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The new evidence from the fingerprint region in FT-IR spectra to indicate the heat treatment of blue sapphire sample

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Abstract. FT-IR spectroscopy is a significant method to detect the heat treatment of gemstones, especially ruby and sapphire. There are a set of certain peaks, i.e., 3309, 3232, and 3185 cm^{-1} in the FT-IR spectra used as an indicator to determine whether the samples have been undergone heat treatment. In this study, however, new evidence has emerged. The O-Al-O bending vibration peak at the fingerprint region around 600-700 cm^{-1} has been suggested as new clues to define the heated stones. The blue sapphire samples were prepared, then the heat treatment was performed separately at 800, 1000, 1200, 1400, and 1650 $^{\circ}\text{C}$ under an oxidizing atmosphere with a soaking time of 1 hour. The energy dispersive X-ray fluorescence (EDXRF) shows that there is no significant difference in the chemical composition of Al_2O_3 , Fe_2O_3 , TiO_2 , and Ga_2O_3 between unheated and heated samples. The alteration of blue color and the UV-Vis absorption spectra are also difficult to classify. When comparing the samples at each heating temperature, the alteration of blue color was not related to one another because the color of the samples was decreased depending on those of the unheated ones. The FT-IR spectra revealed that the broad absorption peak of O-Al-O bending at approximately 650 cm^{-1} was slightly shifted to a lower wavenumber (630 – 635 cm^{-1}) after the samples were heated at higher temperatures. The broad absorption peak also turned into a sharper one when the sample has undergone heating at ≥ 1000 $^{\circ}\text{C}$. It is suggested that the peak is related to the rearrangement of the Al_2O_3 structure of the blue sapphire sample after heat treatment.

1. Introduction

Heat treatment is one of the most efficient methods to improve the quality (color and clarity) of gemstones. The process is carried out by heating the sample in a controlled furnace at different ranges of temperatures, depending on the condition of the raw sample [1]. Normally, after heat treatment, the color of the stone is still caused by its internal chemical composition, thus this technique is accepted in the gem market. However, the undergone heat-treated stone is normally valued less than those of the natural ones [1]. Therefore, the heating process must be revealed at all costs.

Blue Sapphire is an alpha-alumina ($\alpha\text{-Al}_2\text{O}_3$) mineral and one of the most popular stones in the gem market. The blue sapphire is shown in various shades of blue. The expensive one usually contains the deep and vibrant blue color, which nowadays, is rarely found in nature. Thus, heat treatment plays an important role in improving the blue color of the stones. Normally, the heat treatment can be detected using the internal features as well as the alteration of the absorption spectra [2]. However, those indicators would be accurate when compared with the unheated sample. Recently, the FT-IR spectra were also applied to indicate the undergone heat treatment of the sample, especially, the specific peaks



at a -OH stretching region ($3000\text{--}4000\text{ cm}^{-1}$) [3]. Even though the peaks have been useful, they have not seemed to appear in every sample [2].

Therefore, in this study, new evidence for using another set of peaks in FT-IR spectra has been proposed. The peaks in the fingerprint region around $600\text{--}650\text{ cm}^{-1}$ related to the Al_2O_3 structure have been verified to apply the FT-IR spectra for indicating heat treatment of blue sapphire samples.

2. Experiments

Rough blue sapphire samples were collected and prepared. The samples were cut in half, one for referencing (un-heating), another for heating. The cutting direction of the samples is perpendicular to their c-axis and the thickness is polished to less than 2 mm (figure 1). Then the samples were heated separately under the oxidizing atmosphere for an hour at the temperature of 800, 1000, 1200, 1400, and 1650 °C representing the low to high temperature.

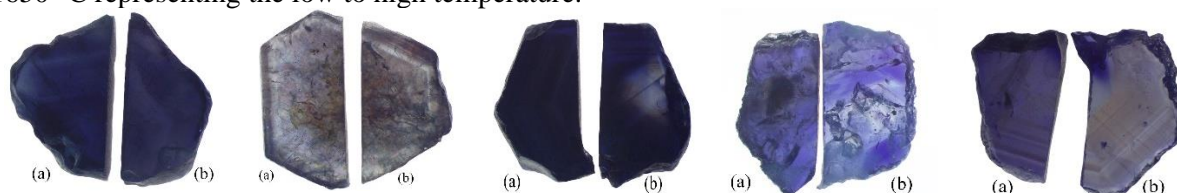


Figure 1. Blue sapphire samples at different heating temperatures from 800 to 1650 °C (a) with their unheated counterpart (b).

The alteration of the blue color before and after heat treatment at each temperature was determined using the Perkin Elmer Lambda 850+ UV-Vis spectrophotometer at the Faculty of Gems, Burapha University Chanthaburi Campus. The absorption spectra were detected in the range of 350 – 800 nm. Then the CIE $L^* a^* b^*$ color measurements were calculated using the color master software. The chemical composition of Al_2O_3 and the trace elements in the blue sapphire samples before and after heating were analyzed by an Energy Dispersive X-ray Fluorescence (EDXRF) at the Burapha Gemological Laboratory, Chanthaburi.

