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Fe oxidation state in heat-treated basaltic blue sapphire samples and its implication to the 3309 cm⁻¹-series peaks in infrared absorption spectra

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Abstract. Ti atoms bond with Fe atoms and exchange their electron particles in the adjacent octahedral sites. This process produces the blue color on the blue sapphire. The Ti content is an important key for the alteration of the 3309, 3232, and 3185 cm⁻¹ (3309 cm⁻¹-series peaks) in infrared absorption (FTIR) spectra of blue sapphire samples. To study the effect of Fe and Ti oxidation state and the behavior of the Ti-related peaks in FTIR spectra during the heating process, the blue sapphire samples from Phrae and Kanchanaburi, Thailand were collected regarding their basaltic origins. The heating experiment was performed. The samples were step-heated at 800, 1000, 1200, 1400, and 1650 °C under an oxidizing atmosphere, with 1 hour soaking time at each temperature. The FTIR spectra and the X-ray absorption spectra (XAS) were measured before and after heating. Before heating, the FTIR spectra showed only the peak at 3309 cm⁻¹ while the side peaks at 3232 cm⁻¹ and 3185 cm⁻¹ start to appear after heating at 800 °C. The 3309 cm⁻¹-series peaks were assigned as -Ti-OH stretching. The intensity of those peaks was slightly decreased after heat-treated. The XAS spectra revealed that the oxidation state of Fe is still Fe³⁺ while Ti is still Ti⁴⁺ in every heating temperature. The results pointed that the alteration of the 3309 cm⁻¹-series peaks does not depend on the Fe and/or Ti oxidation state.

1. Introduction

Blue sapphire is an alpha-alumina (α -Al₂O₃) mineral. The gem-quality of blue sapphire is considered by its color, size, and clarity. Blue sapphire can be originated either by metamorphic or basaltic origins [1]. Naturally, pure Al₂O₃ is colorless; however, the small amount of Fe²⁺-Ti⁴⁺ inter-valence charge transfer can produce blue color on blue sapphire [2]. Generally, the heat treatment has been performed to improve the color and clarity of blue sapphire due to the gem-quality is rare in nature. However, at the same quality, the price of heated blue sapphire could not be higher than the natural ones. For this reason, the heat treatment would be acceptable only when it is revealed.

The 3309 cm⁻¹ and its side peaks at 3232 and 3185 cm⁻¹ aka 3309 cm⁻¹-series peaks in the infrared absorption (FTIR) spectra have been mentioned in blue sapphire identification for decades [3]. The appearance of the peaks was related to the TiO₂ content in Al₂O₃ structure and was assigned to -Ti-OH stretching [4-5]. Whereas there are possibly other variables related to the appearance of the 3309 cm⁻¹-series peaks that still require being clarified such as the oxidation state of Fe and Ti. Nowadays, the oxidation state of those important cations was importantly proved by the X-ray Absorption



Spectroscopy (XAS) technique. The results suggested that the Fe oxidation state in the unheated blue sapphire is mainly trivalent while those of Ti are tetravalent in both unheated and heated stones [6-7]. Although the previous study reported that the Fe oxidation state of heated blue sapphire samples was changed during the heating process [8]; however, the result still not yet to be confirmed by XAS technique.

In this study, therefore, the Fe oxidation state of blue sapphire samples during the heating process and its connection with the alteration of the 3309 cm^{-1} -series peaks have been reported for the better understanding of the peaks into the maximum benefits.

2. Experiments

Rough blue sapphires from Phrae and Kanchanaburi, Thailand were selected as representative samples regarding to the basaltic origins. The samples were cut in a perpendicular direction to their c-axis and were polished into the thickness around 2 mm (figure 1). Then the samples were step heat-treated at 800, 1000, 1200, 1400, and 1650 °C, soaking for 1 hour at each temperature. The heat treatment was performed under the oxidizing atmosphere. The change of color and clarity of the samples after heating at 1650 °C are shown in figure 2.



