

Chemical and Optical Absorption Spectroscopic Study of Colored Tourmalines

유색 전기석의 화학적 및 광학흡수 분광학적 연구

Hee Jong Kim (김희중) · Soo Jin Kim (김수진)

Department of Geological Sciences, Seoul National University, Seoul 151-742, Korea
(서울대학교 지질학과)

ABSTRACT : The chemical and optical absorption spectroscopic characters of pink and colorless tourmalines from San Diego mine in California, U.S.A., blue/green tourmalines from anonymous mine, Brazil, and brownish black tourmalines from Uncheon and Haksan mines in Korea have been studied using X-ray diffractometer, electron microprobe, optical absorption spectroscopy, and heat treatment. Least-squares refinements give unit cell dimensions: $a=15.96-16.01 \text{ \AA}$, $c=7.15-7.16 \text{ \AA}$ for the brownish black tourmalines, $a=15.82-15.87 \text{ \AA}$, $c=7.09-7.10 \text{ \AA}$ for pink tourmalines, and $a=15.88-15.94 \text{ \AA}$, $c=7.12-7.15 \text{ \AA}$ for blue/green tourmalines.

The colors of tourmalines are responsible for the transition elements. The pink color is attributed to the Mn^{3+} ions, the blue/green to Fe^{2+} and Mn^{2+} , bluish green to Cu^{2+} , and the brownish black to Fe^{2+} , $\text{Fe}^{2+}-\text{Fe}^{3+}$, and $\text{Fe}^{2+}-\text{Ti}^{4+}$. The Mn^{3+} ions of pink color tourmalines are stabilized in the Y sites compressed along the $\text{O}(1)\text{H}-\text{O}(3)\text{H}$ axis by Jahn-Teller distortion. Heating removes the pink or red component from tourmalines, producing the colorless stones from the pink and red ones. The bluish green samples change into the greenish blue ones and a certain yellowish green samples change into the light green ones by heat treatment.

In the elbaite-schorl series, the concentration of Fe and Mn are variable depending on the color zones. The green zone is characterized by the high content of Fe, whereas the pink zone by the high content of Mn. Mn increases in deep yellow zone compared with yellow or colorless zones.

요약 : 미국의 샌디에고광산에서 산출되는 분홍색이나 무색의 전기석과 산지가 알려지지 않은 브라질산의 청색 내지 녹색을 띠는 전기석 그리고 국내의 학산, 운천 광산에서 산출되는 흑갈색 전기석들의 화학적 성분과 광물 흡수 분광학적 특성을 연구하기 위하여 X선 회절기, 전자 현미 분석기, 광학적 흡수 분광분석 및 열 처리 실험 등을 이용하였다. 최소 자승법을 활용하여 단위포 크기를 구하면, 흑갈색 전기석 경우 $a=15.96-16.01 \text{ \AA}$, $c=7.15-7.16 \text{ \AA}$ 이며, 분홍색 전기석은 $a=15.82-15.87 \text{ \AA}$, $c=7.09-7.10 \text{ \AA}$ 이며, 청색/녹색 전기석은 $a=15.88-15.94 \text{ \AA}$, $c=7.12-7.15 \text{ \AA}$ 이다. 전기석 광물들이 여러가지 다양한 색을 띠는 주요한 원인은 전이 원소수에 의한 것이다. 분홍색은 망간 3가, 청색 내지 녹색은 철 2가와 망간 2가, 청녹색은 구리 2가, 흑갈색은 철 2가, 철 2가-철 3가, 그리고 철 2가-티타늄 4가에 의해 색을 띠게 된다. 분홍색 전기석 경우, 망간 3가는 압축된 Y자리에서 $\text{O}(1)\text{H}-\text{O}(3)\text{H}$ 축을 따라 잔-텔러 변형으로 안정한 구조를 가지게 된다. 전기석 광물들을 고온으로 열처리하면, 일반적으로 분홍색 혹은 빨간색을 띠는 전기석들은 무색으로 변색이 되며, 청녹색은 녹색으로 색상이 변하며, 황녹색 같은 경우는 일부 샘플들만 열은 녹색으로 바뀌는 모습이 관찰되었다. 엘바이트-흑전기석 계에서는 철과 망간의 함량에 따라 색의 누대구조가 나타난다. 녹색 영역에서는 철의 함량이 높으며 분홍색 영역에서는 망간의 함량이 높다. 망간은 황색이나 무색 영역에서 보다 짙은 황색 영역에서 증가한다.

INTRODUCTION

Tourmaline is the most popular mineral of all colored gemstones. Its attractive appearance, complex composition, and interesting electrical and optical properties have been a subject of intensive research of gemologists and mineralogists. Especially, the wide range of variation in the chemical composition and color of the tourmaline group drew many mineralogists' attention for optical investigation. Tourmaline shows various color chiefly depending on the chemical composition.

Tourmaline is a borosilicate with general formula $XY_3Z_6(BO_3)_3Si_6O_{18}(OH)_4$ and space group R3m (Wilkins et al., 1969). The X site is usually occupied by large cations such as Na^+ , K^+ , Ca^{2+} , while the Y site by smaller cations such as Al, Li, Fe^{2+} , Fe^{3+} , Mg, Mn^{2+} . The Z site is chiefly occupied by Al, but Al can be replaced by Fe^{3+} , Cr^{3+} and V^{3+} (Barton, 1969). Because of a wide substitution in Y site, tourmaline minerals usually have end member; dravite, schorl, and elbaite with Mg, Fe, and (Li, Al) in the Y position, respectively.

There are many important previous works about the origin of colored tourmaline. Colors are usually determined by small amounts of transition elements (Dietrich, 1985). In particular, blue to green color is attributed to various processes involving both Fe^{2+} and Fe^{3+} ions (Mattson and Rossman, 1987) and $Fe^{2+}-Ti^{4+}$ charge transfer (Dietrich, 1985). Cr^{3+} and V^{3+} ions have been identified as coloring agents in green dravite and uvite (Schmetzer and Bank, 1979) but never in elbaite. Several investigators briefly mentioned Cu^{2+} as potential coloring agent in blue and green elbaite on the basis of emission spectrographic analyses (Staatz et al., 1955).

The analysis by electron microprobe of color-zoned samples has permitted a study of the distribution of atoms in these samples and the identification of some characteristics of cationic

solid solution in the elbaite-schorl series. The present study aims to characterize chemical and optical absorption spectroscopic properties of colored tourmalines.

MATERIALS AND METHODS

The majority of pink and colorless tourmaline samples are from San Diego mine in California, U.S.A., the blue/green and pink tourmaline samples from anonymous mine, Brazil, and the brownish black tourmaline samples from Uncheon and Haksan mines in Korea. The color of each specimen appears homogeneous when the polished thin sections are viewed with naked eye. Colors of the studied colored tourmaline specimens were described (Table 1) using the terminology of the Munsell Book of Color (1979). The color was visually determined on parallel-polished slices about 1.5 mm thick which were cut parallel to c axis. Because of tourmaline's strong pleochroism, the face-up color of faceted gemstones might be significantly different from descriptions in Table 1.

Many individual crystals exhibit zoning involving two or more hues and/or color saturations. The color zoning in a given tourmaline mineral may be perpendicular to c, parallel to c, parallel to pyramid faces, irregular or some combination of these. The boundary between different color zones range from abrupt to gradational over a few microns to a few millimeters. Especially the tourmaline samples from the San Diego mine consist of the nearly colorless core and pink rim, or the dark pink core and yellowish green rim. The tourmaline samples from Brazil show color zoning di-colored (green and pink), tri-colored (pink-colorless-pink, or colorless-yellow-deep yellow), and tetra-colored (pink-green-colorless-pink, or brown-green-colorless-pink) (Table 2).

Thin slices cut parallel and perpendicular to c axis were prepared from each mono-colored tourmaline crystal. The crystallographic orien-

Table 1. Color descriptions of colored tourmaline samples.

