CHAPTER 1

INTRODUCTION

1.1 Introduction

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+}, 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 cation occupied in the Y and Z sites (Schmetzer and others, 2007; Dietrich, 1985).

Green tourmaline is a light to intense green variety of gem tourmaline species. In East Africa, tourmaline has been known in the gem trade since the late 1960s, and the green materials have the trade name as chrome and/or vanadium tourmaline (Dirlam and others, 1992; Keller, 1992). The green, yellowish green, greenish blue and bluish green colors in green tourmaline, are mainly caused by V, Fe, Mn, Cr, Cu and Ti (Liu and others, 2011; Bosi, 2008; Da Fonseca-Zang and others, 2008; Laurs and others, 2008; Hainschwang and others, 2007; Sehmetzer and others, 2007). The color of green tourmaline is due to d-d transition of metal ions and intervalence charge transfer process (IVCT) (Dietrich, 1985).

Green tourmaline deposits were discovered from many deposits such as Brazil, USA, Madagascar, Kenya, Tanzania, Afghanistan, Mozambique, Zambia and China (Webster, 1994). In this study, green tourmaline samples are from Madagascar, Mozambique and Tanzania. The basement rocks in the areas of Madagascar and

Mozambique are part of the Mozambique belt (1100-800 Ma) that was deformed during the Pan-Africa tectonic event (950-450 Ma) (Dirlam and others, 1992). The last magmatic cycle of the Pan-Africa orogeny is associated with pegmatite fields and granitic pegmatites crosscut the basement rocks (Laurs and others, 2008; Dirlam and others, 2002; Henn and Milisenda, 2001; Kinnaird and Jackson, 2000; Keller, 1992). Green tourmalines from Tanzania occur in metamorphosed calcium and magnesium-rich rocks such as the politic sediments of the Usagaran and bastment series (Dietrich, 1985). In jewelry industry, green tourmaline varieties are more popular and expensive due to their color and transparency, which are the most important aspect of beauty and value. However, researches on the causes of coloration in different species of green tourmaline have been slightly documented. This study therefore focuses especially on physical, chemical and spectroscopic characteristics of green tourmaline.

1.2 Literature review

1.2.1 Geology of tourmaline

Tourmaline is typically accessory mineral in a wide variety of igneous, metamorphic and sedimentary environments (Falster and others, 2002). The most common and characteristic occurrence of tourmaline is in granitic pegmatites. Tourmaline occur almost in miarolitic cavities in the cores of pegmatites; it may also occur in cavities in the coarse interior units surrounding quartz-rich cores (the core-margin zone) (Figures 1.1-1.2) (Simmons and others, 2012). Most pegmatitic tourmaline is schorl or elbaite and is associated with the common pegmatite minerals, microcline, albite, quartz and muscovite. The dravite and uvite species of tourmaline occur in metamorphic rocks. Uvite is a magnesium and calcium-bearing tourmaline and common found in marbles and schists (Keller, 1992). Tourmaline is a detrital mineral in sediments, different types being found depending on the source. Authigenic tourmaline is from limestone and as secondary growths on well-rounded detrital tourmaline grains in sandstones (Deer and others, 1992). Famous localities for the occurrence of the gem tourmalines are Brazil, Madagascar, Congo, Kenya, Mozambique, Namibia, Nigeria,

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Tanzania, Zambia, Zimbabwe, USA, Italy, Finland, Russia, China, Myanmar, Vietnam, Afghanistan and Pakistan (Figures 1.3-1.4) (Simmons and others, 2012; Klein and Dutrow, 2007). The basement rocks in these areas are part of Mozambique belt (1100-800 Ma) that deformed during the Pan-Africa tectonic event (Dirlam and others, 1992). A large variety of gem deposits are associated with the Mozambique belt. The rocks in this belt underwent metamorphism, folding and faulting during the latter part of the Pan-African orogeny (950-450 Ma) (Dirlam and others, 1992). The last magmatic cycle of the Pan-African occurred from about 570-455 Ma and generated granitic plutons and associated pegmatite fields (Dirlam and others, 2002; Keller, 1992). The gem-bearing pegmatites have formed in the later stage of this cycle.

Pegmatites in Madagascar are hosted by rocks of Itremo Group. The Itremo Group is characterized by a lower unit of gneiss, quartzites, schist and marbles (Dirlam and others, 2002). The tourmaline deposits are related to a large rare element miarolitic pegmatite field (Pezzotta, 2006). The pegmatite composes of quartz, K-feldspar and plagioclase with accessory minerals such as dravite-elbaite-liddicoatite tourmaline, spodumene, spessartine and beryl (Danet, 2006).

In Mozambique, the basement rocks consist of metamorphosed gneiss (migmatite). The rocks were intruded by granitoids and granitic pegmatites. The granitic pegmatites consist of rare metal, industrial mineral and gems such as tourmaline and beryl (Laurs and others, 2008; Laurs and Zwaan, 2007).

The gem deposits of Tanzania consist of schist, gneiss in pegmatites associated with limestone and ultramafics. The basement system in Tanzania (Usagaran system) contains an abundance of gemstone such as tanzanite, ruby, sapphire, emerald, alexandrite, garnet and tourmaline. The elbaite species of tourmaline is found in pegmatites, whereas dravite and uvite occur in metamorphic rocks (Dirlam and others, 1992; Keller, 1992).
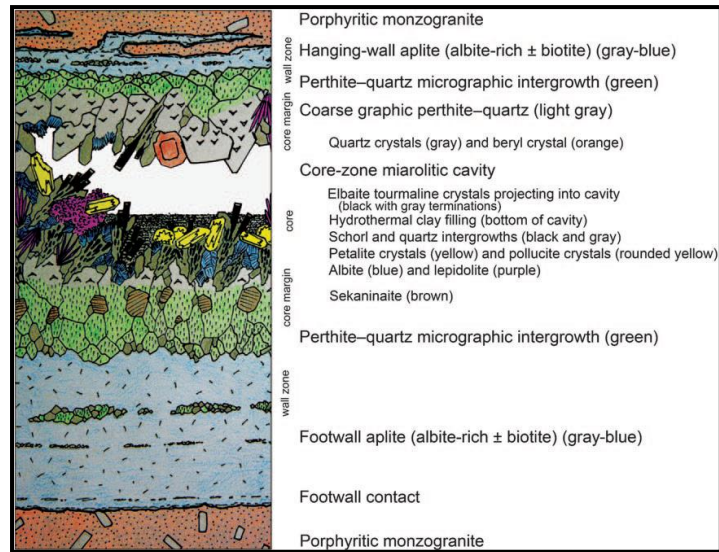
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Figure 1.1 Idealized representation of a miarolitic cavity (Simmons and others, 2012)

