

SPECTROSCOPIC INVESTIGATION OF PROPERTIES OF BLUE SAPPHIRE SAMPLES DEPENDING ON HEATING CONDITIONS**A. Phlayrahan¹, N. Monarumit¹, T. Lhuaamporn²,
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The 3309, 3232, and 3185 cm^{-1} are a series of peaks defined as the 3309 cm^{-1} -series peaks of the functional group absorptions in the mid-infrared region of gem corundum samples, in particular, the blue sapphires. In this study, the 3309 cm^{-1} -series peaks were attributed to $-\text{Ti}-\text{OH}$ stretching. However, the application of revealing these series peaks is still limited because the mechanism of those peaks during the heating process has yet to be clarified. This study showed that the characteristics of the peaks depend strongly on the TiO_2 content in the sapphire samples. Energy dispersive X-ray fluorescence (EDXRF) spectrometry indicated that the samples with Ti content >0.02 wt.% usually show the 3309 cm^{-1} -series peaks with strong intensity. In addition, the X-ray absorption spectra (XAS) revealed that the oxidation state of Fe is Fe^{3+} while Ti is Ti^{4+} for every heating temperature. The UV-Vis-NIR optical absorption showed that the alteration of the bands at 580 and 710 nm, defined as the $\text{Fe}^{3+}/\text{Ti}^{4+}$ pair, was related directly to the atmospheric heating conditions. In contrast, the intensity of the 3309 cm^{-1} -series peaks gradually decreased with increase in heating temperatures in any given atmosphere. This is a result of the mechanism of the bonding between Ti and/or Fe atoms and $-\text{OH}$ in blue sapphire structures caused by the heating.

Keyword: heated blue sapphire, Fourier transform infrared spectroscopy, X-ray absorption spectra, UV-Vis-NIR spectra, 3309 cm^{-1} IR-series peaks.

СПЕКТРОСКОПИЧЕСКОЕ ИССЛЕДОВАНИЕ СВОЙСТВ ОБРАЗЦОВ СИНЕГО САПФИРА В ЗАВИСИМОСТИ ОТ УСЛОВИЙ НАГРЕВА**A. Phlayrahan¹, N. Monarumit¹, T. Lhuaamporn², S. Satitkune¹, P. Wathanakul^{1*}**

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Исследованы спектры поглощения образцов синего сапфира в зависимости от условий нагрева. Максимумы ИК серии на частоте 3309 cm^{-1} отнесены к растяжению $-\text{Ti}-\text{OH}$ -связи. Дисперсно-энергетический рентгеновский флуоресцентный анализ (EDXRF) показал, что образцы с содержанием Ti > 0.02 мас.% обычно обнаруживают высокоинтенсивные максимумы серии 3309 cm^{-1} . Согласно рентгеновским абсорбционным спектрам (XAS), Fe имеет степень окисления Fe^{3+} , тогда как Ti представляет собой ион Ti^{4+} при любой температуре. С помощью методов абсорбционной спектроскопии в УФ, видимой и ИК областях найдено, что изменение определяемых парой $\text{Fe}^{3+}/\text{Ti}^{4+}$ полос на $\lambda = 580$ и 710 нм непосредственно связано с условиями нагревания в атмосфере. Установлено, что интенсивность максимумов серии 3309 cm^{-1} постепенно уменьшается с увеличением температуры атмосферы. Это является результатом вызванной нагревом связи между атомами Ti и/или Fe и $-\text{OH}$ в структуре синего сапфира.

Ключевые слова: нагретый синий сапфир, ИК-Фурье-спектроскопия, рентгеновская абсорбционная спектроскопия, спектры в УФ-видимой-ИК области, серии ИК максимумов при 3309 cm^{-1} .

Introduction. Corundum is alpha-alumina (α -Al₂O₃) occurring in nature. The gem quality of corundum depends on its color and clarity. Pure Al₂O₃ is colorless. The small number of trace elements, i.e., Ga³⁺, Cr³⁺, Fe²⁺, and Ti⁴⁺, can introduce the red and blue color to gem corundum. Generally, red corundum is called ruby and other colored stones are called sapphires [1].

