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ROLE OF Ti CONTENT ON THE OCCURRENCE OF THE 3309 cm^{-1} PEAK IN FTIR ABSORPTION SPECTRA OF RUBY SAMPLES

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The study is based on the determination of trace elements in ruby samples, Ti in particular, using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). The samples were then divided into three groups: high (≥200 ppma), moderate (100–200 ppma) and low (≤50 ppma) Ti content. In addition, X-ray absorption spectroscopy (XAS) was employed to confirm that the Ti oxidation state was Ti^{4+}. The heat experiment conditions were set at 800, 1200, and 1650ºC to investigate the transformation of the –OH vibration in the FTIR spectra of ruby samples. The FTIR spectra showed that samples containing a low Ti concentration did not show the 3309 cm^{-1} absorption peak either before or after heating at any of the designed temperatures. An obvious 3309 cm^{-1} peak appeared only in samples with a moderate to high Ti content after heating at ≥1200ºC. The results also suggest that, in addition Ti^{4+}, the occurrence of the 3309 cm^{-1} peak in the FTIR spectra is strongly affected by the charge compensation of –OH in Al sites, i.e., the structural –OH; thus, the structural –Ti–OH stretching in the ruby samples. Hence, for gemological identification, the 3309 cm^{-1} peak can be applied to indicate whether a ruby has undergone heat treatment if those samples contain enough Ti ions in their structure, i.e., Ti ≥ 100 ppma. This condition is usually found in ruby samples from major deposits such as Mong Hsu and Mogok, Myanmar; Luc Yen, Vietnam; and Montopuez, Mozambique.

Keywords: *structural –Ti–OH stretching, heated ruby, Ti content, FTIR.*

ВЛИЯНИЕ СОДЕРЖАНИЯ ТИТАНА В ОБРАЗЦАХ РУБИНА НА ПОЯВЛЕНИЕ МАКСИМУМА ПРИ 3309 см$^{-1}$ В ИК-ФУРЬЕ-СПЕКТРАХ ПОГЛОЩЕНИЯ

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Следы элементов (в частности, Ti) в образцах рубина определены с помощью масс-спектрометрии с индуктивно-связанной плазмой. По полученным результатам исследуемые образцы разделены на три группы: с высоким (≥200 ppma), средним (100–200 ppma) и низким (≤50 ppma) содержанием Ti. С помощью рентгеновской спектроскопии подтверждено, что титан находится в состоянии Ti^{4+}. Методом ИК-фурье-спектроскопии изучены колебания группы –OH в образцах рубина при температурах 800, 1200 и 1650 ºC. Максимум поглощения на частоте 3309 см$^{-1}$ для образцов с низкой концентрацией Ti не обнаруживается ни при одной из указанных температур, а появляется только в спектрах образцов со средним и высоким содержанием титана при нагревании до температуры ≥1200 ºC. Результаты также свидетельствуют о том, что появление максимума при 3309 см$^{-1}$ помимо наличия ионов Ti^{4+} связано с компенсацией заряда –OH в положениях ионов Al, т. е. с образованием связей –Ti–OH. Следовательно, если в структуре образцов рубина содержится достаточно ионов Ti (≥100 ppma), то по наличию максимума 3309 см$^{-1}$ можно идентифицировать, прошел ли *рубин термическую обработку. Данное условие выполняется для рубина из крупных месторождений, таких как Монг-Хсу и Могок (Мьянма), Люк Йен (Вьетнам) и Монтопес (Мозамбик).*

Ключевые слова: *связь –Ti–OH, нагретый рубин, содержание Ti, ИК-фурье-спектроскопия.*

Introduction. A corundum gem or alpha aluminum oxide (α-Al_2O_3) is classified as one of the most important gemstones in the market. Their varieties are divided into rubies and sapphires depending on their colors. The red color of a ruby is acquired by substitution of a chromium ion (Cr^{3+}) for Al^{3+} in the Al_2O_3 structure. For sapphires, the intervalence charge transfer (IVCT) between iron (Fe^{2+}) and titanium (Ti^{4+}) provides the blue color [1]. Although the Ti ion does not play an important role in the coloration of a ruby, it is usually found as a trace element. The Ti content can be accessed in the ruby crystal structure via blue color zoning (Fe^{2+}–O–Ti^{4+} IVCT), blue sectors, the dark core, and/or as rutile inclusions (TiO_2) [2, 3].