Sample #	Mineral name	Color*	Munsell notation** H V/C	Locality***
AB1	Schorl	brownish black	5B 5/3	a
K1	Schorl	brownish black	5B 5/3	b
K2	Schorl	brownish black	5B 5/3	b
AP1	Elbaite	pink	2RP 7/5	a
AP2	Elbaite	pink	5RP 8/5	a
AWB	Elbaite	light blue	2.5BG 5/2	a
AWG	Elbaite	greenish yellow	10Y 6/4	a
B6	Schorl	light green	10GY 6/5	c
B7	Schorl	bluish green	5BG 4/2	c
B8	Elbaite	pink	5RP 6/1	c
BG1	Schorl	bluish green	2.5BG 6/5	c
BG2	Schorl	green	5G 4/6	c
BG3	Schorl	light bluish green	5BG 6/5	c
BG4	Schorl	light green	8BG 7/7	c
BG6	Schorl	greenish yellow	10Gy 6/5	c
BPB	Elbaite	bluish green	6.5PB 7/5	c

* Color of a 1.5 mm slice containing the c axis.

** H: Munsell hue, V: Munsell value, C: Chroma

*** a: San Diego mine, U.S.A., b: Haksan and Uncheon mine, Korea, c: anonymous mine, Brazil.

Table 2. Color descriptions of color-zoned tourmaline samples.

Sample #	Color-zoned	Locality
CZ-1	Di-colored yellowish green -dark pink)	America
CZ-2	Tri-colored (colorless- yellow-deep yellow)	Brazil
CZ-3	Tri-colored (brown-pink- colorless)	Brazil
CZ-4	Tetra-colored (blue-green- colorless-pink)	Brazil
CZ-5	Tetra-colored (brown-green -colorless-pink)	Brazil

tation of the crystal fragment was determined using striations parallel to c axis on the prisms faces. Each specimen was cut using a diamond saw. Thin slices were mounted on a glass slide with a non-rigid epoxy. After grinding and polishing the one surface, the epoxy and crystal together were lifted from the glass, turned over, and remounted with a non-rigid epoxy upon a glass slide. The thin slice was then ground to the thickness of 0.1–0.2 mm and polished with 1 μ m

alumina powder. Crystal thickness were measured with a micrometer. After grinding and polishing the surface, crystal slice was detached from the glass slide.

Chemical analysis was performed with a wavelength dispersive X-ray spectrometer at an acceleration voltage of 15 kV using A JEOL JCSA 733 Superprobe instrument equipped with a Link automation system. Probe beam current and diameter were 10 nA and 5 μ m, respectively. Data correction was performed using a ZAF correction procedure.

Preliminary X-ray diffraction (XRD) measurements were performed with a Rigaku RAD3-C automatic horizontal goniometer diffractometer equipped with a scintillation counter and a Cu X-ray tube operating at 35kV/20 mA in a continuous scan mode. Slit set was 1°–0.15–1°. Scanning speed was 2°/min. All the experiments were carried out at the XRD room where temperature was adjusted to 20 ± 3°C. Cell parameter refinement was performed with X-ray powder diffraction data using the least squares

program by the Appleman–Evans called LSUCRIPC (Appleman and Evans, 1973; Garvey, 1986). The 2θ range was $10\text{--}80^\circ$.

Optical absorption spectra were recorded using a Cary 5 spectrophotometer with polarizer in the Research Institute for Basic Sciences, Dongeui University. The spectrophotometer has the wavelength range involving ultraviolet, visible, and near infrared (300–2000 nm). Samples were then analysed in the spectroscopic experiment with self-supporting slabs placed on apertures of appropriate size and shape.

Optical absorption spectra were obtained for heat-treated samples in furnace. Temperature was raised from 300°C to 900°C by increasing 100°C per each day for the first three days and 100°C per every two days for the next eight days.

RESULTS AND DISCUSSION

Chemistry of Mono-colored Tourmaline Samples

Results of chemical analyses of 16 samples are presented in the Table 3. The structural formula were calculated on the basis of 24.5 oxygens. Inasmuch as boron is the only cation to be expected in regular triangular coordination (Tsang and Ghose, 1973), it is assumed that there are 3 boron atoms in the structural formula and the weight percent of B_2O_3 necessary to produce the 3 boron atoms was calculated for each analysis. Analyses performed at three random locations on each specimen show only very slightly compositional variation, as might be expected from the fairly uniform coloration. It revealed that the elemental concentrations vary within 5%. Total Fe determined by microprobe analysis is reported as FeO. The Mössbauer analysis shows that iron in all of the blue/green tourmaline samples used in experiment is Fe^{2+} (Kim, 1993).

Cell Parameters of Mono-colored Tourmaline Samples

For illustrating the unit cell parameters of the end members in tourmaline samples, tourmalines with three different colors that are the brownish black, blue/green, and pink were selected. Results of the unit cell determinations are listed in Table 4 and the values of a and c are plotted in Figure 1. All samples are plotted close to the schorl–elbaite and dravite–schorl reference line by Donnay and Barton (1972). Samples with detectable MgO are displaced slightly toward higher values of c parameter. Generally, the brownish black tourmaline samples have $a=15.96\text{--}16.01\text{ \AA}$, $c=7.15\text{--}7.16\text{ \AA}$, pink tourmaline samples $a=15.82\text{--}15.87\text{ \AA}$, $c=7.09\text{--}7.10\text{ \AA}$, and

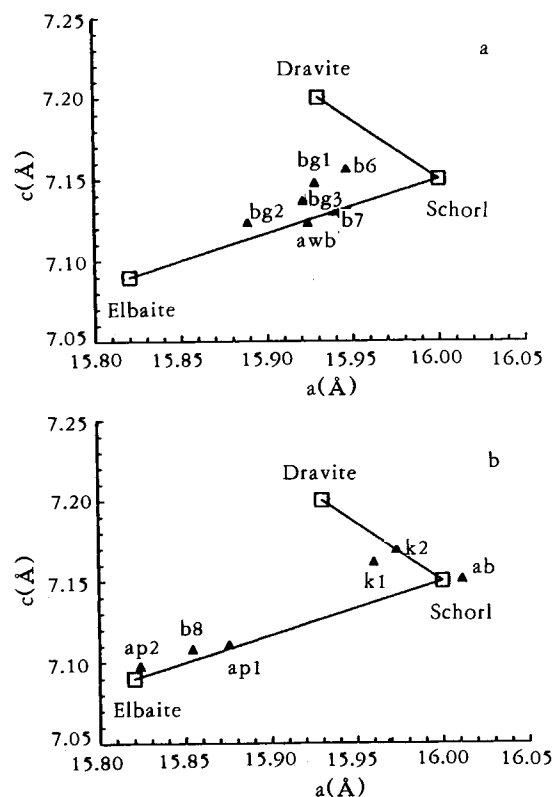


Fig. 1. Unit cell dimensions of tourmaline samples. (a) Blue/green tourmaline samples. (b) Brownish black and pink tourmaline samples.

Table 3. Electron microprobe analyses of colored tourmaline samples (wt%).

Sample	AB	K1	K2	AP1	AP2	B8	AWB	AWG
SiO ₂	34.63	34.64	35.70	38.43	38.14	38.02	37.36	37.78
TiO ₂	0.10	0.02	0.10	0.00	0.00	0.04	0.00	0.00
Al ₂ O ₃	35.37	32.20	34.54	40.71	42.43	43.93	39.50	39.22
FeO	14.43	14.56	9.96	0.05	0.00	0.05	0.19	1.08
MgO	0.19	0.35	2.71	0.00	0.00	0.01	0.00	0.03
MnO	0.51	0.97	0.12	0.56	0.67	0.05	4.31	0.89
CaO	0.05	0.26	0.06	1.76	0.41	0.02	0.41	1.54
Na ₂ O	1.63	2.33	1.56	1.53	1.92	1.80	2.26	1.85
K ₂ O	0.01	0.00	0.04	0.00	0.01	0.01	0.00	0.00
Cr ₂ O ₃	0.08	0.01	0.02	0.02	0.00	0.00	0.07	0.00
CuO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	87.01	85.36	84.80	83.05	83.57	83.92	84.11	82.47