The UV-Vis-NIR spectrophotometer has been used for investigating the cause of color in blue sapphires for decades. However, the absorption band of Fe and Ti as trace elements causing the blue color in the sapphires is difficult to prove because there are many possibilities of alterations in Fe and Ti oxidation states. The most acceptable theory is intervalence charge transfer (IVCT). The overlapping of the d_{z^2} orbital in the Al₂O₃ structure causes the interaction between Fe²⁺ and Ti⁴⁺ at adjacent octahedral sites. The IVCT requires only 0.01% of those ions to create the blue color in sapphire. Due to the spin allowed and $d-d$ transition based on the selection rules, the electron can be transferred between Fe and Ti ions via oxygen-bridging atoms. The extinction of one electron leads to conversion of Fe²⁺ to Fe³⁺ while Ti⁴⁺ gains one to become Ti³⁺. The energy level of the Fe²⁺/Ti⁴⁺IVCT pair is 2.11 eV and causes the absorption bands in the UV-Vis-NIR spectra at 588 and 704 nm [2–4].

Recently, the theory on the cause of color in blue sapphires has been challenged. It has been proposed as the energy band theory using the mixed accepted state of the Fe³⁺/Ti⁴⁺ model. The Fe and Ti oxidation states were proved by X-ray absorption spectroscopy (XAS) [5]. The results suggested that the Fe oxidation state in the sapphire host structure is mainly trivalent, while those of Ti are tetravalent [5–8]. The energy levels of the mixed Fe³⁺/Ti⁴⁺ were calculated as 2.14 and 1.75 eV, causing the UV-Vis-NIR absorption bands at 580 and 710 nm, respectively [5].

Generally, there are three factors involved in the heating process: the temperature-time relationship, the oxidation-reduction reaction, and the trace elements such as Cr, Fe, and Ti [3]. The reducing atmosphere has been used to develop the blue color into the pale sapphire, while the very dark color can be lightened by an oxidizing atmosphere [4, 9]. Thus, the change of color in the gem corundum after heat treatment is influenced by the oxidation-reduction reaction. Even though heat treatment can improve the quality of the stones, the natural unheated stones still command higher prices. Declaration of whether the samples have undergone heating is one of the most critical problems in gem identification. Typically, the alteration of the inclusion and internal features has been used as an indicator. In addition, spectroscopic techniques have been employed to help indicate the heating experience of the sample, particularly when evidence of inclusion is limited.

Origin determination and declaration of treatment are the main topics for gem identification because they affect the desirability and price of the stone. For decades, Fourier transform infrared (FTIR) spectroscopy was classified as an effective technique for gem identification, particularly for ruby and sapphire. There are significant peaks that have always been found especially in blue sapphires such as the 3309, 3232, and 3185 cm⁻¹ peaks (3309 cm⁻¹ IR-series peaks). These peaks have also been used for distinguishing heated stones from unheated ones [10]. Other suggestions on the occurrence of the peaks have been made [10–15]. The previous study [6, 11] disclosed that some important factors such as trace element (especially Ti content), geological origins, and heat treatment conditions affect the characteristics of those peaks.

Application of these series peaks remains limited because of the uncertainty of the behavior caused by the heat treatment. In this study, therefore, a heating experiment of blue sapphire samples was used to reveal the mechanisms of trace elements, in particular TiO₂. We set out to clarify the cause of the occurrences of the 3309 cm⁻¹-series peak in the FTIR spectra of blue sapphire samples under different heating conditions. In addition, the alteration of Fe oxidation state and absorption bands in the UV-Vis-NIR spectra, especially at 580 and 710 nm, during heat treatment are also reported. The application of the 3309 cm⁻¹-series peaks was also unveiled to determine whether the samples had undergone heat treatment.

Experimental. Twenty-nine samples of blue sapphire were collected. The samples were carefully prepared with a thickness around 2.0 mm and were cut perpendicular to the *c*-axis to control the path length and measuring direction.