Figure 1.2 Examples of miarolitic cavities. Top row, left to right: miarolitic cavity containing red elbaite (rubellite) crystals in the Himalaya dike, San Diego present single indicolite tourmaline from this pocket (Simmons and others, 2012).
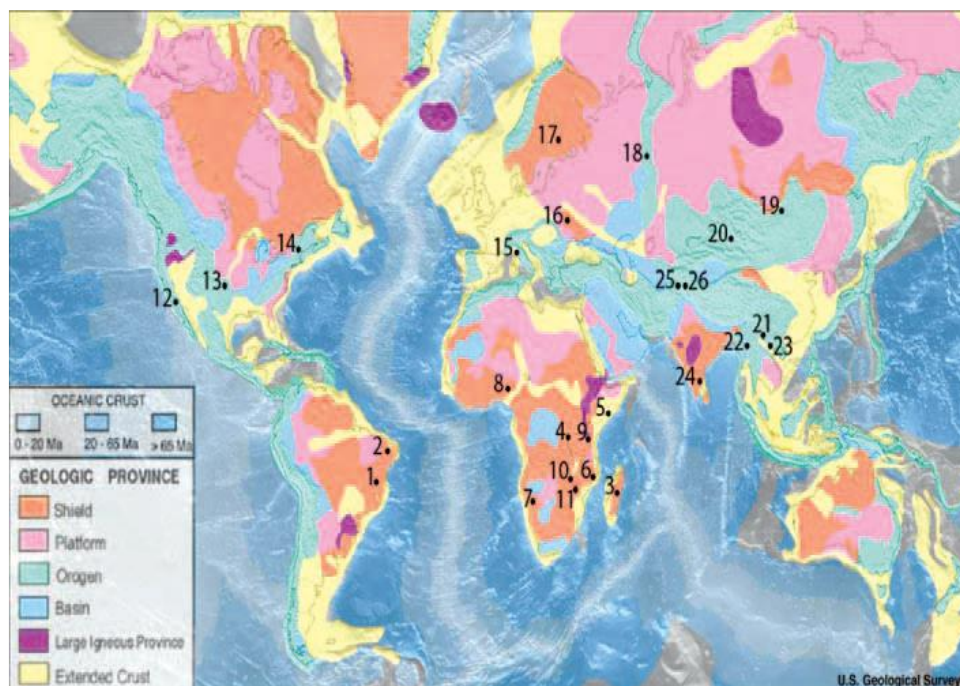
Figure 1.3 Major gem-pegmatite districts of the world; the numbers correspond to the districts in Figure 1.4 (Simmons and others, 2012)

1.* **Brazil**: Minas Gerais
Beryl (aquamarine, morganite, heliodor), topaz, tourmaline, spodumene (kunzite, hiddenite), brazilianite, euclase, quartz (rose, smoky, citrine), amblygonite–montebrasite

2. **Brazil**: Paraíba, Rio Grande do Norte
Tourmaline (Paraíba variety), beryl (aquamarine, morganite, heliodor), euclase, quartz (rose, smoky, citrine), spessartine

3. **Madagascar**: Antananarivo, Fianarantsoa, Toamasina
Tourmaline, beryl (aquamarine), spodumene (kunzite), londonite, pezzottaite, hambergite, orthoclase/sanidine, quartz (rose), spessartine, danburite, phenakite

4. **D. R. Congo**: Katanga, Nord Kivu
Tourmaline

5. **Kenya**: Coast
Tourmaline

6. **Mozambique**: Nampula, Tete, Zambezia
Tourmaline, spessartine, beryl (aquamarine), topaz, spodumene (kunzite), quartz (rose)

7. **Namibia**: Erongo
Tourmaline, beryl (aquamarine), topaz, jeremejevite

8. **Nigeria**: Edo, Kaduna, Kwara, Nassarawa, Oyo, Plateau
Tourmaline, chrysoberyl, topaz, beryl, phenakite, spodumene, spessartine

9. **Tanzania**: Arusha, Morogoro, Tanga
Tourmaline, spessartine

10. **Zambia**: Central, Eastern
Tourmaline, beryl (emerald), spessartine

11. **Zimbabwe**: Mashonaland West
Beryl (aquamarine), topaz, tourmaline

12. **United States**: California, Mesa Grande, Pala, Ramona
Tourmaline, beryl (aquamarine, morganite), spessartine, spodumene (kunzite)

13. **United States**: Colorado Collegiate Range
Beryl (aquamarine), phenakite

14. **United States**: New England, Maine, New Hampshire, Connecticut
Tourmaline, beryl (aquamarine), pollucite

15. **Italy**: Elba
Tourmaline, pollucite

16. **Ukraine**: Zhytomyr
Beryl (heliodor, aquamarine), topaz

17. **Finland**: Luumäki (South Karelia)
Beryl (aquamarine), tourmaline

18. **Russia**: Ural Mountains
Beryl (aquamarine, emerald), topaz, chrysoberyl (alexandrite)

19. **Russia**: Zabaykalsky (Transbaikalia)
Tourmaline, danburite, pollucite, spessartine, beryl (aquamarine), topaz

20. **China**: Xinjiang Uygur
Beryl (aquamarine), tourmaline

21. **China**: Yunan
Tourmaline, beryl (aquamarine), spessartine

22. **Myanmar**: Mogok, Momeik
Tourmaline, phenakite, petalite, pollucite

23. **Vietnam**: Yen Bai
Tourmaline, microcline (amazonite)

24. **India**, Tamil Nadu
Beryl (aquamarine)

25. **Afghanistan**, Kunar, Nuristan
Tourmaline, spessartine, topaz, beryl (emerald, aquamarine), spodumene (kunzite)

26. **Pakistan**, Gilgit-Baltistan
Tourmaline, spessartine, beryl (aquamarine), topaz

* Numbers correspond to map locations in Figure 6.

