CHAPTER 3

RESULTS

3.1 Gemological properties

Gemological properties of green tourmalines from Madagascar, Mozambique and Tanzania are summarized in Tables 3.1-3.3.The specific gravity (S.G.) of all samples varies from 2.98-3.15. Their refractive indices (R.I.) range 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 are inert when exposed under short-wave (SW) and long-wave (LW) ultraviolet radiation.

Table 3.1 Gemological properties of green tourmalines from Madagascar

Sample codes	Weight	S.G.	R.I.		Inclusions	Color grading
			N_o	N_e		
green color						
Tm.Mc.005	1.025	3.07	1.641	1.622	Fracture	G 6/2
Tm.Mc.011	1.141	3.03	1.643	1.623	Healed fracture containing fluid- and/or two-phase (liquid-gas)	G 6/2
Tm.Mc.017	0.970	3.02	1.641	1.623	Fracture, hollow tubes	G 6/2
Tm.Mc.020	1.354	3.02	1.640	1.620	Healed fracture, trichite	G 5/2
bluish green color						
Tm.Mc.001	0.805	3.11	1.645	1.624	Trichite, flat fluid inclusion	bG 7/3
Tm.Mc.002	1.718	3.01	1.644	1.625	Fracture, healed fracture, flat fluid inclusion	vstbG 5/2
Tm.Mc.003	1.099	3.06	1.643	1.625	Healed fracture	vstbG 6/3
Tm.Mc.006	0.806	3.00	1.642	1.624	Hollow tubes, healed fracture	vstbG 6/3
Tm.Mc.007	1.111	3.05	1.642	1.622	Healed fracture	bG 7/3
Tm.Mc.009	0.883	3.09	1.644	1.625	Healed fracture	vstbG 6/3
Tm.Mc.010	0.994	3.11	1.645	1.624	Hollow tubes, healed fracture	vstbG 8/3
Tm.Mc.018	1.004	3.10	1.642	1.623	Healed fracture	vstbG 6/3
Tm.Mc.019	1.228	3.04	1.643	1.625	Healed fracture, fracture	bG 7/3

Table 3.1 (Continued)

Sample codes	Weight	S.G.	R.I.		Inclusions	Color grading
			N_o	N_e		
yellowish green						
Tm.Mc.004	1.705	3.05	1.640	1.623	Hollow tubes	GY/YG 7/3
Tm.Mc.008	1.079	3.04	1.642	1.624	Hollow tubes, healed fracture	styG 3/3
Tm.Mc.012	1.201	3.05	1.640	1.620	Fracture, hollow tubes	styG 6/3
Tm.Mc.013	1.042	3.05	1.642	1.624	Fracture	styG 5/3
Tm.Mc.014	0.692	2.99	1.645	1.625	Fracture	styG 7/3
Tm.Mc.016	0.920	3.11	1.645	1.625	Healed fracture	styG 6/3
watermelon tourmaline						
Tm.Mc.015	1.152	3.10	1.640	1.623	Hollow tubes, healed fracture	styG 7/3, slpR 3/3

Table 3.2 Gemological properties of green tourmalines from Mozambique

Sample codes	Weight	S.G.	R.I.		Inclusions	Color grading
			N_o	N_e		
greenish blue color						
Tm.Mb.001	2.090	3.07	1.641	1.624	Healed fracture, fracture, fluid inclusion	gB 3/3
Tm.Mb.002	1.279	3.05	1.640	1.623	Fractures filled with ion stains, hollow tubes, healed fracture	gB 3/3
Tm.Mb.003	0.891	3.06	1.642	1.624	Healed fracture	vstgB 2/3
Tm.Mb.004	1.329	3.07	1.640	1.623	Healed fracture	vstgB 2/3
Tm.Mb.005	1.664	3.05	1.642	1.624	Trichite, fracture, healed fracture	vstgB 2/3
Tm.Mb.006	0.973	3.07	1.641	1.621	Fractures filled with ion stains, hollow tubes, healed fracture	vstgB 2/3
Tm.Mb.007	0.947	3.07	1.641	1.621	Healed fracture	vstgB 2/3
Tm.Mb.008	0.795	3.08	1.640	1.622	Hollow tubes, fluid inclusion	vstgB 3/2
Tm.Mb.009	0.679	3.10	1.640	1.620	Healed fracture, fluid inclusion	vstgB 3/2
Tm.Mb.010	0.855	3.08	1.642	1.624	Trichite, fracture, healed fracture	vstgB 7/2
Tm.Mb.011	0.785	3.05	1.642	1.624	Healed fracture	vstgB 3/2
Tm.Mb.012	1.448	2.99	1.641	1.624	Hollow tubes, healed fracture	vstgB 3/2
blue color						
Tm.Mb.013	0.915	3.12	1.643	1.624	Hollow tubes, fluid inclusion	B 5/1
Tm.Mb.014	0.683	3.11	1.642	1.621	Fractures filled with ion stains, healed fracture	B 5/2
green color						
Tm.Mb.015	1.590	3.06	1.642	1.624	Flat fluid inclusion, healed fracture	GB/BG 2/2
Tm.Mb.016	0.792	3.10	1.640	1.621	Healed fracture	GB/BG 4/2

Table 3.2 (Continued)

Sample codes	Weight	S.G.	R.I.		Inclusions	Color grading
			N_o	N_e		
Tm.Mb.017	1.010	3.06	1.643	1.625	Fractures filled with ion stains, healed fracture	GB/BG 6/1
Tm.Mb.018	1.419	3.09	1.642	1.625	Hollow tubes, fluid inclusion	GB/BG 6/1
bi-color tourmaline						
Tm.Mb.019	2.778	3.04	1.640	1.621	Fractures filled with ion stains, hollow tubes, healed fracture	vstgB 3/3, vslgB 2/3
Tm.Mb.020	1.399	3.08	1.640	1.620	Healed fractures containing fluid- and/or two-phase (liquid-gas)	B 4/2, vslgB 2/3

Table 3.3 Gemological properties of green tourmalines from Tanzania

Sample codes	Weight	S.G.	R.I.		Inclusions	Color grading
			N_o	N_e		
yellowish green color						
Tm.Tz.001	1.280	3.06	1.641	1.624	Fractures filled with ion stains	slyG 8/3
Tm.Tz.002	2.057	3.15	1.644	1.624	Healed fracture, fracture	styG 6/4
Tm.Tz.003	1.148	3.01	1.644	1.624	Fractures	styG 6/4
Tm.Tz.004	2.183	3.02	1.642	1.624	Hollow tubes, fracture	styG 7/3
Tm.Tz.005	1.407	3.05	1.643	1.623	Healed fracture	yG 3/3
Tm.Tz.006	2.580	2.98	1.644	1.624	Fractures filled with ion stains	styG 6/4
Tm.Tz.007	2.070	2.97	1.640	1.621	Crystal inclusion	styG 6/4
Tm.Tz.008	1.757	2.98	1.642	1.624	Healed fracture	yG 4/3
Tm.Tz.009	1.638	2.99	1.641	1.621	Fractures	yG 6/4
Tm.Tz.010	2.036	2.98	1.641	1.621	Fractures filled with ion stains	yG 2/3
Tm.Tz.011	1.548	3.01	1.644	1.624	Healed fracture	slyG 8/3
Tm.Tz.012	1.345	3.02	1.642	1.624	Hollow tubes, fractures filled with ion stains	styG 7/3
Tm.Tz.013	1.267	2.99	1.644	1.624	Fractures	yG 7/3
Tm.Tz.014	2.002	3.00	1.642	1.621	Healed fracture	yG 7/3
Yellow- Green color						
Tm.Tz.015	1.375	2.98	1.643	1.625	Liquid inclusion, negative inclusion	YG/GY 6/3
Tm.Tz.016	1.484	3.00	1.642	1.624	Fractures filled with ion stains	YG/GY 7/3
Tm.Tz.017	1.295	3.03	1.643	1.625	Healed fracture, fracture, fluid inclusion	YG/GY 6/3
green color						
Tm.Tz.018	1.479	3.02	1.644	1.624	Fractures	G 4/2
Tm.Tz.019	2.087	2.99	1.641	1.624	Fractures filled with ion stains	G 6/4
Tm.Mc.020	0.743	2.98	1.644	1.624	Hollow tubes, fluid inclusion	G 6/2

3.2 Internal microscopic characteristics

The main internal characteristics of the samples from Madagascar, Mozambique and Tanzania are typical of tourmaline, such as partially healed fissures, fluid inclusion, hollow tubes, and small fractures. The most inclusions from Madagascar consist of partially healed fissures, which presented wide variations. The samples have healed fractures containing fluid- and/or two-phase (liquid-gas) inclusions (Figure 3.1 a). The specimens occurred as trichite contain fluid-filled cavities linked by networks of very thin capillaries (Figure 3.1 b). The inclusions of flat fluid inclusion (Figure 3.2 a), hollow tubes, oriented parallel to the C-axis, are common found (Figure 3.2 b). The fractures were observed in some samples (Figure 3.3). Most samples from Mozambique contain numerous hollow tubes (Figure 3.4 a) and partially healed fractures (Figure 3.4 b), were quite common. Often they occurred as trichite. The capillaries were irregular and wispy (Figure 3.5 a). Flat fluid inclusion (Figure 3.5 b) and fractures with filled with ion stains were evident in a few samples (Figure 3.6). Microscopic observation samples from Tanzania revealed internal features that are normally of tourmaline, such as fluid inclusion (Figure 3.7 a), negative crystals (Figure 3.7 a), partially healed fissures (Figure 3.7 b), crystal inclusion (Figure 3.8 a) and fracture with filled with ion stains (Figure 3.8 b).

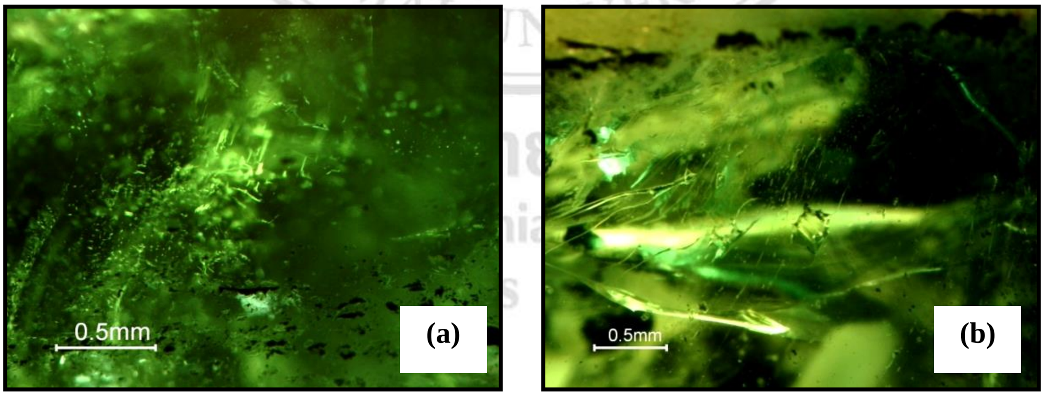

Figure 3.1 Healed fractures containing fluid- and/or two-phase (liquid-gas) inclusions in Tm.Mc.011 (a) and trichite, which fluid-filled cavities linked by networks of very thin capillaries in Tm.Mc.001 (b).

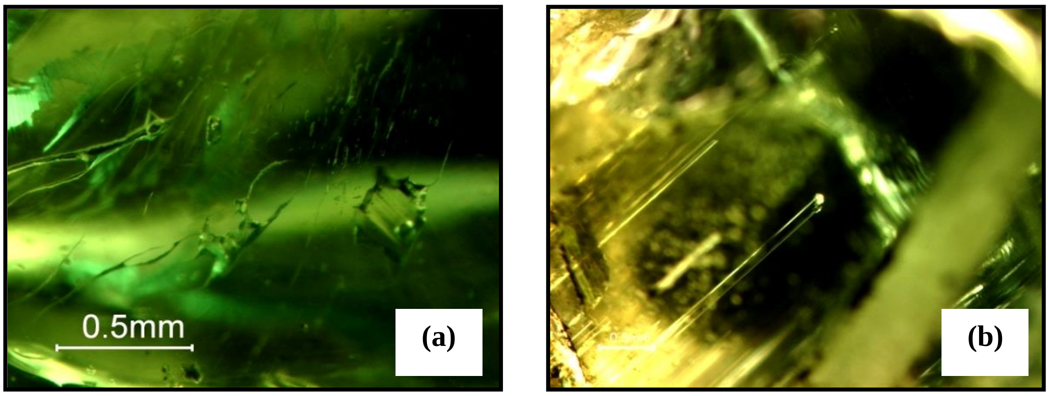

Figure 3.2 Flat fluid inclusions in Tm.Mc.001 (a) and hollow tubes, oriented parallel to the C-axis in Tm.Mc.004 (b).

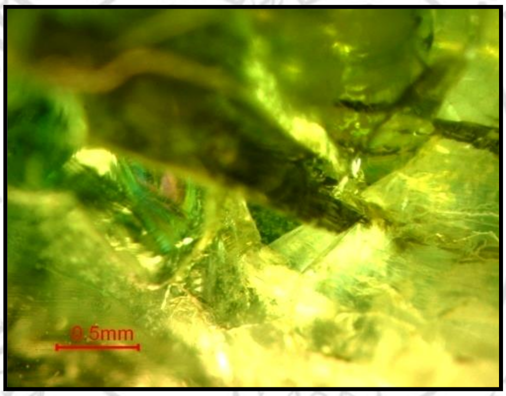

Figure 3.3 Fractures in Tm.Mc.014

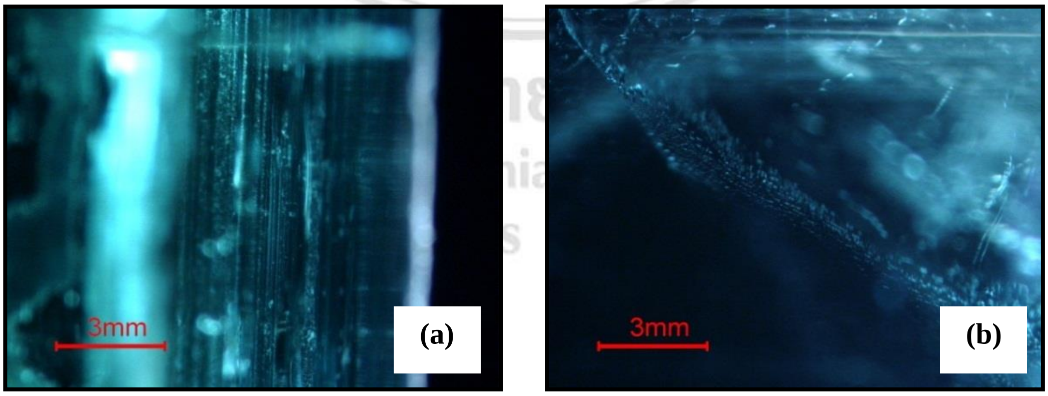

Figure 3.4 Hollow tubes, oriented parallel to the C-axis in Tm.Mb.018 (a) and healed fractures containing fluid- and/or two-phase (liquid-gas) inclusions in Tm.Mb.020 (b).