Cation normalized to oxygen 24.5

Si	5.79	5.96	5.96	6.16	6.06	5.98	6.06	6.16
Ti	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00
Al	6.98	6.54	6.80	7.70	7.95	8.16	7.55	7.55
Fe	2.02	2.09	1.39	0.01	0.00	0.01	0.03	0.15
Mg	0.05	0.09	0.67	0.00	0.00	0.00	0.00	0.01
Mn	0.07	0.14	0.02	0.08	0.09	0.01	0.59	0.14
Ca	0.01	0.05	0.01	0.30	0.07	0.00	0.07	0.27
Na	0.53	0.78	0.51	0.48	0.59	0.55	0.71	0.59
K	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
Cr	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Sample	B6	B7	BG1	BG2	BG3	BG4	BG6	BPB
SiO ₂	36.73	36.70	36.95	37.67	36.07	37.31	37.69	37.37
TiO ₂	0.04	0.00	0.00	0.09	0.02	0.00	0.00	0.00
Al ₂ O ₃	36.66	36.98	36.36	38.04	36.16	35.93	37.14	40.14
FeO	4.86	7.57	7.04	4.48	5.61	6.21	6.05	0.00
MgO	0.23	0.07	0.02	0.29	0.01	1.99	0.21	0.00
MnO	0.85	0.37	0.25	1.31	0.63	0.22	0.64	2.15
CaO	0.13	0.08	0.04	0.21	0.15	0.07	0.11	0.35
Na ₂ O	2.83	2.61	3.02	2.84	2.73	2.72	2.96	2.24
K ₂ O	0.02	0.02	0.02	0.01	0.02	0.01	0.02	0.01
Cr ₂ O ₃	0.01	0.03	0.02	0.01	0.00	0.00	0.00	0.00
CuO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.60
Total	82.34	84.43	83.74	84.97	81.39	84.45	84.81	82.32

Cation normalized to oxygen 24.5

Si	6.15	6.06	6.14	6.11	6.13	6.12	6.15	6.10
Ti	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
Al	7.24	7.21	7.13	7.28	7.25	6.96	7.16	7.73
Fe	0.68	1.05	0.98	0.61	0.80	0.85	0.83	0.00
Mg	0.06	0.02	0.01	0.07	0.00	0.49	0.05	0.00
Mn	0.12	0.05	0.04	0.18	0.09	0.03	0.09	0.30
Ca	0.02	0.01	0.01	0.04	0.03	0.01	0.02	0.06
Na	0.92	0.84	0.97	0.89	0.90	0.86	0.94	0.71
K	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.07

AP1, AP2, AWB, AWG, B8, and BPB, are elbaite. AB1, K1, K2, B6, B7, BG1, BG2, BG3, BG4, and BG6 are schorl.

blue/green tourmaline samples $a=15.88-15.94 \text{ \AA}$,
 $c=7.12-7.15 \text{ \AA}$.

Chemistry of Color-zoned Tourmaline Samples

Color-zoned tourmaline samples of the elbaite-schorl series were analyzed using electron microprobe. The distribution of elements in color-zoned minerals gives an important information on the chemical environment of their formation. The composition in the color-zoned tourmaline samples are of particular interest since they reflect the trends of chemical variation. In the analyzed samples, the Mn and Fe contents increase with decreasing Al content. The major compositional variation is due to the substitution of $(\text{Li}+\text{Al})$ for $(\text{Fe}^{2+} + \text{Mg} + \text{Mn})$ in the Y site (Ramberg, 1952; Henry and Guidotti, 1985). In this respect, we can deduce the behavior of the cations in relation to the changes of color. Mn plays an important role in the pink and colorless zones. In the blue/green and brown zones, Fe give a great influence on the changes of color.

Sample CT-1 tourmaline is di-colored with yellowish green and dark pink zones. The Al content is inversely related to Fe, Mn, Mg, and Ca contents. Al tends to increase toward the yellowish green zone, whereas Fe, Mn, Mg, and Ca decrease toward the dark pink zone. Si shows no distinct variation. In the dark pink zone, Mn and Mg are very low, and Fe is nearly absent. $\text{Mn}/(\text{Fe} + \text{Mg} + \text{Mn})$ ratios are high in the dark pink zone (0.85-1) compared with the yellowish green zone (0.5-0.6) (Figs. 2a and 3a).

Sample CT-2 tourmaline is tri-colored with colorless, yellow, and deep yellow zones. Si and Na show no distinct variation in all three zones. Al tends to decrease in the deep yellow zone (Fig. 2b). Mg tends to decrease slightly in the yellow and deep yellow zones whereas Mn increases in the deep yellow zone. Fe is variable in the same zone, especially in the yellow and deep yellow

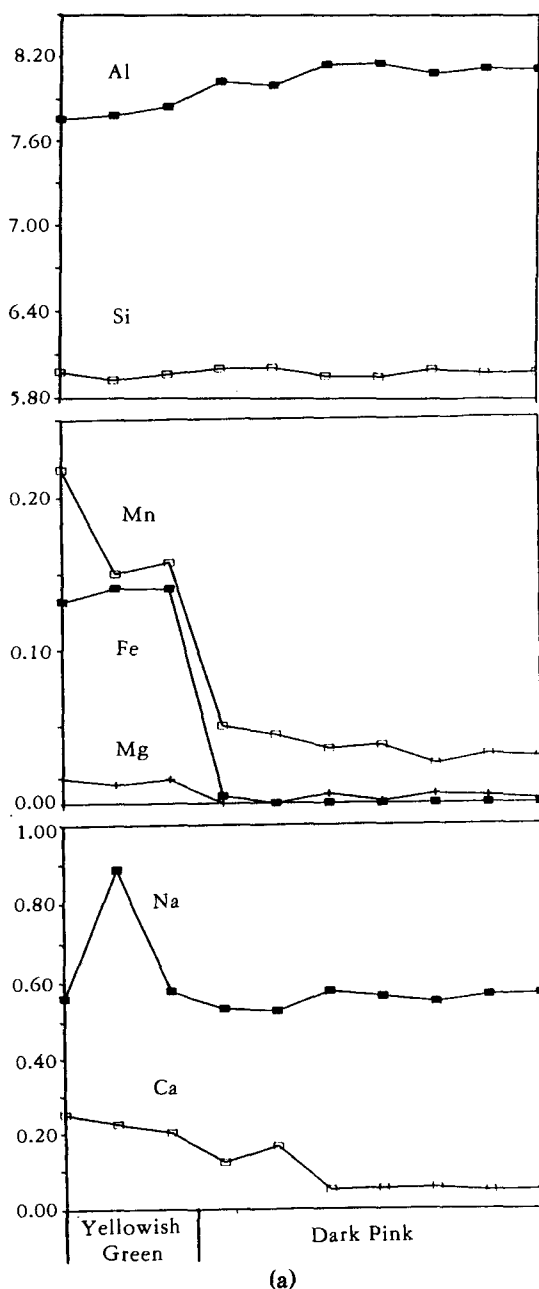
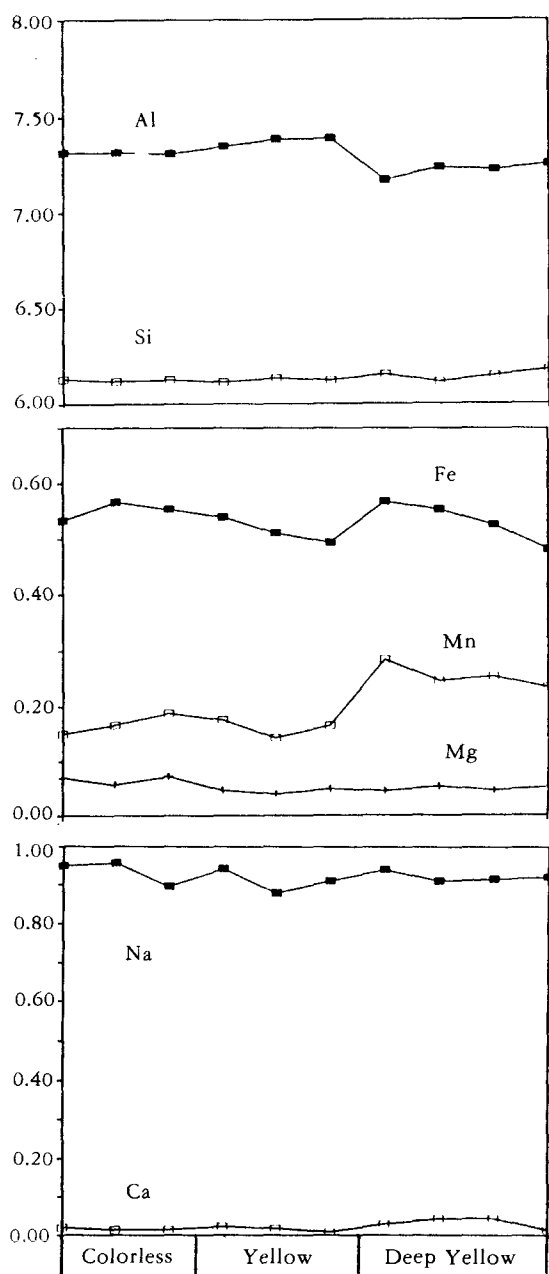