The chemical composition, particularly TiO₂ and Fe₂O₃, of sapphires was analyzed by the energy dispersive X-ray fluorescence (EDXRF) technique using the EAGEL III model at The Gem and Jewelry Institute of Thailand (GIT).

The heating experiment was used to determine the spectroscopic behaviors, in particular of the UV-Vis-NIR spectra and FTIR 3309 cm⁻¹-series peaks, including 3309, 3232, and 3185 cm⁻¹ as well as the alteration of color during the heating process. The experiment was performed using an electric digital furnace invented by The Gem and Mineral Science Special Research Unit, Kasetsart University, Bangkok, Thailand. The samples were separated into two groups and heated at different atmospheric conditions. The first group was

heated at oxidizing (air) atmosphere while the second one was heated at reducing atmosphere using an argon-filled environment. Both groups were heated at the same temperature at 800, 1000, 1200, 1400, and 1650°C with a soaking time of 1 h.

The UV-Vis-NIR absorption spectra before and after heat treatment at each temperature were obtained by a Perkin Elmer Lambda 900 UV-Vis-NIR spectrophotometer. The absorption spectra were taken at 200–1400 nm. The FTIR spectra were acquired by a Perkin Elmer 400 FT-IR spectrometer. The spectra were recorded from 400 to 4000 cm^{-1} with a spatial resolution of 4 cm^{-1} and 32 samples to a scan. The diffused reflectance was used as an accessory throughout the experiment. To avoid the polarization effect, samples were measured in the direction parallel to the *c*-axis. Then, the spectra were plotted by the Origin Pro8 software. The baseline of the spectra was normalized. The intensities of the significant peaks were fitted and analyzed using the Gauss function (area version of Gaussian function).

The oxidation state of Ti in blue sapphire has already been shown to be due to Ti^{4+} by XAS technique in previous research [7–8]. In this study, we considered the Fe *K*-edge X-ray absorption near edge the structure (XANES) region in fluorescence measurement. The intensity of fluorescence X-ray was detected using a 13-array Ge detector. The suitable energy range was selected by a Ge (220) double crystal monochromator. In addition, the Fe oxidation state of a chemical standard was selectively collected from FeO and Fe_2O_3 regarding Fe^{2+} and Fe^{3+} , respectively. Fe foil was used to calibrate the energy of the Fe zero oxidation state. The photon energy scan of the samples was set from 7075 to 7275 eV with 508 points per scan. The experiment was performed at the Synchrotron Light Research Institute (SLRI), Nakhonrachasima, Thailand. The Fe *K*-edge XAS spectra were analyzed by Athena software.

Results and discussion. *Chemical composition.* The chemical composition of blue sapphire averaged from 29 samples is shown in Table 1, based on the results obtained by EDXRF. Al_2O_3 is the main component in the samples. As to the trace element content, they possess quite low V_2O_5 and Cr_2O_3 , on average 0.1 wt.%, while bearing a high amount of Fe_2O_3 in every sample. In addition, the average amounts of Ga_2O_3 and TiO_2 are 0.04 and 0.05 wt.% respectively.

TABLE 1. The Average Chemical Composition (wt.%) Obtained by EDXRF of the Main and Trace Elements in Blue Sapphire Samples

Al_2O_3	TiO_2	Fe_2O_3	V_2O_5	Cr_2O_3	Ga_2O_3
99.27	0.05	0.52	0.01	0.01	0.04
99.14–99.51	0.02–0.10	0.39–0.76	0.01–0.02	0.00–0.01	0.02–0.11

UV-Vis-NIR absorption spectra. To understand the trace element mechanisms affecting the blue color in sapphires during the heating experiment, the UV-Vis-NIR absorption spectra of unheated and heated samples under different atmospheric conditions (oxidation and reduction) were measured. The normalized UV-Vis-NIR spectra of the representative blue sapphire samples are shown in Fig. 1.