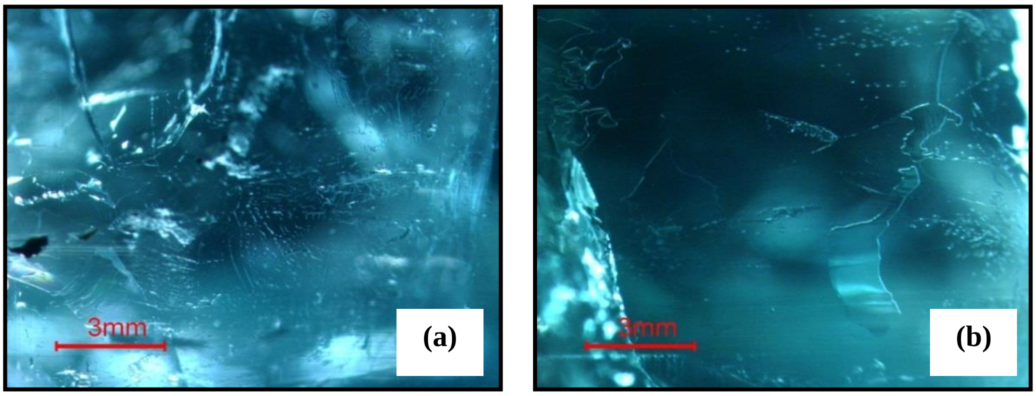

Figure 3.5 Trichite, which fluid-filled cavities linked by networks of very thin capillaries in Tm.Mb.005 (a) and Tm.Mb.015 (b).

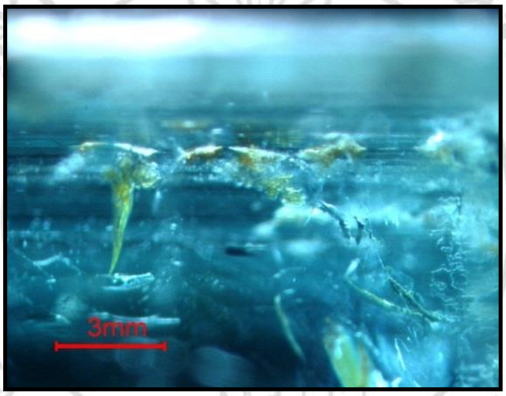

Figure 3.6 Fractures filled with ion stains in Tm.Mb.002

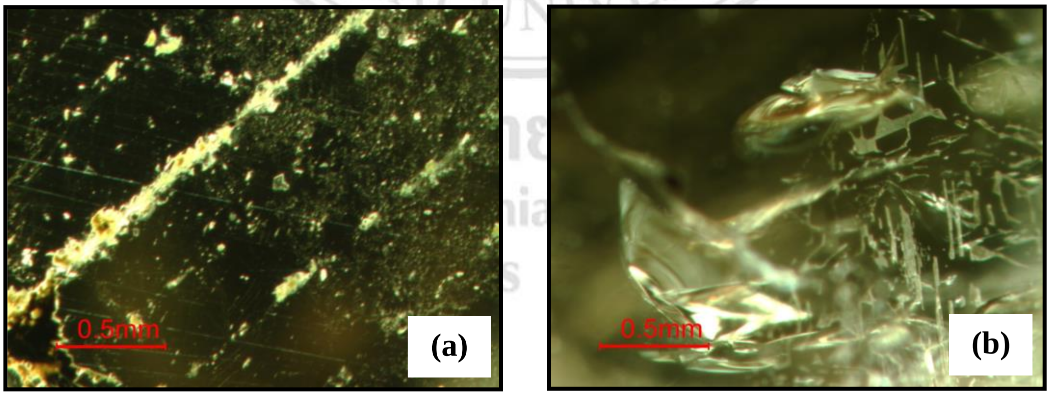

Figure 3.7 Fluid inclusion and negative inclusion in Tm.Tz.015 (a) and healed fractures containing fluid- and/or two-phase (liquid-gas) inclusions in Tm.Tz.008 (b).

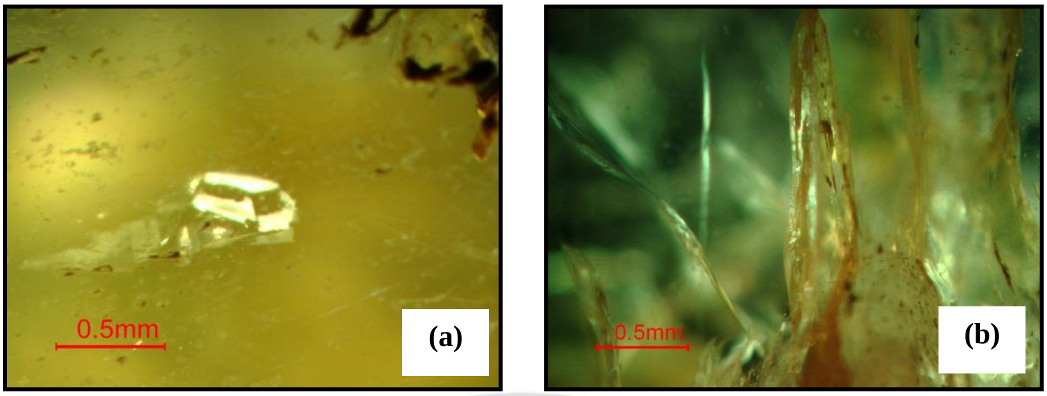

Figure 3.8 Crystal inclusion in Tm.Tz.007 (a) and fractures filled with ion stains in Tm.Tz.001 (b).

3.3 Ultraviolet-Visible-Near Infrared (UV-Vis-NIR) spectra

The UV-Vis-NIR absorption spectra of all samples were investigated the cause of coloration in green tourmaline. The typical absorption spectra of each locality are presented in Figures 3.9 to 3.23.

The absorption spectra were recorded at room temperature in a range of 250 nm to 1500 nm at a scan speed of 300 nm per minute, with 2 mm of slit width. The spectra were saved in absorbance mode. All samples were measured in the ordinary and extraordinary rays. The data from this analysis were processed by Hitachi spectrophotometer UV solution program.

The absorption spectrum of green tourmaline from Madagascar (Figures 3.9 to 3.13) and Mozambique (Figures 3.14 to 3.18) displays similar spectral range. Absorption bands are assigned to Mn^{2+} from d-d transitions at 350 to 443 nm (weakly in the violet regions of the visible light range). A low intensity Mn^{3+} band was observed in a few samples from Madagascar near 510, 517 and 520 nm. The strong broad bands at 686 to 793 nm are related to Fe^{2+}-Fe^{3+} intervalence charge transfer (IVCT) (orange and red regions of the visible light range). These present transmission the green region of the visible light range resulting in the blue, greenish blue, bluish green, green and yellowish green colors. The bands between at 918 to 1292 nm are attributed to Fe^{2+} octahedral in Y site. In the near infrared region, the spectra of the samples show intense bands around 1400 to 1473 nm, associated with hydroxyl groups. Because these absorptions (Fe^{2+}octahedral in Y site and hydroxyl groups) lie outside of the visible light range, they cannot affect the perceived color. The green tourmaline from Tanzania (Figures 3.19 to 3.23) displays absorption spectra of the main transition metal at 313 to 448 nm (violet and blue regions of the visible light range) and 601 to 610 nm (orange regions of the visible light range) that are attributed to V^{3+} on octahedral site. A small peak at 417, 422 and 425 nm (violet regions of the visible light range) is related to Cr^{3+} with transmission in green, yellowish green and yellow-green colors. The absorption bands at 1421 to 1528 nm are due to hydroxyl groups. The detail of UV-Vis-NIR absorption spectra of green tourmaline samples are given in Appendix A.

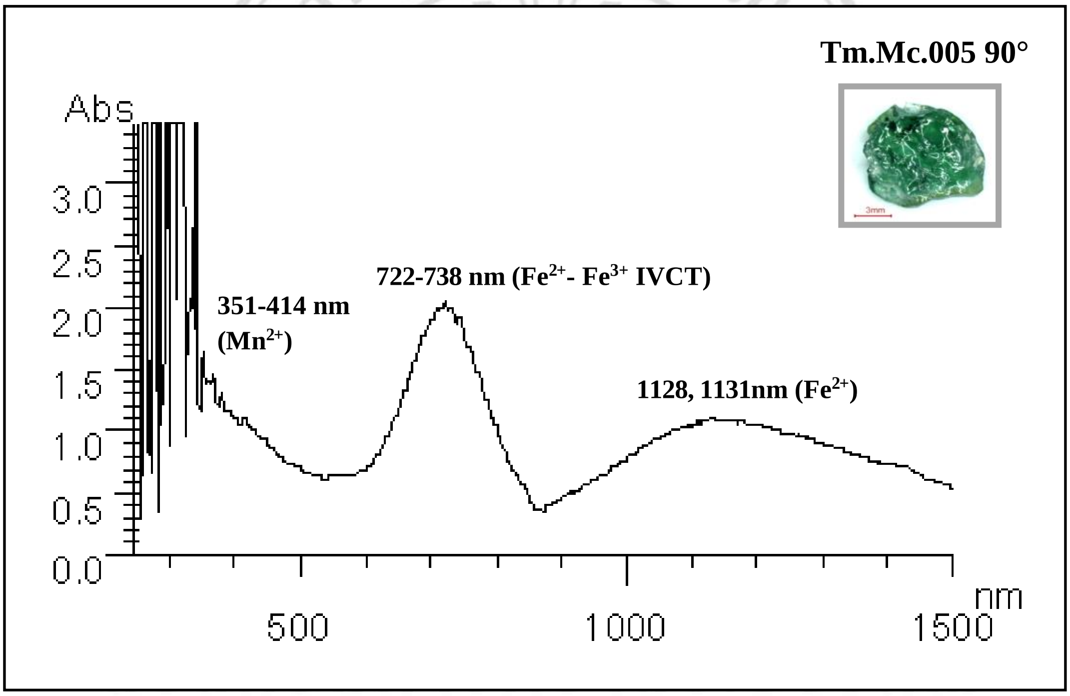

Figure 3.9 UV-Vis-NIR absorption spectra of sample from Madagascar (Tm.Mc.005; green color)

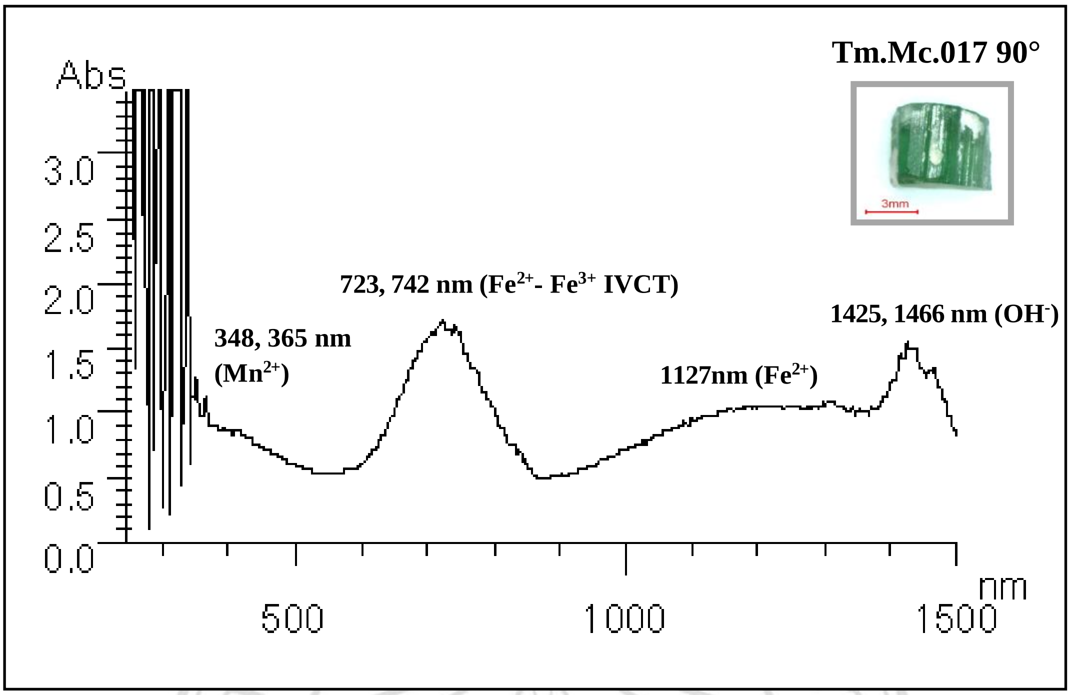

Figure 3.10 UV-Vis-NIR absorption spectra of sample from Madagascar (Tm.Mc.017; green color)

