

## EFFECT OF HEAT TREATMENT ON MADAGASCAR DRAVITE TOURMALINE: UV-VISIBLE AND DIFFUSE REFLECTANCE INFRARED SPECTROSCOPIC CHARACTERIZATION

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*The color change and chemical behavior of Madagascar dravite when subjected to heating in air atmosphere were studied by energy-dispersive X-ray fluorescence spectrometry, UV-visible (UV-vis) spectroscopy and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. Heat treatment was performed with temperatures of 500, 600, and 700°C for 2 h. Colors and color differences were measured and evaluated using CIELAB color measurement. The origin of color and its change after treatment are assessed via UV-vis spectra. The diffuse reflectance infrared spectra of the dravites revealed major absorption bands of OH, BO<sub>3</sub>, Si<sub>6</sub>O<sub>18</sub>, and R–OH (where R = Fe, Mg). The variation of infrared spectra with increasing temperature indicates the deformation of R–OH bonds in an octahedron and, further, the deformation of BO<sub>3</sub> and Si<sub>6</sub>O<sub>18</sub>. The results of color change may be utilized to enhance the color or clarity in dravite tourmaline and for generating satisfactory color.*

**Keywords:** dravite, tourmaline, heat treatment, diffuse reflectance infrared Fourier transform spectroscopy, UV-visible spectroscopy.

**Introduction.** Tourmaline is an extremely popular semiprecious stone because of its wide variety of colors, including black, brown, green, red, pink, blue, yellow, orange, purple, gray, and clear. It is a group of chemically complex borosilicate minerals, whose generalized structural formula is presented as XY<sub>3</sub>Z<sub>6</sub>(Si<sub>6</sub>O<sub>18</sub>)(BO<sub>3</sub>)<sub>3</sub>V<sub>3</sub>W, where X = Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>; Y = Li<sup>+</sup>, Mg<sup>2+</sup>, Fe<sup>2+</sup>, Mn<sup>2+</sup>, Al<sup>3+</sup>, Cr<sup>3+</sup>, Fe<sup>3+</sup>, Ti<sup>4+</sup>; Z = Al<sup>3+</sup>, Fe<sup>3+</sup>, Cr<sup>3+</sup>, V<sup>3+</sup>, Mg<sup>2+</sup>; V = OH<sup>-</sup>, O<sup>2-</sup>; W = OH<sup>2-</sup>, F<sup>-</sup>, O<sup>-</sup> [1, 2]. Tourmaline is divided into various species depending on its specific chemical composition. The most well-known species of tourmalines are schorl, elbaite, and dravite species [1]. Schorl is the sodium iron (divalent) tourmaline end member of the group, which is the most common species of tourmaline in nature. Most colors of schorl are brownish black to black. Elbaite species is a lithium tourmaline that includes a variety of colors such as red or pinkish-red (called the rubellite variety), light blue to bluish green (called the indicolite variety), green (called the verdelite variety), and colorless. Dravite is the sodium–magnesium-rich tourmaline end member. The color of dravite is dark yellow to brownish black. Because of the complex structure of tourmaline, the cause of its color is not yet clear. There are some known causes of color based on defects, such as the Mn<sup>2+</sup>–O<sup>-</sup>–Ti<sup>4+</sup> charge transfer and Mn<sup>2+</sup> causing greenish yellow and yellowish green, respectively [3, 4]. The cause of blue color in iron-bearing tourmaline is Fe<sup>2+</sup>–Fe<sup>3+</sup> or Fe<sup>2+</sup>–Ti<sup>4+</sup> intervalence charge transfer [4–6]. Meanwhile, Fe<sup>2+</sup> is related to green tourmaline, and Mn<sup>3+</sup> is related to pink tourmaline and rubellite [7–9]. Green and pink Mn-rich tourmalines from Brazil have been investigated and classified as a tourmaline group [9]. These tourmalines show a strong broad band of Mn(II) ions in UV-vis spectra. However, their infrared spectra present the band position of green and pink tourmalines as differing slightly owing to compositional variations. In view of the complex tourmaline structure, which can incorporate total or partial substitution of a great variety of elements, the slightest changes in the composition might result in a completely different color.