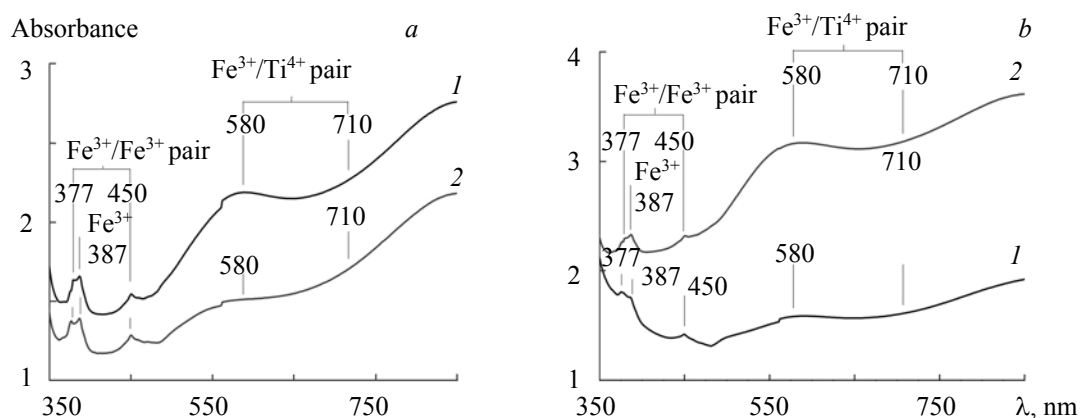


Fig. 1. UV-Vis-NIR spectra representative of two different blue sapphire samples unheated (1) and heated at 1650°C (2) under oxidizing (a) and reducing (b) atmospheres.

The oxidizing atmosphere. The spectra of unheated and heated samples at oxidizing atmosphere show absorption peaks at 387, 377, and 450 nm. Those peaks were assigned to the $\text{Fe}^{3+}/\text{Fe}^{3+}$ pair, the single Fe^{3+} , and the $\text{Fe}^{3+}/\text{Fe}^{3+}$ pair, respectively [16]. The broad absorption band at 580 nm, also appears in the spectra. This band has been defined as the $\text{Fe}^{3+}/\text{Ti}^{4+}$ pair [5]. The intensity of the band depends on the concentration of the Fe_2O_3 and TiO_2 [17], which relate to the color of the samples. The unheated dark blue samples usually show strong 580 nm absorption, and the band was slightly decreased in those samples heated at 1650°C. Correspondingly, the absorption band at 710 nm, which was also assigned to the $\text{Fe}^{3+}/\text{Ti}^{4+}$ pair [5], decreased as well.

The reducing atmosphere. In the case of reducing atmosphere, the sample shows similar peak and band positions as in those spectra obtained from heating samples in the oxidizing condition but with inverse intensity. The UV-Vis-NIR spectra of heating samples at 1650°C indicated stronger absorptions at 387, 377, 450, 580, and 710 nm. With the lower temperature of heating, the intensity of the peaks and bands was slightly changed. The blue color of the sapphire samples also changed through the heating experiment. This was dependent on the atmospheric heating conditions. In the oxidizing condition, the blue colors faded from dark blue to a paler shade, while blue colors changed to a darker hue in the reducing environment.

XANES spectra. The alteration of Fe oxidation state in blue sapphire samples throughout the heating process has been proved by XANES spectra. The zero oxidation state of Fe was calibrated at 7112.39 eV by Fe metal foil. The Fe *K*-edge XANES spectra of FeO and Fe_2O_3 the standard chemical compound showed the Fe *K*-edge energy position at 7119.20 and 7123.12 eV for the di- and trivalences of Fe, respectively. The Fe^0 , Fe^{2+} , and Fe^{3+} oxidation states measured by reference standards are shown in Fig. 2a.

As seen from the Fe *K*-edge XANES spectra, the Fe^{3+} oxidation state appears on both unheated and heated blue sapphires under an oxidizing atmosphere. The Fe *K*-edge energy position of the samples was compared with those of the Fe_2O_3 standard around 7123 eV, as shown in Fig. 2b.

