

## Gemological and Chemical Characteristics of Green Tourmaline from Madagascar, Mozambique, and Tanzania

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### Abstract

Green tourmalines from Madagascar, Mozambique, and Tanzania were investigated for their gemological properties, spectroscopic characteristics, and chemical compositions. The studied specimens were green, bluish green, yellowish green to brownish green, greenish blue, and blue. Their gemological properties were in a typical range of natural tourmaline. Microscopic examination displayed internal features which were normal of inclusion in tourmaline, such as growth tubes, hollow tubes, healed fractures, fluid inclusions, 2-phase (liquid-gas) inclusions, and small fractures. The cause of coloration in green tourmaline was examined by observing their Ultraviolet-visible-near infrared (UV-Vis-NIR) absorption spectra. The samples from Madagascar and Mozambique exhibited the same spectral range. The absorption bands at near 332, 385, 400 and 415 nm were related to  $Mn^{2+}$  from d-d transitions at the octahedral site. The intensity of absorption bands at 720 and 732 nm were attributed to  $Fe^{2+} - Fe^{3+}$  intervalence charge transfer (IVCT), while strong bands between 918 to 1220 nm were associated with the  $Fe^{2+}$  octahedral in the Y site. The samples from Tanzania displayed absorption spectra at 307 to 628 nm due to  $V^{3+}$  on the octahedral sites (Z-sites) and a weak peak at 417 nm associated with  $Cr^{3+}$ . The green tourmalines from this study exhibit intense bands around 1425 nm that are attributed to hydroxyl groups. Fourier Transform Infrared (FTIR) absorption spectra in the range 4000 - 500  $cm^{-1}$  were used to identify the stretching vibration of  $Si_6O_{18}$  rings (1200 - 820  $cm^{-1}$ ) and the  $BO_3$  (1350 to 1250  $cm^{-1}$ ) and hydroxyl groups (3700 to 3400  $cm^{-1}$ ) in the structure of tourmaline. Chemical analyses from electron probe micro-analysis (EPMA) revealed that samples from Madagascar and Mozambique had chemical compositions of elbaite end-members (lower in Ca content and richer in Na content), whereas the samples from Tanzania (Ca-Mg rich tourmaline) were of uvite end-members. This study proposes chemical fingerprinting by the Laser Ablation-Inductively coupled plasma-mass spectroscopy (LA-ICP-MS) technique, useful for differentiating green tourmalines from 3 different localities. The Madagascar samples contained Li, Fe, Zn, Ga, Sn, Pb and Bi, the Mozambique samples contained Li, Fe, Zn and Sn, and the Tanzania tourmalines contained Ti, V, Cr and Sr.

**Keywords:** Tourmaline, green tourmaline, gemological characteristics, chemical characteristics, spectroscopic characteristics

### Introduction

Green tourmaline is a light to intense green variety of the tourmaline gem species. In East Africa, tourmaline has been known in the gem trade since the late 1960s, and the green material has the trade name of chrome and/or vanadium tourmaline [1]. Green tourmaline deposits were discovered in many places, such as Brazil, USA, Madagascar, Kenya, Tanzania, Afghanistan, Mozambique, Zambia, and China [2]. In the jewelry industry, green tourmaline varieties are more popular and expensive due to their color and transparency, which are the most important aspects of beauty and value. Tourmaline is a mineral group and has a chemically complex composition. The basic chemical formula can be written as  $XY_3Z_6(T_6O_{18})(BO_3)_3V_3W$ . The X-site contains  $Na^+$ ,  $Ca^{2+}$ , and vacancies. The Y-site is occupied by  $Fe^{2+}$ ,  $Mg^{2+}$ ,  $Mn^{2+}$ ,  $Al^+$ ,  $Cr^{3+}$ ,  $V^{3+}$  and  $Fe^{3+}$ . The Z-site is substituted by Mg,  $Al^{3+}$ ,  $Fe^{3+}$ ,  $V^{3+}$ ,  $Cr^{3+}$ . The T-site is occupied by Si, Al, B). The V-site contains  $O^{2-}$  and  $OH^-$ , while the W-site is occupied by  $O^{2-}$ ,  $OH^-$  and  $F^-$ . Tourmaline is classified based on different cations occupied in the Y and Z sites [3,4]. This study therefore focuses especially on gemological characteristics, the causes of coloration, and chemical composition in green tourmaline.