Dravite is a dark yellow to brown variety of tourmaline. It contains sodium magnesium aluminum borosilicate mineral with the general chemical formula NaMg<sub>3</sub>Al<sub>6</sub>(BO<sub>3</sub>)<sub>3</sub>Si<sub>6</sub>O<sub>18</sub>(OH)<sub>4</sub> [1, 2, 10]. Generally, dravite is found in translucent to opaque forms, but transparent is uninteresting to gem collectors. Although the colored and transparent forms of dravite

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are in extreme demand and can be sold for premium prices, *there* has been much *less research* investigating the color change of dravite tourmaline. Some studies on dravite tourmaline have previously been reported [10–12]. Dravite from India was studied to record some preliminary information by X-ray and infrared (in the 3000–4000  $\text{cm}^{-1}$  region). The minor discrepancies in the crystal structure of the India dravites can be explained in terms of Mg Al in the octahedral Y position and high Ca contents in their structure. Tourmalines of various colors from Madagascar were irradiated and subsequently heat-treated under only one condition at 550°C for 3 h in air, while the samples were analyzed by UV-vis, mid-infrared, and wavelength dispersive X-ray fluorescence (WDXRF) spectroscopy [11]. The absorption spectra of some brown tourmalines taken at room temperature (293 K) to helium temperature (5.5 K) were studied. The spectra in the 20,000–27,000  $\text{cm}^{-1}$  region enable the temperature dependence of the assigned  $\text{Fe}^{2+} + \text{Ti}^{4+} \rightarrow \text{Fe}^{3+} + \text{Ti}^{3+}$  and  $\text{Fe}^{3+} + \text{Fe}^{3+} \rightarrow \text{Fe}^{3+} + \text{Fe}^{2+}$  charge transfer [12], to be studied.

Since color and transparency are the most important aspects in evaluating the beauty and value of gemstones, heat treatment is the most commonly used process to increase the clarity and alter the color of gemstones. Good-quality tourmaline can be used as gem material; however, some of the raw materials need to be color- and clarity-enhanced to improve their quality. Some studies on thermal treatment of tourmaline have previously been reported. The black color of schorl tourmalines was changed to brown at 700°C and to reddish brown at 900°C mainly owing to oxidation of Fe [13]. In addition, heating at 600°C can remove both the natural and the irradiation-induced pink color in elbaite [14]. For blue tourmaline, heat treatment in air at 700°C for 48 h can produce a red color owing to oxidation of ferrous iron at the octahedral site [9]. For dravite tourmaline, no successful heat treatment of it has been obtained and its color change has not been reported.

Therefore, the objective of this article is to perform heat treatment on dravite tourmalines and to investigate their color change and other effects of heat treatment. The mineralogical studies were carried out with energy-dispersive X-ray fluorescence spectrometry (EDXRF), UV-vis spectrophotometry, and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. The combination of these techniques allowed the chemical characterization of the tourmaline samples to delineate the origin of the color, the color change after heat treatment, and the determination of the temperature at which the sample undergoes major modification.

**Experimental.** The samples were gem quality faceted brownish yellow dravites (0.100–1.900 cts.) from Madagascar. Representative samples are shown in Fig. 1. Basic gemological instruments were used to determine the gemological properties of the dravite samples, including the specific gravity, refractive index, birefringence, and ultraviolet fluorescence. After that, the samples were divided into three groups for heating at different temperatures. The samples were heated at 500, 600, and 700°C in an electric furnace with an oxidation condition. The holding time for the heating temperature was 2 h. The heating rate to achieve these holding temperatures was 10°C/min. After heat treatment, the samples were cooled in the furnace.