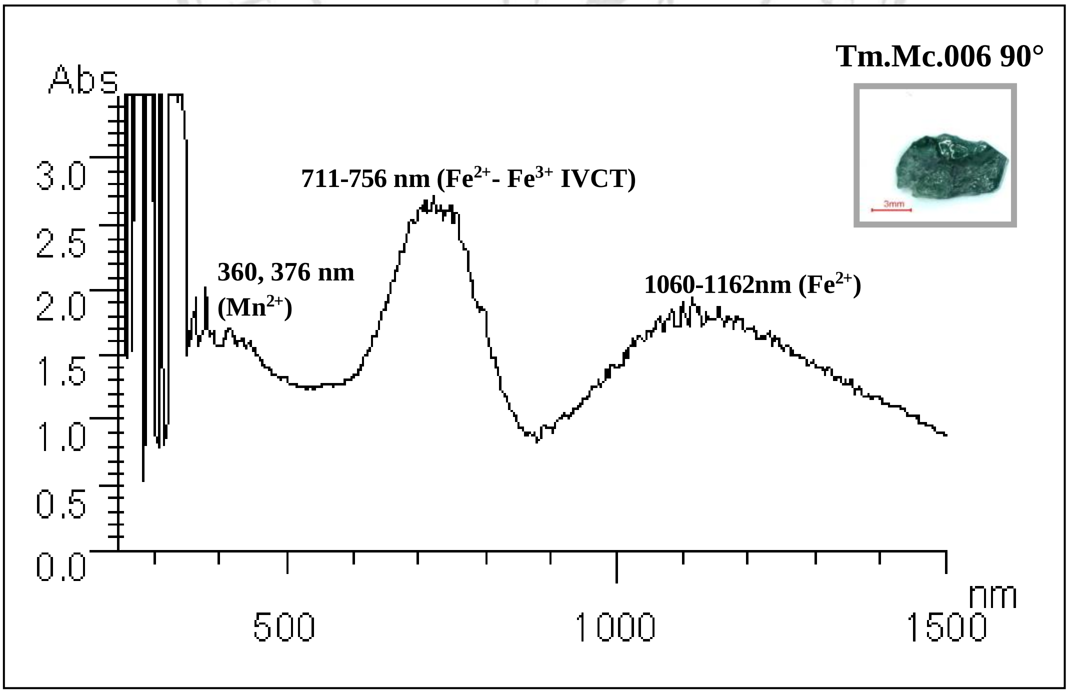

Figure 3.11 UV-Vis-NIR absorption spectra of sample from Madagascar (Tm.Mc.006; bluish green color)

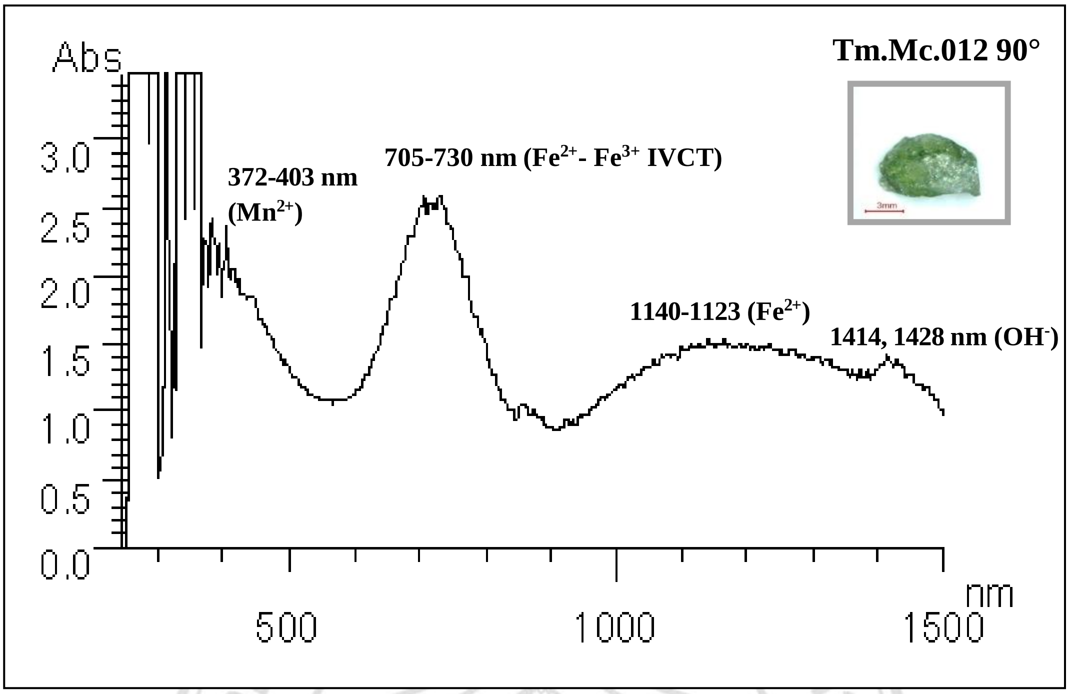

Figure 3.12 UV-Vis-NIR absorption spectra of sample from Madagascar (Tm.Mc.012; yellowish green color)

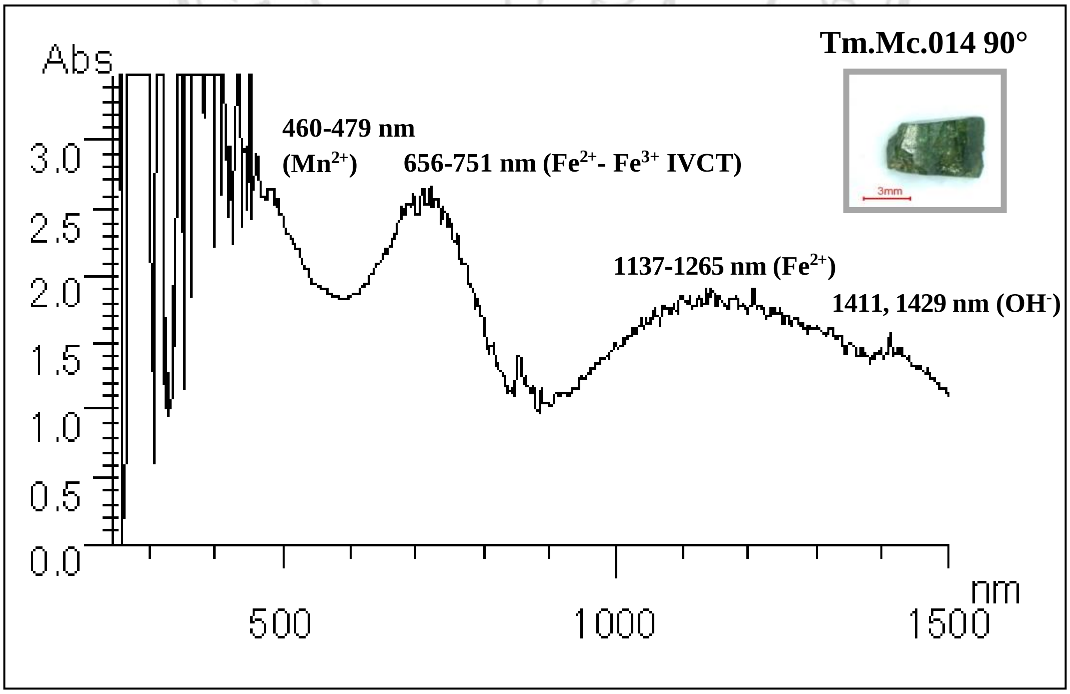

Figure 3.13 UV-Vis-NIR absorption spectra of sample from Madagascar (Tm.Mc.014; yellowish green color)

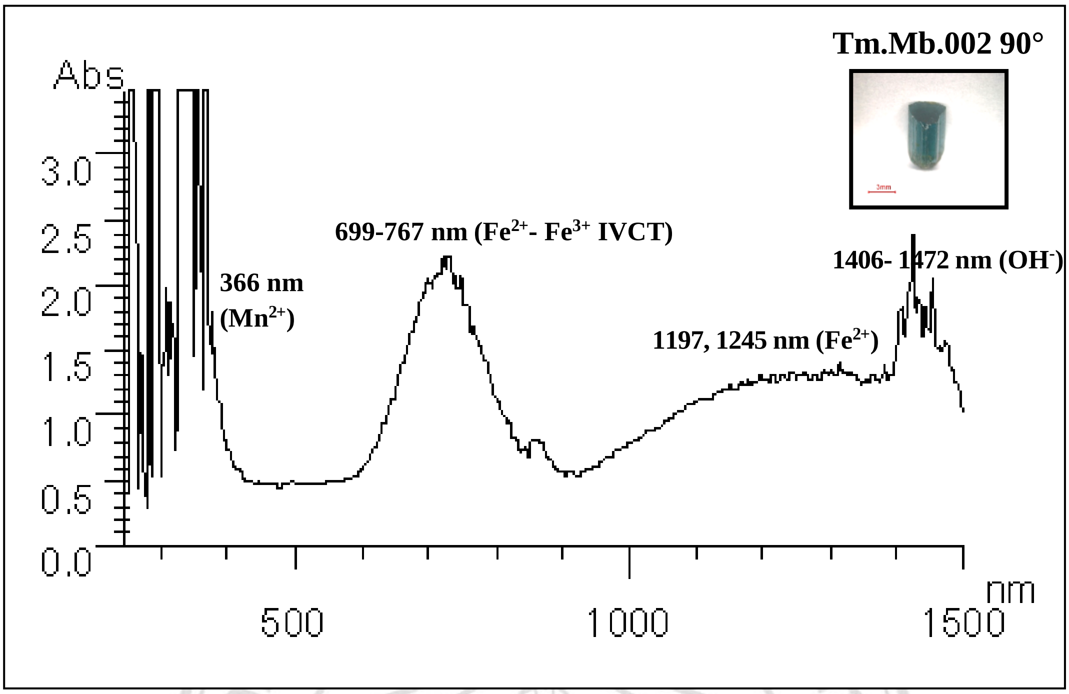

Figure 3.14 UV-Vis-NIR absorption spectra of sample from Mozambique (Tm.Mb.002; greenish blue color)

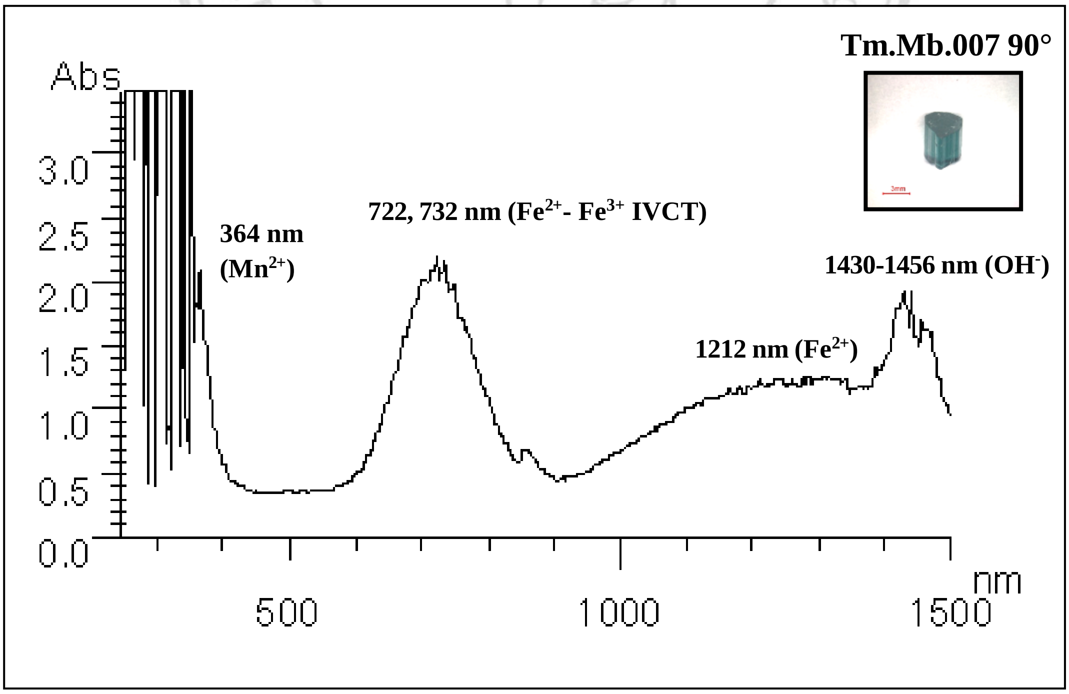

Figure 3.15 UV-Vis-NIR absorption spectra of sample from Mozambique (Tm.Mb.007; greenish blue color)

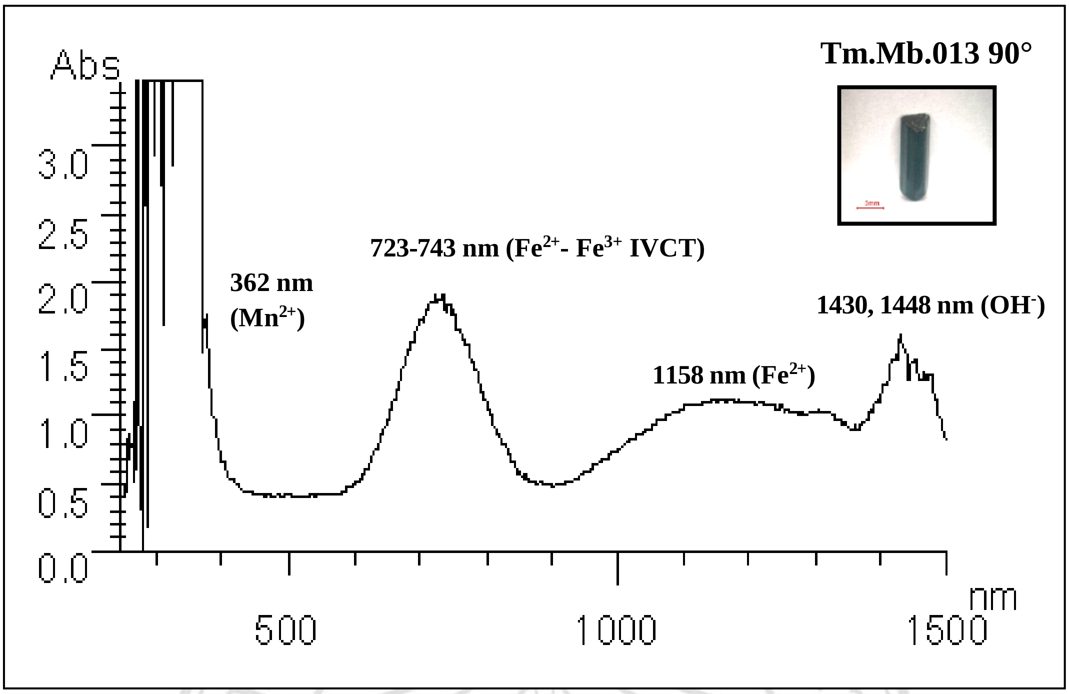

Figure 3.16 UV-Vis-NIR absorption spectra of sample from Mozambique (Tm.Mb.013; blue color)