Fig. 2. Diagrams showing the chemical variation with change of color in the color-zoned tourmalines. Numvers represent the cation-normalized values to oxygen 24.5. (a) Di-colored tourmaline(sample CZ-1) (b) Tri-colored tourmaline(sample CZ-2) (c) Tri-colored tourmaline(sample CZ-3) (d) Tetra-colored tourmaline(sample CZ-4) (e) Tetra-colored tourmaline (sample CZ-5)

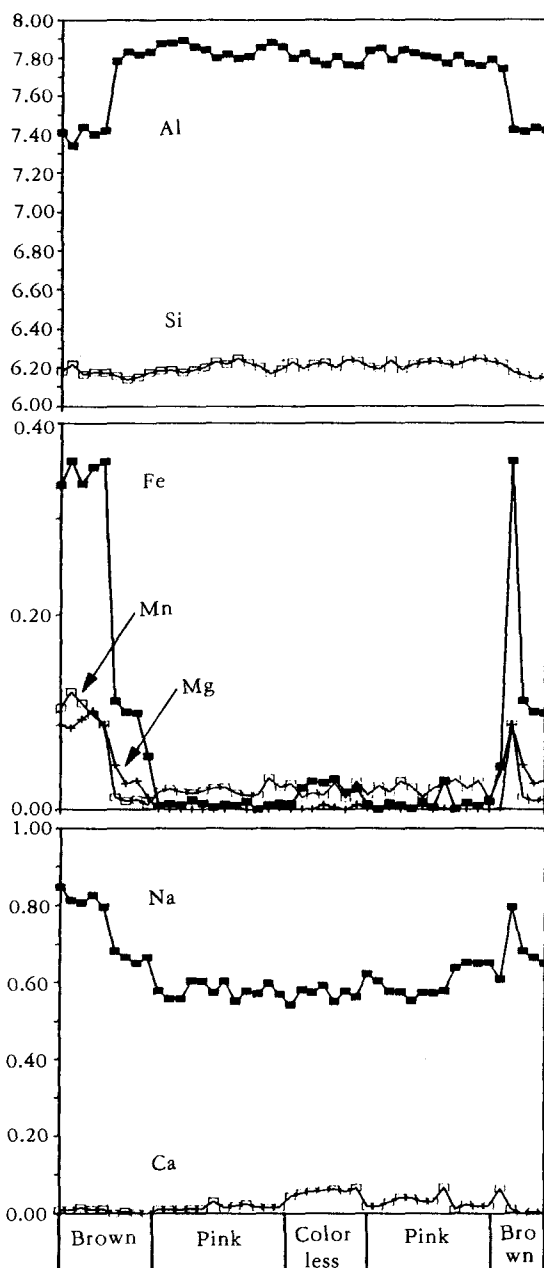
Chemical and Optical Absorption Spectroscopic Study of Colored Tourmalines



(b)

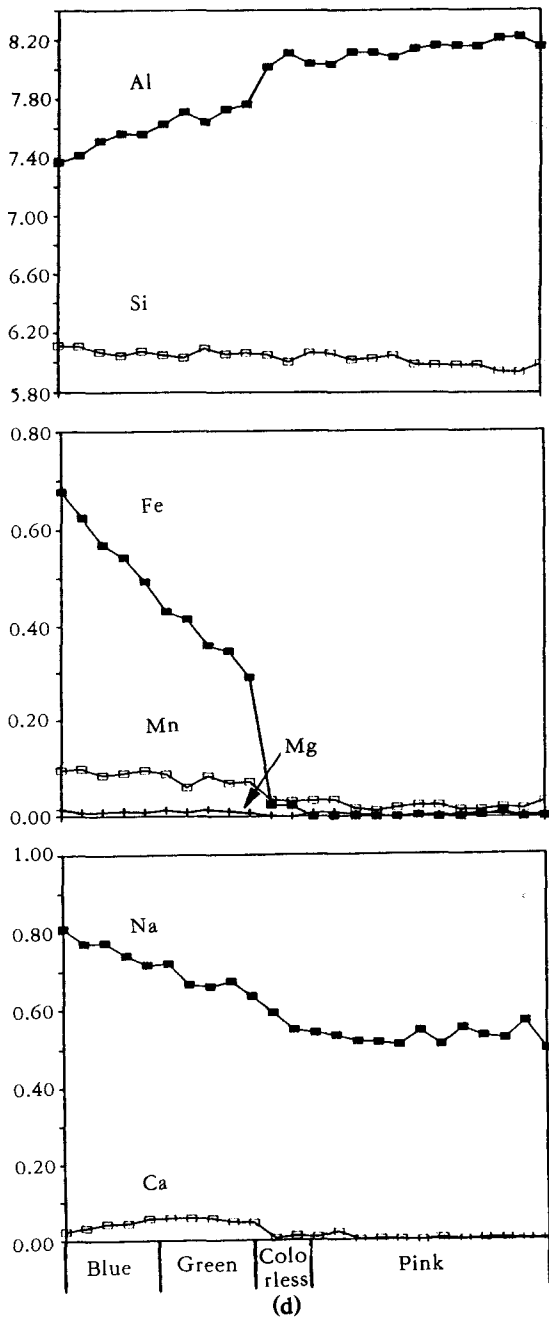
zones. Of course, $Mn/(Fe + Mg + Mn)$ values are high in the deep yellow zone (0.23) compared with other zones (0.17) (Fig. 3b).

Sample CT-3 tourmaline is tri-colored with brown, pink, and colorless zones. This sample shows symmetric color zoning of brown-pink-

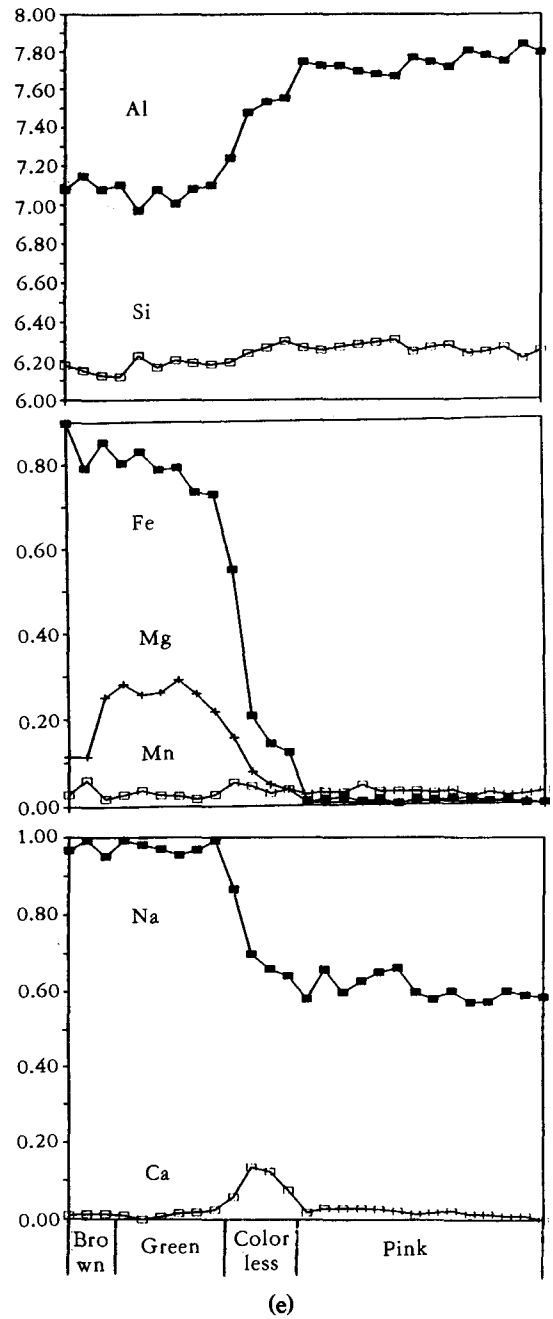


(c)

colorless-pink-brown. The variation of Si content does not show definite relationships to color. In the pink and colorless zones, Al is very high, whereas Fe, Mn, Mg, and Na are very low compared with the brown zone. Ca increases slightly in the colorless zone (Figs. 2c and 3c).