A quantitative chemical analysis was performed using an Orbis Micro-XRF Analyzer. The XRF was utilized at Burapha Gems Laboratory (BGL), Chanthaburi, Thailand. The spectrometer was used for analyzing major oxides and trace elements in the tourmaline samples. The sample was excited by X-ray (Mo tube) at 50 kV and 50 W focused by a spot size of 100  $\mu\text{m}$ .

A Hitachi U4100 UV-vis spectrophotometer was employed for the UV-vis measurements of unheated and heated samples to investigate their color change and causes of coloration. The UV-vis spectra were obtained in transmission mode with wavelengths ranging from 300 to 800 nm at a scan speed of 100 nm/min. The color changes of the samples at the different temperatures were analyzed using the CIELAB method and the UV-vis spectrophotometer with a D65 light source and 2° detection angle. CIELAB is a color space that describes all the visible colors using three coordinates:  $L^*$ ,  $a^*$ , and  $b^*$ . The  $L^*$  means the lightness that represents the darkest black ( $L^* = 0$ ) and the brightest white ( $L^* = 100$ ). The  $a^*$  value represents red/green opponent colors, negative  $a^*$  values indicate green, and positive  $a^*$  values indicate red. The  $b^*$  value represents yellow/blue opponent colors, negative  $b^*$  values indicate blue, and positive  $b^*$  values indicate yellow. Further parameters from the CIELAB color measurement were calculated using these data to detect color and hue differences in heated samples.

A Bruker Alpha FT-IR spectrometer equipped with a smart diffuse reflectance accessory was employed for all FT-IR measurements. The gemstones were characterized as received without an additional sample preparation except cleaning. A spectral resolution of 4  $\text{cm}^{-1}$  with 64 Co-addition scans was employed. The observed spectra in the mid-infrared region (4000–400  $\text{cm}^{-1}$ ) were baseline-corrected before further analysis. For all diffuse reflectance measurements, a faceted dravite was placed on the sample holder with the table facet face down; the infrared radiation was coupled into the gemstone at a near normal angle of incidence. The diffuse reflected radiation was then collected, while the absorption of the gemstone was expressed in Kubelka–Munk units. Since the observed diffuse reflectance spectrum was greatly influenced by the gemstone arrangements, several spectra for different gemstone arrangements were collected. The observed spectrum with the

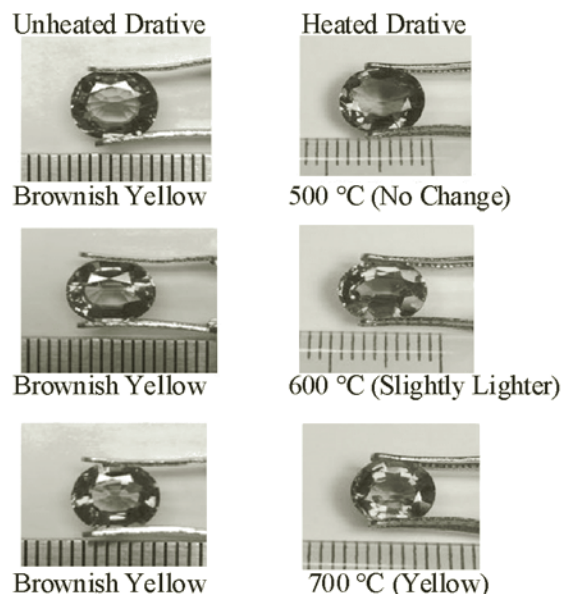


Fig. 1. Heat treatment results for representative dravite samples. The measured samples were quality faceted dravite gems (0.100–1.900 cts.).

best signal-to-noise ratio was employed for further spectral analysis. The UV-vis spectra and diffuse infrared spectra were measured before and after heat treatment.

