 263–27.

McMillan N.J., Curry J., Dutrow B.L. and Henry D.J. (2018) Identification of the host lithology of tourmaline using laser-induced breakdown spectroscopy for application in sediment provenance and mineral exploration. The Canadian Mineralogist, 56, 393–410.

Mihaliová B., Gasharova B. and Konstantinov L. (1996) Influence on non-tetrahedral cations in Si-O vibrations in complex silicates. Journal of Raman Spectroscopy, 27, 829–833.

Novák M., Povondra P. and Selway J.B. (2004) Schorl-oxy-schorl to dravite-oxydravite tourmaline from granitic pegmatites; examples from the Moldanubicum, Czech Republic. European Journal of Mineralogy, 16, 323–333.

Novák M., Škoda P., Filip J., Macek I. and Vaculovic T. (2011) Compositional trends in tourmaline from intragranitic NYF pegmatites of the Třebíč Pluton, Czech Republic; electron microprobe, Mössbauer and LA-ICP-MS study. The Canadian Mineralogist, 49, 359–380.

Novák M., Ertl A., Povondra P., Vašinová Galiová M., Rossman G.R., Pristažová F. and Selway J.B. (2010) Darrelhenryite, Na (LiAl3)Al9(BO3)SiO10(OH)2, a new mineral from the tourmaline supergroup. American Mineralogist, 98, 1886–1892.

Paquette J.L. and Nédélec A. (1998) A new insight into Pan-African tectonics in the East–West Gondwana collision zone by U–Pb zircon dating of granites from central Madagascar. Earth and Planetary Science Letters, 155, 45–56.

Pezzotta F. (1999) Madagaskar – Das Paradies der Mineralien und Edelsteine. Extra Lapis, 17, 56–59 [in German].

Pezzotta F. and Frančík M. (1997) Miorolitic shallow depth pegmatites of the Betafo and Antsirabe areas, central Madagascar; genetic inferences. P. 71 in: Proceedings of the UNESCO-IUGS-IGCP-348/IGCP-368 International Field Workshop on Proteroizic Geology of Madagascar, Antananarivo, August 16–30 (R. Cox and L.D. Ashwal, editors). Gondwana Research Group Miscellaneous Publication No. 5.

Pezzotta F. and Lauris B.M. (2011) Tourmaline: The kaleidoscopic gemstone. Elements, 7, 331–336.

Pouchou J.L. and Pichoir F. (1991) Quantitative analysis of homogeneous or stratified microvolumes applying the model “PAP”. Pp. 31–75 in: Electron Probe Quantitation (K.F. Heinrich and D.E. Newbury, editors). Plenum, New York.

Reddy B.J., Frost R.L., Martens W.N., Wain D.I. and Klopogge J.T. (2007) Spectroscopic characterization of Mn-rich tourmalines. Vibrational Spectroscopy, 44, 42–49.

Reddy B.J. and Rossman G.R. (1988) Role of natural radiation in tourmaline coloration. American Mineralogist, 73, 822–825.

Sheldrick G.M. (2015) Crystal structure refinement with SHELXL. Acta Crystallographica, C71, 3–8.

Skogby H., Bosi F. and Lazor P. (2012) Short-range order in tourmaline: a vibrational spectroscopic approach to elbaite. Physics and Chemistry of Minerals, 39, 811–816.

Strunz H. (1979) Anjanabonoana, Fundont schönter Tourmaline. Lapis, 1, 24–27, 47–48 [in German].

Sweetapple M.T. and Tassios S. (2015) Laser-induced breakdown spectroscopy (LIBS) as a tool for in situ mapping and textural interpretation of lithium in pegmatite minerals. American Mineralogist, 100, 2141–2151.

Tempesta G. and Agrogi G. (2016) Standaridless, minimally destructive chemical analysis of red beryls by means of laser induced breakdown spectroscopy. European Journal of Mineralogy, 28, 571–580.

Tempesta G., Bosi F. and Agrogi G. (2020) Crystal chemical characterisation of red beryl by ‘standaridless’ laser-induced breakdown spectroscopy and single-crystal refinement by X-ray diffraction: an example of validation of an innovative method for the chemical analysis of minerals. Geostandards and Geoanalytical Research, 44, 685–693.

van Hinsberg V.J., Henry D.J. and Dutrow B.L. (2011a) Tourmaline as a petrologic forensic mineral: a unique recorder of its geologic past. Elements, 7, 327–332.

van Hinsberg V.J., Henry D.J. and Marschall H.R. (2011b) Tourmaline: an ideal indicator of its host environment. The Canadian Mineralogist, 49, 1–16.

Webber K.L., Simmons W.B. and Falster A.U. (2002) Tourmaline from the Antandrokomy and Fianarantsoa Pegmatites, Madagascar. Mineralogical Record, 33, 82.

Watenphul A., Burgdorf M., Schlüter J., Horn I., Malcherek T. and Mihailova B. (2016a) Exploring the potential of Raman spectroscopy for crystallo-chemical analyses of complex hydrous silicates: II. Tourmalines. American Mineralogist, 101, 970–985.

Watenphul A., Schlüter J., Bosi F., Skogby H., Malcherek T. and Mihailova B. (2016b) Influence of the octahedral cationic-site occupancies on the framework vibrations of Li-free tourmalines, with implications for estimating temperature and oxygen fugacity in host rocks, American Mineralogist, 101, 2554–2563.