Sample CT-4 tourmaline is tetra-colored with blue, green, colorless, and pink zones. This type is called the water-melon tourmaline; it has a pink core and a green rim. From the blue via green to colorless and pink, Al tends to increase, whereas Si, Na, Fe, and Mn decrease. The pink or colorless



zone in characterized by the low contents of Fe, Mn, and Ca(Figs. 2d and 3d).

Sample CT-5 tourmaline is tetra-colored with brown, green, colorless, and pink zones. This sample shows chemical variations similar to sample CT-4 tourmaline, but Si content increases

in the colorless and pink zones. The Ca content increases only in the colorless zone. The Mn

content is nearly constant (Figs. 2e and 3e).

Optical Absorption Spectroscopy

Color of mineral comes from differential absorption and transmission of light waves. Thin slices of tourmaline samples which were cut either parallel or perpendicular to the c axis were used for the measurement of absorption properties. The slices do not have the same thickness, so it was difficult to compare the relative absorption in the spectra. But regardless of color, it was known that E_⊥c spectrum of tourmaline was generally more intense and absorptive than E_∥c spectrum.

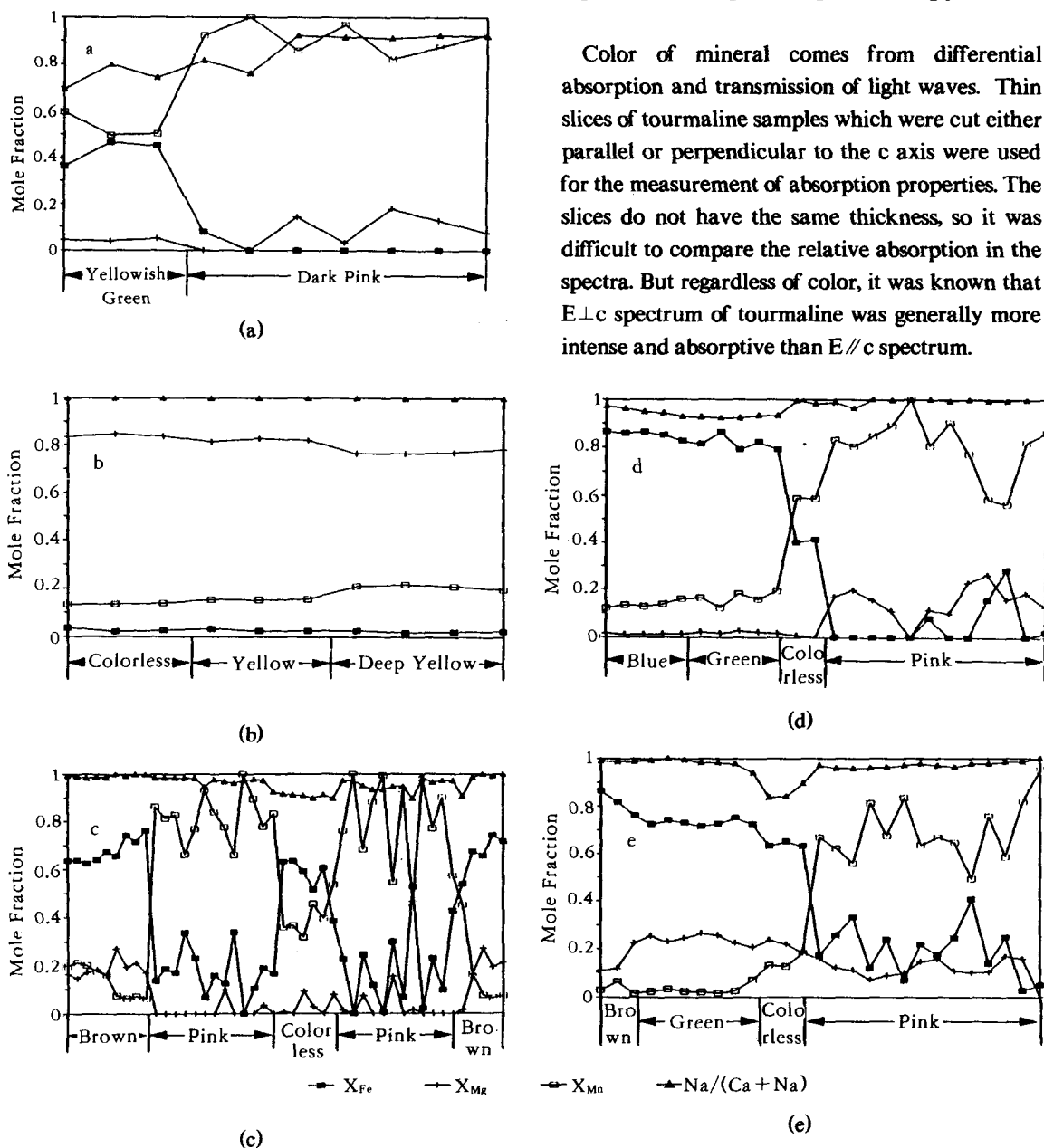


Fig. 3. Diagrams showing the variation in mole fractions of cations in Y site with different color in the color-zoned tourmalines. (a) Di-colored tourmaline (sample CZ-1), (b) Tri-colored tourmaline (sample CZ-2), (c) Tri-colored tourmaline (sample CZ-3), (d) Tetra-colored tourmaline (sample CZ-4), and (e) Tetra-colored tourmaline (sample CZ-5).

Pink Tourmaline

Pink tourmalines show several absorption bands between 300 and 2000 nm that have been extensively studied by Manning (1968, 1969, and 1973). The color of pink tourmaline is due to the absorption of light in the green and blue regions of the spectrum so that the emergent light from the crystal is enriched in red and pink. The color also changes in intensity and tonality from sample to sample.

Mn and Fe cations are present in pink tourmaline samples. However, the Fe concentration is generally low. The color is probably due to the absorption of light by the Mn cation. 392 and 520 nm peaks which appear in the sample AP2 (Fig. 4) are due to Mn^{3+} at the Y site (Isotani, 1988). In $E//c$ spectra of room temperature, 520 nm absorption peak of sample B8 is more intense than sample AP2 because of high Mn content (Figs. 4 and 5). Bands in the 1400 to 1500 nm and 1800 to 2000 nm regions are a typical harmonics of OH combinations, respectively (Wickersheim et al., 1959).

Many studies concerning the effects of heating on tourmaline samples have been performed. When the pink tourmaline was heated, 512 nm peak shown by Mn in the Y site disappeared at 500 °C (Fig. 5). Heating experiment was also carried out on the sample B8. Temperature was raised to 500 °C from the starting 300 °C by increasing 100 °C per each day. The spectrum of heat-treated sample does not show 520 nm peak owing to Mn^{3+} in the Y site. Therefore, the pink color turns to colorless. Heating at 500 °C eliminates the pink color, but the yellow color is not affected.

The Mn^{3+} ion is stabilized in the Y site by a Jahn-Teller distortion along the $O(1)H-O(3)H$ axis. By using the method by Isotani (1988), these bands are assigned to the Mn^{3+} absorption in the Y site compressed along the $O(1)H-O(3)H$ axis.