**Results and Discussion.** *Gemological properties and chemical composition.* The specific gravity of all samples varied from 3.02 to 3.10 g/cm<sup>3</sup>. Their refractive indices ranged from 1.624 to 1.644 with a birefringence of 0.017–0.021. All dravite samples were inert when exposed to long-wave and short-wave ultraviolet radiation. The chemical compositions of the dravite samples measured by EDXRF are follows (wt.% average): SiO<sub>2</sub> 41.491, Al<sub>2</sub>O<sub>3</sub> 29.473, MgO 22.788, CaO 4.767, K<sub>2</sub>O 0.102, TiO<sub>2</sub> 0.584, V<sub>2</sub>O<sub>5</sub> 0.090, MnO 0.162, Fe<sub>2</sub>O<sub>3</sub> 0.142, and B<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O not detected. They contained the major oxides Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> with significant amounts of MgO. The Madagascar dravites have a very high quantity of MgO, at about 22 wt.%. Other oxides, such as K<sub>2</sub>O, CaO, Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>, and MnO, were detected in subordinate concentrations in samples. However, the essential lighter elements of dravite, B, and Na, were not detected owing to the limitations of this method. The EDXRF analysis indicated that the samples were dravite tourmaline [1, 10].

*Color change.* The colors of unheated and heated dravite samples under different heating temperatures are presented in Fig. 1. The unheated samples displayed an intense brownish yellow color. In the heated dravites, the visual appearance of the samples showed almost no color change after heating at 500°C for 2 h in an oxidation condition. At 600°C, all samples showed a slight change to a more yellow color. In terms of visual appearance, a significant color change was clearly observed when the heating temperature was increased to 700°C. The original brown color of dravite decreased and trended toward yellow. Meanwhile, the clarity of all heated dravite increased with all heating temperatures.

To characterize the color and color change, the CIELAB color method was performed before and after heating. Regarding  $a^*$  and  $b^*$  indices, the change in color of dravite tourmaline at different heating temperatures is shown in Fig. 2a. For most dravites, the unheated samples showed positive  $a^*$  and  $b^*$  values corresponding to a brownish yellow color. For the  $a^*b^*$  indices of the heated samples, the value of  $a^*$  shows a slightly positive shift to a higher red value, while the  $b^*$  value indicates a shift to yellow with increasing temperature. This means that the color of the heated stones tended to appear a more yellow to orange color than that of the unheated samples. Meanwhile, it can be concluded that the green tone disappeared after heating. Regarding the lightness ( $L^*$ ), the average of the samples heated at different temperatures is shown in Fig. 2b. After heat treatment, the samples revealed a greater lightness than the unheated samples. There were clear trends in the change of lightness ( $L^*$  value) for the heated stones, suggesting that the stone became lighter with increasing temperature. As a result, it can be concluded that at a heating temperature of 500–700°C, the dravites became lighter and had a yellow color.

To determine the total color difference ( $\Delta E^*$ ) between all three indices, the  $\Delta E^*$  of dravites at different temperatures was calculated as  $\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}$ . As seen in Fig. 2c,  $\Delta E^*$  showed a clearly increasing trend with increasing

