

Effect of heat treatment on spectroscopic properties of tanzanite

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Abstract. Tanzanite is blue to violet gem variety of mineral zoisite. It is a very popular jewelry gemstone in gems trade. Due to the unique beautiful color of tanzanite is rarely natural; almost tanzanites are usually has been heat treated to enhance the beautiful color. In this research, color enhancement of natural tanzanite from Tanzania was performed by heat treatment and its spectroscopic characterization was determined. The stones were heat-treated in an atmosphere with the heating temperatures at 400, 500 and 600°C, soaked for 2 hours. Basic gemological equipment was applied to identify the unheated and heated tanzanite sample. In order to study the color change of tanzanite after heat treatment, colors and color differences were measured and evaluated using CIELAB color measurement. The cause of color change and chemical behavior of tanzanite were studied by energy-dispersive X-ray fluorescence spectrometry, UV-visible spectroscopy and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. The results of color change and spectral properties may be utilized to enhance the satisfactory color and identification of heated tanzanite.

1. Introduction

Gemstone is currently one of important products in the world market because of its economic value. Tanzanite is the trading name of blue to violet zoisite, $\text{Ca}_2\text{Al}_3(\text{SiO}_4)_3(\text{OH})$. It is the most famous gem-variety of vanadium rich zoisite due to its unique color, and rarity. Since a small quantity of blue natural tanzanite is discovered, most of tanzanites that enter the gem trading system are actually brown or violet zoisites that has been heated to blue color [1-2]. Gemologist may attempt to discriminate between natural tanzanite and heated tanzanite because the treated gems may influences the trading market value. Although pleochroism is now only indicator for differentiating between natural tanzanite and heated brown zoisites, it cannot use for differentiating between natural tanzanite and heated tanzanite [2-3]. Therefore, vibrational spectroscopy has been used as a powerful tool for gems identification and utilized for differentiating various natural and heated gemstones. To study effect of heat treatment on spectroscopic properties in tanzanite, the unheated and heated tanzanites were identified using energy-dispersive X-ray fluorescence (EDXRF) spectroscopy, UV-visible spectroscopy, and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy.

2. Experiment

The samples were gems quality rough violet tanzanite collected from Tanzania. The samples were cut and polished for preparing to spectroscopic experiments. Basic gemological instruments were used to determine the gemological properties of tanzanite, including the specific gravity, refractive index,

birefringence and pleochroism. The samples were treated with different heating temperatures at 400, 500, 600°C in an electric furnace with an oxidation condition. The heating rate to achieve these holding temperatures was 10°C/min and the holding time was 1 hour.

A quantitative chemical analysis was performed using an Orbis Micro-XRF Analyzer. The EDXRF was utilized at Burapha Gems Laboratory (BGL), Chanthaburi, Thailand. A Hitachi U4100 UV-Vis spectrophotometer was employed for investigating color change and causes of coloration of samples. The UV-vis spectra were obtained in transmission mode from 300 nm 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 with a D65 light source and 2° detection angle. A Bruker Alpha FT-IR spectrometer equipped with a smart diffuse reflectance accessory was employed for all FT-IR measurements. A spectral resolution of 4 cm⁻¹ with 64 Co-addition scans was employed. The observed spectra in the mid-infrared region (4000–400 cm⁻¹) were baseline-corrected before further analysis.

3. Results and discussion

3.1. Gemological Properties and Chemical Composition

The specific gravity of all samples varied from 3.40 to 3.41 g/cm³. Their refractive indices ranged from 1.690 to 1.700 with a birefringence of 0.010–0.011. Pleochroisms of unheated and heated samples are similar dichroism with reddish violet and blue color. The chemical compositions of the tanzanite samples measured by EDXRF contained major oxides as Al₂O₃ (28.752%), SiO₂ (36.865%) and CaO (32.733%). Some minor elements that were possible chromophores of tanzanite together with REEs also revealed. Other oxides including TiO₂ (0.716%), V₂O₅ (0.396%), Ce₂O₃ (0.021%), Ga₂O₃ (0.024%), Nd₂O₃ (0.016%), Fe₂O₃ (0.115%), Eu₂O₃ (0.096%), Cr₂O₃(0.002%) and SrO (0.262%), were detected in subordinate concentrations in samples.

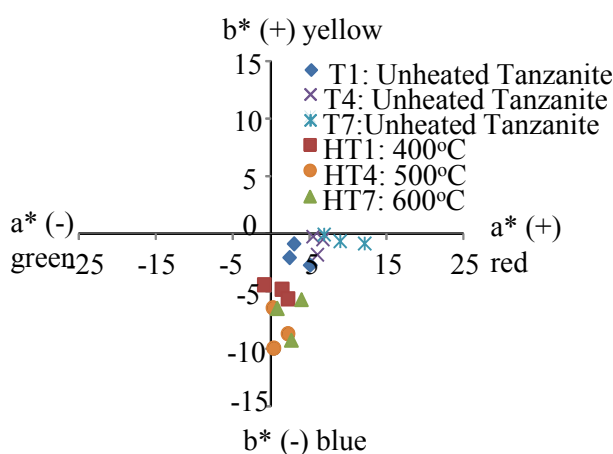


Figure 1. Color change of heated tanzanite at different heating temperatures measured via CIELAB color measurement.