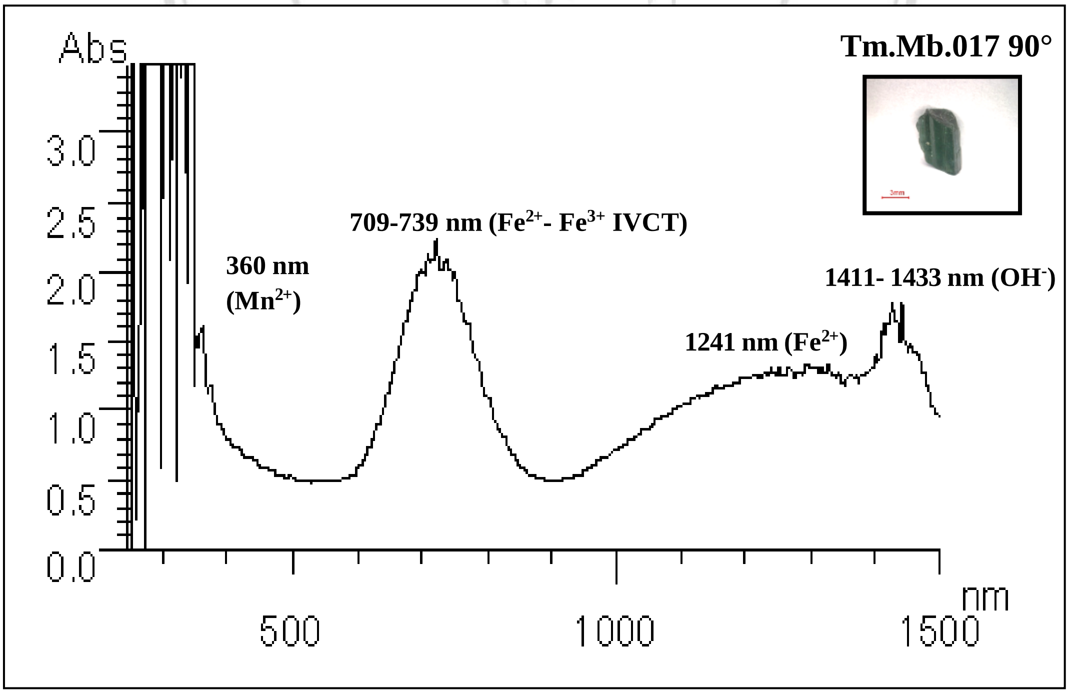

Figure 3.17 UV-Vis-NIR absorption spectra of sample from Mozambique (Tm.Mb.017; green color)

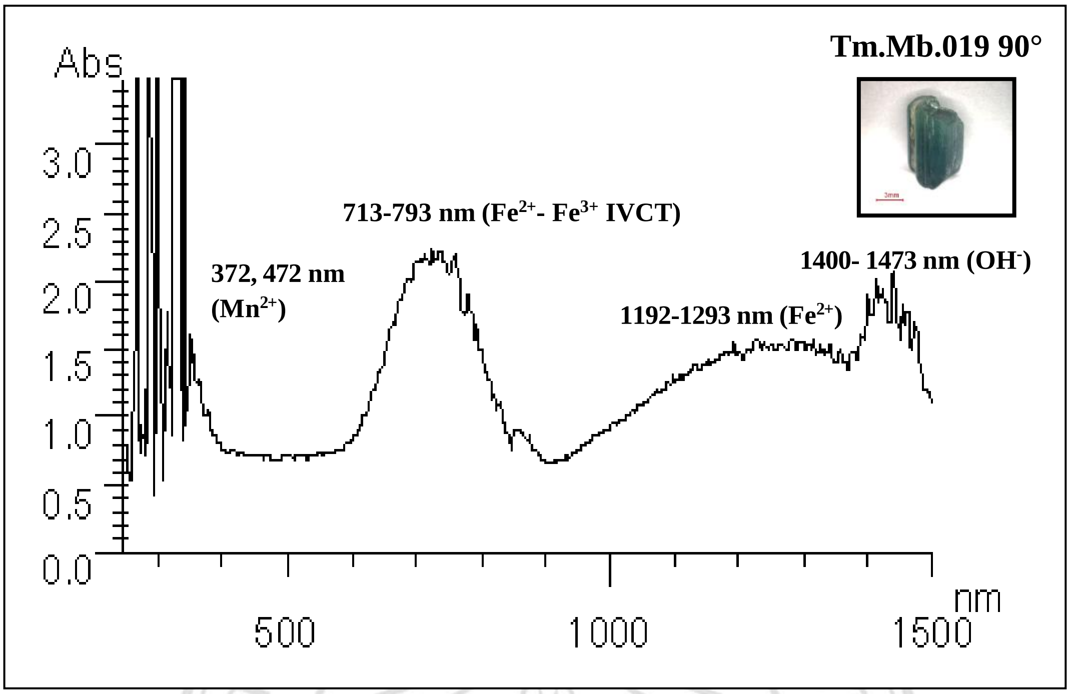

Figure 3.18 UV-Vis-NIR absorption spectra of sample from Mozambique (Tm.Mb.019; bi-color)

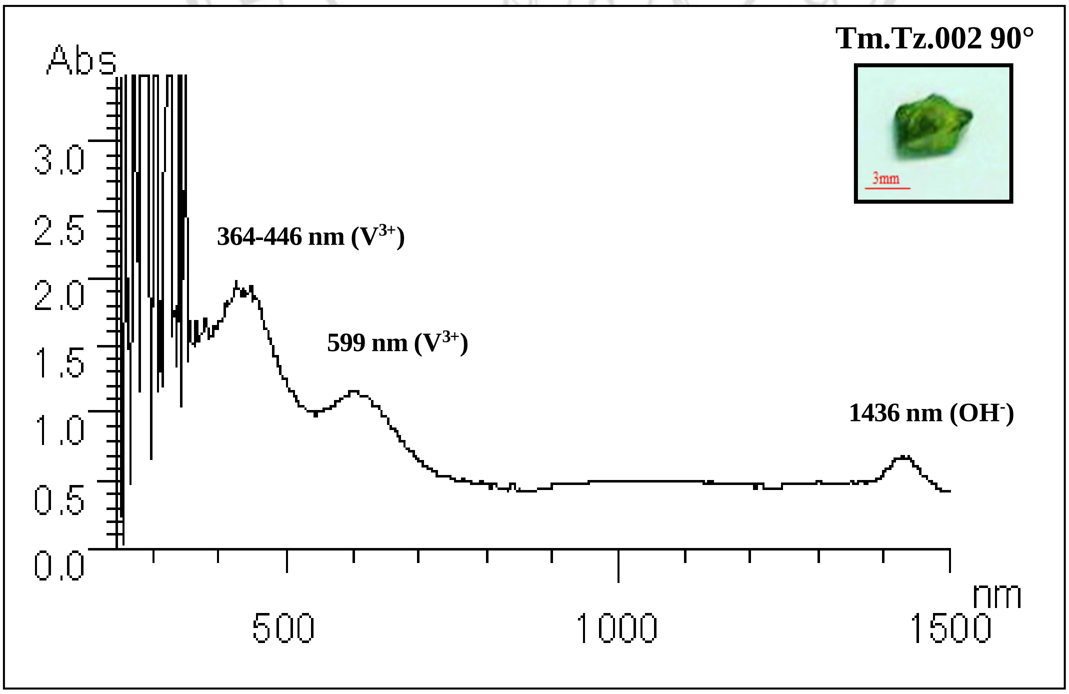

Figure 3.19 UV-Vis-NIR absorption spectra of sample from Tanzania (Tm.Tz.002; yellowish green color)

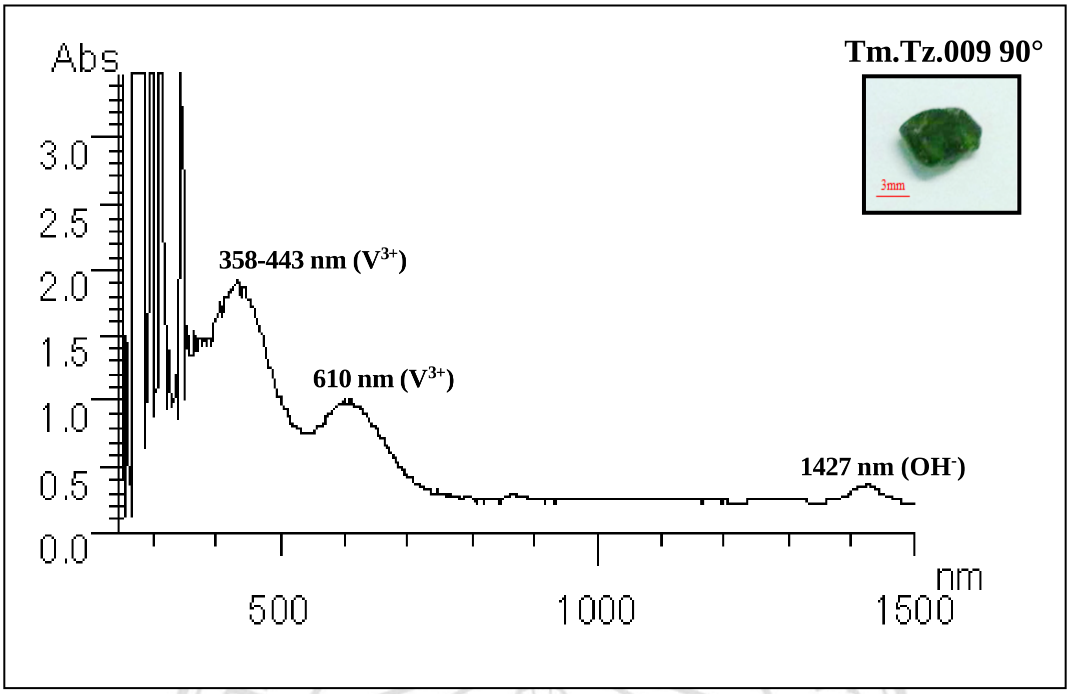

Figure 3.20 UV-Vis-NIR absorption spectra of sample from Tanzania (Tm.Tz.009; yellowish green color)

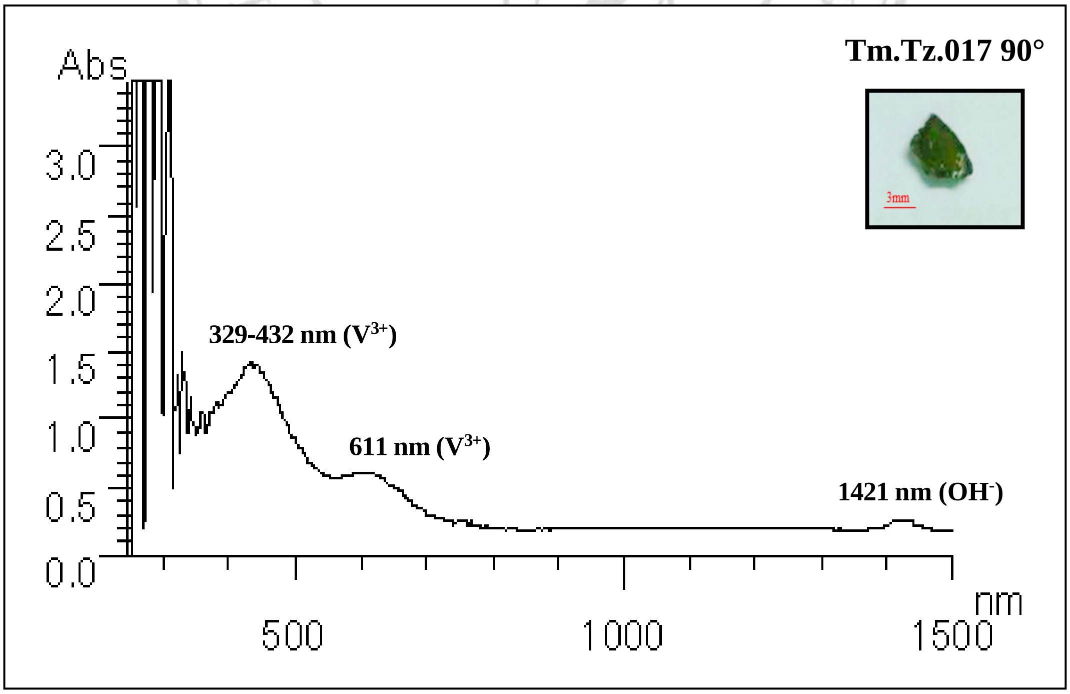

Figure 3.21 UV-Vis-NIR absorption spectra of sample from Tanzania (Tm.Tz.017; Yellow-Green color)

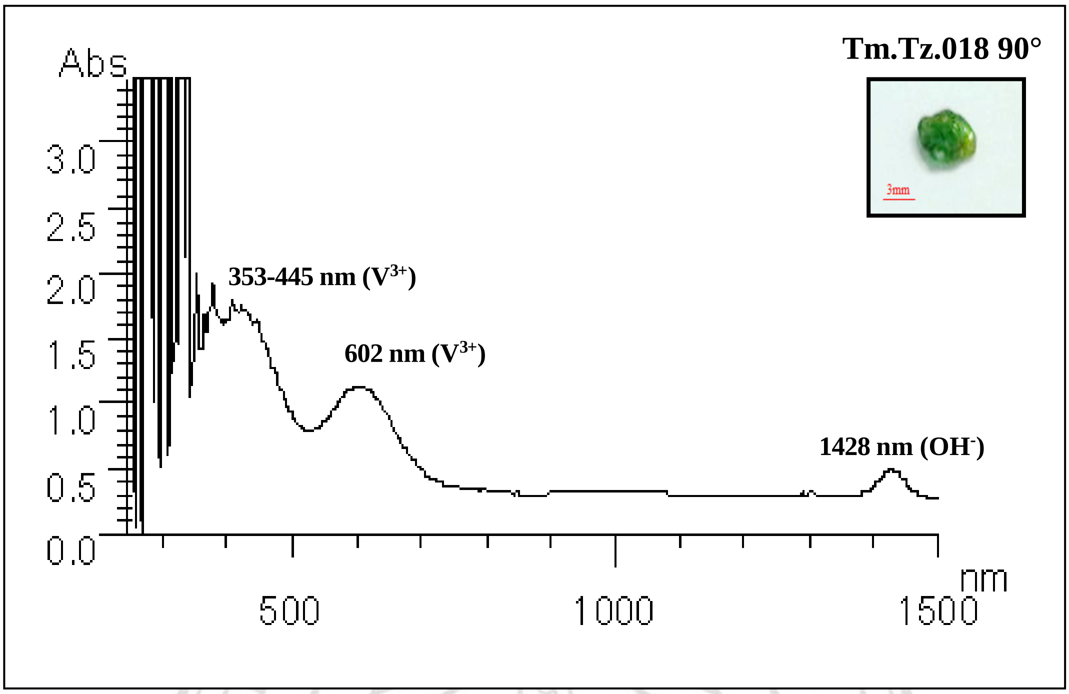

Figure 3.22 UV-Vis-NIR absorption spectra of sample from Tanzania (Tm.Tz.018; green color)