Sources: Clifford et al. 2011; Cornejo and Bartorelli 2010; Groat et al. 2007; Falster et al. 2002, 2005; Pezzotta 2001; Shigley et al. 2010; Simmons 2007

Figure 1.4 Major gem-pegmatite districts and notable gem minerals (Simmons and others, 2012)

1.2.2 Crystallography, physical properties and optical properties of tourmaline

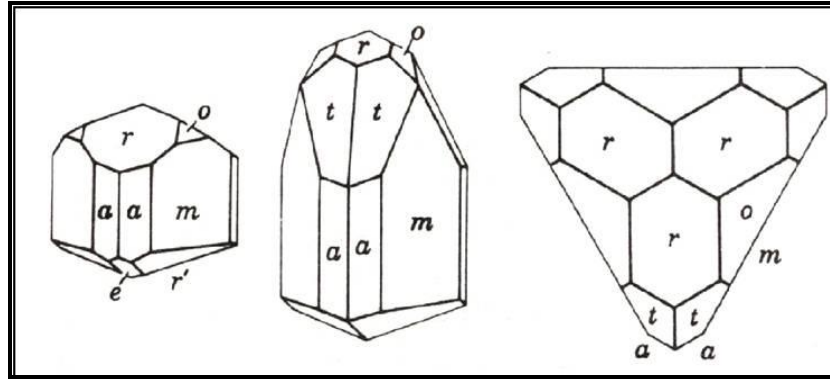|	
Crystallography	Hexagonal; 3m. Usually in prismatic crystals with a prominent trigonal prism and subordinate hexagonal prism, $\{11\bar{2}0\}$, vertically striated. The many different prism faces may round into each other giving the crystals a cross section like a spherical triangle. When doubly terminated, crystals usually present different forms at the opposite ends of the vertical axis due to the polar nature of the structure (Figure 1.5) (Klein and Dutrow, 2007).
Crystal habit	parallel and elongated, acicular prisms, sometimes radiating, Massive, scattered grains (in granite).
Color	most commonly black, but can range from colorless, brown, violet, yellow, orange, blue, red, green, pink, or bi-colored, or even tri-colored
Cleavage	Indistinct
Fracture	uneven, small conchoidal, brittle
Hardness	7-7.5
Luster	vitreous, sometimes resinous
Specific gravity	3.06 (+.20 -.06)
Optical properties	double refractive, uniaxial negative
Refractive index	n_ω=1.635–1.675, n_ε=1.610–1.650
Birefringence	0.018 to 0.040; typically about 0.020 but in dark stones it may reach 0.040
Pleochroism	typically moderate to strong red tourmaline: definite; dark red, light red green tourmaline: strong; dark green, yellow-green brown tourmaline: definite; dark brown, light brown blue tourmaline: strong; dark blue, light blue
Dispersion	0.017
Ultraviolet fluorescence	pink stones—inert to very weak red to violet in long and short wave

Figure 1.5 Tourmaline crystals (Klein and Dutrow, 2007)

1.2.3 Structure and chemistry of tourmaline

Tourmaline is a borosilicate mineral group and has a chemically complex composition. Its chemical formula is $XY_3Z_6 (T_6O_{18})(BO_3)_3V_3W$ with space group of R3m. There are 14 valid from the International Mineralogical Association's Commission on New Minerals, Nomenclature and Classification (IMA-CNMNC) approved species classified (Hawthorne and Henry, 1999). Because of 14 species are isostructural, ionic substitution and solid solution befalls between these end-members. The tourmaline structure consists of (Si_6O_{18})-rings of corner-shared (SiO_4)-tetrahedral, which are linked to planar (BO_3)-groups. These structural elements of silicon- and boron-polyhedral are linked by different cations on X-, Y- and Z-sited of the tourmaline structure. The X-site is coordinated by nine anions and two types of octahedral coordinated are the Y-sites and the smaller distorted Z-sites, which share edges to form brucite-like fragments. The OH^- is different located, where $W(O_1)$ site is located at the center of hexagonal rings whereas $V(O_3)$ site is located at the corner of the brucite-like fragments of the three edge-sharing octahedral (Ahn and others, 2013). The $W(O_1)$-site only contain O^{2-}, OH^- while the $V(O_3)$-site can contain O^{2-}, OH^- and F^- (Figure 1.6). Tourmalines are classified based on different cations occupied in the Y and Z sites (Schmetzer and others, 2007; Deer and others, 1992; Dietrich, 1985).

X	=	Na^+, Ca^{2+}, K^+, [ ] (vacancy)
Y	=	Li^+, Mg^{2+}, Fe^{2+}, Mn^{2+}, Al^{3+}, Fe^{3+}, Cr^{3+}, V^{3+}, (Ti^{4+})
Z	=	Al^{3+}, Mg^{2+}, Fe^{2+}, Cr^{3+}, V^{3+}, (Fe^{2+})
T	=	Si^{4+}, Al^{3+}, (B^{3+})

B	=	B^{3+}, Si^{4+}, [ ](vacancy)
$V(O_3)$	=	(OH^-), O^{2-}
$W(O_1)$	=	(OH^-), F^-, O^{2-}

Tourmaline species are defined with the dominant-valency rule by can be separated into several groups and subgroups, which led to the several compositional diagrams in classification of the tourmaline-supergroup minerals (Hawthorne and Henry, 1999). The primary groups are based on occupancy of X-site such as alkali, calcic and X-vacant groups and can be plotted on the simple ternary diagram in Figure 1.7. The primary X-site groups are defined as follows: alkali if $(Na^+ + K^+) \geq Ca^{2+}$ and $(Na^+ + K^+) \geq {}^x\square$; calcic if $Ca^{2+} > (Na^+ + K^+)$ and $Ca^{2+} > {}^x\square$; and X-vacant if ${}^x\square > (Na^+ + K^+)$ and ${}^x\square > Ca^{2+}$. Tourmaline group minerals are defined on the dominant occupancy of the Y-site and Z-site. Inside each group, there are several subgroups therefore there is more than tourmaline species within subgroups. Ternary plots for the most common substitution or solid-solution series for the Y-site in each of the three groups. The alkali group diagram shows the range of composition for elbaite, dravite and schorl; the calcic group for liddicoatite, uvite and feruvite; the X-vacant group for rossmanite, magnesiofoitite and foitite (Figure 1.8) (Henry and others, 2011; Hawthorne and Henry, 1999; Dietrich, 1985).
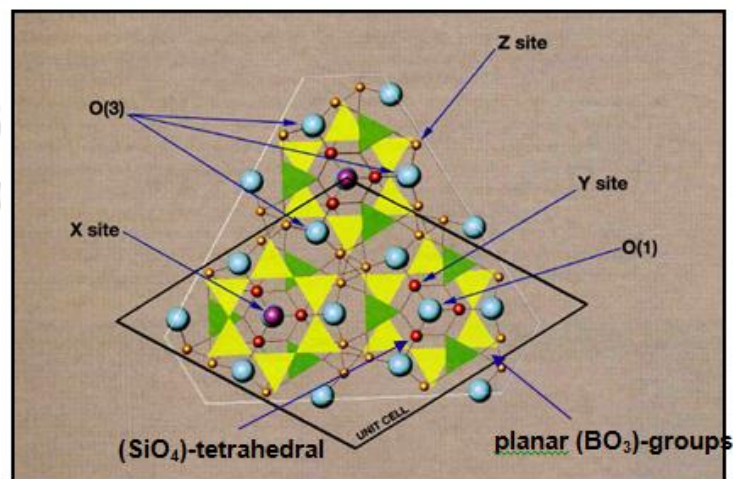
Figure1.6 The tourmaline structure projected parallel to the (0001) plane
(Schmetzer and others, 2007)