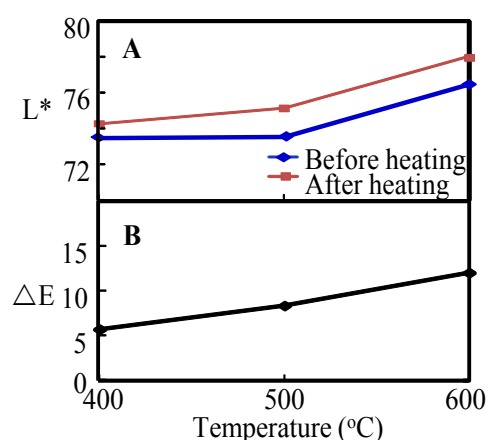


Figure 2. (A) Change of L* (lightness); and (B) trends in color difference (ΔE^*) of tanzanite at different heating temperatures.

3.2. Color Change

To characterize the color and color change after heat treatment, the CIELAB color method was performed before and after heating. Regarding a* and b* indices, the change in color of tanzanite at different heating temperatures is shown in figure 1. For most tanzanites, the unheated samples showed positive a* and b* values corresponding to a violet color. For the a*b* indices of the heated samples, the values of a* and b* show a slightly negative shift to a lower value indicates a shift to blue color with increasing temperature. It can be conclude that the original violet color of tanzanite decreased and trended toward blue color in heated tanzanite. Regarding the lightness (L*), the heated samples with all heating temperatures revealed a greater lightness than the unheated samples, as shown in figure 2.

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

3.3. 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. The UV-vis absorption spectra of unheated and heated tanzanites are shown in figure 3. The spectra of all unheated tanzanites exhibited strong absorption band at 300-400 nm, which corresponds to VO_2^+ absorption [4]. The absorption bands at 505 and 531 nm caused by Fe^{2+} and V^{2+} , and a wide absorption band between 440, 580 and 610 nm caused by V^{3+} . The absorption band located at about 790 nm related to the presence of V^{4+} in the crystal structure of the blue zoisite which produces a blue color [5]. After heating, heated tanzanite spectra revealed that a broad band below 400 nm of VO_2^+ dramatically decreased and the band of V^{3+} slightly decreased. In addition, the strong band attributed to octahedral V^{4+} species at 390 nm increased corresponding to increasing of blue color in heated tanzanite [4-5].

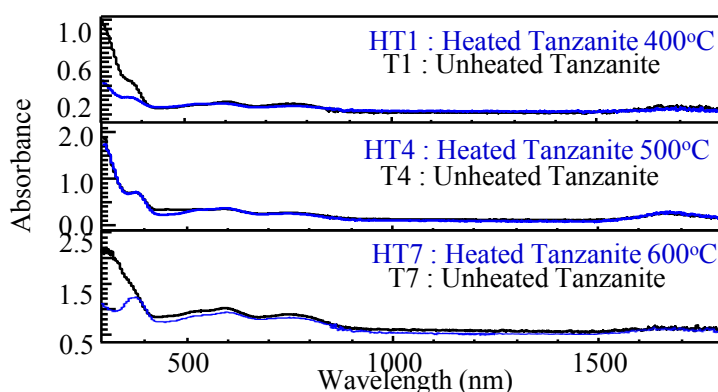


Figure 3. UV-vis spectra of unheated (T1, T4, T7) and heated (HT1, HT4, HT7) tanzanites at different temperatures.

3.4. FTIR spectroscopy

The diffuse reflectance spectra of unheated and heated tanzanites at different temperatures are presented in figure 4A-4C. Regarding the infrared spectra of unheated tanzanite, two well-defined spectral regions are observed. The first region is the absorption bands at $3300\text{--}3800\text{ cm}^{-1}$, and the second included the bands at $500\text{--}1500\text{ cm}^{-1}$. In the first region, an obvious band appeared including the broad absorption band around 3460 cm^{-1} which could be attributed to the possible presence of OH groups in the tanzanite structure. At the second region in $500\text{--}1500\text{ cm}^{-1}$, the infrared absorption in tanzanite is mainly caused by vibrations of Si-O-Si bond of the SiO_4 , Al-O mode and Ca-O mode of aluminium hydroxyl sorosilicate, $\text{Ca}_2\text{Al}_3(\text{SiO}_4)_3(\text{OH})$. The strong band at 1180 cm^{-1} is attributed to the Si-O-Si stretching vibration of the $[\text{SiO}_4]$. The small absorption band of OH librational mode which was found in some layer silicates at about 930 cm^{-1} was also observed [6]. The registered peak at 735 cm^{-1} and small band at 785 cm^{-1} were assigned as R-O mode [R= Al, V, Fe] [7]. The absorption of Si-O-Si bending also overlapped with R-OH in the $640\text{--}780\text{ cm}^{-1}$ regions. The metal hydroxyl (R-OH) vibration and translation were registered to the band at 645 (shoulder) and 595 cm^{-1} [7].