A corundum gem's quality is based on clarity and color, and high-quality examples are hard to find in nature. However, clarity and color can be improved by heat treatment. The technique is commonly acceptable in the gem market as long as it has been disclosed at every point of sale because clarity and color affects a gem's price. Generally, the changes of the internal features of a ruby by heat treatment are detectable using a gemological microscope. However, some advanced techniques such as Fourier transform infrared (FTIR) spectroscopy can also provide confirmation [4].

The FTIR spectrum represents the specific vibrational frequency between the bonding of atoms or molecules. This technique can be applied to analyze bonding of the light elements such as hydrogen, carbon, oxygen, and boron, as well as their functional groups, e.g., O–H, C–H, C–N, and C–O [5]. In mineralogical research, FTIR spectroscopy has been widely used to characterize the molecular water and the hydroxyl group in several minerals, such as silicates, clays, aluminum oxides, and iron oxides [6, 7]. However, in gemology, particularly with rubies and sapphires, the FTIR spectra can also be applied to determine the molecular and/or structural vibration of –OH. This vibration is the result of reflections from OH-bearing mineral inclusions, such as boehmite, diaspore, goethite, and mica [8, 9]. With this advantage, the transformation of some specific absorption around 3000–3500 cm^{-1}, particularly the 3309 cm^{-1} peak during the heating process, can be presumably used to identify whether a corundum gem has undergone heat treatment.

The 3309 cm^{-1} peak in the FTIR spectra was introduced in the 1970s [7, 10]. This peak usually appears in blue sapphires and in some conditions of rubies. Some gemologists have speculated that this peak can be used to identify heat treated samples [9, 11]. Thus, this peak has been widely discussed and mentioned in gem identification. However, the cause of the 3309 cm^{-1} peak has not been clarified yet. The principles explaining the occurrence of the 3309 cm^{-1} peak have been reported in several hypotheses. For example, reports suggest that it is related to the impurity of Ti atoms during the heat synthesis [10], the defect of $(\mathrm{Ti}^{\circ}_{\mathrm{Al}}\,\mathrm{V}'''_{\mathrm{Al}}\mathrm{OH}^{\circ}_{\mathrm{O}}\mathrm{Ti}^{\circ}_{\mathrm{Al}})^{x}$ in α-Al_2O_3 of synthetic sapphire [12], the increase of the hydroxyl group (OH^-) by dehydration of hydrous mineral inclusions (boehmite and/or diaspore) in natural ruby samples [13], the charge compensation of H^+ after heat treatment [14], and/or the vacancy in the Al sites [15].

Based on previous research [16], it can be noted that there are some specific conditions of rubies that usually show the peak at 3309 cm^{-1} in the FTIR spectra, such as rubies with a metamorphic origin, i.e., Mong Hsu, Mogok (Myanmar) and Luc Yen (Vietnam) rubies. Normally, these samples contain blue zoning, a dark core and/or blue sectors in which they normally look purplish red because they possess high Fe^{2+}/Ti^{4+} IVCT in their structure. Consistently, these ruby samples also possess relatively high Ti content. Therefore, samples of metamorphic origin are often heated at high temperature to eliminate the blue hue, and thus enhance the red color. Accordingly, the 3309 cm^{-1} peak in the FTIR spectra is evident only in samples that have undergone heating at high temperature ($\geq$1200°C). Thus, there is a possibility that the Ti content and heat treatment are likely related to the occurrence of the 3309 cm^{-1} peak in the FTIR spectra in ruby samples [16].