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Primary Tourmaline Groups
X site
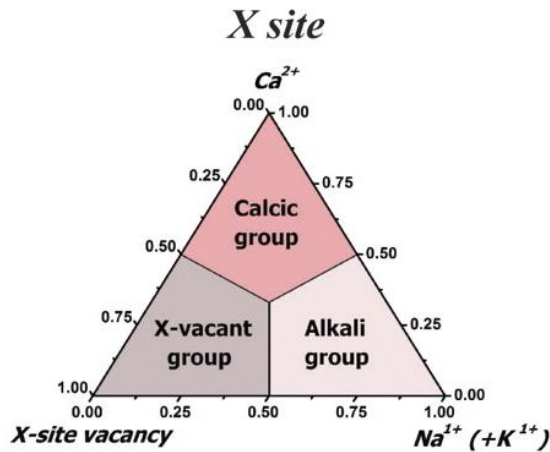
Figure 1.7 Ternary systems for the primary tourmaline groups based on the dominant occupancy of the X-site (Henry and others, 2011).

Alkali Group
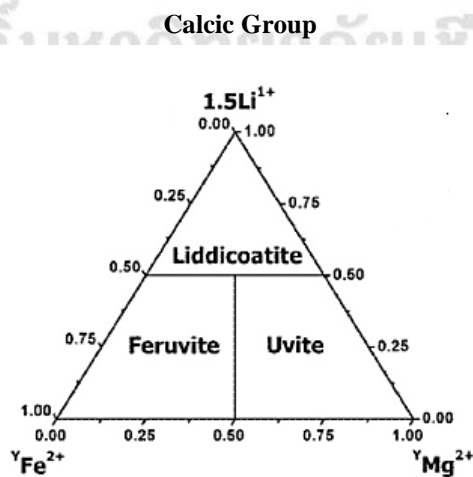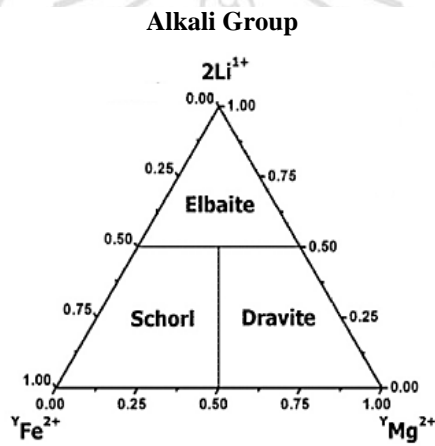
Calcic Group

Figure 1.8 Ternary subsystem species tourmaline within each subgroup on the dominant occupancy of the Y-site and Z-site (Henry and others, 2011).

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Figure 1.8 (Continued)
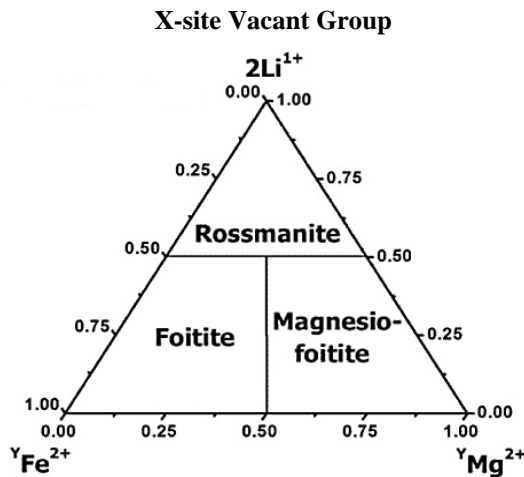
In green tourmaline, it could consisted of alkali group and calcic group such as dravite, elbaite, uvite, liddicoatite species and nearly complete solid solution between Elbaite – Liddicoatite series and Dravite-Uvite series (Table 1.1) (Dietrich, 1985).

Dravite	$NaMg_3Al_6B_3Si_6O_{27}(OH)_3(OH)$
Elbaite	$[Na][(Li,Al)_3][Al_6][(OH)_3|OH|(BO_3)_3|Si_6O_{18}]$
Liddicoatite	$[Ca][Li_2Al][Al_6][(OH)_3|F|(BO_3)_3|Si_6O_{18}]$
Uvite	$[Ca][(Mg,Fe^{2+})_3][MgAl_5][(OH)_3|F|(BO_3)_3|Si_6O_{18}]$

Table 1.1 Chemical compositions of green tourmaline species (Dietrich, 1985).

| Species	(X)	(Y_3)	(Z_6)	T_6O_18	(BO_3)_3	V_3	W
Alkali Group							
Elbaite	Na	$[Li_{1.5}Al_{1.5}]$	Al_6	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	(OH)
Dravite	Na	Mg_3	Al_6	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	(OH)
Calcic Group							
Liddicoatite	Ca	$[Li_2Al]$	Al_6	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	F
Uvite	Ca	Mg_3	Al_6	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	F

1.2.4 The causes of coloration in tourmaline

The variety of colors in tourmaline group is due to chromophoric metal cations, charge transfer interactions and color centers (Table 1.2).