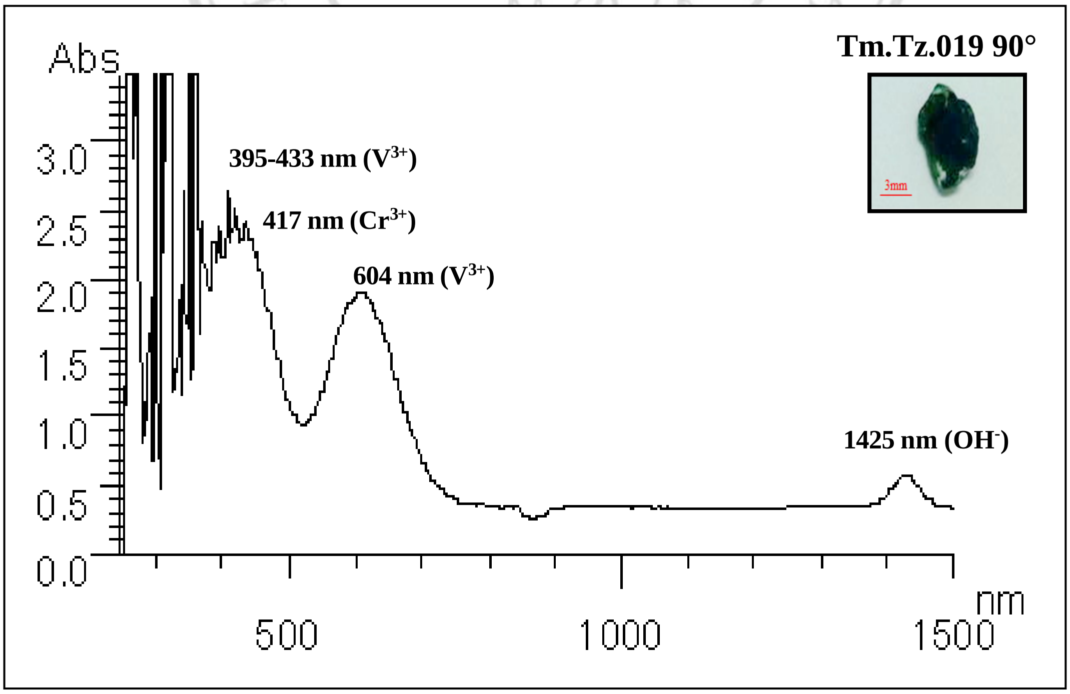

Figure 3.23 UV-Vis-NIR absorption spectra of sample from Tanzania (Tm.Tz.019; green color)

3.4 Fourier Transform Infrared (FTIR) spectra of samples

FTIR absorption spectra were measured in the range 4000-500 cm^{-1} region using Bruker Tensor 27 FTIR spectrometer. These spectra were obtained the stretching vibration of Si-O, BO_3 and hydroxyl groups in the structure of typical green tourmaline samples. Experiment was executed at room temperature using a liquid nitrogen cooled cell. The measurements were saved in oriented single crystal (E//c).

The vibration absorption bands around 1200-820 cm^{-1} are assigned to the stretching vibration of Si_6O_{18} rings. The band at 1110 cm^{-1} is attributed to MgOH bending modes. The sharp bands at around 1350 and 1250 cm^{-1} are related to the stretching vibration modes of BO_3 groups. The stretching modes of hydroxyl groups are observed in the range from 3700 to 3400 cm^{-1} (Figures 3.24 to 3.38). The detail of FTIR absorption spectra of green tourmaline samples are given in Appendix B.

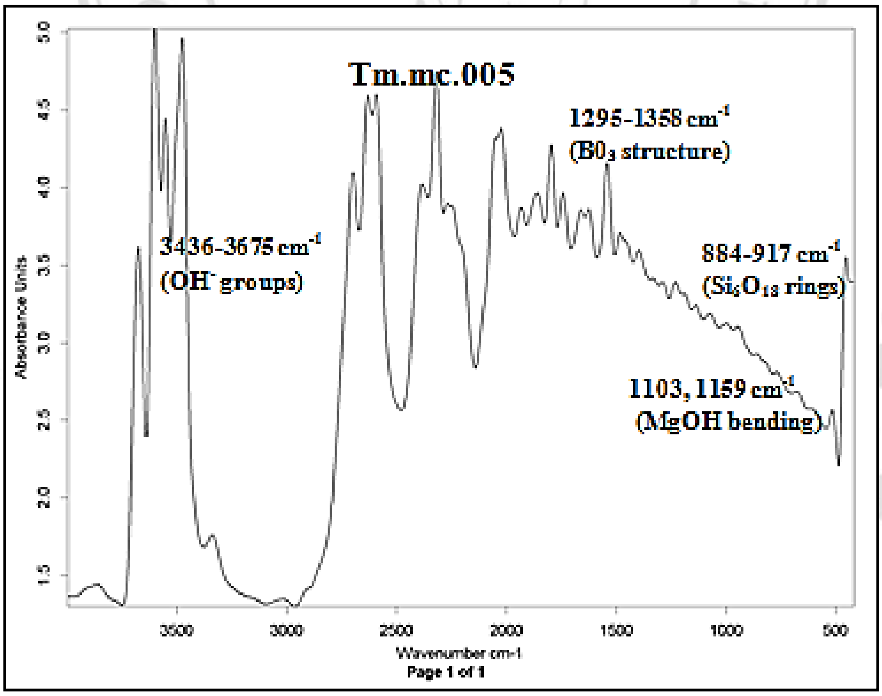

Figure 3.24 Polarized FTIR absorption spectra of sample from Madagascar (Tm.Mc.005)

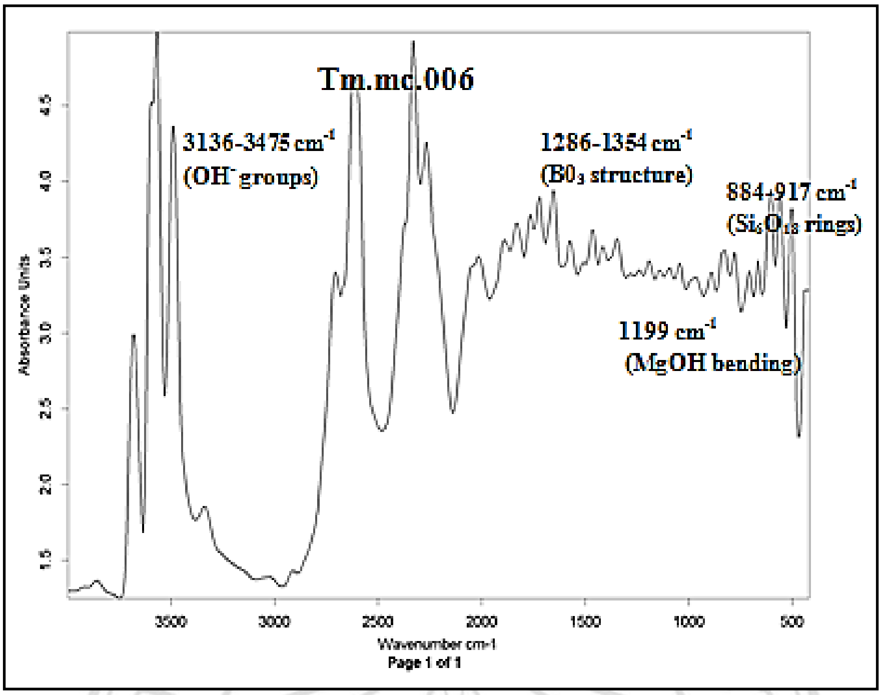

Figure 3.25 Polarized FTIR absorption spectra of sample from Madagascar (Tm.Mc.006)

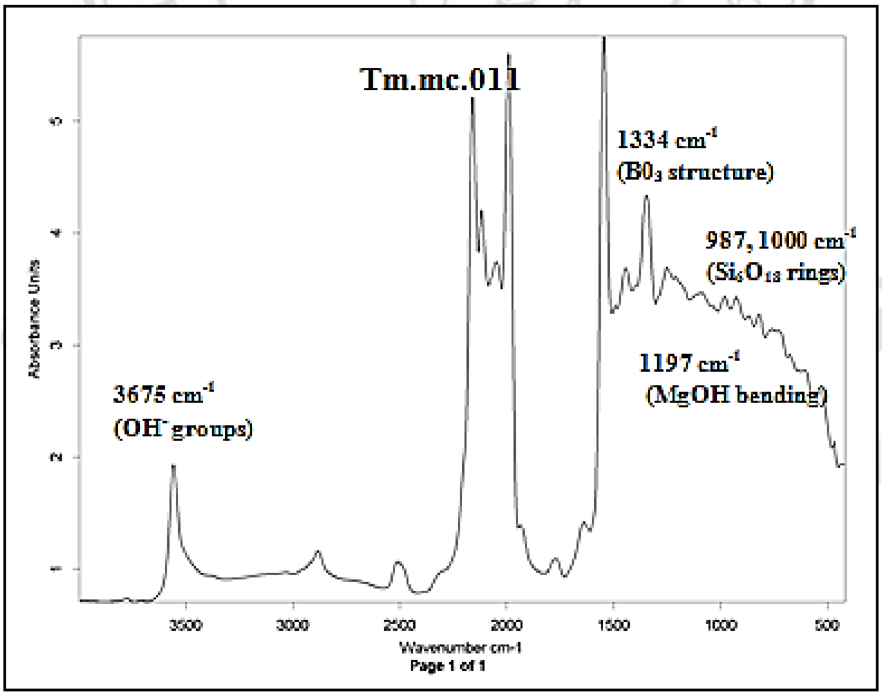

Figure 3.26 Polarized FTIR absorption spectra of sample from Madagascar (Tm.Mc.011)

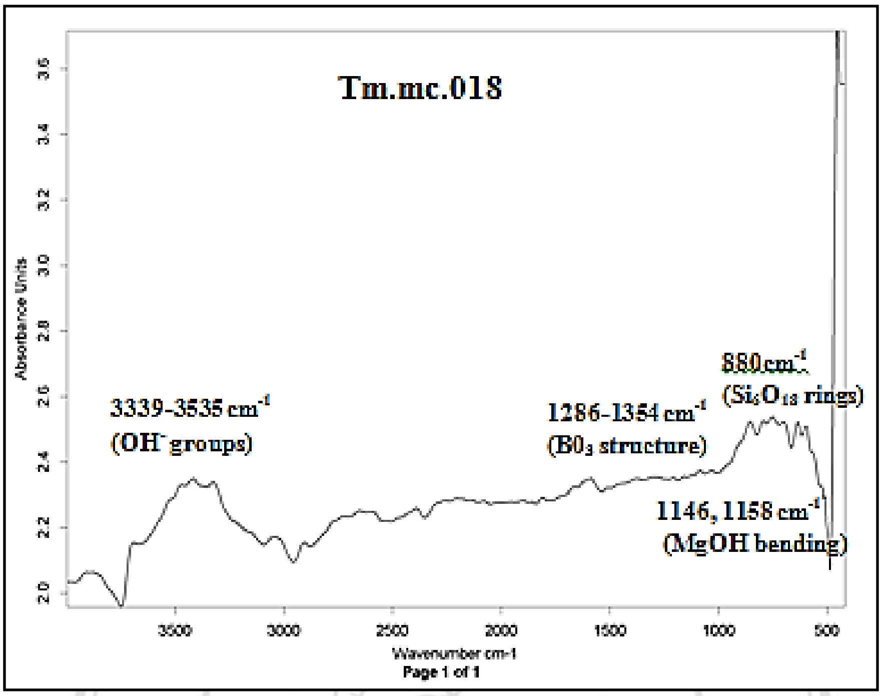

Figure 3.27 Polarized FTIR absorption spectra of sample from Madagascar (Tm.Mc.018)

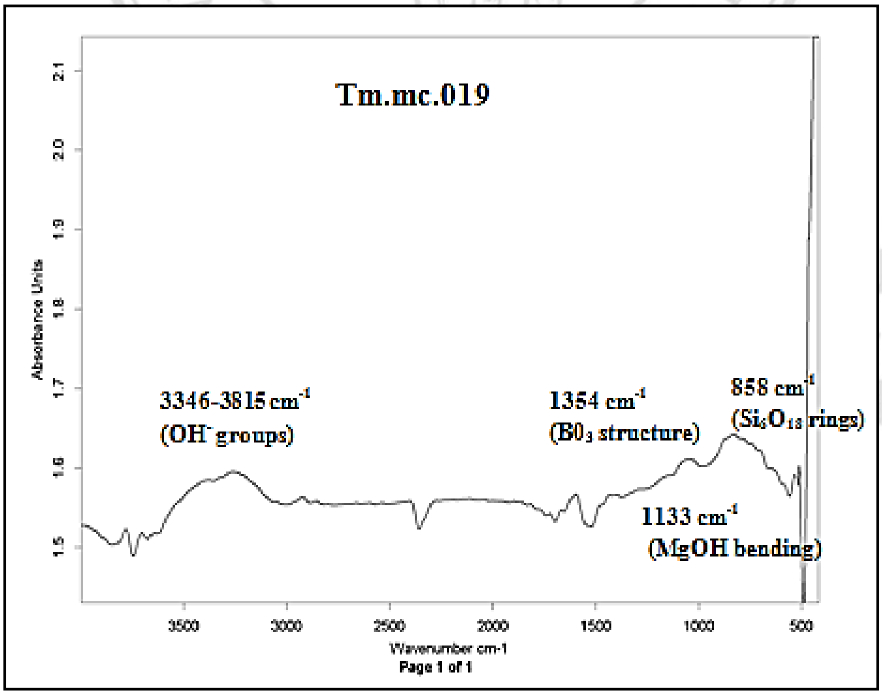

Figure 3.28 Polarized FTIR absorption spectra of sample from Madagascar (Tm.Mc.019)