In this study, using ruby samples with different levels of Ti content, heat treatment experiments and the alteration of –OH stretching vibration are discussed for clarifying the cause of the 3309 cm^{-1} peak in the FTIR spectra. In addition, the application of this peak for determining whether ruby samples have undergone heat treatment is considered.

Experimental. A group of ruby samples of different conditions based on their Ti content was collected. The samples were cut perpendicular along the c-axis with a thickness of around 0.2–0.4 cm. To determine the influence of Ti content on the occurrence of the 3309 cm^{-1} peak, the samples were examined by laser ablation inductively coupled plasma mass spectroscopy (LA-ICP-MS) using an Agilent 7500 series spectroscope at The Gem and Jewelry Institute of Thailand (GIT), Bangkok, Thailand and then divided into three groups based on high (NRH01-NRH05), moderate (NRM01-NRM05), and low Ti content (NRL01-NRL05). The samples with moderate and high Ti content showed a significant dark core and/or blue color zoning.

Both of these groups also indicated the mineral inclusion of boehmite (γ-AlO(OH)) and/or diaspore (α-AlO(OH)). X-ray absorption spectroscopy (XAS) was also used to confirm the oxidation state of Ti. The technique focused on the Ti *K*-edge XANES region in fluorescence mode by a 13-array germanium detector. The X-ray photon energy was manipulated by a Ge (220) double crystal monochromator connected to a synchrotron storage ring at the Synchrotron Light Research Institute (SLRI), Nakhon Ratchasima, Thailand [17].

Heating experiments were used to investigate the alteration of the –OH stretching vibration. The experiments were carried out at high temperatures in an electric digital furnace invented by The Gem and Mineral Science Special Research Unit, Department of Earth Sciences, Faculty of Science, Kasetsart University, Bangkok, Thailand. The samples were heated in a normal atmosphere, i.e., oxidization at 800, 1200, and 1650ºC, representing the low, medium, and high temperature conditions, respectively. After reaching the desired temperature, the soaking time for each experiment was set at 1 h. Afterwards, the samples were allowed to cool in the furnace until reaching 600ºC. They were then removed and allowed to cool to room temperature outside the furnace.

The FTIR spectra of the samples were acquired by a NEXUS 470 FTIR spectrometer in transmission mode with a Collector™ II diffuse reflectance accessory at Department of Earth Sciences, Faculty of Science, Kasetsart University, Thailand. The spectra were recorded from 4000–1500 cm^{-1} with a spectral resolution of 4 cm^{-1} and 256 scans. In this study, the samples were measured with the IR beam parallel to the *c*-axis. The surrounding air was always measured as background spectra.

Results and discussion. The chemical composition with % uncertainties of ruby samples obtained by LA-ICP-MS is summarized in Table 1. The average of the trace element concentrations is reported in atom mole parts per million (ppma) unit. Most of the ruby samples show a high range of Cr content (~1500–2100 ppma) as the main trace element. For Ti content, the average is ~240 ppma in high Ti content samples (NRH), ~120 ppma in moderate Ti content samples (NRM), and the low Ti content samples (NRL) have an average of ~23 ppma. In addition, the low Ti content samples contain the highest amount of Fe, at ~730 ppma.

The heated high Ti content sample (NRH01) was used as a representative and measured for the oxidation state of Ti using the XAS (Fig. 1). A calculation method by the first derivative is used for determining the binding energy of the Ti *K*-edge. The Ti atoms in the NRH01 sample show the Ti *K*-edge energy position at 4982 eV, which is assigned to Ti^{4+} similar to that of the rutile (TiO_2) standard. This result is also confirmed by the highest peaks in the first derivative spectrum at the same position. Therefore, it can be assumed that the Ti oxidation state in the ruby sample is Ti^{4+}.