## Materials and methods

A total of 60 green tourmaline samples from Madagascar, Mozambique, and Tanzania used in this study were purchased from dealers at the Bangkok Gems and Jewelry Fair. Then, the samples were classified into groups based on their color. The color of samples can be described with the GIA Gem Set. The basic gemological instruments were applied to determine the gemological properties of the samples, including the specific gravity, refractive index, birefringence, ultraviolet fluorescence, and microscopic features. UV-Vis-NIR spectroscopy (250 - 1500 nm) was used to investigate the causes of coloration. Fourier Transform Infrared (FTIR) spectroscopy ( $4000 - 500 \text{ cm}^{-1}$ ) was used to characterize the stretching vibrations of Si-O and the  $\text{BO}_3$  and the hydroxyl groups in the structure. All samples were carried out using instruments at the Department of Geological Sciences, Faculty of Science, Chiang Mai University, Chiang Mai, Thailand. Quantitative chemical analyses in this study were obtained using an electron probe micro-analyzer (EPMA) and Laser Ablation-Inductively coupled plasma-mass spectroscopy (LA-ICP-MS). Quantitative chemical analyses were measured using a JEOL Electron Probe Micro-Analyzer with wavelength dispersive (WD) analyzer at the Department of Geology, Faculty of Science, Chulalongkorn University, Bangkok, Thailand. In this study, 3 point locations on 10 samples of all color groups from different localities were analyzed for  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{V}_2\text{O}_3$ ,  $\text{MnO}$ ,  $\text{TiO}_2$ , F,  $\text{B}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{FeO}_{(\text{total})}$ , CaO, MgO,  $\text{Na}_2\text{O}$ , CuO and  $\text{K}_2\text{O}$ . Some elements in tourmalines cannot be measured by EPMA, such as  $\text{Li}_2\text{O}$  and  $\text{H}_2\text{O}$ , and were recalculated as per their mineral structural formula based on stoichiometric principles. The analytical results are typically a data table of weight percent oxides to atom per formula unit (apfu) bases on 31 anions (O, OH, F). The tourmaline chemical formulas were processed using Microsoft Excel spreadsheets developed by Selway and Xiong [5]. The chemical analyses were measured using an Agilent 7500a (ICP-MS) joined to the New Wave UP-213 laser-ablation adjustment at the Gem and Jewelry Institute of Thailand (Public Organization), Bangkok, Thailand. In this study, 3 random locations on 10 representative samples of all color groups from different localities were analyzed for minor and trace elements of Li, Be, Sc, Ti, V, Cr, Fe, Ni, Zn, Ga, Ge, Sr, Nb, Mo, Sn, Sb, Ta, Pb and Bi. This method can give amounts measurable in the range of parts per million (ppm).