Table 1.2 Causes of color in the tourmaline group (Falster and others, 2002)

Color	Species	Cause of color	References
colorless	elbaite, dravite, uvite	no or extremely small amounts of transition metals or color centers	Wilkins and others, 1969
pink-red	elbaite, liddicoatite, olenite, tsilaisite	Mn^{3+} (associated with exposure to ionizing radiation) Mn^{2+}- Mn^{3+} IVCT color center electron trap in vacant anion position	Manning, 1969, 1973; DeCamargo and Isotani, 1988 DeCamargo and Isotani, 1988 Bershov and others, 1969; Nassau, 1975
red	Dravite	Fe^{3+} pairs	Mattson and Rossman, 1984
yellow	Elbaite	hole traps of type O^- in interaction with two Al nuclei caused by irradiation	Krambrock and others, 2002
yellow-brown	dravite, uvite, schorl, buergerite dravite-uvite series	Fe^{3+} and/or Mn^{2+} Ti^{4+} Fe^{2+}- Ti^{4+} IVCT	Wilkins and others, 1969 Smith, 1977 Mattson and Rossman, 1984
brown	Dravite	Ti^{3+}- Ti^{4+} IVCT	Manning, 1969
green and blue	elbaite, dravite, schorl, uvite	Fe^{2+} and/or Fe^{3+} Fe^{2+}- Fe^{3+} IVCT	Dunn and others, 1977 Leckebusch, 1978
green	dravite, uvite elbaite-liddicoatite elbaite	V^{3+} and/or Cr^{3+} Fe^{2+}- Ti^{4+} IVCT Fe^{3+} in tetrahedral site	Schmetzer, 1978, 1982 Faye and others, 1974 Manning, 1973
yellow-green	Elbaite	Mn^{2+}- Ti^{4+} IVCT	Rossman and Mattson, 1986
blue	Elbaite	Cu^{2+} in octahedral site	Zang and others, 2001; Rossman and others, 1991

The colors of green tourmaline are due to d-d transition of metal ions (V, Fe, Mn, Cr and Ti) in the Y- and Z- octahedral site and intervalence charge transfer processes (IVCT) (Dietrich, 1985). The Fe^{2+}or Fe^{3+} are the main transition metal of these cause the green coloration. The result of Fe^{2+} or combination of Fe^{2+} and the Fe^{2+}- Ti^{4+} IVCT is associated with green hues such as bluish green, greenish blue (Da Fonseca-Zang and others, 2008; Hainschwang and others, 2007; Reddy and others, 2007; Castaneda and others, 2006; Simmons and others, 2001). The color of green tourmaline depends on V^{3+} and/or Cr^{3+} on octahedral aluminium sites. The V^{3+} is the principle coloring agent presented with less amount of Cr^{3+} (Hainschwang and others, 2007; Schmetzer and others, 2007). Green tourmalines from East Africa have higher V^{3+} than Cr^{3+}content and thus are vanadian dravites and uvites species (Schmetzer and Bank, 1979). The Mn^{2+} is the source of yellow-green color in tetrahedral coordination (Schmetzer and Bank, 1984). The Mn^{2+}- Ti^{4+} IVCT is related to yellowish green hues in elbaite species (Dietrich, 1985).

1.2.5 UV-Vis-NIR Spectroscopy of tourmaline

The absorption spectrum of the green vanadium-bearing tourmalines from Madagascar comprise of two strong absorption band at 599 and 441 nm in the spectrum parallel to c-axis and at 610 and 418 nm in the spectrum perpendicular to c-axis, are assigned to V^{3+} on octahedral aluminium-sites (Z-sites) of the tourmaline structure (Figure 1.9). The absorption bands of chromium occur at 588 and 417 nm, which are in the same spectral range as vanadium (Hainschwang and others, 2007; Schmetzer and others, 2007). Therefore, the two overlay absorptions cannot be separated. The green tourmalines show absorption spectra (Figure 1.10) at 450, 470, 540, 720, and 1150 nm are related to Fe^{2+} in Y-octahedral site, where as the bands at 415, 420, 600, 650, 988 and 1180 nm are related to Fe^{3+} (Liu and others, 2011; Merkel and Breeding, 2009; Da Fonseca-Zang and others, 2008; Castaneda and others, 2006).

The optical absorption spectrum of green tourmaline are associated with d-d transition of Mn^{2+} in Y-site at 400, 415 nm and the band at 392, 517, 520, nm are