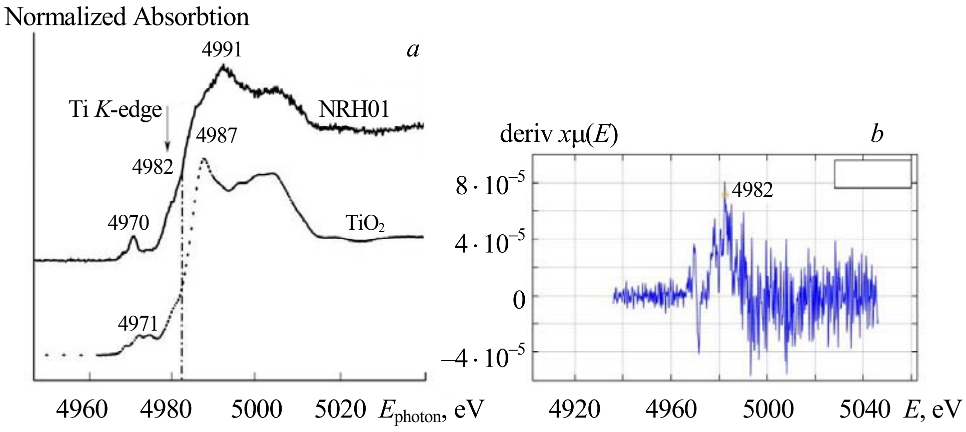

Fig. 1. The Ti *K*-edge XANES spectrum of rutile (TiO_2) standard and NRH01 sample (a) and the first derivative spectrum showing the binding energy at the same position at 4982 eV (b).

The FTIR spectra were recorded in the functional group region between 4000 and 1500 cm^{-1}. In this study, the polarized FTIR spectra were measured parallel to the *c*-axis of the samples. This was done to minimize the structural influence of the samples when measured from different directions. In addition, based on the previous research, the 3309 cm^{-1} peak shows obvious and strong intensity in the *c*-axis direction [13, 16].

The FTIR spectra of the ruby samples show the group of peaks around 2920 and 2850 cm^{-1}, which have been assigned for the C–H stretching of organic matter. However, it must be noted here that these peaks usually appear in the FTIR spectra of rubies and blue sapphires in particular. Most research in gemology has mentioned that the occurrence of these peaks is related to the oil from the cutting and polishing process. Although the samples are carefully cleaned to remove contaminants, the peaks still appear. Therefore, it is possible that the occurrence of the peaks is not only related to the cutting or polishing process, but also related to the organic matter acquired from the geological origin and/or mineral inclusions. Another group of peaks that usually presented in the FTIR spectra of samples are those around 2350–2335 cm^{-1} of C–O stretching (CO_2) from the environment during the experiment.

The representative samples of high (NRH01) and moderate (NRM01) Ti content (Fig. 2) showed a broad FTIR absorption band of molecular water around 3500–3100 cm^{-1} in both the unheated samples and those heated at 800ºC. The band then turned to sharp peaks with the highest intensity after the samples were heated at 1200ºC. The appearance of those peaks could be caused by the dissolution of molecular water, in which its absorption overlaid the peaks before heating. However, both samples exhibited a significant peak at 3309 cm^{-1}, though in different patterns. At 1200ºC, the NRH01 sample demonstrated the 3309 cm^{-1} peak with side peaks at 3367, 3232, 3185 cm^{-1} with a ratio of 10:1:3:1, respectively. The peaks at 3367 and 3185 cm^{-1} eventually disappeared when the sample was heated at 1650ºC. However, the NRM01 sample exhibited only a low intensity 3309 cm^{-1} peak without any side peaks, and it was no longer apparent when the sample was heated at the highest temperature (1650ºC); the decrease of the 3309 cm^{-1} peak could be influenced again by the dissolution of –Ti–OH in the structure because of the high temperature of the heating.