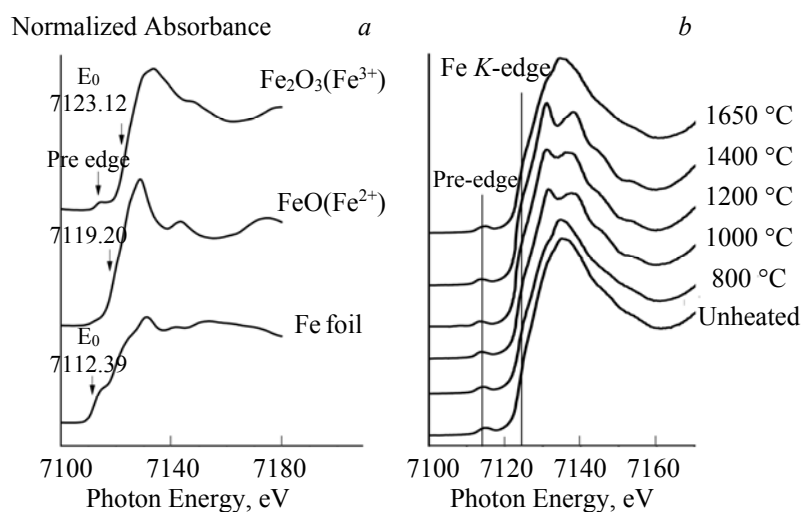


Fig. 2. The Fe *K*-edge XANES spectra of Fe^0 , Fe^{2+} , and Fe^{3+} as reference chemical standards (a) and those of unheated and heated (800–1650°C) blue sapphire samples (b) under an oxidizing atmosphere appear at 7123 eV revealing the trivalent oxidation state of Fe at every heating temperature.

The linear combination fitting at -20 to $+30$ eV around this position was calculated in order to confirm the similarity of the Fe oxidation state between Fe^{2+} and Fe^{3+} (Table 2). The Fe^{3+} proportion was close to 1 on both unheated and heated samples. Thus, it was suggested that the Fe oxidation state of blue sapphires at the ground state was still present as Fe^{3+} whether or not the samples had undergone heating under the oxidizing atmosphere.

Previous research [6–8] revealed that the Ti oxidation state of natural sapphire is tetravalent Ti. The results showed that the Ti *K*-edge XANES spectra of rutile mineral standard have a binding energy position at 4982 eV. This is the same position as those in the unheated and heated samples. Therefore, the Ti oxidation state in sapphire samples before and after heating is still Ti^{4+} .

TABLE 2. The Linear Combination Fitting of Fe Chemical Standards Compared to Those of Blue Sapphire Samples at Different Heating Temperatures

Heating condition, °C	Proportional Weight		Fe <i>K</i> -edge
	FeO	Fe ₂ O ₃	
Unheated	0.000±0.032	1.000±0.032	7123.01
800	0.000±0.022	1.000±0.022	7123.20
1000	0.000±0.023	1.000±0.023	7122.82
1200	0.000±0.020	1.000±0.020	7122.79
1400	0.000±0.021	1.000±0.021	7123.27
1650	0.000±0.021	1.000±0.021	7122.98

The FTIR spectra. The FTIR spectra were recorded in the region from 400 to 4000 cm⁻¹. In this study, however, the spectra were plotted and reported only at 3000 to 3500 cm⁻¹ to emphasize the significant peaks of the 3309 cm⁻¹-series peaks. Normalized FTIR spectra of the two representative blue sapphire samples at different heating temperatures and atmospheric environments are shown in Fig. 3. The spectra indicated a significant peak at 3309 cm⁻¹, which has been attributed to Ti–OH stretching [6, 10, 11]. The heated samples from both atmospheres also indicated the peaks at 3232 and 3185 cm⁻¹. These peaks have been assigned to Ti–OH in the different direction of stretching from 3309 cm⁻¹ [10, 11].