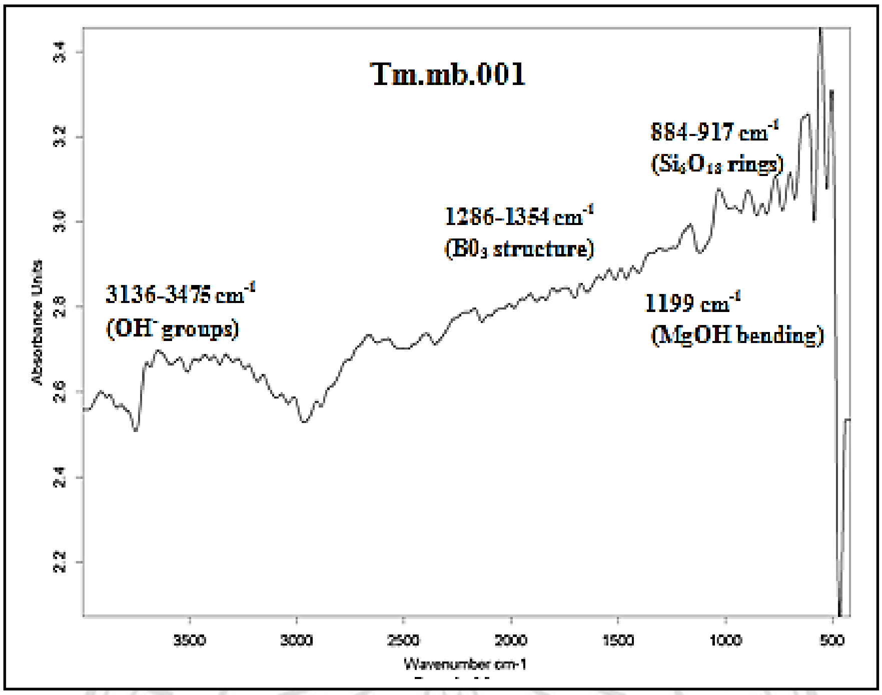

Figure 3.29 Polarized FTIR absorption spectra of sample from Mozambique (Tm.Mb.001)

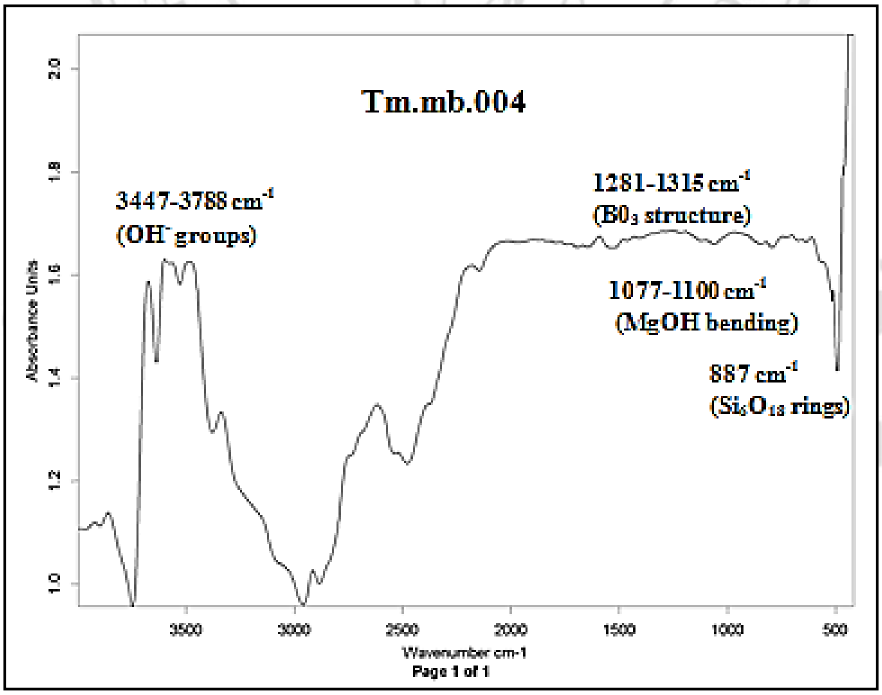

Figure 3.30 Polarized FTIR absorption spectra of sample from Mozambique (Tm.Mb.004)

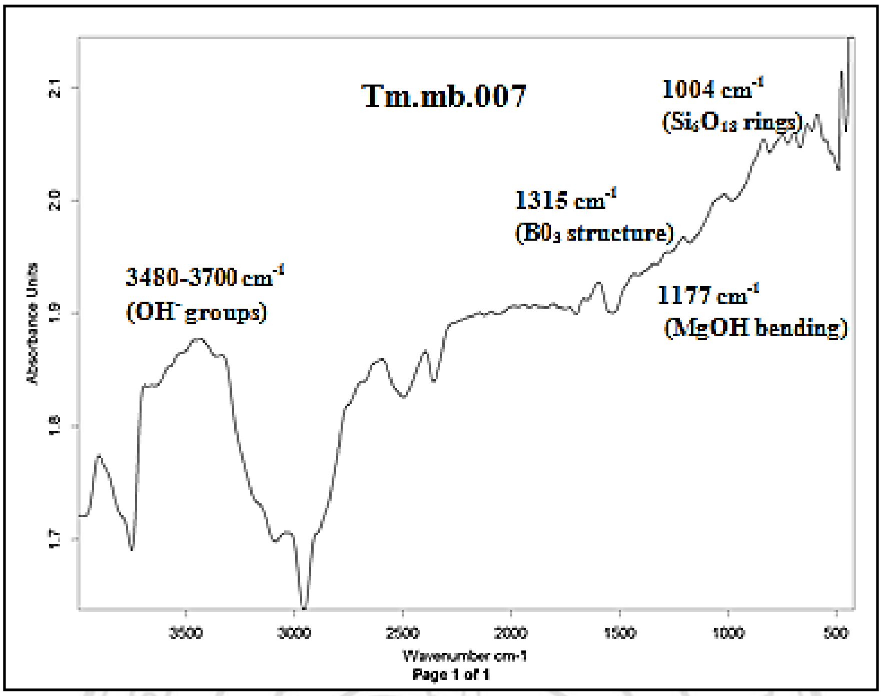

Figure 3.31 Polarized FTIR absorption spectra of sample from Mozambique (Tm.Mb.007)

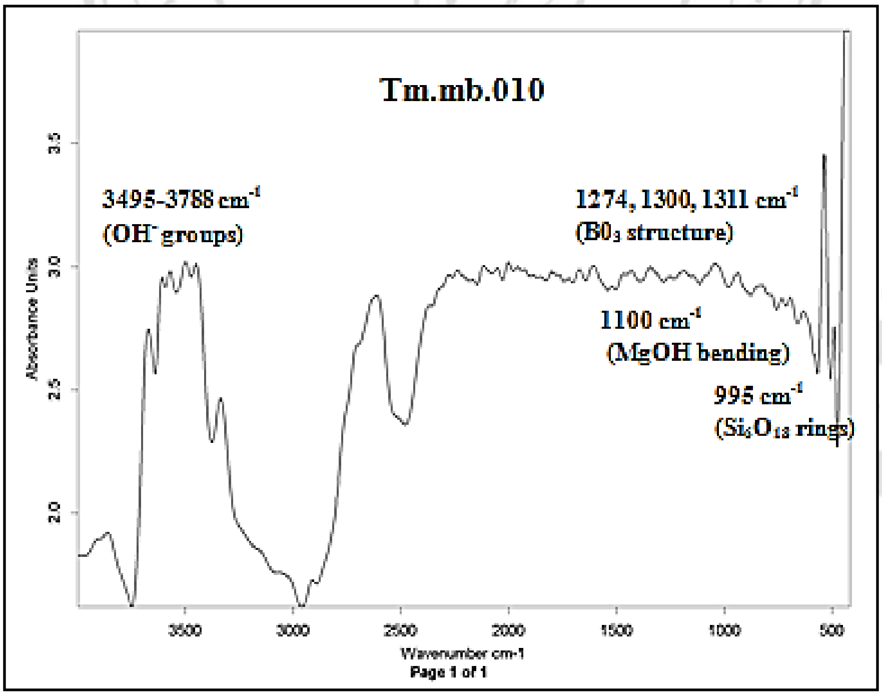

Figure 3.32 Polarized FTIR absorption spectra of sample from Mozambique (Tm.Mb.010)

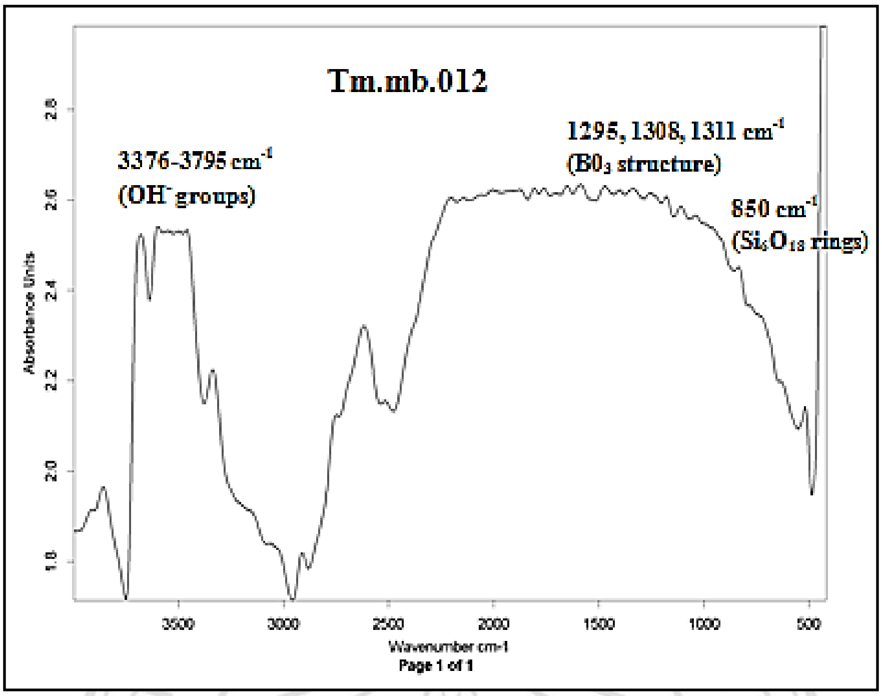

Figure 3.33 Polarized FTIR absorption spectra of sample from Mozambique (Tm.Mb.012)

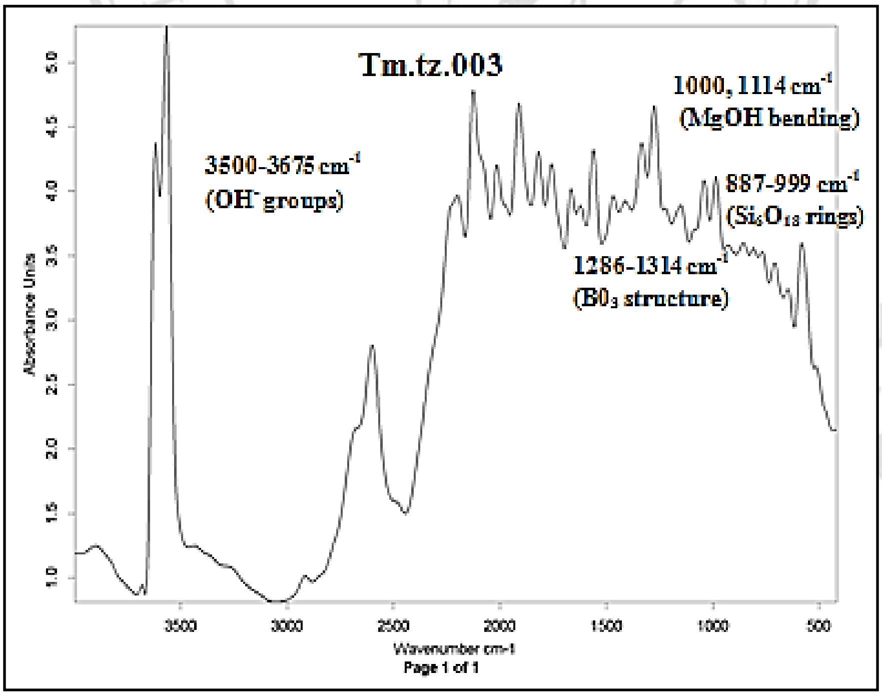

Figure 3.34 Polarized FTIR absorption spectra of sample from Tanzania (Tm.Tz.003)

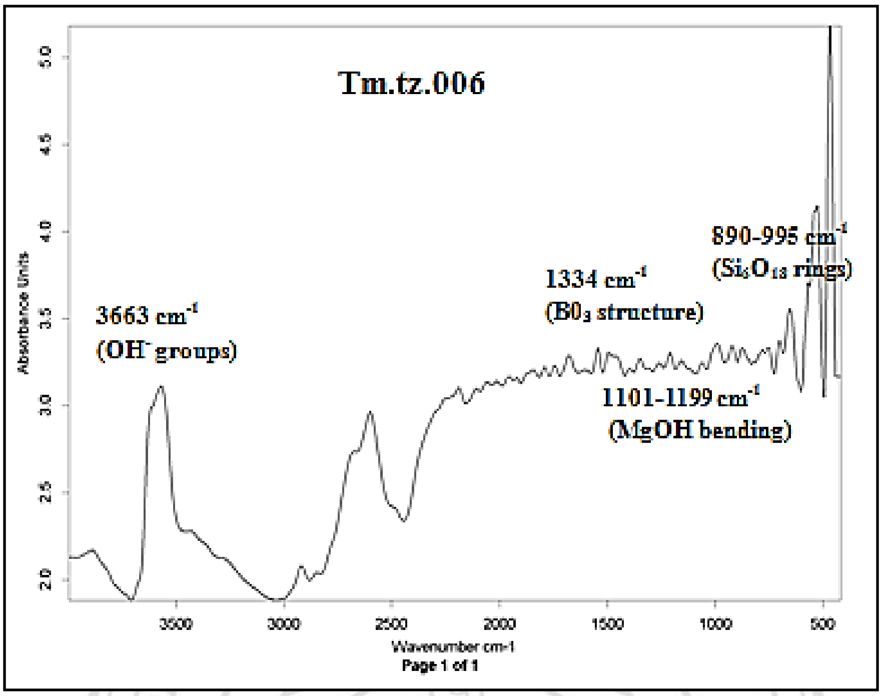

Figure 3.35 Polarized FTIR absorption spectra of sample from Tanzania (Tm.Tz.006)