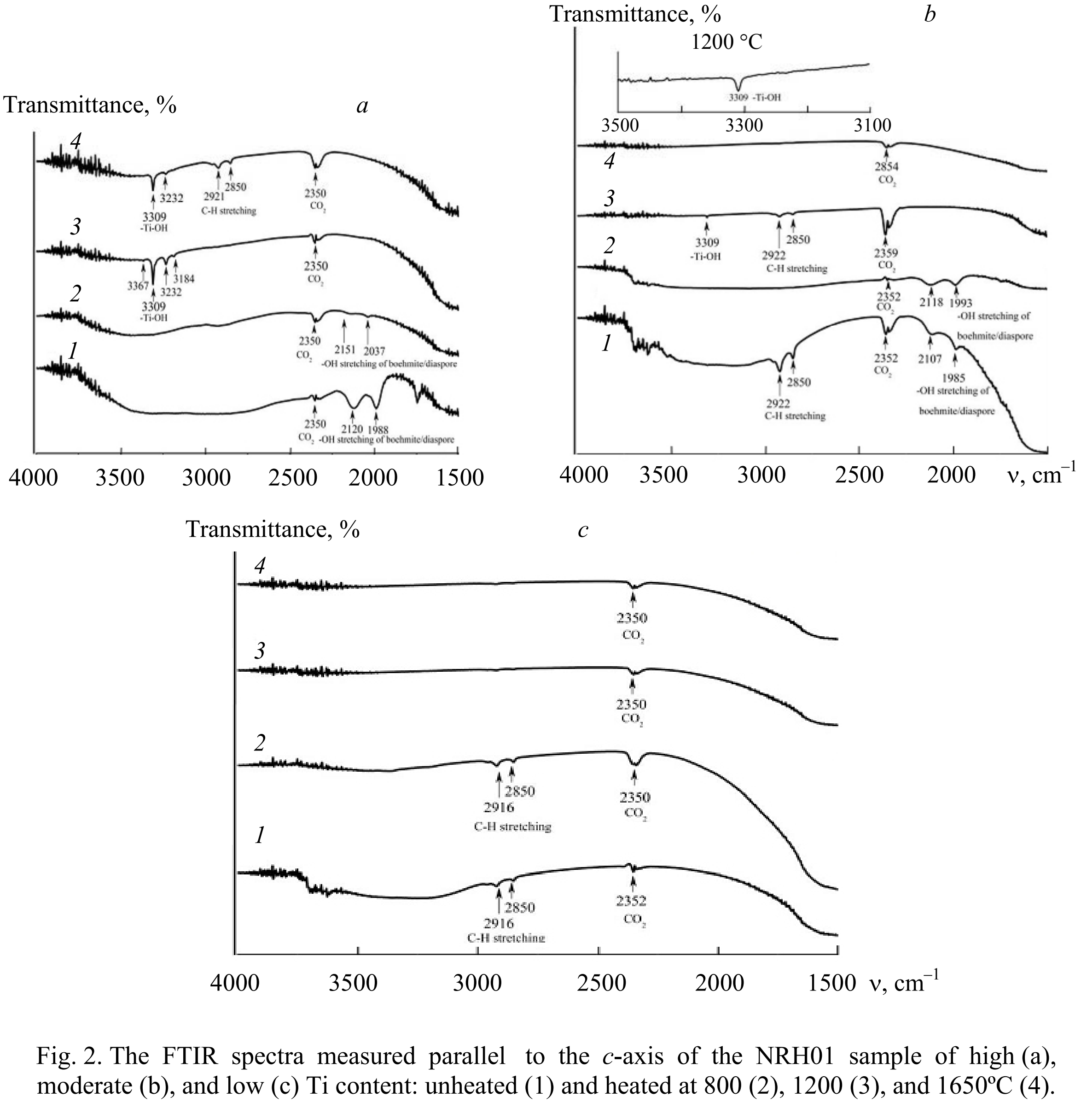

Fig. 2. The FTIR spectra measured parallel to the *c*-axis of the NRH01 sample of high (a), moderate (b), and low (c) Ti content: unheated (1) and heated at 800 (2), 1200 (3), and 1650ºC (4).

The side peaks at 3367, 3232 and 3184 cm^{-1} could be also related to the Ti content because those peaks only appear in the FTIR spectra of samples with high Ti content. In addition, either increasing or decreasing the intensity of the side peaks during the heating process demonstrates the relationship as the reciprocal proportion. This result agrees with other research [12].