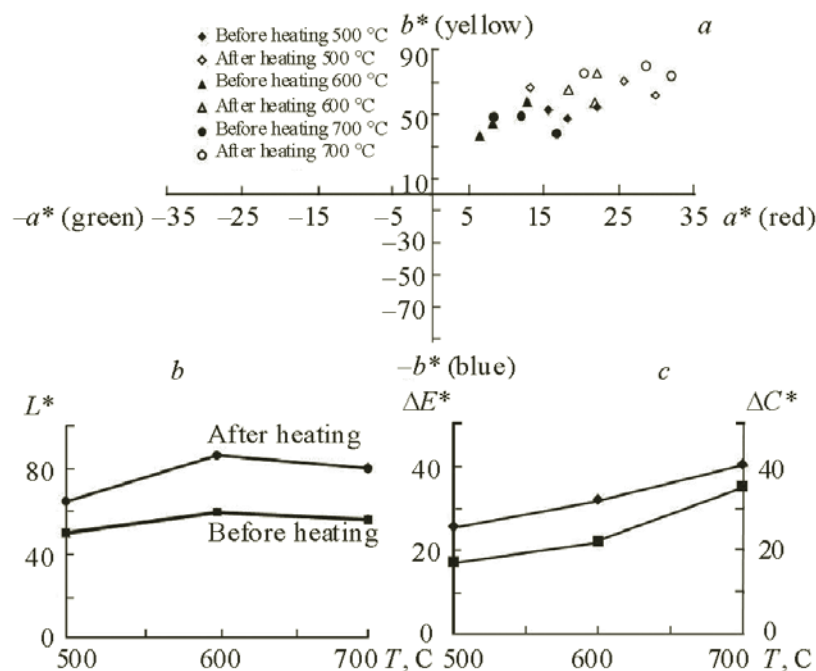


Fig. 2. Color change of heated dravite tourmalines at different heating temperatures measured via CIELAB color measurement. a) Indices of  $a^*$  (red-green) and  $b^*$  (yellow-blue); b) change in  $L^*$  (lightness); c) trends in color difference ( $\Delta E^*$ ,  $\blacklozenge$ ) and chroma difference ( $\Delta C^*$ ,  $\blacksquare$ ).

temperature. In addition, the chroma difference value ( $\Delta C^*$ ) was calculated as  $\Delta C^* = (\Delta a^{*2} + \Delta b^{*2})^{1/2}$ , in which positive  $\Delta C^*$  indicates brighter, and negative  $\Delta C^*$  indicates duller. By comparing the  $\Delta C^*$  of heated dravites treated at different heating temperatures, the  $\Delta C^*$  tended to slightly increase to a positive value with increasing heating temperature, as shown in Fig. 2c. This implied that increasing temperature led to increasing color and chroma difference. Thus, it can be concluded that heated dravites gain more lightness and a brighter yellow color tone when heated at temperatures between 500 and 700 °C for 2 h in an air atmosphere.

**UV-visible spectroscopy.** It is well known that the natural color of a gemstone depends on its mineral composition. UV-vis spectroscopy is a powerful instrument for studying the color of minerals containing transition metals. Tourmaline is a complex borosilicate mineral, in which the color is affected by transition metals [4, 15]. The results of the UV-vis absorption spectra we measured of unheated and heated dravites are shown in Fig. 3. The UV-vis spectra of most unheated dravites exhibited strong absorption band at 445 nm, which corresponds to  $\text{Fe}^{2+}\text{-O-Ti}^{4+}$  absorption, as shown by the solid line in Fig. 3.  $\text{Fe}^{2+}\text{-O-Ti}^{4+}$  charge transfer is the source of the brown color in tourmaline [4, 5, 12]. An additional strong absorption band at 325 nm rising toward the ultraviolet end of the spectrum was determined to be the  $\text{Mn}^{2+}\text{-O-Ti}^{4+}$  that is observed in yellow-green Mn-rich tourmaline [4]. The UV-vis spectra also showed a small absorption band at 633 nm, which is the absorption band of Mn [3, 4]. The  $\text{Mn}^{2+}$  can produce a yellow-green color in tourmaline [4, 5, 16]. Moreover, the spectra show a small absorption band at 715 nm; several different interpretations of this band have been suggested and reported in previous works [5, 6, 11, 12, 17]. Some indicate that this band can be assigned to an intervalence charge transfer of  $\text{Fe}^{2+}\text{-Fe}^{3+}$  or even a  $\text{Mn}^{2+}\text{-Fe}^{3+}$  or  $\text{Mn}^{2+}\text{-Mn}^{3+}$  electronic transition [9, 17]. In some cases, this band occurs owing to the presence of  $\text{Cu}^{2+}$ , which produces a greenish blue color [16]. Because there is a lack of copper oxide found by EDXRF, a possible reason for this absorption band ( $\sim 715$  nm) may be the exchange interaction  $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ , as suggested by Ahn et al. [11].