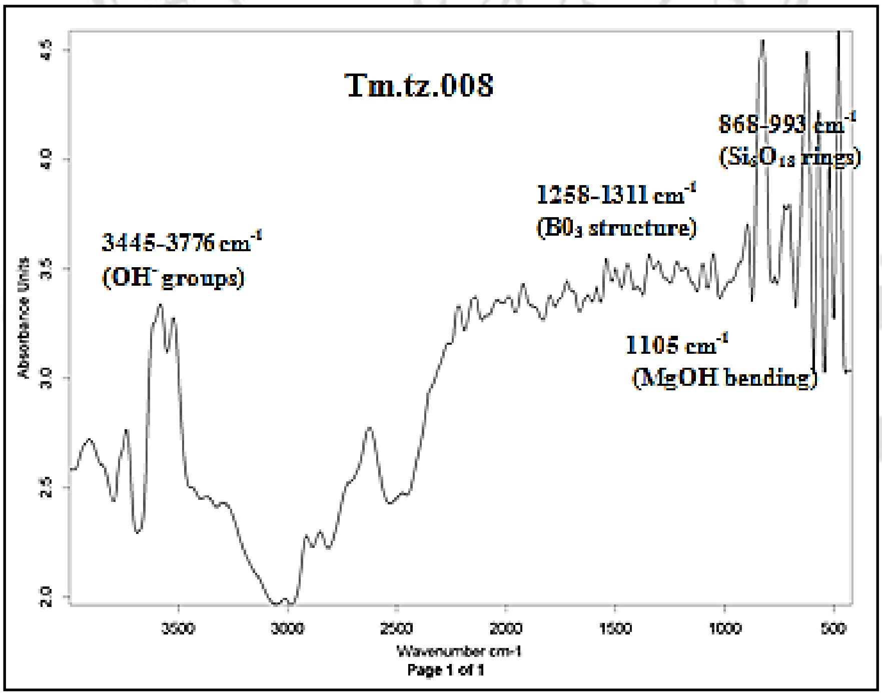

Figure 3.36 Polarized FTIR absorption spectra of sample from Tanzania (Tm.Tz.008)

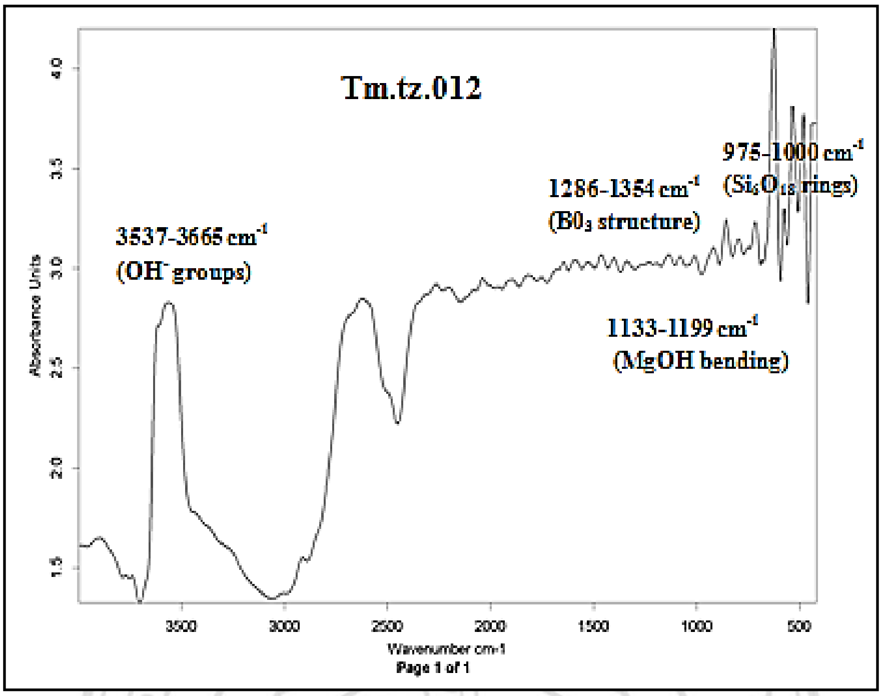

Figure 3.37 Polarized FTIR absorption spectra of sample from Tanzania (Tm.Tz.012)

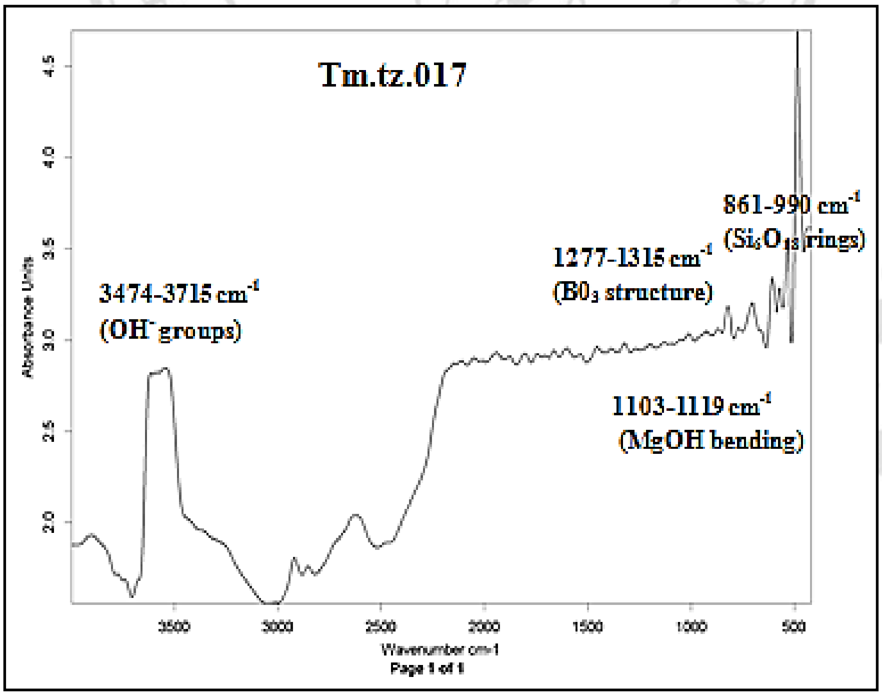

Figure 3.38 Polarized FTIR absorption spectra of sample from Tanzania (Tm.Tz.017)

3.5 Chemical analyses using electron probe micro-analyser (EPMA)

Quantitative chemical analyses were measured using a JEOL Electron Probe Micro-Analyser with wavelength dispersive (WD) analyser. In this study, three point locations on 10 samples of all color groups from different localities were analyzed for Al_2O_3, SiO_2, V_2O_3, MnO, TiO_2, F, B_2O_3, Cr_2O_3, $FeO_{(total)}$, CaO, MgO, Na_2O, CuO, K_2O. Since some elements in tourmalines cannot be measured by EPMA such as Li_2O and H_2O, which can be recalculated as 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 Julie Selway & Jian Xiong. A detail of chemical analyses of three random locations on ten representative green tourmaline samples are given in Appendix C.

3.5.1 Group I : The samples from Madagascar

The analytical results of green tourmalines from Madagascar showed that all samples were elbaite. The chromophoric elements Fe and Mn were typically in the samples from Madagascar. They range in color from green, yellowish green and watermelon tourmaline (pink cores and green rims). The T, B and Z sites: SiO_2 ranges from 36.12 to 38.67 wt.% and 5.746 to 6.076 apfu Si at the T-site. B_2O_3 ranges from 10.61 to 11.10 wt.% at B-site with 2.878 to 3.063 apfu B. The Al totals quantities are between 40.04 to 40.40 wt.% Al_2O_3. Y-site Al: This has a range from 1.311 to 1.472 apfu Al. The Ti content was very low or below detection limit in these samples ranges from 0.01 to 0.02 wt.% TiO_2 and 0.001 to 0.002 apfu. The Mg contents were ranging from 0.05 to 0.10 wt.% MgO and 0.012 to 0.023 apfu, in all analyses Mg was very low to below the limit of detection. The Mn content is a wide range in the various colors of samples. The Mn ranges from 0.54 to 1.66 wt.% MnO and 0.073 to 0.224 apfu. The high content of Mn was observed in green and watermelon tourmaline (spot in pink core) samples.

The samples from Madagascar have Fe contents ranging from 3.02 to 3.57 wt.% FeO (all iron reported as FeO) and 0.396 to 0.475 apfu. The highest Fe values were found in green, yellowish green to brownish green and watermelon tourmaline. The Li contents were calculated ranging from 1.51 to 1.80 wt.% Li_2O and 0.952 to 1.157 apfu. The yellowish green to brownish green sample has the highest Li concentrations, followed by the green and watermelon tourmaline samples. The X-site totals: Ca content has a range from 0.17 to 0.72 wt.% CaO and 0.029 to 0.123 apfu. The Na-rich were found in X-site a range from 1.75 to 2.36 wt.% Na_2O and 0.532 to 0.728 apfu Na, whereas quantities increase at green color. The K is low contents of green elbaite samples. It contained 0.02 wt.% K_2O and 0.004 apfu. The hydroxyl anion and calculated water: The wt.% of calculated H_2O varies from 3.41 to 3.59, whereas OH ranges from 3.636 to 3.766 apfu at the V and W-sites. Fluorine: The F content varies from 0.20 to 0.30 wt.% and 0.234 to 0.364 apfu F. The EPMA analyses of green tourmalines of various colors from Madagascar are summarized in Table 3.4.

Table 3.4 EPMA analyses of green tourmaline of various colors from Madagascar

Chemical composition	Madagascar			
	yellowish Green to brownish Green	Green	Watermelon	
			yellowish Green	Purplish Red
Oxide (wt.%)				
Al_2O_3	40.04	40.35	40.10	40.40
SiO_2	36.12	36.12	38.67	38.35
V_2O_3	bdl	bdl	bdl	bdl
MnO	0.54	1.66	1.05	1.17
TiO_2	0.02	bdl	bdl	0.01
F	0.72	0.68	0.47	0.58
B_2O_3	11.10	11.02	10.61	10.73
Cr_2O_3	bdl	bdl	bdl	bdl
FeO	3. 26	3.57	3. 25	3.02
CaO	0.72	0.36	0.17	0.45
MgO	0.05	bdl	0.09	0.10
Na_2O	1.99	2.36	1.84	1.75
CuO	0.01	bdl	0.02	0.02
K_2O	0.02	0.02	0.02	0.02
Li_2O calc.	1.80	1.55	1.56	1.51
H_2O calc.	3.41	3.45	3.59	3.55
Subtotal	99.80	101.14	101.44	101.66
-O=F	0.30	0.29	0.20	0.24
Total	**99.50**	**100.85**	**101.24**	**101.42**
Ions per 31 (O,OH,F)				
T: Si	5.775	5.746	6.076	6.018
Al	0.225	0.254	0.000	0.000
B	3.063	3.026	2.878	2.906
Z: Al	6.000	6.000	6.000	6.000
Mg	0.000	0.000	0.000	0.000
Cr	0.000	0.000	0.000	0.000
Fe^{3+}	0.000	0.000	0.000	0.000
Y: Al	1.320	1.311	1.426	1.472
Ti	0.002	0.000	0.000	0.001
V	0.000	0.000	0.000	0.000
Cr	0.000	0.000	0.000	0.000
Fe^{3+}	0.000	0.000	0.000	0.000
Mg	0.012	0.000	0.021	0.023
Mn	0.073	0.224	0.140	0.156
Fe^{2+}	0.436	0.475	0.427	0.396
Zn	0.000	0.000	0.000	0.000
Li*	1.157	0.990	0.986	0.952
?Y	3.000	3.000	3.000	3.000
X: Ca	0.123	0.061	0.029	0.076
Na	0.617	0.728	0.561	0.532
K	0.004	0.004	0.004	0.004
r	0.256	0.207	0.407	0.388
OH	3.636	3.658	3.766	3.712
F	0.364	0.342	0.234	0.288
Cl	0.000	0.000	0.000	0.000
Mineral name	Elbaite	Elbaite	Elbaite	Elbaite

Abbreviation: bdl = below detection limit
Li_2O, H_2O were calculated as mineral structural formula based on stoichiometric principles

3.5.2 Group II : The samples from Mozambique

The analytical results of green tourmalines from Mozambique showed that all samples consist of elbaite. The chromophoric elements Fe and Mn exhibited strong correlation with color. They range in color from greenish blue, blue, green and bi-color tourmaline. The T, B and Z sites: SiO_2 ranges from 35.01 to 36.19 wt.%. and 5.604 to 5.918 apfu Si at the T-site. B_2O_3 ranges from 10.52 to 11.28 wt.% at B-site with 2.942 to 3.101 apfu B. The Al totals quantities are between 40.26 to 40.93 wt.% Al_2O_3 and filled at T-sites between 0.082 to 0.399 apfu and Z-sites with 6.000 apfu. The Y-site Al: This has a range from 0.082 to 0.399 apfu Al. The Ti content was very low or below detection limit in these samples ranges from 0 to 0.01 wt.% TiO_2 and 0 to 0.001 apfu. The Mg contents were ranging from 0 to 0.06 wt.% MgO and 0 to 0.014 apfu, in all analyses Mg was very low to below the limit of detection and increased in green color. The Mn content is a wide range in the various colors of samples. Mn ranges from 0.82 to 2.20 wt.% MnO and 0.108 to 0.298 apfu. The highest Mn values were found in blue color of bi-color tourmaline. The Fe content ranging from 2.22 to 3.74 wt.% FeO (all iron reported as FeO) and 0.297 to 0.499 apfu. Fe content was highest in green color and was lowest in blue color of bi-color tourmaline. The Li contents were calculated ranging from 1.36 to 1.85 wt.% Li_2O and 0.884 to 1.161 apfu. The blue sample has the highest Li concentrations, followed by the green, bi-color tourmaline and greenish blue samples. The X-site totals: The samples revealed lower Ca content. The Ca content has a range from 0.23 to 0.57 wt.% CaO and 0.039 to 0.098 apfu. The Na-rich were found in X-site a range from 1.08 to 2.40 wt.% Na_2O and 0.599 to 0.754 apfu Na. The Na content was highest in greenish blue color. The K is low contents of green elbaite samples. Its varies from 0.01 to 0.02 wt.% K_2O and 0.002 to 0.004 apfu. The hydroxyl anion and calculated water: The wt.% of calculated H_2O varies from 3.34 to 3.62, whereas OH ranges from 3.611 to 3.763 apfu at the V and W-sites. Fluorine: The F content varies from 0.20 to 0.32 wt.% and 0.237 to 0.389 apfu. The EPMA analyses of green tourmalines of various colors from Mozambique are summarized in Table 3.5.