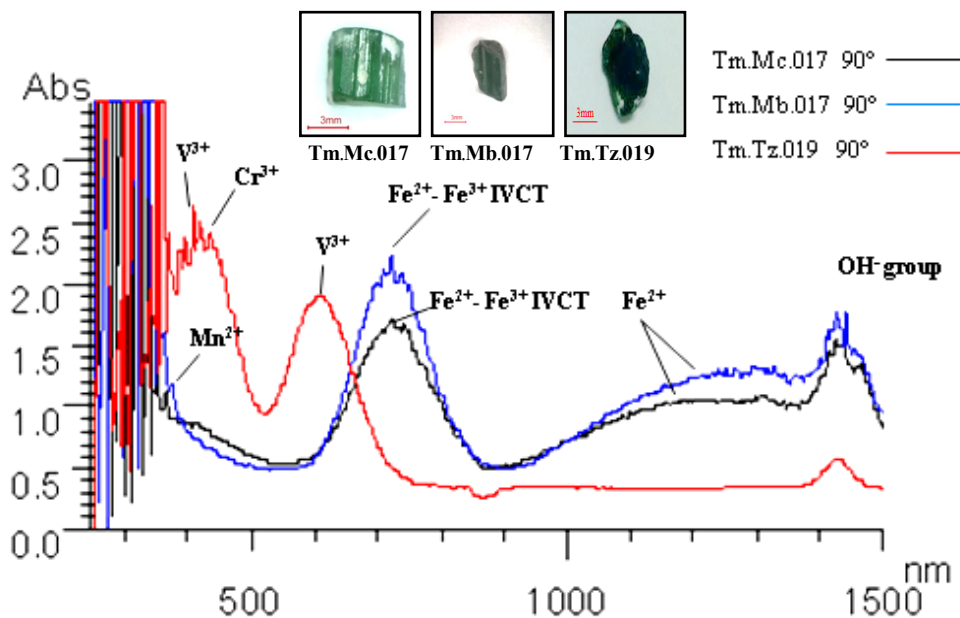
## Results and discussion

### Gemological properties

The specific gravity (S.G.) of all samples varied from 2.98 - 3.15. Their refractive indices (R.I.) ranged from 1.640 - 1.645 for  $N_o$ , and from 1.620 - 1.625 for  $N_e$ , with a birefringence of 0.017 - 0.021. All samples were inert when exposed under short-wave (SW) and long-wave (LW) ultraviolet radiation. Microscopic examination revealed internal features that were typical of inclusion in tourmaline, such as growth tubes, hollow tubes, healed fractures, fluid inclusions, 2-phase (liquid-gas) inclusions, and small fractures [2,4,6].

### UV-Vis-NIR absorption spectroscopy

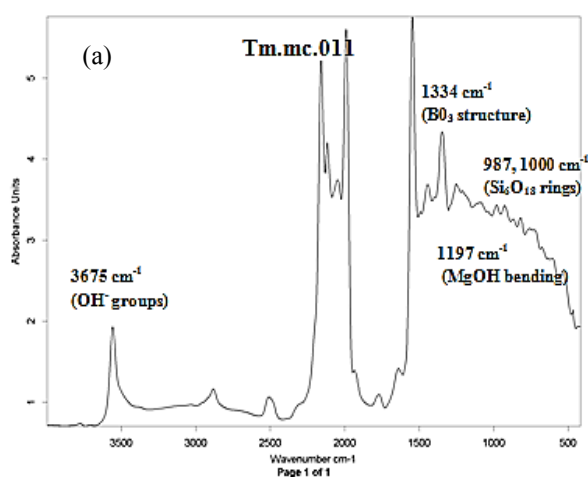
The absorption spectrum of green tourmaline from Madagascar and Mozambique presented a similar spectral range. The narrow band near 332, 385, 400 and 415 nm was attributed to  $\text{Mn}^{2+}$  from d-d transitions at the octahedral site [7,8]. A low intensity  $\text{Mn}^{3+}$  band was observed in a few samples from Madagascar near 510, 517 and 520 nm [9]. Reddy *et al.* [10] reported that the band at 520 nm was due to  $\text{Mn}^{3+}$  ions in the high spin state, distorted octahedral sites. A strong band centered at 720 nm related to  $\text{Fe}^{2+}$ - $\text{Fe}^{3+}$  intervalence charge transfer (IVCT), and the spectrum ordinary ray ( $90^\circ$ ) had a higher concentration of iron [10,11]. There are reports that assigned the band to the  $\text{Fe}^{2+}$  octahedral in the Y site [7,12,13], while Camargo and Isotani [14] reported the band presence of  $\text{Fe}^{2+}$  at the Z site. The strong bands between 918 to 1220 nm were related to the  $\text{Fe}^{2+}$  octahedral in the Y site [12]. The sharp absorption bands in the 1400 - 1500 nm were attributed to hydroxyl groups, noticeably parallel to the c-axis [15]. Schmetzer [16] noted that chromium and vanadium both cause absorption bands at the same position in the UV-Vis-NIR spectra. The green tourmaline from Tanzania showed absorption spectra of the main transition metal at 307, 390, 432, 448, 608 and 628 nm, attributed to  $\text{V}^{3+}$  on the octahedral coordinated aluminum-sites (Z-sites) [16,17]. A small peak at 417 nm was related to  $\text{Cr}^{3+}$ , which is in the same spectral range of vanadium [18]. Schmetzer *et al.* [3] reported that the spectra of  $\text{V}^{3+}$  and  $\text{Cr}^{3+}$  causes the green coloration in uvite samples. The ratio of V: Cr determined by chemical analyses presented that had higher vanadium than chromium contents, and the UV-Vis-NIR spectra shown characterized by the 2 broad bands related to  $\text{V}^{3+}$ . Absorption band at 1425 nm is due to hydroxyl groups (**Figure 1**).