The UV-vis spectra of heated dravites at different temperatures are represented in Fig. 3 (dashed line). The absorption bands at 445 and 325 nm that correspond to  $\text{Fe}^{2+}\text{-O-Ti}^{4+}$  and  $\text{Mn}^{2+}\text{-O-Ti}^{4+}$ , respectively, decreased after they had been heated at 500 °C (dashed line in Fig. 3a). Those bands tend to show a continuous decrease with increase in temperature to 600 and 700 °C (Fig. 3b,c). The dramatic decrease in the relative intensity of the  $\text{Fe}^{2+}\text{-O-Ti}^{4+}$  band at 445 nm corresponds to a decreased brown color in heated dravites. In addition, the increase in the  $\text{Fe}^{2+}\text{-Fe}^{3+}$  band at 715 nm after heat treatment

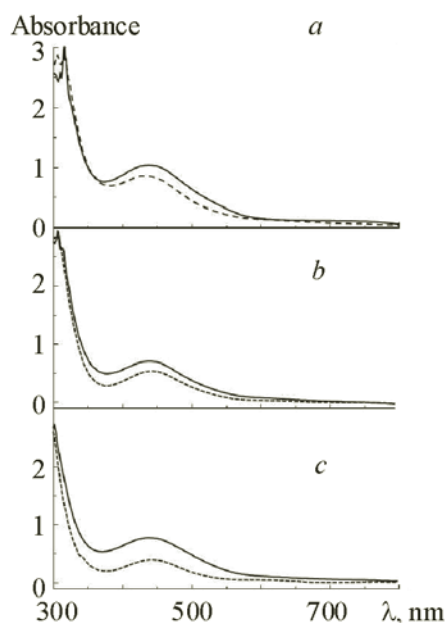


Fig. 3. UV-vis spectra of unheated (solid line) and heated (dashed line) dravites at 500 (a), 600 (b), and 700°C (c).

is in agreement with the color change of yellowish brown to yellow. Moreover,  $\text{Mn}^{2+}-\text{Ti}^{4+}$  produced at 325 nm was strongly decreased after heating to 700°C. Since  $\text{Mn}^{2+}-\text{Ti}^{4+}$  is related to the green color of tourmaline, a decrease in this band resulted in a sample color change from green to red, which is indicated by the  $a^*$  value in Fig. 2a. Additionally, the appearance of a small shoulder at 345 nm can be detected in the spectra of the heated dravite at 700°C. This band corresponds to absorption of the Mn(II) ion in tourmaline. As a result, it can be concluded that partial oxidation of  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  seems to occur during heat treatment at 700°C in air, where oxidation can increase the intensity of the absorption band at 715 and 345 nm, respectively. Therefore, the variation of UV-vis absorption spectra was related to the obtained color of the heated dravites. Moreover, it is well known that iron is a strong luminescence element, and luminescence of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  may occur in luminescence spectra. Therefore, besides the thermal treatment affecting the UV-vis absorption spectra of dravite, it also influenced the luminescence properties of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  [18].

**FTIR spectroscopy.** FTIR spectroscopy is a well-known molecular spectroscopic technique for gem analysis [19–23]. In particular, it is used in the characterization of treated gemstones with different treatment processes. FTIR spectral fingerprint regions provide information directly related to the chemical structure, chemical composition, and impurities in the analyzed materials. The transmission method is a classical sampling technique that is very popular for collecting infrared spectra. For gemstone characterization, a thin slab of stones or the KBr pellet technique is required [20, 24, 25]. Because the techniques are destructive, they are not suitable for faceted gemstones of high commercial value. For high-thickness faceted stones, the transmission spectrum is often exhibited over the absorption band in the fingerprint region. Additionally, transmission measurement using a beam condenser is complicated in the characterization of a faceted gemstone owing to the sample arrangement and the complex reflection from its cut and polished surfaces [26]. Thus, the diffuse reflectance technique was devised for faceted gem analysis in order to address the problems associated with thickness, cutting, or different facets of gemstones. In this research, the diffuse reflectance technique was employed for characterization of faceted dravites, and their spectral features associated with structure and heat treatment processes were discussed.