To investigate the behavior of the peaks in FT-IR spectra throughout the heating process, the spectra were acquired by the Thermo Scientific Nicolet iS50 FT-IR spectrometer in the absorption mode with the diffuse reflectance accessory at the Faculty of Gems, Burapha University, Chanthaburi Campus. The spectra were recorded from $400\text{--}4000\text{ cm}^{-1}$ with a spectral resolution of 4 cm^{-1} and 32 number of scans. To avoid the polarization effect, the FT-IR spectra were measured in a parallel direction to the c-axis of the samples.

3. Results and discussion

The chemical composition of blue sapphire samples before and after heating at different temperatures obtained by EDXRF is shown in table 1. The result indicates that Al_2O_3 is a main component of the blue sapphire. The trace elements responsible for the blue color of these samples are Fe_2O_3 and TiO_2 . The Ga_2O_3 is also presented in every sample. It is noteworthy that the chemical composition of the samples before and after heat treatment is slightly different. Therefore, only the chemical composition cannot be used as evidence for identifying the undergone heating.

Table 1. Chemical composition obtained by the EDXRF of main and trace element of blue sapphire samples.

Chemical Composition	Percentage by weight (% wt)									
	un	800	un	1000	un	1200	un	1400	un	1650
Al_2O_3	99.24	99.32	98.93	98.94	99.36	99.42	98.18	98.09	97.54	97.74
TiO_2	0.15	0.16	0.02	0.02	0.10	0.09	0.09	0.10	0.07	0.05
Fe_2O_3	0.58	0.49	1.03	1.02	0.52	0.47	1.71	1.79	2.37	2.19
Ga_2O_3	0.03	0.03	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02

The alteration of the color and clarity of the samples after heat treatment can be observed by the naked eyes as shown in figure 1. The unheated samples possessed a greenish-blue color. However, after experiencing heat treatment, the green color vanished, and the blue color was increased in the samples. The clarity of the samples was also improved. It became clearer than those of the unheated ones. This result is correspondingly well with the L^* a^* and b^* factors of color measurement as shown in table 2. The lightness (L^*) possesses a higher value after heat treatment except at 800 °C, corresponding when observed with naked eyes. The blue color representing as $-b^*$ also increased when the samples were heated. However, at a high temperature (≥ 1200 °C), the $-b^*$ value does not show a significant change.

Table 2. CIE L^* a^* b^* color measurement of blue sapphire samples comparing between unheated and heated samples.

Heating Condition (°C)	CIE color measurement					
	unheated			heated		
	L^*	a^*	b^*	L^*	a^*	b^*
800	18.845	-8.256	-6.391	10.809	-0.095	-23.062
1000	18.143	-8.681	-8.489	30.145	-5.025	-25.084
1200	3.751	-1.408	-0.587	20.735	-4.954	-1.198
1400	30.069	-1.022	-5.305	61.235	0.113	-5.685
1650	38.829	-3.871	-12.325	52.892	-2.823	-13.704

The UV-Vis absorption spectra of unheated and heated samples at different heating temperatures were measured to investigate the mechanisms of trace elements related to the blue color in sapphire during the heating processes. The UV-Vis absorption spectra of the representative blue sapphire samples are shown in figure 2. The spectra of unheated and heated samples at 800 and 1650 °C show the absorption peaks at 387 nm and 450 nm defining the single Fe^{3+} [4]. The broad absorption band at 560 nm also appears in the spectra. This band has been assigned as Fe^{3+}/Ti^{4+} pair [5]. The intensity of the band depends on the amount of Fe_2O_3 and TiO_2 relating to the cause of the blue color of the sapphire [6]. However, the UV-Vis absorption spectra were hardly changed throughout the heating process. It could be more reliable when compared only with the unheated counterpart. Thus, the UV-Vis absorption spectra are only useful as a supporting clue to verify the heat treatment.

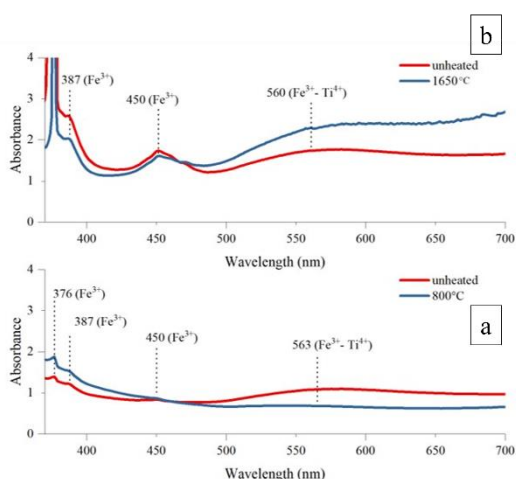


Figure 2. UV-Vis spectra of the representative blue sapphire samples comparing between unheated and heated sample at 800 (a) and 1650 °C (b).