Blue/Green Tourmaline

The spectra of blue/green tourmalines are

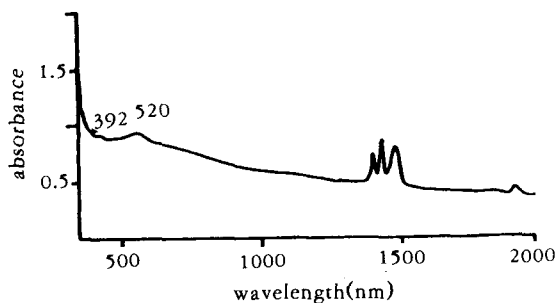


Fig. 4. Optical absorption spectra of pink tourmaline (sample AP2) at room temperature. $E//c$ polarization. Sample thickness is 0.24 mm.

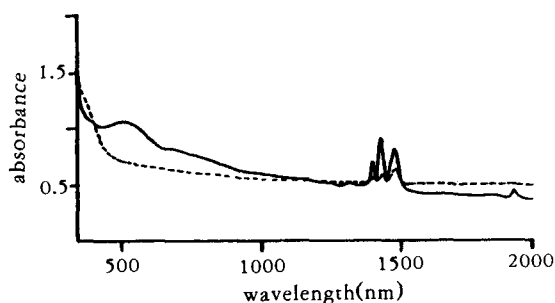


Fig. 5. Optical absorption spectra of pink tourmaline (sample B8) at room temperature (solid line) and 500 °C (broken line). Sample thickness is 0.24 mm ($E//C$).

clearly polarization-dependent and very intense for polarized light perpendicular to the c axis. This $E\perp c$ spectrum of blue/green tourmaline contains two broad bands of comparable intensity centered at 720 and 1100 nm. According to Faye et al. (1968), Burns (1972), and Burns and Simon (1973), the peak at 720 nm arises from Fe^{2+} ions in the smaller Z octahedra, while transitions within Fe^{2+} ions in the larger Y octahedra give rise to absorption bands around 1100 nm. The $E//c$ spectrum shows broader band at 1100 nm than $E//c$ spectrum and contains sharp peaks due to first harmonic OH vibrations at 1410, 1440, and 1470 nm. Weak bands in the 1800–2000 nm region are due to OH combinations (Fig. 6).

Fe^{2+} is by far the most common transition element ion in most analysed tourmaline samples. Figure 7 shows the optical absorption absorption

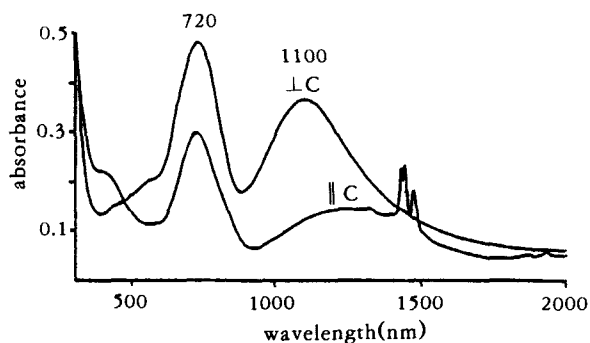


Fig. 6. Optical absorption spectra of blue/green tourmaline (sample B7) at room temperature. Sample thickness ($E \perp c$) is 0.20 mm. Sample thickness ($E // c$) is 0.25 mm.

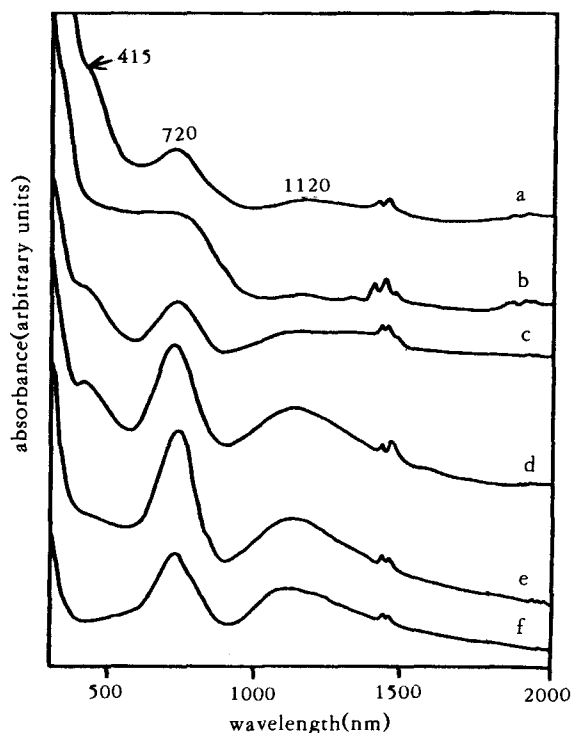


Fig. 7. Optical absorption spectra of blue/green tourmaline samples at room temperature. All sample were cut parallel to the c axis. (a) Sample AWG, sample thickness; 0.33 mm, (b) Sample AGY, sample thickness; 0.20 mm, (c) Sample BG2, sample thickness; 0.22 mm, (d) Sample B6, sample thickness; 0.49 mm, (e) Sample BG3, sample thickness; 0.13 mm, and (f) Sample BG1, sample thickness; 0.15 mm.

Table 4. Unit cell dimensions of selected tourmaline samples.

Sample #	color	a (Å)	c (Å)	V (Å ³)	number of peaks used
AB	brownish black	16.011	7.150	1551.8	25
K1	brownish black	15.960	7.161	1579.9	25
K2	brownish black	15.973	7.168	1583.9	33
AP1	pink	15.875	7.109	1551.8	20
AP2	pink	15.823	7.096	1538.9	19
B8	pink	15.854	7.107	1547.1	27
ABW	light blue	15.929	7.122	1565.1	20
B6	light green	15.946	7.155	1575.7	29
B7	bluish green	15.938	7.129	1568.3	23
BG1	bluish green	15.927	7.147	1570.3	25
BG2	green	15.889	7.122	1557.2	26
BG3	green	15.920	7.135	1566.4	32

spectra of a blue/green tourmaline samples which were cut to the $//c$ orientation. Chemical analysis shows that samples have both Mn and Fe (Table 3). As Mn/Fe ratio decreases, the color of the samples changes from yellowish green through green to bluish green (Table 5). In this spectrum, 415 nm peak is caused by Mn^{2+} in the Y site, and 720 and 1110 nm by Fe^{2+} .

The change of color by heat treatment in the green tourmaline samples was examined. Generally it was observed that the blue/green tourmaline samples can be lightened by heating to 650 °C (Anon, 1932) but in this work most green tourmaline samples show no color change when it was heated at 600 °C for five days and at 700 °C for two days. When it was heated at 800 °C, it changed to thick and opaque brown or red (Figs. 8 and 9). But in the sample BG6, the yellowish green color changed to light green (Fig. 9). The Mössbauer analysis shows that all Fe ions in the Fe-bearing tourmaline samples are ferric when heating at 800 °C but the sample BG6 shows the hyper fine effect unlike other samples (Kim, 1993). Hence, it is inferred that it has different proton environment compared with other heat-treated samples.

Table 5. Correlation between Mn/Fe ratio and various colors in blue/green tourmaline samples.

sample #	Color	HV/C	Mn (Mole%)	Fe (Mole%)	Mn/Fe ratio
AWG	greenish yellow	10Y 6/4	0.14	0.15	0.93
AGY	yellowish green	7.5GY 8/5	0.04	0.09	0.44
BG2	green	5G 4/6	1.31	4.48	0.29
B6	light green	10gy 6/5	0.85	4.86	0.17
BG3	light bluish green	5BG 6/5	0.63	5.61	0.11
BG1	bluish green	2.5BG 6/5	0.25	7.04	0.03

Bluish Green Tourmaline

The optical absorption spectra of the bluish green tourmalines are characterized by two features; a pair of strong broad bands in the 740 and 931 nm region (absorbing more strongly in the $E \perp c$ direction), and a series of weak sharp bands in the 1400 to 1500 nm region and very weak peaks in the 1800–2000 nm region strongly polarized in the $E // c$ direction (Fig. 10). Bands in the 1400 to 1500 nm region are a typical harmonics of OH vibrations which are present in all of the observed spectra. The $E // c$ spectrum contains weak bands in the 1800–2000 nm region owing to OH combinations.