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assigned to Mn^{3+} ions in the high spin state, distorted octahedral sites (Liu and others, 2011; Reddy and others, 2007; Castaneda and others, 2006). The Cu^{2+} absorption band of green tourmaline (Figure 1.11) show peaks at 700, 900 nm (Laurs and others, 2008). Green color is associated with absorption bands of Ti^{4+} ions at 24000 cm^{-1} (416 nm) in Y- octahedral site and Z-octahedral site (Da Fonseca-Zang and others, 2008). The green tourmalines that show absorption spectra at 715 nm, implies intervalence charge transfer (IVCT) between Fe^{2+}-Fe^{3+} ions (Reddy and others, 2007), the IVCT- transitions may be described as Ti^{3+}-Ti^{4+} and Fe^{2+}-Ti^{4+} or Ti^{3+}-Ti^{4+}-Fe^{3+} causing absorbance at around 14000 cm^{-1} (714 nm) (Da Fonseca-Zang and others, 2008) and the 438-444 nm band due to Fe^{2+}-Ti^{4+} (Hainschwang and others, 2007).
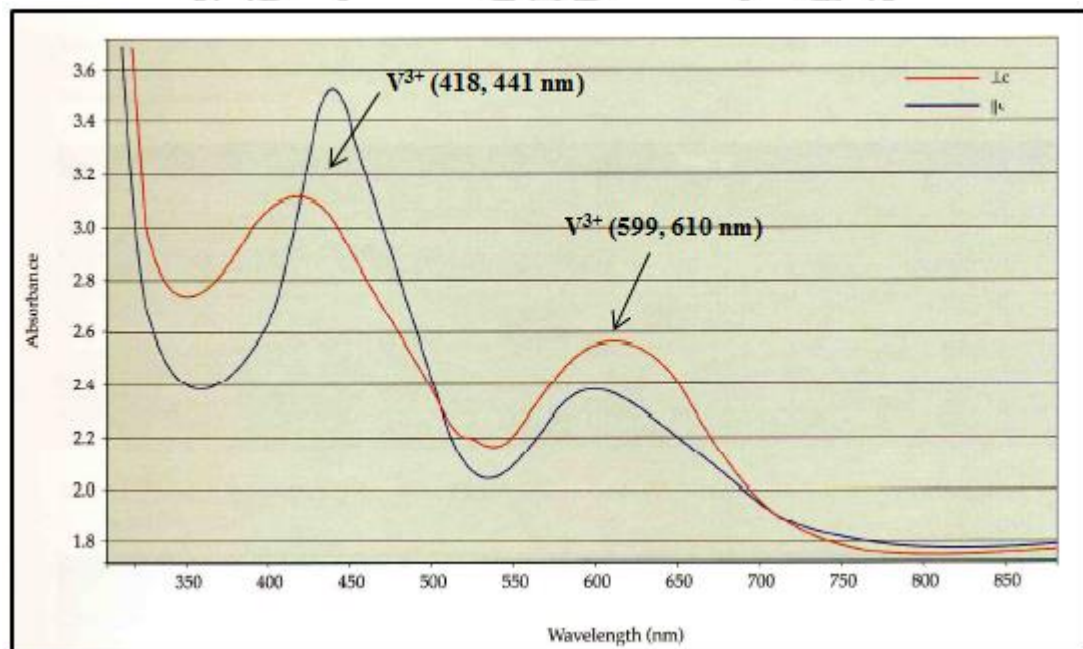
Figure 1.9 UV-Vis-NIR absorption spectra of vanadium-bearing, iron free
tourmaline from southern Madagascar (Schmetzer and others, 2007).
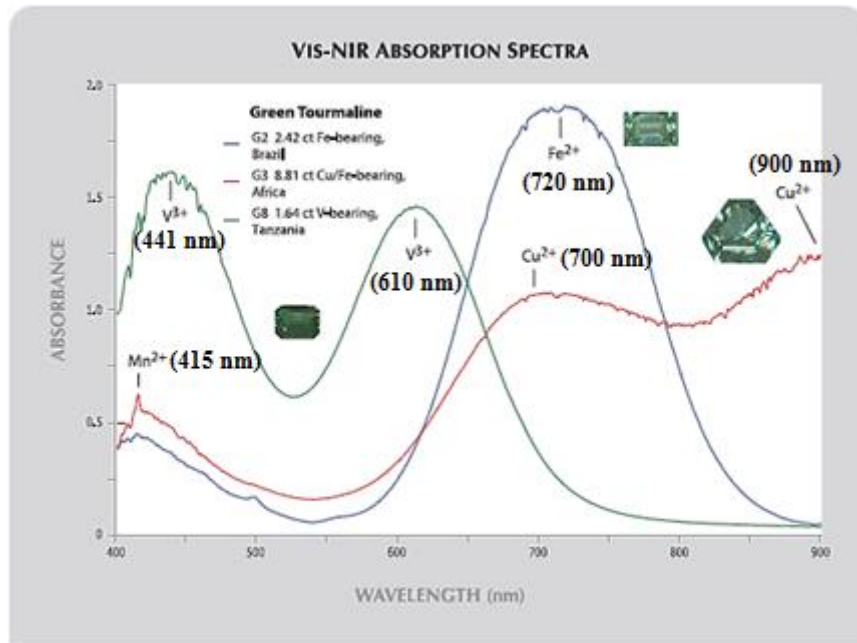
Figure 1.10 UV-Vis-NIR absorption spectra of green tourmaline are from Brazil (G2), Africa(G3) and Tanzania(G8) (Merkel and Breeding, 2009).
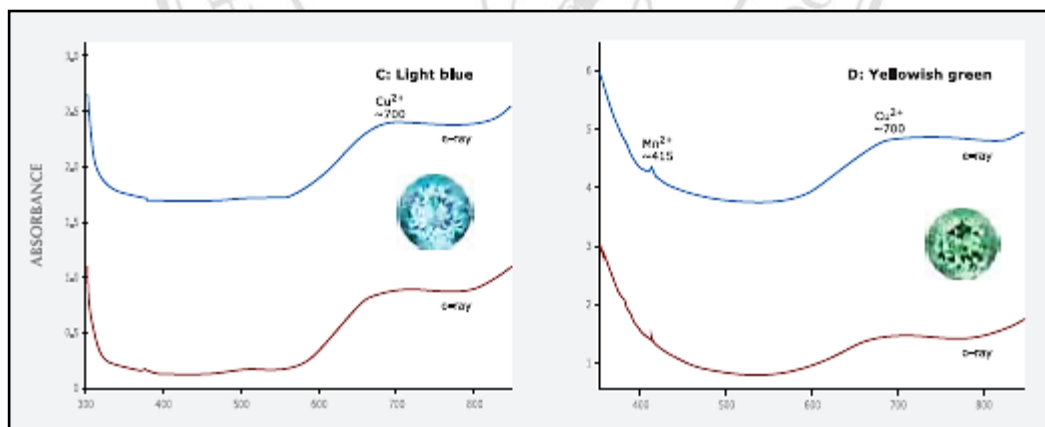
Figure 1.11 UV-Vis-NIR absorption spectra are presented Cu-bearing tourmaline from Mozambique show peaks at 700, 900 nm (Laurs and others, 2008).

1.2.6 Fourier Transform Infrared Spectroscopy (FTIR) of tourmaline

FTIR absorption spectra were obtained in the range 4000-500 cm^{-1} due to the stretching vibration of Si-O, BO_3 and hydroxyl groups (Hainschwang and others, 2007). The band located at 3657 cm^{-1} can be assigned to the O-H stretching vibration at $W(O_1)$ site and the band at 3475 cm^{-1} show OH^- vibration at $V(O_3)$ site (Skogby and others, 2012). The OH^- groups (OH^-1and OH^-3) are distributed in two different sites (Y- and Z- cation sites) and the bands are due to occupancy of octahedral site. The bands in the range of 3560-3600 cm^{-1} are concerned with O-H stretching vibration. The band at 3555 cm^{-1} can be due to the vibrations OH^- groups connected with Al in Z site and Fe, Mn or Mg in Y- sites. The bands around 1300 cm^{-1} belongs to BO_3 groups, the band near 1000 cm^{-1} are related to stretching vibration of Si_6O_{18} rings and the band at 1100 cm^{-1} is attributed to $MgOH^-$ bending modes (Reddy and others, 2007) (Figures 1.12-1.13).
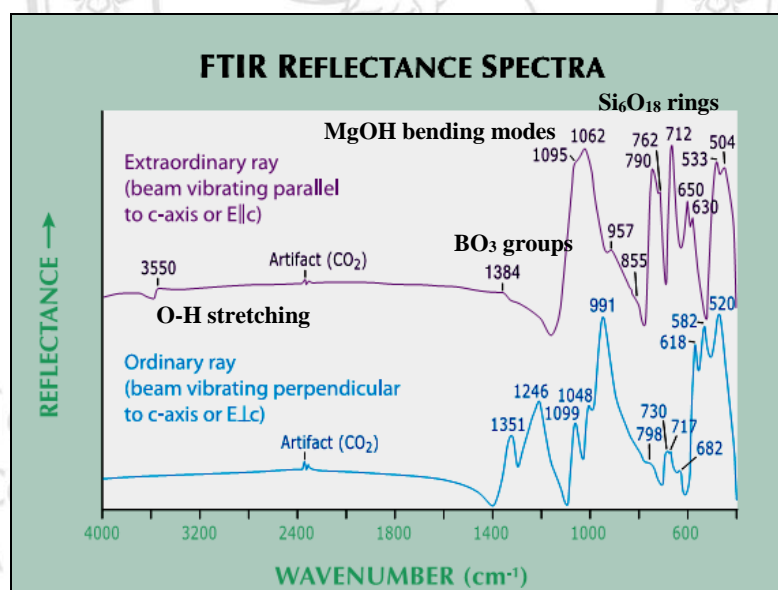
Figure 1.12 Infrared spectra Trapiche Tourmaline from Zambia show O-H
stretching region 3550 cm^{-1} and the widely varying intrinsic bands
between 1500 –450 cm^{-1} (Hainschwang and others, 2007).