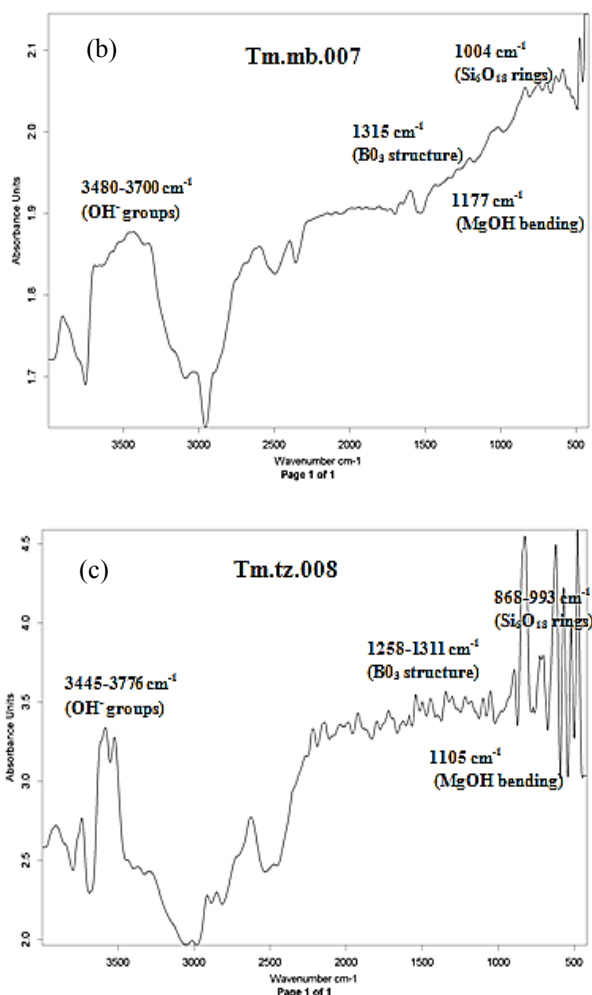


**Figure 1** UV-Vis-NIR absorption spectra comparisons of green tourmaline samples from Madagascar, Mozambique, and Tanzania.

#### Infrared absorption spectroscopy

Infrared absorption spectroscopy obtained the stretching vibrations of Si-O, the  $\text{BO}_3$  groups, and the hydroxyl groups in the structure of typical green tourmaline samples. The absorption spectrum of green tourmaline from Madagascar, Mozambique and Tanzania presented a similar spectral range. The vibration absorption bands around  $1200 - 820 \text{ cm}^{-1}$  were attributed to the stretching vibrations of the  $\text{Si}_6\text{O}_{18}$  rings [10,19]. The bands between  $1105$  and  $1197 \text{ cm}^{-1}$  were attributed to MgOH bending modes [10]. The sharp bands at around  $1350$  and  $1250 \text{ cm}^{-1}$  were identified as the stretching vibration modes of the  $\text{BO}_3$  groups [19]. The stretching modes of the hydroxyl groups were observed in a range from  $3700$  to  $3400 \text{ cm}^{-1}$  [20] (**Figure 2**).





**Figure 2** Polarized FTIR absorption spectra comparisons of sample from (a) Madagascar, (b) Mozambique, and (c) Tanzania.