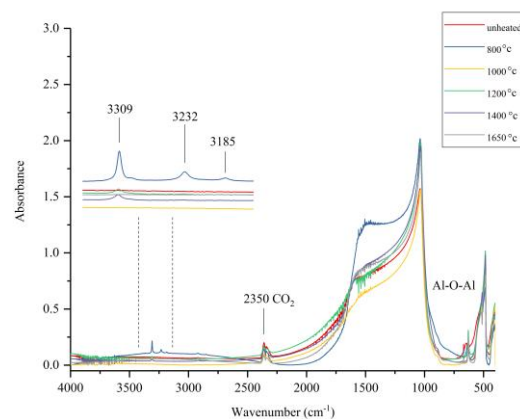


Figure 3. FT-IR spectra measured at 400-4000 cm^{-1} of blue sapphire samples at different heating temperatures.

The FTIR spectra of blue sapphire samples are shown in figure 3. The spectra were recorded at 400-4000 cm^{-1} the common range for analyzing a blue sapphire. The spectra in the -OH stretching region (3000-3500 cm^{-1}) present the peaks at 3309, 3232, and 3185 cm^{-1} assigned to -Ti-OH stretching vibration [2-3]. The peaks are normally used as one of the important indicators to classify the undergone heating of the samples. It should be noted that the peaks are not present in every sample but seem to appear only in the sample heating at low temperatures (≤ 800 $^{\circ}\text{C}$) and disappear when the samples are heated at a higher one. Thus, it is not suitable for identifying the heat treatment at high temperatures, which is a usual method to improve the quality of the blue sapphire.

The absorption peaks in the fingerprint region around 600 - 700 cm^{-1} (figure 4) in the FT-IR spectra are related strongly to the Al-O structure of the blue sapphire. The spectra show the peak at 668 cm^{-1} of Al-O stretching in every heating temperature corresponding to the vibration of Al in the octahedral structure and of the blue sapphire. Simultaneously, in this study, the alteration of the peaks around 625-650 cm^{-1} has been proposed to be applied as a new indicator to classify whether the blue sapphire has been undergone heating. The peaks have been defined as O-Al-O bending vibration relating to the arrangement of the Al_2O_3 in the blue sapphire structure [7]. The unheated sample possesses a broad absorption band centered at 648 cm^{-1} . After the samples were heated at a higher temperature, the peak had been slightly shifted to a higher wavenumber. The feature of the peak also slightly changed from broad absorption to a sharper one. The alteration of the peak responsible for the main structure of blue sapphire in the fingerprint region depends on the temperature of heating. After heating, the disordered atoms, particularly, the Al and O in the blue sapphire structure were rearranged and caused the shift of the peak [6]. Since the Al-O is always present in the blue sapphire as the main component, therefore, the peaks relating to them are more reliable than those in the -OH stretching region, which is associates with the trace elements.

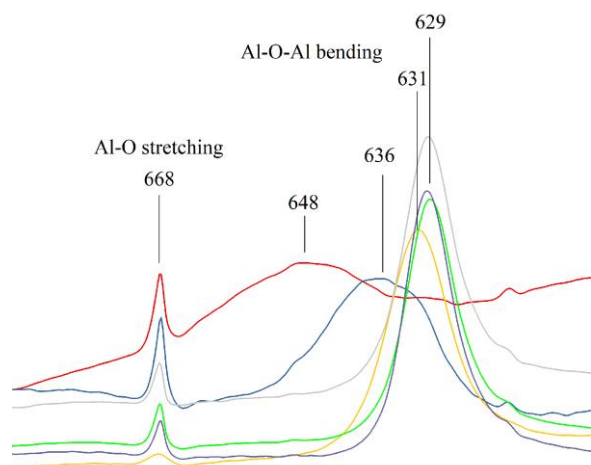


Figure 4. The expanded FT-IR spectra of blue sapphire samples showing the shifted position of Al-O-Al stretching at different heating temperatures; red line = unheated, blue line = 800 $^{\circ}\text{C}$, yellow line = 1000 $^{\circ}\text{C}$, green line = 1200 $^{\circ}\text{C}$, violet line = 1400 $^{\circ}\text{C}$, and gray line = 1650 $^{\circ}\text{C}$

4. Conclusion

The alteration of the O-Al-O bending vibration peak around 625-650 cm^{-1} in FT-IR spectra of blue sapphire has been suggested as one of the new evidence for identifying whether the samples have been undergone heat treatment. The peak is related to the rearrangement of the disordered Al and O atoms caused by heat treatment. This result can be applied in the blue sapphire heating at every range of temperatures.

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