Additionally, –OH stretching vibration peaks around 2100–1980 cm^{-1} of hydrous mineral inclusions, such as boehmite and diaspore [9], also appeared in both samples. In the unheated condition the peaks appeared at 2120–1988 and 2116–1985 cm^{-1} in the NRH01 and NRM01 samples, respectively. However, when the samples were heated at 800°C those peaks slightly shifted to the higher wavenumber because of the phase transformation of boehmite and/or diaspore. Finally, the peaks disappeared when the samples were heated at higher temperatures (>800°C). Consequently, the shift of the –OH stretching peaks in this region to a few higher wavenumbers could also confirm whether certain ruby samples have undergone heat treatment at a low temperature [13].

In contrast to the high and medium Ti content samples, the FTIR spectrum of the representative low Ti content sample (NRL01) does not exhibit the 3309 cm^{-1} peak in every heating temperature. Even though the broad absorption of molecular water would help to identify unheated samples, it would be unable to confirm whether samples have undergone heat treatment at 800°C. There are C–H and C–O stretching peaks as well as the small broad absorption band in the unheated sample, but the alteration of those peaks is insignificant. It can be assumed that the occurrence of the 3309 cm^{-1} peak is not related to other trace elements, such as Cr and Fe (as shown in Table 1); no peaks appear in those samples with high Fe content (low Ti content). Even when the samples possess a high Cr content, the 3309 cm^{-1} peak still does not appear in the FTIR spectra of those samples. Therefore, the Ti content has been shown to play an important role in the occurrence of the 3309 cm^{-1} peak in the FTIR spectra of ruby samples. Accordingly, heat treatment at high temperature could dissolve some mineral inclusions such as rutile, boehmite, and/or diaspore, thus providing the free radical –OH in the ruby structure. In addition, the actual existence of the 3309 cm^{-1} peak is also revealed by the disappearance of the molecular water broad absorption band around 3500–3000 cm^{-1}. Furthermore, the oxidation atmosphere during heat treatment at high temperature (≥1200ºC) facilitates the transfer of Fe^{2+} to Fe^{3+}. Thus, the probabilities of the Fe^{2+}/Ti^{4+} IVCT in the dark core and/or blue color zoning areas in the ruby samples were decreased [18], corresponding to the fading of those features after heating at ≥1200ºC. This is likely because the loss of an Fe^{2+}electron to Fe^{3+} in the ruby structure requires the bonding of Ti^{4+} with –OH. Consequently, at the appropriate temperature (≥1200ºC), the Ti^{4+} and –OH created the unique vibrational frequency at 3309 cm^{-1} in the FTIR spectra. The intensity of the 3309 cm^{-1} peak depended on the amount of Ti content and structural –OH in the ruby structure.

TABLE 1. The Average Data (ppma) of Trace Elements (Cr, Ti, and Fe) in Ruby Samples Analyzed Using Laser Ablation Induce Coupled Plasma Mass Spectroscopy (LA-ICP-MS)

Element	High Ti (NRH)	Moderate Ti (NRM)	Low Ti (NRL)	% Uncertainties
Cr	2082	1519	1563	3.8
Ti	242	120	23	5.6
Fe	18	141	730	21.8

Conclusion. The 3309 cm^{-1} peak in the FTIR absorption spectra of rubies could be interpreted as structural –Ti–OH stretching vibration. This research revealed that the peak is useful for identifying whether a gem has been heated. The Ti content, heat treatment, and the structural –OH stretching vibration are factors that affect the occurrence of the 3309 cm^{-1} peak. Nevertheless, it has been found that this peak can be used for indicating the heat treatment only in those samples that have Ti content ≥100 ppma. An advantage of this research is that the results can be applied to most rubies from major deposits. For example, rubies from Mong Hsu and Mogok, Myanmar usually have a Ti content ≥200 ppma; those of Luc Yen, Vietnam have ≥120 ppma, and Montopuez, Mozambique have ≥100 ppma.

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