### Chemical composition

Quantitative chemical analyses in this study were obtained using an EPMA and LA-ICP-MS. Major elements of green tourmalines from Madagascar: SiO<sub>2</sub> (36.12 to 38.67 wt.%), Al<sub>2</sub>O<sub>3</sub> (40.04 to 40.40 wt.%), and B<sub>2</sub>O<sub>3</sub> (10.61 to 11.10 wt.%) were similar to natural tourmaline [21]. Chemical analyses in this study correspond to elbaite position. The elbaite samples analyzed showed higher Na content (1.75 to 2.36 wt.%) than Ca content (0.17 to 0.72 wt.%). The most Ca-rich (4.15 wt.%) and Na-poor (0.96 wt.%) was liddicoatite from Madagascar [21]. Akizuki *et al.* [22] published their findings, containing Ca content (4.69 wt.%) and Na content (0.54 wt.%). Tourmaline from Madagascar can be identified with both elbaite and liddicoatite because tourmaline solid solutions involve the occupancy of equivalent structural sites by difference ions. Moreover, it can be expected in members of any mineral group with cation sites in which substitutions are possible [4]. In the case of the chemical substitution, this locality occurs from the elbaite-liddicoatite series, based on Na<sup>+</sup>: Ca<sup>2+</sup> differences in the X-site, which are composed of charge compensating differences between Al<sup>3+</sup> and Li<sup>+</sup> in the Y-sites [23]. Dunn *et al.* [24] reported that liddicoatite cannot be differentiated from elbaite by its optical and physical characteristics. Quantitative chemical analyses are required to confirm the tourmaline species. The chromophoric elements Fe, Mn and Ti are typically in Madagascar tourmaline [21]. These chromophorics affect the coloration of liddicoatite in the same way they affect elbaite [4]. The highest Fe values (3.02 to 3.57 wt.%) were found in green color [25]. The Mn content has a wide range in the various colors of samples. The high content of Mn was observed in green and watermelon tourmaline (spot in pink core) samples. The Ti content is very low or below detection limit in these samples. The most abundant trace elements in this study were Zn, Ga, Sn, Pb and Bi. Trace element amounts of Zn and Pb are more common in green and blue elbaite [4].

Multicolored tourmalines (pink, purple, red, olive green, yellow-brown, and yellow) from the Antseny pegmatite, Madagascar, have been found to have trace elements of Bi and Pb, whereas multicolored tourmalines from the Anjahamiary pegmatite, Madagascar have been found to have only Pb [26].

Major element contents of green tourmalines from Mozambique contain SiO<sub>2</sub> (35.01 to 36.12 wt.%), Al<sub>2</sub>O<sub>3</sub> (40.26 to 40.93 wt.%), and B<sub>2</sub>O<sub>3</sub> (10.52 to 11.28 wt.%), and are similar to natural tourmaline [27]. The analyses fell in the elbaite field of alkali tourmaline. The samples were elbaite components, mostly lower in Ca content (0.23 to 0.57 wt.%), and richer in Na content (1.08 to 2.40 wt.%) [28]. The chromophoric elements Fe, Mn and Ti exhibited strong correlation with color. Fe is the most important trace element. The next-highest Fe values (3.18 to 3.74 wt.%) were found in green and greenish blue color tourmaline, similar to tourmaline from Mt. Mica, USA (1.79 to 4.46 wt.% FeO) [28]. All samples had very low Ti contents. Mn was highest in bi-color and greenish blue. By comparison, the Mn contents of the samples from Mozambique had the same range with the samples from Madagascar (0.54 to 2.20 wt.%). Shigley *et al.* [29] noted that elbaite containing minor amounts of Mn are common, and appear to be of pegmatitic origin, including green color. The most abundant trace elements of Zn and Sn were detected in the samples from Mozambique.

Chemical composition identified the samples from Tanzania as Ca-Mg tourmaline. Chemical analyses corresponded with end-member uvite [20]. They were Ca-rich, as found in the X-site, ranging from 3.74 to 4.64 wt.% CaO, and high Mg contents ranged from 12.12 to 13.30 wt.% MgO. Schmetzer *et al.* [3] reported that the magnesium-bearing calcic tourmalines with Al < 6 and Mg > 3 apfu (atoms per formula unit), was consistent with the composition of uvite. The specimen Al content ranged from 5.152 to 5.170 apfu, and the Mg content ranged from 2.916 to 3.234 apfu. Therefore, the samples in this study can be designated as uvite. Henry and Guidotti [30] noted that tourmaline with Al < 6 and Mg > 3 apfu (uvite) originate from metacarbonates and meta-pyroxenites. The chromophoric elements were vanadium, with a minor influence from chromium [31]. The highest V values (0.19 to 0.25 wt.%) were found in green color. The ratio of V: Cr determined by chemical analyses showed that vanadium is strongly dominant [16,31]. The trace elements of green tourmalines from Tanzania presented high value quantities of Ti, V, Cr and Sr. Representative EPMA analyses and LA-ICP-MS chemical data of green tourmaline of various colors from Madagascar, Mozambique, and Tanzania are shown in **Tables 1** and **2**.