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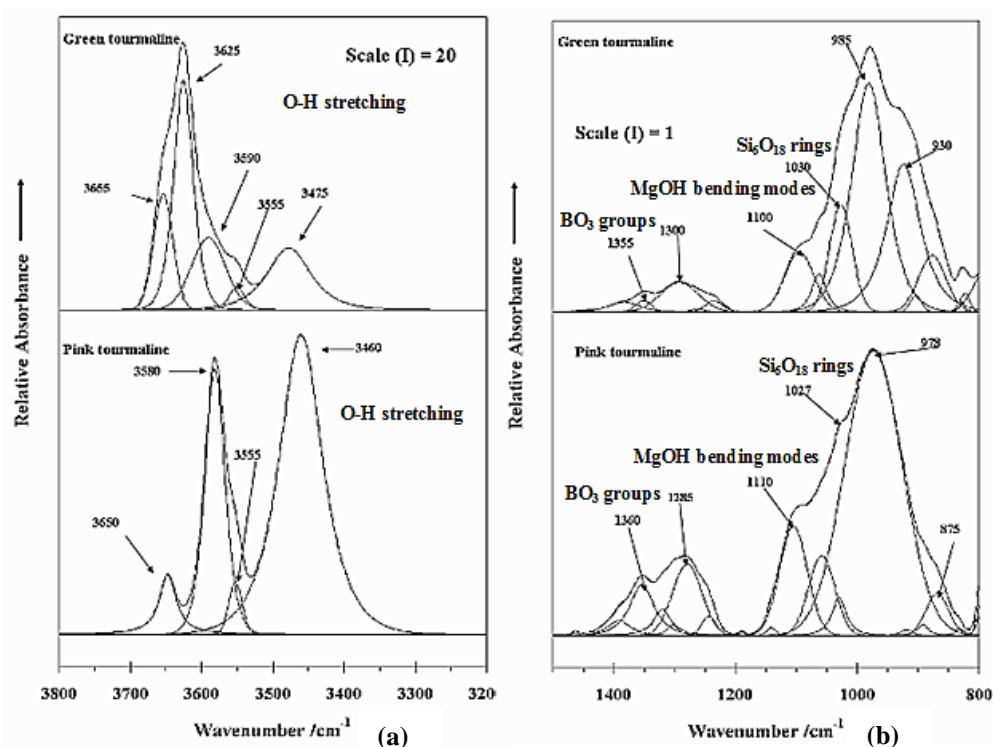
Figure 1.13 Mid-infrared spectra of green and pink tourmaline in (a) O-H
        stretching region 3800-3200cm^{-1} and (b) low wavenumber region
        1500-800 cm^{-1} (Reddy and others, 2007).

1.2.7 Electron probe micro-analyser (EPMA) and Laser Ablation-Inductively Coupled Plasma-Mass Spectroscopy (LA-ICP-MS)

The chemical compositions of tourmaline can be obtained by Electron Probe
Micro-Analyser (EPMA) and Laser Ablation-Inductively Coupled Plasma-Mass
Spectroscopy (LA-ICP-MS), which are applied for the determination of major, minor and
trace elements in solid (Abduriyim and Kitawaki, 2006). The bluish green to greenish
blue tourmaline from Mozambique contained Cu and Mn contents (up to 3.21 wt% CuO
and 4.81 wt% MnO). The trace elements show high contents of Sc, Ga and Pb. Only
minute amounts of Mg detect in a few of Mozambique stones (Abduriyim and others,
2006). The Madagascar green tourmalines range in composition from Ca-rich and Na-
poor liddicoatite, and it has been found abundance only in Madagascar (4.69 wt% CaO
and 0.54 wt% Na$_2$O) (Superchi and others, 2006; Dirlam and others, 2002). The
chemical analyses of tourmalines from Tanzania indicate uvite-dravite series (Dirlam
and others, 1992).

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The trace elements in green tourmalines may be responsible for or correlative with coloration. The trace amounts of Pb, Ba, Be, Cu, Cr and Ni are more common in red than in yellow, green and blue elbaites whereas Ge and Zn are more common in green and blue elbaites. The trace elements of few tourmalines occur as major constituents of the other tourmalines e.g. Li is a trace element in dravite whereas a major component in liddicoatite, elbaite and elbaite-schorls (Dietrich, 1985). For chemical data on tourmaline from other localities, see Table 1.3.

Table 1.3 Chemical composition of tourmaline from other localities

Chemical composition	USA[1]						Rwanda[2]	Zambia[3]
	Light green	Green	Yellow-Green	Olive green	Blue-Green	Blue	Green	Green
Oxide (wt.%)								
Al_2O_3	41.78	38.67	41.93	41.57	39.55	38.49	39.66	26.73
SiO_2	36.79	36.59	36.63	36.76	36.55	36.78	38.27	36.03
V_2O_3	nd	nd	nd	nd	nd	nd	nd	0.34
MnO	0.44	1.70	0.41	0.82	0.43	1.20	0.66	0.01
TiO_2	bdl	0.08	bdl	0.18	bdl	bdl	0.01	0.33
F	0.88	1.14	1.09	0.95	0.88	1.31	0.92	1.12
B_2O_3	10.99	10.80	10.97	11.00	10.79	10.83	11.12	10.55
Cr_2O_3	nd	nd	nd	nd	nd	nd	nd	0.15
FeO	1.33	4.46	0.96	1.79	4.35	5.22	1.89	0.01
CaO	0.32	0.15	0.22	0.14	0.06	0.75	0.29	5.03
MgO	0.03	0.03	bdl	0.02	bdl	bdl	nd	15.12
Na_2O	2.07	2.38	2.22	2.12	2.10	2.00	2.06	0.43
CuO	nd	nd	nd	nd	nd	nd	nd	nd
K_2O	0.02	bdl	0.02	0.02	0.02	0.03	0.01	nd
Li_2O calc.	1.82	1.43	1.87	1.71	1.48	1.49	2.21	nd
H_2O calc.	3.33	3.18	3.27	3.35	3.31	3.12	3.40	3.11
Subtotal	99.91	100.60	99.61	100.42	99.52	101.22	100.51	98.96
-O=F	0.41	0.48	0.46	0.40	0.37	0.55	0.39	0.47
Total	**99.50**	**100.12**	**99.15**	**100.02**	**99.15**	**100.67**	**100.12**	**98.49**
Mineral name	Elbaite	Elbaite	Elbaite	Elbaite	Elbaite	Elbaite	Elbaite	Uvite