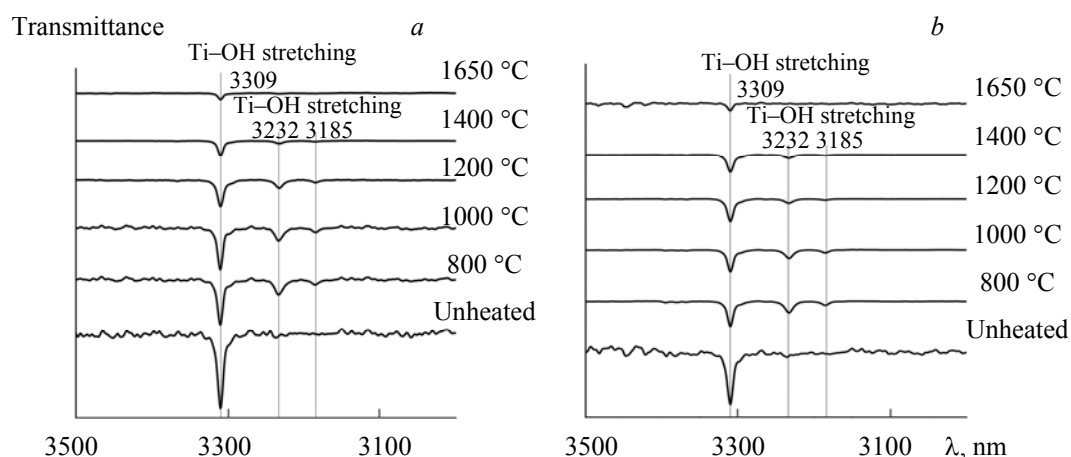


Fig. 3. FTIR spectra of the two representative unheated and heated (800 to 1650°C) blue sapphire samples under the oxidizing (a) and reducing (b) atmospheres. The TiO₂ content in both samples is 0.09 wt.%.

Even though the atmospheric conditions could be related to the decreasing intensity of the peaks in the UV-Vis-NIR absorption spectra, this hardly affected the appearance of the 3309 cm⁻¹-series peaks in the FTIR spectra. In contrast, the different concentrations of TiO₂ in the blue sapphires play an important role in the appearance of the peaks [6]. The FTIR spectra of the blue sapphire sample possess a low TiO₂ content, ≤0.02 wt.% (Fig. 4a), showing the peak only at 3309 cm⁻¹. The peak was observed to have the highest intensity in the unheated condition, decreasing after the samples were heated at higher temperatures (800–1650°C).

Samples with higher TiO₂ content, i.e., >0.02 wt.%, usually display the 3309 cm⁻¹ peak in the strong absorption in unheated samples. In addition, these groups of samples also show side peaks at 3232 and 3185 cm⁻¹ after heating (Fig. 4b,c). However, the peaks present only in heated samples at 800 to 1400°C then disappeared at 1650°C. Moreover, the intensity of the side peaks decreased when the samples were heated at higher temperatures. The samples possess TiO₂ content of around 0.05 but <0.08 wt.%, and the 3309 cm⁻¹ peak almost disappears (very weak absorption) after experiencing heating at 1650°C (Fig. 4b).

The result suggested that the different occurrence of the 3309 cm⁻¹-series peaks is related to the TiO₂ content. The previous study also revealed that the orientation of Ti and hydroxyl (-OH) dipole moment in the Al₂O₃ structure play an important role in the position of the Ti-related stretching peaks [6, 11, 13]. General-

ly, the -Ti and -OH vibrations were perpendicular to the *c*-axis direction [18]. Accordingly, when the spectra were detected in that direction, the possibility of finding the 3309 cm⁻¹-series peaks is higher and more accurate than those of the other measurement directions [12, 19].

Naturally, the Al₂O₃ structure in the unheated state is disordered. The possibility of Fe-O-Ti bonding is less than that of the Ti-OH stretching. This result causes the strong intensity of the 3309 cm⁻¹ peak in unheated samples. The bonding of -Ti-OH was broken during heat treatment. The Ti ions and -OH could be re-bonded in different directions in the corundum structure. As a result, the intensity of the 3309 cm⁻¹ peak decreased. At the same time, the peaks at 3232 and 3185 cm⁻¹ were introduced into the spectra of heated samples.