**Table 1** EPMA analyses of green tourmaline of various colors from Madagascar, Mozambique, and Tanzania.

Chemical composition	Madagascar				Mozambique				Tanzania			
	yellowish Green to brownish Green	Green	Watermelon		Blue	greenish Blue	Green	Bi-color		Yellow-Green	yellowish Green	Green
			yG	pR				B	bG			
<b>Oxide (wt.%)</b>												
Al <sub>2</sub> O <sub>3</sub>	40.04	40.35	40.10	40.40	40.70	40.93	40.26	40.33	40.61	27.18	27.15	27.19
SiO <sub>2</sub>	36.12	36.12	38.67	38.35	37.93	35.14	36.12	36.19	35.01	38.23	38.96	38.58
V <sub>2</sub> O <sub>3</sub>	bdl	bdl	bdl	bdl	bdl	0.01	bdl	bdl	0.02	0.19	0.20	0.25
MnO	0.54	1.66	1.05	1.17	0.82	1.26	0.99	2.20	1.74	0.01	0.02	bdl
TiO <sub>2</sub>	0.02	bdl	bdl	0.01	bdl	0.01	0.01	bdl	bdl	0.12	0.12	0.20
F	0.72	0.68	0.47	0.58	0.48	0.76	0.52	0.54	0.62	0.54	0.53	0.15
B <sub>2</sub> O <sub>3</sub>	11.10	11.02	10.61	10.73	11.28	10.52	11.14	10.84	11.23	10.57	10.42	10.85
Cr <sub>2</sub> O <sub>3</sub>	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.02	0.08	0.07	0.09
FeO	3.26	3.57	3.25	3.02	2.51	3.18	3.74	2.22	3.39	0.03	0.01	bdl
CaO	0.72	0.36	0.17	0.45	0.37	0.27	0.23	0.57	0.39	4.64	3.74	3.76
MgO	0.05	bdl	0.09	0.10	bdl	bdl	0.06	0.01	0.03	13.36	13.20	12.12
Na <sub>2</sub> O	1.99	2.36	1.84	1.75	1.08	2.40	2.17	2.08	2.37	0.88	1.24	1.16
CuO	0.01	bdl	0.02	0.02	0.01	0.03	bdl	0.03	bdl	bdl	bdl	0.02
K <sub>2</sub> O	0.02	0.02	0.02	0.02	0.02	0.01	0.02	0.02	0.02	0.03	0.03	0.07
Li <sub>2</sub> O calc.	1.80	1.55	1.56	1.51	1.85	1.36	1.61	1.57	1.62	0.89	1.09	1.32
H <sub>2</sub> O calc.	3.41	3.45	3.59	3.55	3.62	3.34	3.52	3.49	3.45	3.47	3.51	3.65
Subtotal	99.80	101.14	101.44	101.66	101.57	99.22	100.38	100.09	100.52	100.21	100.76	99.39
-O=F	0.30	0.29	0.20	0.24	0.20	0.32	0.22	0.23	0.26	0.23	0.22	0.06
<b>Total</b>	<b>99.50</b>	<b>100.85</b>	<b>101.24</b>	<b>101.42</b>	<b>101.37</b>	<b>98.90</b>	<b>100.16</b>	<b>99.86</b>	<b>100.26</b>	<b>99.98</b>	<b>100.54</b>	<b>99.33</b>
<b>Ions per 31 (O,OH,F)</b>												
T: Si	5.775	5.746	6.076	6.018	5.918	5.694	5.758	5.790	5.601	6.161	6.216	6.217
Al	0.225	0.254	0.000	0.000	0.082	0.306	0.242	0.210	0.399	0.000	0.000	0.000
B	3.063	3.026	2.878	2.906	3.038	2.942	3.065	2.993	3.101	2.940	3.000	3.018
Z: Al	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	5.162	5.105	5.164
Mg	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.838	0.895	0.836