Table 3.5 EPMA analyses of green tourmaline of various colors from Mozambique

Chemical composition	Mozambique				
	Blue	greenish Blue	Green	Bi-color	
				Blue	greenish Blue
Oxide (wt.%)					
Al_2O_3	40.70	40.93	40.26	40.33	40.61
SiO_2	37.93	35.14	36.12	36.19	35.01
V_2O_3	bdl	0.01	bdl	bdl	0.02
MnO	0.82	1.26	0.99	2.20	1.74
TiO_2	bdl	0.01	0.01	bdl	bdl
F	0.48	0.76	0.52	0.54	0.62
B_2O_3	11.28	10.52	11.14	10.84	11.23
Cr_2O_3	bdl	bdl	bdl	bdl	0.02
FeO	2.51	3.18	3.74	2.22	3.39
CaO	0.37	0.27	0.23	0.57	0.39
MgO	bdl	bdl	0.06	0.01	0.03
Na_2O	1.08	2.40	2.17	2.08	2.37
CuO	0.01	0.03	bdl	0.03	bdl
K_2O	0.02	0.01	0.02	0.02	0.02
Li_2O calc.	1.85	1.36	1.61	1.57	1.62
H_2O calc.	3.62	3.34	3.52	3.49	3.45
Subtotal	101.57	99.22	100.38	100.09	100.52
-O=F	0.20	0.32	0.22	0.23	0.26
Total	**101.37**	**98.90**	**100.16**	**99.86**	**100.26**
Ions per 31 (O,OH,F)					
T: Si	5.918	5.694	5.758	5.790	5.601
Al	0.082	0.306	0.242	0.210	0.399
B	3.038	2.942	3.065	2.993	3.101
Z: Al	6.000	6.000	6.000	6.000	6.000
Mg	0.000	0.000	0.000	0.000	0.000
Cr	0.000	0.000	0.000	0.000	0.000
Fe^{3+}	0.000	0.000	0.000	0.000	0.000
Y: Al	1.403	1.510	1.322	1.394	1.258
Ti	0.000	0.001	0.001	0.000	0.000
V	0.000	0.001	0.000	0.000	0.003
Cr	0.000	0.000	0.000	0.000	0.003
Fe^{3+}	0.000	0.000	0.000	0.000	0.000
Mg	0.000	0.000	0.014	0.002	0.007
Mn	0.108	0.173	0.134	0.298	0.236
Fe^{2+}	0.328	0.431	0.499	0.297	0.454
Zn	0.000	0.000	0.000	0.000	0.000
Li*	1.161	0.884	1.031	1.009	1.040
?Y	3.000	3.000	3.000	3.000	3.000
X: Ca	0.062	0.047	0.039	0.098	0.067
Na	0.599	0.754	0.671	0.645	0.735
K	0.004	0.002	0.004	0.004	0.004
r	0.335	0.197	0.286	0.253	0.194
OH	3.763	3.611	3.738	3.727	3.686
F	0.237	0.389	0.262	0.273	0.314
Cl	0.000	0.000	0.000	0.000	0.000
Mineral name	Elbaite	Elbaite	Elbaite	Elbaite	Elbaite

Abbreviation: bdl = below detection limit

Li_2O, H_2O were calculated as mineral structural formula based on stoichiometric principles

3.5.3 Group III : The samples from Tanzania

The analytical results of green tourmalines from Tanzania showed that all samples consist of uvite. The chromophoric elements V and Cr were typically in the samples from Tanzania. They range in color from yellowish green, yellow-green and green. The T, B and Z sites: SiO_2 ranges from 38.23 to 38.96 wt.% and 6.225 to 6.619 apfu Si at the T-site. The B_2O_3 ranges from 10.42 to 10.85 wt.% at B-site with 2.896 to 3.022 apfu B. Al totals quantities are between 27.15 to 27.18 wt.% Al_2O_3 and filled at Z-sites between 5.152 to 5.170 apfu. The Mg content was ranging from 0.830 to 0.848 apfu at Z-sites. The Y-site: Ti content has a range from 0.12 to 0.20 wt.% TiO_2 and 0.015 to 0.024 apfu Ti. The high Mg contents were ranging from 12.12 to 13.30 wt.% MgO and 2.086 to 2.386 apfu. The Mn content was very low to below the limit of detection in the various colors of samples. The Mn ranges from bdl to 0.02 wt.% MnO and 0.000 to 0.003 apfu. The V content was very low from 0.19 to 0.25 wt.% V_2O_3 and 0.025-0.032 apfu. The highest V values were found in green color. The Cr contents in various colors were measured between 0.07 to 0.09 wt.% Cr_2O_3 and 0.009 to 0.011 apfu. The highest Cr values were found in green color sample. The Fe content was very low from 0.01 to 0.03 wt.% FeO (all iron reported as FeO) and 0.000 to 0.004 apfu. The Fe content was highest in yellow-green color and was lowest in green color. The Li contents were calculated ranging from 0.89 to 1.32 wt.% Li_2O and 0.573 to 0.856 apfu. The green sample has the highest Li concentrations, followed by the yellowish green and yellow-green samples. The X-site totals: The Ca-rich were found in X-site a range from 3.74 to 4.64 wt.% CaO and 0.645 to 0.802 apfu Ca. The Ca content was highest in yellow-green color. The Na content has a range from 0.88 to 1.24 wt.% Na_2O and 0.275 to 0.387 apfu. The K contents varies from 0.03 to 0.07 wt.% K_2O and 0.006 to 0.014 apfu. The hydroxyl anion and calculated water: The wt.% of calculated H_2O varies from 3.47 to 3.65, whereas OH ranges from 3.725 to 3.924 apfu at the V and W-sites. Fluorine: The F content varies from 0.06 to 0.23 wt.% and 0.077 to 0.276 apfu F. The EPMA analyses of green tourmalines of various colors from Tanzania are summarized in Table 3.6.

Table 3.6 EPMA analyses of green tourmaline of various colors from Tanzania

Chemical composition	Tanzania		
	Yellow- Green	yellowish Green	Green
Oxide (wt.%)			
Al_2O_3	27.18	27.15	27.19
SiO_2	38.23	38.96	38.58
V_2O_3	0.19	0.20	0.25
MnO	0.01	0.02	bdl
TiO_2	0.12	0.12	0.20
F	0.54	0.53	0.15
B_2O_3	10.57	10.42	10.85
Cr_2O_3	0.08	0.07	0.09
FeO	0.03	0.01	bdl
CaO	4.64	3.74	3.76
MgO	13.36	13.20	12.12
Na_2O	0.88	1.24	1.16
CuO	bdl	bdl	0.02
K_2O	0.03	0.03	0.07
Li_2O calc.	0.89	1.09	1.32
H_2O calc.	3.47	3.51	3.65
Subtotal	100.21	100.76	99.39
-O=F	0.23	0.22	0.06
Total	**99.98**	**100.54**	**99.33**
Ions per 31 (O,OH,F)			
T: Si	6.161	6.216	6.217
Al	0.000	0.000	0.000
B	2.940	3.000	3.018
Z: Al	5.162	5.105	5.164
Mg	0.838	0.895	0.836
Cr	0.000	0.000	0.000
Fe^{3+}	0.000	0.000	0.000
Y: Al	0.000	0.000	0.000
Ti	0.015	0.014	0.024
V	0.025	0.026	0.032
Cr	0.010	0.009	0.011
Fe^{3+}	0.000	0.000	0.000
Mg	2.372	2.245	2.076
Mn	0.001	0.003	0.000
Fe^{2+}	0.004	0.001	0.000
Zn	0.000	0.000	0.000
Li*	0.573	0.702	0.856
?Y	3.000	3.000	3.000
X: Ca	0.801	0.639	0.649
Na	0.275	0.384	0.362
K	0.006	0.006	0.014
r	0.000	0.000	0.000
OH	3.725	3.733	3.924
F	0.275	0.267	0.076
Cl	0.000	0.000	0.000
Mineral name	Uvite	Uvite	Uvite

Abbreviation: bdl = below detection limit

Li_2O, H_2O were calculated as mineral structural formula based on stoichiometric principles

3.6 Chemical analyses using Laser Ablation-Inductively coupled plasma-mass Spectroscopy (LA-ICP-MS)

The chemical analyses were measured using a using an Agilent 7500a (inductively coupled plasma-mass spectrometer) joined to the New Wave UP-213 laser-ablation adjustment. In this study, three random locations on ten representative samples of all color groups from different localities were analyzed minor and trace elements for Li, Be, Sc, Ti, V, Cr, Fe, Ni, Zn, Ga, Ge, Sr, Nb, Mo, Sn, Sb, Ta, Pb and Bi. This method can be measured in the range of parts per million (ppm). The results are described for each of color groups from Madagascar, Mozambique and Tanzania, which is summarized in Tables 3.7 to 3.9. A detail of chemical analyses of three random locations on ten representative green tourmaline samples are given in Appendix D.

3.6.1 Group I : The samples from Madagascar

The analytical results of green tourmalines from Madagascar showed that all samples were elbaite. They range in color from green, yellowish green to brownish green and watermelon tourmaline (pink core and green rim). The most abundant trace elements were Li, Fe, Zn, Ga, Sn, Pb and Bi. Samples contained high level of Li contents ranging from 1424.74 to 1722.44 ppm. The high contents of Li were observed in watermelon tourmaline (pink core and green rim). The Fe content is a wide range in the various colors of samples. The Fe range from 283.54 to 55462 ppm and highest values were found in green color. The Zn range from 29.32 to 150.87 ppm and showed high amounts in yellowish green to brownish green sample. The high concentrations of Ga were detected in watermelon tourmaline and ranging from 14.94 to 69.08 ppm. The Sn content has a range from 5.52 to 26.89 ppm. The Sn-rich were found in green color. The Pb content varies from 3.80 to 58.34 ppm and presented high values quantities in green color. The Bi has high contents between 0.66 to 71.76 ppm in watermelon tourmaline (pink core). The LA-ICP-MS chemical data of green tourmalines of various colors from Madagascar are summarized in Table 3.7.

Table 3.7 LA-ICP-MS chemical data of green tourmaline of various colors from Madagascar

Trace element (ppm)	Madagascar			
	yellowish Green to brownish Green	Green	Watermelon	
			yG	pR
Li	1619	1424	1655	1722
Be	3.52	2.61	4.06	6.95
Sc	8.74	8.42	8.11	8.07
Ti	29.05	14.96	86.57	52.25
V	0.68	0.43	0.77	1.28
Cr	7.49	5.98	11.20	16.20
Fe	46845	55462	947	283
Ni	2.97	2.12	4.59	6.01
Zn	150.87	77.89	140.64	29.32
Ga	28.78	14.94	69.08	58.80
Ge	5.83	3.59	5.81	9.18
Sr	4.55	2.42	0.55	0.72
Nb	1.09	0.49	0.42	0.76
Mo	2.74	1.70	3.13	5.06
Sn	9.12	26.89	5.52	8.23
Sb	4.06	1.06	2.41	3.21
Ta	0.88	0.51	0.53	0.75
Pb	44.39	58.34	3.80	5.76
Bi	15.98	0.66	37.3	71.76

3.6.2 Group II : The samples from Mozambique

The analytical results of green tourmalines from Mozambique showed that all samples consist of elbaite. They range in color from greenish blue, blue, green and bi-color tourmaline. The high trace elements Li, Fe, Zn and Sn were detected in the samples from Mozambique.

The bi-color tourmaline had the highest Li contents ranging from 1277.61 to 1940.82 ppm. The Fe content ranging from 14608 to 39368 ppm and the highest Fe values were revealed in green color. The Zn contents were ranging from 32.17 to 667.13 ppm and increased in greenish blue color. The bi-color tourmaline sample had the highest Sn concentrations from 13.52 to 29.18 ppm. The LA-ICP-MS chemical data of green tourmalines of various colors from Mozambique are summarized in Table 3.8.

Table 3.8 LA-ICP-MS chemical data of green tourmaline of various colors from Mozambique

Trace element (ppm)	Mozambique				
	Blue	greenish Blue	Green	Bi-color	
				Blue	greenish Blue
Li	1451.21	1304.49	1277.61	1413.09	1940.82
Be	4.66	6.74	3.42	2.98	3. 23
Sc	7.01	7.54	6.36	6.23	6.51
Ti	8.85	7.92	25.11	7.20	8.17
V	0.58	0.56	0.69	0.63	0.63
Cr	9.81	6.86	7.10	8.04	7.69
Fe	26596	34647	39368	14608	20110
Ni	4.94	4.52	3.14	2.96	2.67
Zn	128.08	667.13	258.77	32.17	51.41
Ga	13.66	12.20	18.40	10.24	8.43
Ge	5.61	10.21	9.92	6.19	4.05
Sr	0.91	6.29	0.32	1.14	1.23
Nb	0.41	0.40	0.53	0.54	0.37
Mo	2.54	2.45	2.28	3.23	1.51
Sn	21.22	16.30	13.52	29.18	25.88
Sb	1.88	1.29	1.53	1.44	1.54
Ta	0.62	1.42	0.45	0.39	0.41
Pb	11.72	31.81	9.52	2.27	2.13
Bi	0.97	0.67	1.02	0.70	0.87

3.6.3 Group III : The samples from Tanzania

The analytical results of green tourmalines from Tanzania showed that all samples consist of uvite. They range in color from yellowish green, yellow-green and green. The trace elements of green tourmalines from Tanzania are presented high values quantities of Ti, V, Cr and Sr. The Ti contents were measured between 555.03 to 690.10 ppm and displayed the high Li contents in green color. The high V contents were ranging from 170.72 to 645.25 ppm. The green color has the highest V concentrations. The Cr content was varies in various color from 18.21 to 492.66 ppm and showed high contents in green color. The Sr-rich were found in yellow-green color and varies from 64.76 to 201.05 ppm. The LA-ICP-MS chemical data of green tourmalines of various colors from Tanzania are summarized in Table 3.9.

Table 3.9 LA-ICP-MS chemical data of green tourmaline of various colors from Tanzania

Trace element (ppm)	Tanzania		
	Yellow- Green	yellowish Green	Green
Li	4.05	12.98	6.39
Be	6.13	2.34	2.26
Sc	5.40	6.19	6.11
Ti	555.03	607.27	690.10
V	170.72	552.47	645.25
Cr	18.21	249.92	492.66
Fe	66.30	28.56	25.69
Ni	8.42	2.31	3.27
Zn	17.55	6.29	5.41
Ga	2.91	0.84	6.79
Ge	8.33	3.27	2.99
Sr	201.05	92.18	64.76
Nb	0.78	0.32	0.33
Mo	4.00	1.56	2.37
Sn	4.93	1.63	2.02
Sb	3.26	1.12	1.48
Ta	0.82	0.39	0.37
Pb	3.68	1.01	1.34
Bi	1.49	0.63	0.66