Figure 1. A representative unheated blue sapphire samples.



Figure 2. A representative heated at 1650 °C blue sapphire samples.

To investigate the behavior of the Ti-related peaks (3309 , 3232 , and 3185 cm^{-1}) in FTIR spectra throughout the heating process, the spectra were examined by Perkin Elmer 400 FT-IR spectrometer at Department of Physics, Faculty of Science, Kasetsart University, Thailand. The spectra were detected from 400 cm^{-1} to 4000 cm^{-1} ranging with the spatial resolution of 4 cm^{-1} and 32 numbers of a scan. The diffused reflectance was used as an accessory throughout the experiment. To control the polarization effect, the samples were measured in a parallel direction to the c-axis.

Due to the bonding of Fe and Ti atoms cause the blue color on blue sapphire. In addition, the Fe-Ti bonding also related to the alteration of the 3309 cm^{-1} -series peaks in FTIR spectra [5]. In this study, the Fe oxidation state of the blue sapphire samples was investigated by XAS technique in the Fe *K*-edge x-ray absorption near edge structure (XANES) region at the Synchrotron Light Research Institute (SLRI), Thailand. The XAS experiment was set in a fluorescence measurement to carry out the x-ray absorption intensity using a 13-array Ge detector, as well as, to select a suitable energy range using a Ge (220) double crystal monochromator. In addition, the Fe oxidation state of the Fe chemical standard was selectively recorded from FeO and Fe₂O₃ representing to Fe²⁺ and Fe³⁺, respectively. The energy calibration for Fe zero oxidation state was calibrated from Fe foil. The photon energy scan of each sample was set from 7075 eV to 7275 eV with 508 points per scan. The Fe *K*-edge XANES spectra were analyzed by Athena software.

3. Results and Discussion

The FTIR spectra were recorded in the region between 400 cm^{-1} to 4000 cm^{-1} . In this study, however, the spectra were emphasized only at 3500 cm^{-1} to 3000 cm^{-1} for the significant peaks at 3309 , 3232 and 3185 cm^{-1} . The spectra showed the significant peak at 3309 cm^{-1} and its side peaks at 3232 and 3185 cm^{-1} as shown in figure 3. These peaks have been defined as -Ti-OH stretching in the different crystallographic axis [4-5]. The normalized spectra indicated that the side peaks at 3232 and 3185 cm^{-1} were begun to appear in the heating temperatures from 800 °C to 1200 °C then they were disappeared at higher temperatures. It is noteworthy that, the intensity of the peaks was decreased when the

samples were heated at high temperatures. The decreasing of intensity and the disappearing of the side peaks were affected by the concentration and the arrangement of Ti atoms and the hydroxyl group in Al_2O_3 structure [3-5].

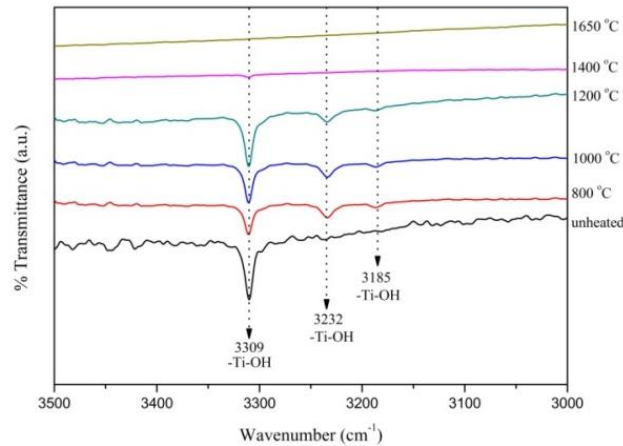


Figure 3. Normalized FTIR spectra of representative unheated and heated from 800 to 1650 °C blue sapphire samples.