[1]Simmons and others, 2005; [2]Henn and Schmitz, 2014; [3]Hainschwang and others, 2007

Table 1.3 (Continued)

Chemical composition	Nigeria[4]			Namibia[4]	Congo[4]	Brazil[5]
	yellowish-Green	Pale green	Bluish Green	Dark green	Green	Green
Oxide (wt.%)						
Al_2O_3	39.80	40.44	39.93	39.29	38.47	38.57
SiO_2	38.25	38.07	38.11	37.85	37.22	36.94
V_2O_3	0.03	0.01	bdl	bdl	bdl	nd
MnO	0.56	0.10	0.28	1.00	1.01	1.32
TiO_2	bdl	bdl	bdl	0.06	0.24	0.08
F	1.03	1.24	1.25	1.10	1.04	nd
B_2O_3	10.98	11.10	11.08	10.97	10.86	10.84
Cr_2O_3	nd	nd	nd	nd	0.03	nd
FeO	0.68	0.28	0.48	2.76	3.10	3.23
CaO	0.67	2.09	2.27	0.45	0.26	0.55
MgO	0.05	bdl	bdl	0.07	0.46	0.45
Na_2O	1.72	1.41	1.48	2.09	2.50	2.45
CuO	nd	nd	nd	nd	nd	nd
K_2O	bdl	0.01	0.01	0.02	bdl	0.03
Li_2O calc.	2.19	2.42	2.45	1.79	1.70	1.35
H_2O calc.	3.30	3.24	3.23	3.26	3.25	3.69
Subtotal	99.27	100.39	100.58	100.71	100.16	99.85
-O=F	0.43	0.52	0.53	0.46	0.44	0.00
Total	**98.84**	**99.87**	**100.06**	**100. 24**	**99.72**	**99.85**
Mineral name	Elbaite	Elbaite	Elbaite	Elbaite	Elbaite	Elbaite

[4]Giller, 2003; [5]Castaneda and others, 2006

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Table 1.3 (Continued)

Chemical composition	Kenya[6]		Mogok, Myanmar[6]	Austria[6]
	yellowish Green	Green	Green	Green
Oxide (wt.%)				
Al_2O_3	27.53	26.69	30.02	34.36
SiO_2	36.39	36.52	35.59	36.47
V_2O_3	0.294	0.244	0.614	0.84
MnO	0.004	0.01	0.001	0.03
TiO_2	0.49	1.02	0.16	0.44
F	1.589	1.66	1.03	nd
B_2O_3	10.48	10.51	10.59	10.99
Cr_2O_3	0.10	0.14	0.05	0.17
FeO	0.06	bdl	bdl	0.11
CaO	3.46	3.26	3.29	1.30
MgO	13.24	13.74	12.61	10.24
Na_2O	0.98	1.25	1.19	1.94
CuO	nd	nd	nd	nd
K_2O	nd	nd	nd	0.05
Li_2O calc.	0.34	0.34	0.23	0.34
H_2O calc.	2.86	2.84	3.17	3.79
Subtotal	98.83	98.25	98.57	101.07
-O=F	0.67	0.70	0.43	0.00
Total	**97.16**	**97.55**	**98.14**	**101.07**
Mineral name	Uvite	Uvite	Uvite	Dravite

[6]Ertl and others, 2008

1.3 Aim and objectives

The main aim of this study is to determine the spectroscopic characteristics and chemical compositions of green tourmalines from Madagascar, Mozambique and Tanzania. The detailed study of physical properties, optical properties, chemical compositions of green tourmalines from Madagascar, Mozambique and Tanzania were carried out. This leads to investigate the cause of coloration in green tourmalines, spectroscopic characteristics, and this can be helpful to understand the geological formation of the area where the tourmaline is located.

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1.4 Research plan

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┌─────────────────────────┐
│     Research Plan       │
└─────────────────────────┘
         │
         ├──→ ┌─────────────────────┐
         │    │  Literature review  │
         │    └─────────────────────┘
         │
         ├──→ ┌─────────────┐   ┌────────────────────────────────────┐
         │    │   Scope     │──→│ Purchased samples from Bangkok Gems │
         │    └─────────────┘   │ and Jewelry Fair                   │
         │                      └────────────────────────────────────┘
         │
         ├──→ ┌─────────────┐   ┌────────────────────────────────────┐
         │    │ Sampling and│──→│ ➤ All samples were cleaned         │
         │    │ preparation │   │ ➤ All samples were polished in     │
         │    └─────────────┘   │   perpendicular to C-axis          │
         │                      │ ➤ All samples were classified into │
         │                      │   each groups on the basis of their│
         │                      │   colors                           │
         │                      └────────────────────────────────────┘
         │
         │                   ┌──────────────┐  ┌─────────────────────────┐
         │                 ┌→│Basic analytical│→│ ➤ Hydrostatic balance  │
         │                 │ │ techniques    │  │ ➤ Refractometer        │
         ├──→┌────────────┐│ └──────────────┘  │ ➤ Ultraviolet lamp     │
         │   │ Analytical ││                    │ ➤ Gemological microscope│
         │   │ techniques ││                    └─────────────────────────┘
         │   └────────────┘│ ┌──────────────┐  ┌─────────────────────────┐
         │                 └→│Advanced analytical│→│ ➤ UV-Vis-NIR          │
         │                   │ techniques    │  │ ➤ FTIR                  │
         │                   └──────────────┘  │ ➤ EPMA                  │
         │                                      │ ➤ LA-ICP-MS             │
         │                                      └─────────────────────────┘
         ├──→ ┌─────────────────────┐
         │    │ Interpretation and  │
         │    │ data processing     │
         │    └─────────────────────┘
         │
         ├──→ ┌─────────────────────┐
         │    │   Thesis writing    │
         │    └─────────────────────┘
         │
         └──→ ┌─────────────────────┐
              │ Oral defense of thesis│
              └─────────────────────┘
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