Cu is the principal coloring agent in elbatite. Electron microprobe analyses (Table 3) show that this tourmaline contains little or no Ti, Cr, or Fe except Cu and Mn as major transition elements. Cu^{2+} ion is responsible for two strong absorption bands around 695 and 940 nm, which result in a bluish green color. The bands in the 695 and 940 nm regions are interpreted as arising from absorption by the Cu^{2+} ion (Warner, 1935; Staatz et al., 1955; Rossman, 1991).

Additional absorption around 580 nm is questionable. The absorption peak of Mn^{3+} in the Y site generally appears in 520 nm which is

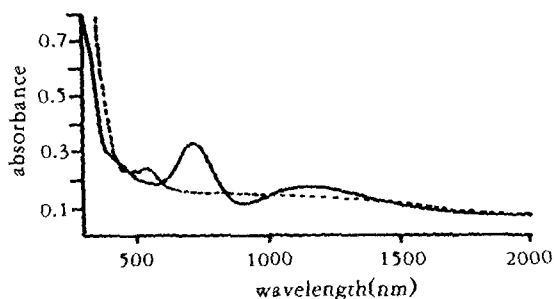


Fig. 8. Optical absorption spectra of light green tourmaline (sample BG4) at room temperature (solid line) and 800 °C (Broken line). Sample thickness is 0.20 mm ($E // c$).

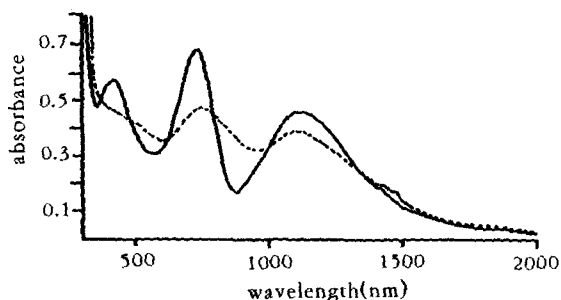


Fig. 9. Optical absorption spectra of greenish yellow tourmaline (sample BG6) at room temperature (solid line) and 800 °C (Broken line). Sample thickness is 0.23 mm ($E // c$).

shifted to 580 nm in this spectrum (Fig. 10). Therefore, the further study is needed to reveal whether or not this peak is due to Mn.

Unique greenish blue appeared when the bluish green samples were heated at 600 °C. The major cause of this color change is the shifting of 960 nm peak by Cu^{2+} in the Y site to 890 nm (Fig. 11). The weak 580 nm disappeared when it is heated at 600 °C. Therefore, the color changes by heat treatment is related to the increase of the crystal field strength of octahedral Cu in Y site.

Brownish Black Tourmaline

The basic characteristics of Fe^{2+} absorption spectra in tourmaline are illustrated in Figure 12. The 430 nm band in $E \perp c$ spectrum is due to $Fe^{2+} - Ti^{4+}$ charge transfer interaction. The broad

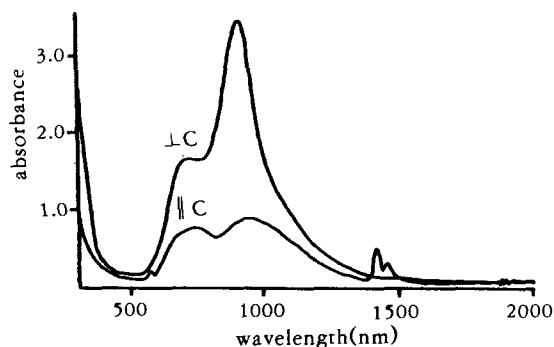


Fig. 10. Optical absorption spectra of bluish green tourmaline (sample BPB) at room temperature. Sample thickness ($E \perp c$) is 0.30 mm. Sample thickness ($E // c$) is 0.31 mm.

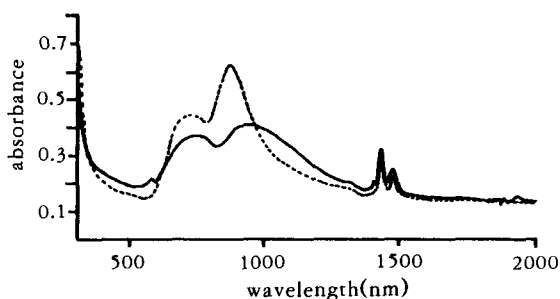


Fig. 11. Optical absorption spectra of bluish green tourmaline (sample BPB) at room temperature (solid line) and 800°C (broken line). Sample was cut parallel to the c axis. Sample thickness is 0.02 mm.

bands centered at 720 and 1100 nm can be assigned to components of the Fe^{2+} transition (${}^6T_2 \rightarrow {}^5E$) split by the non-cubic crystal field (Smith, 1978). The sharp bands between 1300 and 1500 nm are vibrational transitions.

The brownish black tourmaline samples contain on the whole more iron than another tourmaline samples (Table 3). According to the Mössbauer analysis, Fe^{2+} in sample K2 is predominantly partitioned into the Y site and partly in the Z site (Kim, 1993). Sample K1 unlike other samples has Fe^{3+} (Kim, 1993) and its optical spectrum shows absorption peaks at 594 and 635 nm peaks (Fig. 13). A comparison of this spectrum with that of a typical tourmaline (Fig. 12) shows the basic

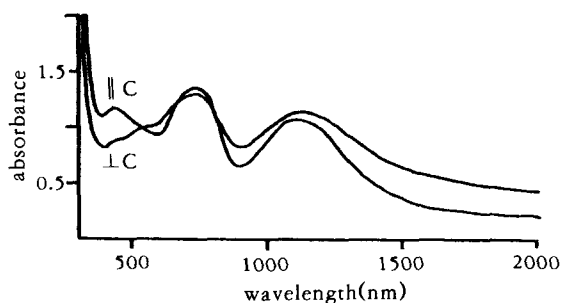


Fig. 12. Optical absorption spectra of brownish black tourmaline (sample K2) at room temperature. Sample thickness ($E \perp c$) is 0.23 mm. Sample thickness ($E // c$) is 0.26 mm.

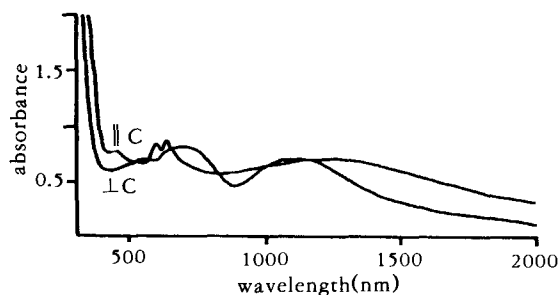


Fig. 13. Optical absorption spectra of brownish black tourmaline (sample K1) at room temperature. Sample thickness ($E \perp c$) is 0.20 mm. Sample thickness ($E // c$) is 0.21 mm.

features of $Fe^{2+} - Fe^{3+}$ interactions in tourmaline. $Fe^{2+} - Fe^{3+}$ charge transfer has been assigned to the comparatively weak features at 550–670 nm (Smith, 1978; Faye et al., 1974; Townsend, 1970; Mattson et al., 1987). The polarization of ion-pair transitions along intercation vectors is a familiar aspect of charge transfer transitions. The dominant distribution of $Fe^{2+} - Fe^{3+}$ pairs in tourmaline is in site combinations with vectors perpendicular to the c axis. This effect produces the visible pleochroism of tourmaline. $Fe^{2+} - Fe^{3+}$ charge transfer is not a prominent feature of tourmaline spectra. $Fe^{2+} - Fe^{3+}$ charge transfer would be expected to be especially intense in those tourmaline samples with significant amounts of both Fe^{2+} and Fe^{3+} .

Table 6. Summary of spectroscopic studies for various colored tourmaline samples.