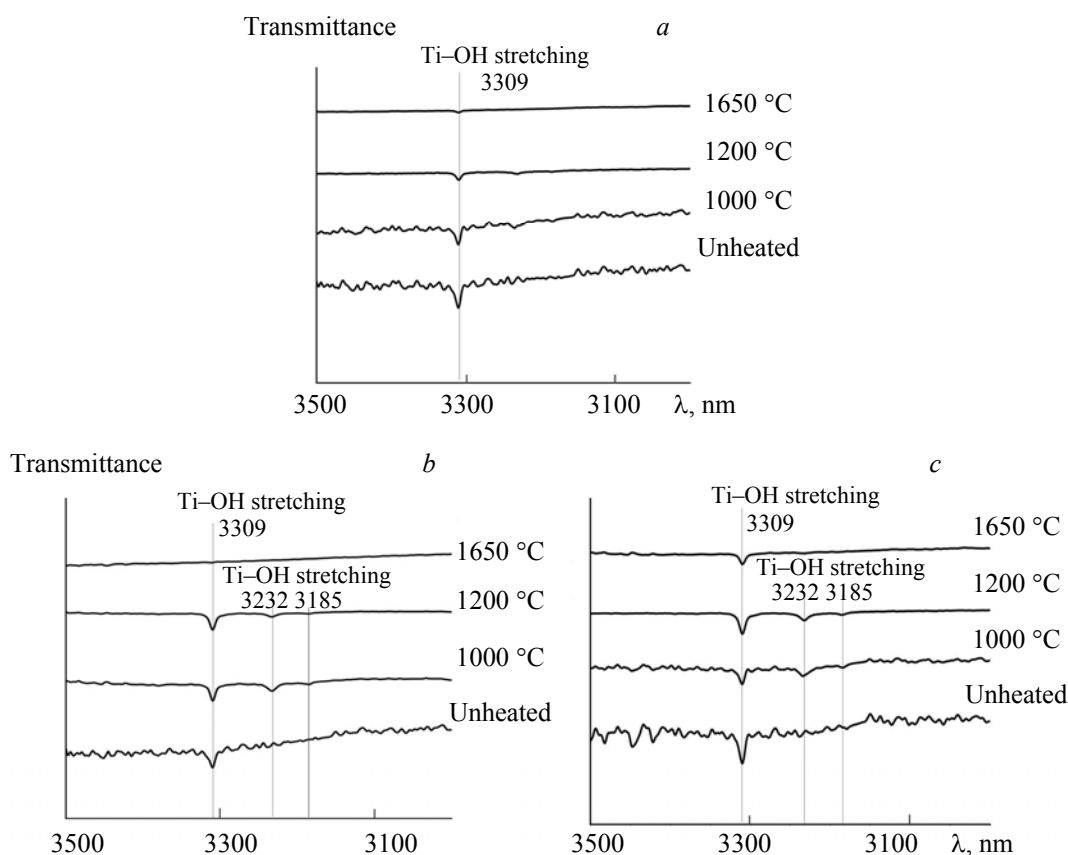


Fig. 4. FTIR spectra of the blue sapphire sample with TiO₂ content of 0.02 wt.% (a) showing the peak only at 3309 cm⁻¹; together with the FTIR spectra of the blue sapphire samples with TiO₂ content >0.02 wt.% (b, c), displaying the peak at 3309 cm⁻¹ with the side peaks at 3232 and 3185 cm⁻¹ while heating. However, this sample had a TiO₂ content of 0.05 wt.% (b), and the 3309 cm⁻¹ peak disappeared after heating at 1650 °C.

It is noteworthy that the heating atmospheres (oxidizing or reducing) were differently affected by the decreasing of the 3309 cm⁻¹-series peaks in the FTIR spectra of blue sapphire samples. There are some studies suggesting that this could be related to the alteration of the Fe oxidation state during the heat treatment [20]. Based on the IVCT theory, oxidizing and reducing atmospheres could change the Fe and Ti oxidation state according to:



However, in this study, the XANES spectra revealed that the Fe oxidation state in the host structure of blue sapphire throughout the heating process under the oxidizing atmosphere is Fe³⁺. Meanwhile, the Ti oxidation state before and after heat treatment is Ti⁴⁺ [6, 8]. The results suggested that the oxidation state of the Fe/Ti pair causing the blue color in sapphire could be Fe³⁺/Ti⁴⁺ [5].