The diffuse reflectance spectra of unheated and heated dravite at different temperatures are presented in Fig. 4, and the band assignments are summarized in Table 1. Regarding the infrared spectra of unheated dravite (solid lines in Fig. 4), three well-defined spectral regions are observed. The first region is the absorption bands at 3300–3800  $\text{cm}^{-1}$ , the second at 800–1200  $\text{cm}^{-1}$ , and the third included the bands below 800  $\text{cm}^{-1}$ .

In the first region, two bands appeared, including the sharp peak at 3590  $\text{cm}^{-1}$  and the broad absorption band around 3360  $\text{cm}^{-1}$ . The typical band of dravite in this range can be due to the local vibrations of OH groups connected with Al in Z sites and Fe, Mn, or Mg in Y sites [8, 11, 22, 25]. The bands are assigned as OH stretching vibrations, which could be

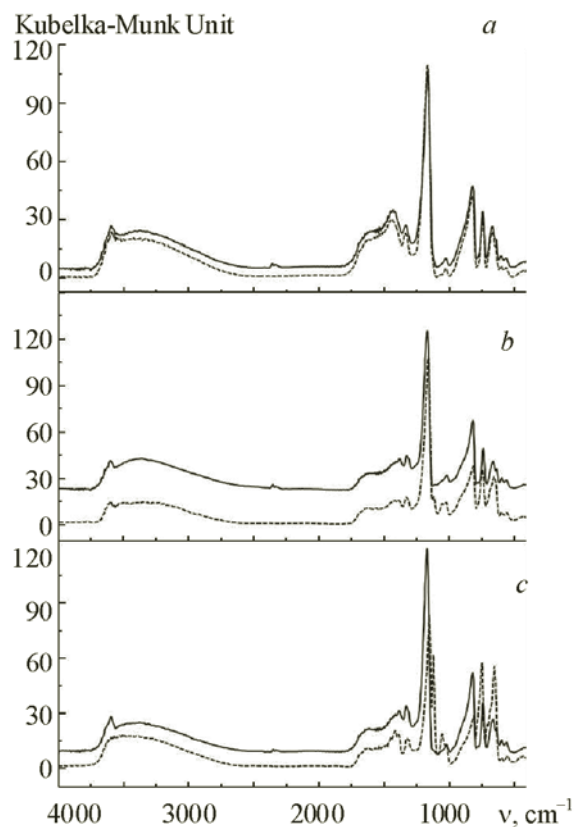


Fig. 4. Diffuse reflectance spectra of unheated (solid line) and heated (dashed line) dravites at 500 (a), 600 (b), and 700°C (c).

TABLE 1. Wavenumber ( $\nu$ ,  $\text{cm}^{-1}$ ) and Possible Assignments of Bands Observed in Diffuse Reflectance Spectra of Unheated and Heated Dravites

$\nu$	Assignment	$\nu$	Assignment
3590	OH stretching	1115	MgO
3360		785	Si–O–Si stretching
1650	OH bending	735	Si–O–Si bending
1265	B–O stretching	535	
1360		460	
1055	Si–O stretching	435	R–OH
1020		645	
968		505	

attributed to the possible presence of two different OH groups in the tourmaline structure. The broad band at  $3360\text{ cm}^{-1}$  is not involved in the hydrogen bond, while the intense sharp peak at  $3590\text{ cm}^{-1}$  was ascribed to hydroxyl groups involved in hydrogen bonds [8, 11, 24]. According to Reddy et al. [8] and [24], the weak band at  $3590\text{ cm}^{-1}$  resulted from the OH stretching, involving Fe in the Y octahedral site of the dravite tourmaline structure.

At the second region in  $800\text{--}1200\text{ cm}^{-1}$ , the infrared absorption in tourmaline is mainly caused by vibrations of the Si–O bond, Si–O–Si bond of the  $[\text{SiO}_4]$  tetrahedron, B–O bond of the  $[\text{BO}_3]$  triangle, and R–O bond of an octahedron (where R = Al, Mg, or Fe) [21, 22, 27]. The strong band at  $1150\text{ cm}^{-1}$  is attributed to the Si–O–Si stretching vibration of the  $\text{Si}_6\text{O}_{18}$ .