After heating (figure 4A), the obtained infrared spectra look similar to those of unheated samples. However, small absorption band at $1100\text{--}800\text{ cm}^{-1}$ related to Si-O and Si-O-Al vibrations and at $650\text{--}700\text{ cm}^{-1}$ related to Si-O-Si bending and R-OH showed different spectral features. Considering to the increasing of heating temperature to 700°C in figure 4D and 4E, small band of OH mode in silicates at 930 cm^{-1} was shifted to lower wavenumber. In addition, the sharp peak at about 740 cm^{-1} were observed corresponding to the change of Si-O-Si and R-OH in heated tanzanite. It can indicate that heat treatment can change some chemical bonds in tanzanite structure involving Si-O-Si and R-OH.

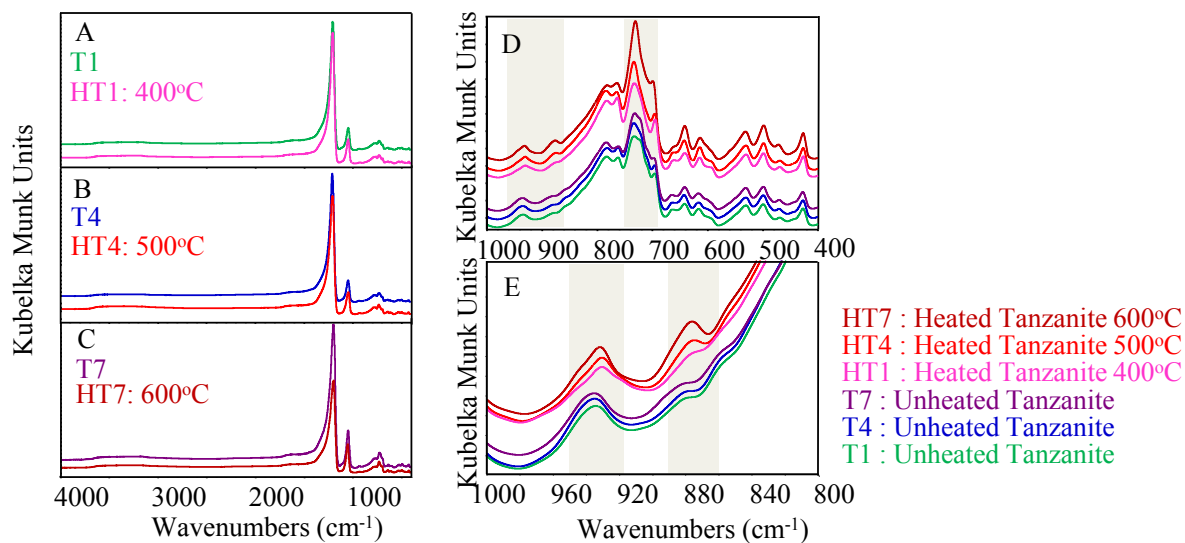


Figure 4. Diffuse reflectance spectra of unheated (T1, T4, T7) and heated (HT1, HT4, HT7) tanzanites at different temperatures; (A-C) the range of 4000-400 cm^{-1} ; D) zoom in 1000-400 cm^{-1} ; and E) zoom in 1000-800 cm^{-1} .

4. Conclusion

The effects of heat treatment on the color and spectroscopic properties of violet tanzanite from Tanzania were investigated. The samples were heated at temperatures of 400, 500, and 600°C for 1 hour in atmosphere. Regarding the color change after heating, the lightness of heated tanzanite was increased and their color changed from violet to bluish violet color with increasing temperature. In comparison to unheated tanzanite, the UV-vis absorption spectra of heated tanzanite showed an increasing of V^{4+} attributed to obtained blue color after heating. The temperature-dependent FTIR spectra showed variation band at about 980 -700 cm^{-1} with increasing temperature correspond to Si-OH mode of silicate. It can be concluded that the variation of UV-vis and infrared spectra showed evidence of internal structure change as an effect of heat treatment. Accordingly, appropriate heating conditions can be utilized as enhancement for improving tanzanite color and value.

Acknowledgments

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