Chemical composition	Madagascar				Mozambique				Tanzania			
	yellowish Green to brownish Green	Green	Watermelon		Blue	greenish Blue	Green	Bi-color		Yellow-Green	yellowish Green	Green
			yG	pR				B	bG			
Cr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Fe <sup>3+</sup>	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Y: Al	1.320	1.311	1.426	1.472	1.403	1.510	1.322	1.394	1.258	0.000	0.000	0.000
Ti	0.002	0.000	0.000	0.001	0.000	0.001	0.001	0.000	0.000	0.015	0.014	0.024
V	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.003	0.025	0.026	0.032
Cr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.003	0.010	0.009	0.011
Fe <sup>3+</sup>	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Mg	0.012	0.000	0.021	0.023	0.000	0.000	0.014	0.002	0.007	2.372	2.245	2.076
Mn	0.073	0.224	0.140	0.156	0.108	0.173	0.134	0.298	0.236	0.001	0.003	0.000
Fe <sup>2+</sup>	0.436	0.475	0.427	0.396	0.328	0.431	0.499	0.297	0.454	0.004	0.001	0.000
Zn	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Li*	1.157	0.990	0.986	0.952	1.161	0.884	1.031	1.009	1.040	0.573	0.702	0.856
?Y	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000
X: Ca	0.123	0.061	0.029	0.076	0.062	0.047	0.039	0.098	0.067	0.801	0.639	0.649
Na	0.617	0.728	0.561	0.532	0.599	0.754	0.671	0.645	0.735	0.275	0.384	0.362
K	0.004	0.004	0.004	0.004	0.004	0.002	0.004	0.004	0.004	0.006	0.006	0.014
r	0.256	0.207	0.407	0.388	0.335	0.197	0.286	0.253	0.194	0.000	0.000	0.000
OH	3.636	3.658	3.766	3.712	3.763	3.611	3.738	3.727	3.686	3.725	3.733	3.924
F	0.364	0.342	0.234	0.288	0.237	0.389	0.262	0.273	0.314	0.275	0.267	0.076
Cl	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Mineral name	Elbaite	Elbaite	Elbaite	Elbaite	Elbaite	Elbaite	Elbaite	Elbaite	Elbaite	Uvite	Uvite	Uvite

Abbreviation: bdl = below detection limit  
 Li<sub>2</sub>O, H<sub>2</sub>O were calculated as mineral structural formula based on stoichiometric principles

**Table 2** LA-ICP-MS chemical data of green tourmaline of various colors from Madagascar, Mozambique, and Tanzania.

Trace element (ppm)	Madagascar				Mozambique				Tanzania			
	yellowish Green to brownish Green	Green	Watermelon		Blue	greenish Blue	Green	Bi-color		Yellow-Green	yellowish Green	Green
			yG	pR				B	bG			
Li	1619.23	1424.74	1655.42	1722.44	1451.21	1304.49	1277.61	1413.09	1940.82	4.05	12.98	6.39
Be	3.52	2.61	4.06	6.95	4.66	6.74	3.42	2.98	3.23	6.13	2.34	2.26
Sc	8.74	8.42	8.11	8.07	7.01	7.54	6.36	6.23	6.51	5.40	6.19	6.11
Ti	29.05	14.96	86.57	52.25	8.85	7.92	25.11	7.20	8.17	555.03	607.27	690.10
V	0.68	0.43	0.77	1.28	0.58	0.56	0.69	0.63	0.63	170.72	552.47	645.25
Cr	7.49	5.98	11.20	16.20	9.81	6.86	7.10	8.04	7.69	18.21	249.92	492.66
Fe	46845	55462	947	283	26596	34647	39368	14608	20110	66.30	28.56	25.69
Ni	2.97	2.12	4.59	6.01	4.94	4.52	3.14	2.96	2.67	8.42	2.31	3.27
Zn	150.87	77.89	140.64	29.32	128.08	667.13	258.77	32.17	51.41	17.55	6.29	5.41
Ga	28.78	14.94	69.08	58.80	13.66	12.20	18.40	10.24	8.43	2.91	0.84	6.79
Ge	5.83	3.59	5.81	9.18	5.61	10.21	9.92	6.19	4.05	8.33	3.27	2.99
Sr	4.55	2.42	0.55	0.72	0.91	6.29	0.32	1.14	1.23	201.05	92.18	64.76
Nb	1.09	0.49	0.42	0.76	0.41	0.40	0.53	0.54	0.37	0.78	0.32	0.33
Mo	2.74	1.70	3.13	5.06	2.54	2.45	2.28	3.23	1.51	4.00	1.56	2.37
Sn	9.12	26.89	5.52	8.23	21.22	16.30	13.52	29.18	25.88	4.93	1.63	2.02
Sb	4.06	1.06	2.41	3.21	1.88	1.29	1.53	1.44	1.54	3.26	1.12	1.48
Ta	0.88	0.51	0.53	0.75	0.62	1.42	0.45	0.39	0.41	0.82	0.39	0.37
Pb	44.39	58.34	3.80	5.76	11.72	31.81	9.52	2.27	2.13	3.68	1.01	1.34
Bi	15.98	0.66	37.3	71.76	0.97	0.67	1.02	0.70	0.87	1.49	0.63	0.66