Sample		Absorption(nm)	Assignment	Pleochroism
pink tourmaline	E//C	392 520 1384, 1402, 1431 1465 1845, 1878, 1902	Mn ³⁺ (Y site) Mn ³⁺ (Y site) first harmonic OH vibrations OH combinations	weak pink
	E⊥C	525 1386, 1398, 1427 1845, 1878, 1902	Mn ³⁺ (Y site) first harmonic OH vibrations OH combinations	pink
blue/green tourmaline	E//C	415 720 1110 1419, 1437, 1464 1859, 1921	Mn ²⁺ (Y site) Fe ²⁺ (Z site) Fe ²⁺ (Y site) first harmonic OH vibrations OH combinations	blue/green
	E⊥C	415 717 1111 1422, 1466	Mn ²⁺ (Y site) Fe ²⁺ (Z site) Fe ²⁺ (Y site) first harmonic OH vibrations	intensive blue/ intensive green
bluish green tourmaline	E//C	580 740 931 1379, 1470 1837, 1866, 1921	Cu ²⁺ (Y site) Cu ²⁺ (Y site) first harmonic OH vibrations OH combinations	bluish green
	E⊥C	580 738 841	Cu ²⁺ (Y site) Cu ²⁺ (Y site)	slight grayish green
brownish black tourmaline	E//C	430 594, 640 720 1115	Fe ²⁺ -Ti ⁴⁺ Fe ²⁺ -Fe ³⁺ Fe ²⁺ (Z site) Fe ²⁺ (Y site)	brownish black
	E⊥C	720 1100	Fe ²⁺ (Z site) Fe ²⁺ (Y site)	dark bluish black

Table 6 shows the summary of spectroscopic studies for various colored tourmaline samples.

CONCLUSIONS

Least-squares refinements give unit cell dimensions: a=15.96-16.01 Å, c=7.15-7.16 Å for the brownish black tourmaline samples, a=15.82-15.87 Å, c=7.09-7.10 Å for the pink tourmaline samples, and a=15.88-15.94 Å, c=7.12-7.15 Å

for the blue/green tourmaline samples.

The colors of tourmalines are responsible for the transition elements. Pink color is attributed to the Mn³⁺ ions, blue/green to Fe²⁺, bluish green to Cu²⁺, and brownish black to Fe²⁺, Fe²⁺-Fe³⁺, and Fe²⁺-Ti⁴⁺. The Mn³⁺ ions of pink color tourmalines are stabilized in the Y sites compressed along the O(1)H-O(3)H axis by the Jahn-Teller distortion. Heating removes the pink or red component from tourmalines, producing

colorless stones from the pink and red ones. The bluish green samples change into the greenish blue ones and a certain yellowish green samples change into the light green ones by heat treatment.

Chemical analyses of color-zoned tourmaline samples show that the concentration of Fe and Mn are variable depending on the color zones in the elbaite-schorl series. The green zone is characterized by the high content of Fe, whereas the pink zone by the high content of Mn. Mn increases in the deep yellow zone compared with the yellow and colorless zones.

REFERENCES

- Anon (1932) Improving the colour of tourmalines. *Gemmologist*, 1, 213.
- Appleman, D.E. and Evance, H.Y.Jr. (1973) Job 9214: Indexing and least-squares refinement of powder diffraction data. *U.S. Geol. Surv., Computer Contrib.*, 20, U.S. National Technical Information Surv., Doc. PB2-16188.
- Barton, R.Jr. (1969) Refinement of the crystal structure of buergerite and the absolute orientation of tourmalines. *Acta Crystallographica*, B25, 1525-1533.
- Buerger, M.F., Burngm, C.W., and Pecor, D.R. (1962) Assessment of several structures proposed for tourmaline. *Acta Crystallographica*, B25, 1525-1533.
- Burns, R.G. (1972) Mixed valencies and site occupancies of iron in silicate minerals from mössbauer spectroscopy. *Canadian Journal of Spectroscopy*, 17, 52-59.
- Burns, R.G. and Simon, H.F. (1973) Cation disorder in tourmalines. *Geological Society of America abstracts with Programs*, 5, 563-564.
- Dietrich, R.V. (1985) The tourmaline group. Van Nostrand Reinhold, New York.
- Donnay, G. and Barton, R.Jr. (1972) Refinement of the crystal structure of elbaite and the mechanism of tourmaline solid solution. *Tschermaks Mineralogische und Petrographische Mitteilungen*, 18, 273-286.
- Faye, G.H., Manning, P.G., Gosselin, J.R., and Tremblay, R.J. (1974) The optical absorption spectra of tourmaline: Importance of charge-transfer processes. *Canadian Mineralogist*, 12, 370-380.
- Faye, G.H., Manning, P.G., and Nickel, E.H. (1968) An interpretation of the polarized optical absorption spectra of tourmaline cordierite, chloritoid, and vivianite: Fe^{2+} - Fe^{3+} electronic interaction as a source of pleochroism. *American Mineralogist*, 53, 1174-1201.
- Henry, D.J. and Guidotti, C.V. (1985) Tourmaline as a petrogenetic indicator mineral: an example from the staurolite-grade metapelites of NM Maine. *American Mineralogist*, 70, 1-15.
- Isotani, M.B.C.S. (1988) Optical absorption spectroscopy of natural and irradiated pink tourmaline. *American Mineralogist*, 73, 172-180.
- Kim, H.J. (1993) Chemical and spectroscopic studies of tourmaline minerals. Master thesis, Seoul National University, Korea.
- Manning, P.G. (1968) Absorption spectra of the manganese-bearing chain series, pyroxmangite, rhodonite, bustanite and serandite. *Canadian Mineralogist*, 9, 348-357.
- Manning, P.G. (1969) An optical absorption study of the origin of color and pleochroism in pink and brown tourmalines. *Canadian Mineralogist*, 9, 678-690.
- Manning, P.G. (1973) Effect of second-nearest-neighbour interaction on Mn^{3+} absorption in pink and brown tourmalines. *Canadian Mineralogist*, 9, 971-977.
- Mattson, S.M. and Rossman, G.R. (1987) Fe^{2+} - Fe^{3+} interactions in tourmaline. *Physics and Chemistry of Minerals*, 14, 163-171.
- Munsell book of color (1979) Matte finish collection. Munsell Color, Macbeth Division

- of Kollmorgen Corp., Baltimore, Maryland.
- Ramberg, H. (1952) Chemical bonds and distribution of cations in silicates. *Journal of Geology*, 60, 331–355.
- Rausell, F.A., Sanz, J., Fernandez, M., and Serratosa, J.M. (1979) Distribution of octahedral ions in phlogopites and biotites. In: Mortland MM and Farmer VC (ed) *Development in Sedimentology 27*. Elsevier, Amsterdam, 27–36.
- Rossmann, G.R., Fritsch, E., and Shigley, J.E. (1991) Origin of color in curprian elbaite from Sao Jose de Batalha, Paraiba, Brazil. *American Mineralogist*, 76, 1479–1484.
- Schmetzer and Bank (1979) East African tourmalines and their nomenclature. *Journal of Gemmology*, 16–5, 310–311.
- Smith, G. (1978) A reassessment of the role of iron in the 5000–3000 cm^{-1} region of the electronic spectra of tourmaline. *Physics and Chemistry of Minerals*, 3, 343–373.
- Staatz, M.H., Murata, K.J., and Glass, J.J. (1955) Variation of composition and physical properties of tourmaline with its position in the pegmatite. *American Mineralogist*, 40, 789–804.
- Townsend, M.G. (1970) On the dichroism of tourmaline. *Journal of Physics and Chemistry of Solids*, 1, 2481–2488.
- Tsang, T. and Ghose, S. (1973) Nuclear magnetic resonance of ^1H , ^7Li , ^{11}B , ^{23}Na , and ^{27}Al in tourmaline (elbaite). *American Mineralogist*, 58, 224–229.
- Warner, T.W. (1935) Spectrographic analysis of tourmalines with correlation of color and composition. *American Mineralogist*, 20, 531–536.
- Wickersheim, K.A. and Buchanan, R.A. (1959) The near infrared spectrum of beryl. *American Mineralogist*, 44, 440–443.
- Wilkins, R.W.T., Farrell, E.F., and Naiman, C.S. (1969) The crystal field spectra and dichroism of tourmaline. *Journal of Physics and Chemistry of Solids*, 30, 43–56.