The results could be summarized by noting that the bonding between Ti and -OH was weakened after heating. The possibility of Ti-O and/or Fe-O bonding is high. However, the bonding does not cause the occurrence of any absorption peaks in the -OH stretching region ($4000\text{--}3000\text{ cm}^{-1}$), although it does elsewhere, usually below 1500 cm^{-1} [21, 22]. In addition, Fe and Ti ions form mineral inclusions such as rutile (TiO_2), hematite (Fe_2O_3), and/or ilmenite (FeTiO_3), which were not yet dissolved at the low heating temperatures [23, 24]. The low amount of oxygen in the reducing environment forced the Ti atoms to bond with -OH again. However, some of those ions could probably be formed in another direction in the Al_2O_3 structure. This can be explained by the decreasing intensity of 3309 cm^{-1} peaks and the side peaks produced at 3232 and 3185 cm^{-1} in the heated samples. At high heating temperature, the mineral inclusions were dissolved and added some amount of Fe^{3+} and Ti^{4+} into the structure. A sufficient quantity of those ions can re-bond and increase the $\text{Fe}^{3+}/\text{Ti}^{4+}$ pairs as well as the $\text{Fe}^{3+}/\text{Fe}^{3+}$ pairs. These results caused the strong absorption at 580 and 710 nm in the UV-Vis-NIR spectra as well as emitting the darker blue color. In addition, the small amount of Ti can also bond with the -OH in the host structure, which presents with weak absorption of the 3309 cm^{-1} peak in FTIR spectra.

After heating in the oxygen environment (oxidizing), there is a possibility that the Fe and Ti ions could be formed and exchange an electron with O^{2-} in the structure. The $\text{Fe}^{3+}/\text{Ti}^{4+}$ pair in the UV-Vis-NIR spectra and the 3309 cm^{-1} -series peaks decreased through the heating process. The fading of the blue color of the samples after heating can be related to the broken bond of the $\text{Fe}^{3+}/\text{Ti}^{4+}$ pair. However, at the high heating temperature there is some amount of Fe and Ti from the dissolved minerals inclusion that is added in the structure. Titanium can bond with -OH and create the stretching of -Ti-OH at the 3309 cm^{-1} -series peaks in the FTIR spectra. Nevertheless, the high concentration of Fe_2O_3 in the structure might cause the -Fe-OH stretching to bond more than -Ti-OH stretching, which created the absorption peaks over the 3600 cm^{-1} [21]. It consequently affected the decreasing of the 3309 cm^{-1} -series peaks and the absorption band at 580 and 710 nm in the UV-Vis-NIR spectra in the heated blue sapphire samples under the oxidizing atmosphere. The bonding of Fe-OH and/or Ti-OH occurred instead of the $\text{Fe}^{3+}/\text{Ti}^{4+}$ pair, which resulted in fading of the blue color.

Conclusion. The Fe oxidation state of blue sapphire throughout the experimental heating process was still mainly Fe^{3+} , as shown by the XAS technique. In addition, in this study, the 3309 cm^{-1} -series peaks have been confirmed again as -Ti-OH stretching. The different characteristics of the 3309 cm^{-1} -series peaks in FTIR spectra are dependent on the TiO_2 content and the atmospheric heating conditions. Thus, the results suggested that the intensity of the 3309 cm^{-1} -series peaks could be applied to identify whether or not the samples have undergone heat treatment. This interpretation depends on the initial intensity of the 3309 cm^{-1} -series peaks and hence, is related to the TiO_2 content. In the meantime, the cause of the absorption band at 580 and 710 nm in the UV-Vis-NIR spectra also supports the previous theory of the $\text{Fe}^{3+}/\text{Ti}^{4+}$ energy band model. The alterations (decrease or increase) of those bands depend on the concentration of the $\text{Fe}^{3+}/\text{Ti}^{4+}$ pair in the host structure.

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