Two bands at 1265 and around 1330  $\text{cm}^{-1}$  are identified as  $\text{BO}_3$  stretching [24]. The band at 1115  $\text{cm}^{-1}$  as a shoulder on the band at 1150  $\text{cm}^{-1}$  is attributed to MgOH bending modes [8, 13, 24, 25].

In the last region below 800  $\text{cm}^{-1}$ , an assignment of the band appeared below 800  $\text{cm}^{-1}$  that is often overlapped and overlaid [25, 28]. The registered peak at 735  $\text{cm}^{-1}$  and small band at 785  $\text{cm}^{-1}$  were assigned as R–O mode [R = Al, Mg, Fe] [24]. The absorption of Si–O–Si bending also overlapped with R–OH in the 640–700  $\text{cm}^{-1}$  regions. The characteristic bands of dravite were also observed at 535  $\text{cm}^{-1}$  and attributed to Si–O [28]. The metal hydroxyl (R–OH) vibration and translation were registered to the band at 645 (shoulder) and 595  $\text{cm}^{-1}$  [28].

After heating at 500°C (dashed line in Fig. 4a), the obtained infrared spectra look similar to those of unheated dravites. With heating to 600°C (dashed line in Fig. 4b), the intensity of OH stretching absorption around 3590  $\text{cm}^{-1}$  slightly decreased, while this band disappeared with heating temperatures increasing to 700°C (dashed line in Fig. 4c). This implied that the vibration of the OH group connected with Fe(II) was reduced with this high temperature. Moreover, some bands showed different features after heating the sample to higher temperatures. In the region of 400–1200  $\text{cm}^{-1}$ , the intensities of Mg–OH at 1115  $\text{cm}^{-1}$  significantly increased with increased heating temperature. This indicates that the anharmonic vibration of Mg–OH is enhanced with increasing temperature. In addition, the small absorption band at 1100–800  $\text{cm}^{-1}$  related to Si–O and Si–O–Al vibrations and at 650–700  $\text{cm}^{-1}$  related to Si–O–Si bending and R–OH showed different spectral features. Moreover, a deformation stretching vibration of  $\text{BO}_3$  at 1330  $\text{cm}^{-1}$  was broadened with increasing temperature. This means that the anharmonic vibration of  $\text{BO}_3$  was large at higher temperatures. Accordingly, the variation of infrared spectra in dravite tourmalines with rising temperature indicated the deformation of Fe–OH and Mg–OH bonds in the Y octahedron and the deformation of the  $[\text{BO}_3]_3^-$  polyhedron and  $[\text{Si}_6\text{O}_{18}]_{12}^-$  ring, which are connected with the octahedron site [22].

**Conclusions.** The effects of heat treatment on the color and clarity of brownish yellow dravite tourmaline from Madagascar were investigated. Madagascar dravite has a very high quantity of MgO trace elements. The tourmalines were heated at temperatures of 500, 600, and 700°C for 2 h in the atmosphere. In comparison to unheated dravites, the UV-vis absorption spectra of heated dravites showed a decreasing absorption of  $\text{Fe}^{2+}$ – $\text{Ti}^{4+}$  and  $\text{Mn}^{2+}$ – $\text{Ti}^{4+}$ . The temperature-dependent FTIR spectra showed a decreased peak absorption at 3590  $\text{cm}^{-1}$  and increased MgOH absorption band at 1115  $\text{cm}^{-1}$  with increased temperature. Further, variations of the infrared spectra of Si–O and  $\text{BO}_3$  were also observed in the region of 1000–800  $\text{cm}^{-1}$ . Accordingly, the variation of UV-vis and infrared spectra showed evidence of internal structure change as an effect of heat treatment. Regarding the color change after heating, the lightness of heated dravite was increased and the color changed from brownish yellow to yellow with increased temperature. As such, appropriate heating conditions can be utilized as an alternative gemstone enhancement technique for improving dravite color and value.

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