## Conclusions

1) Green tourmalines from Madagascar, Mozambique, and Tanzania show color in green, bluish green, yellowish green to brownish green, greenish blue, and blue. Their gemological properties are typical in the range of natural tourmaline. Internal features are normal of inclusion in tourmaline, such as growth tubes, hollow tubes, healed fractures, fluid inclusions, 2-phase (liquid-gas) inclusions, crystal inclusions, and small fractures.

2) The cause of coloration in green tourmaline was analyzed by UV-Vis-NIR absorption spectral. Samples from Madagascar and Mozambique present the same spectral range. The absorption bands near 332, 385, 400 and 415 nm are attributed to  $Mn^{2+}$  from d-d transitions at the octahedral site. The intensity of absorption bands at 720 and 732 nm are related to  $Fe^{2+} - Fe^{3+}$  IVCT, while strong bands between 918 to 1220 nm are related to the  $Fe^{2+}$  octahedral in the Y site. The samples from Tanzania show absorption spectra at 307 to 628 nm due to  $V^{3+}$  on the octahedral sites (Z-sites) and a weak peak at 417 nm is related to  $Cr^{3+}$ . The green tourmalines from 3 localities present intense bands centered at 1425 nm, attributed to hydroxyl groups.

3) The FTIR absorption spectra in the range 4000 - 500  $cm^{-1}$  were used to characterize the stretching vibrations of  $Si_6O_{18}$  rings (1200 - 820  $cm^{-1}$ ) and the  $BO_3$  (1350 to 1250  $cm^{-1}$ ) and the hydroxyl groups (3700 to 3400  $cm^{-1}$ ) in the structure of tourmaline.

4) EPMA samples from Madagascar and Mozambique present the same chemical compositions that correspond to near end-member elbaite, mostly lower in Ca content and richer Na content, whereas the samples from Tanzania identified as Ca-Mg rich tourmaline are related to end-member uvite. The chromophoric elements Fe and Mn were usually found in Madagascar and Mozambique tourmaline. Fe is the most important trace element in both these localities and was found in green color. The main chromophoric element of green tourmaline from Tanzania was vanadium, with a minor influence from chromium. The green samples contained the highest V concentration.

5) This study presented chemical fingerprinting using the LA-ICP-MS technique, which is helpful for differentiating green tourmalines from the various localities. The Madagascar samples showed high contents of Li, Fe, Zn, Ga, Sn, Pb and Bi, whereas the Mozambique samples were enriched in Li, Fe, Zn and Sn. The green tourmalines from Tanzania contained amounts of the trace elements Ti, V, Cr and Sr. The minor and trace elements of samples from Madagascar and Mozambique are more common in green and blue elbaite, and are associated with characteristic occurrences of tourmaline in granitic pegmatites, whereas samples from Tanzania are associated with occurrences in metamorphic rocks.

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