The XAS spectra of blue sapphire samples have confirmed the alteration of Fe oxidation state at different heating temperature. The result shows that the Fe zero oxidation state from Fe foil was calibrated at 7112.39 eV. The Fe^{2+} and Fe^{3+} oxidation states were classified using the Fe K -edge XANES spectra of FeO and Fe_2O_3 referring to the binding energy (E_0) value at 7119.20 eV and 7123.12 eV as shown in figure 4. According to the Fe K -edge XANES spectra of the samples, the Fe oxidation state of the unheated blue sapphire was similar to those of heated ones showing Fe^{3+} . The binding energy position (E_0) of the samples derived from the first derivative calculation was detected nearby the same position of Fe_2O_3 chemical standard around 7123 eV as shown in figure 5. To confirm this result, the linear combination fitting from -20 eV to +30 eV around E_0 position was helpful to evaluate the similarity of the Fe oxidation state between Fe^{2+} and Fe^{3+} as shown in table 1. The probability of Fe^{3+} oxidation state was nearby 1 detected from both unheated and heated samples. Therefore, it was clearly mentioned that the Fe oxidation state of blue sapphire samples was not changed after heating whether the different temperature.

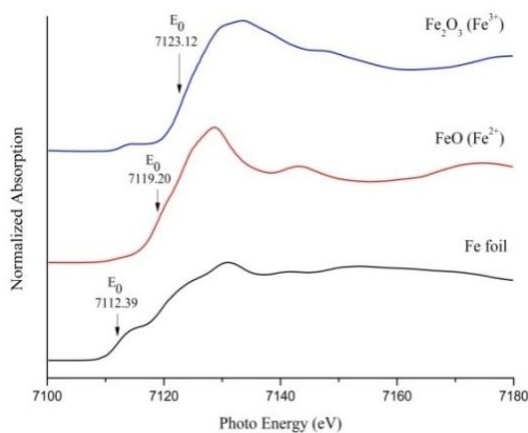


Figure 4. Fe K -edge XANES spectra of Fe chemical standard.

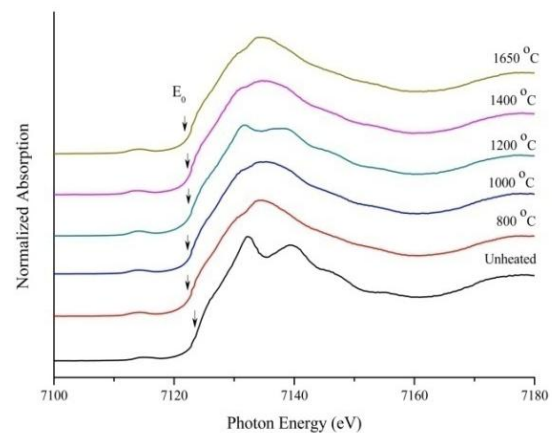


Figure 5. Fe K -edge XANES spectra of blue sapphire samples at different heating temperatures.

Table 1. A linear combination fitting of the blue sapphire samples with Fe chemical standard.

Sample	Standard	Weight	E0 (eV)
Unheated	FeO (Fe ²⁺)	0.000 ± 0.032	7123.88
	Fe ₂ O ₃ (Fe ³⁺)	1.000 ± 0.032	
Heated at 800 °C	FeO (Fe ²⁺)	0.000 ± 0.022	7122.95
	Fe ₂ O ₃ (Fe ³⁺)	1.000 ± 0.022	
Heated at 1000 °C	FeO (Fe ²⁺)	0.000 ± 0.023	7122.95
	Fe ₂ O ₃ (Fe ³⁺)	1.000 ± 0.023	
Heated at 1200 °C	FeO (Fe ²⁺)	0.000 ± 0.020	7123.25
	Fe ₂ O ₃ (Fe ³⁺)	1.000 ± 0.020	
Heated at 1400 °C	FeO (Fe ²⁺)	0.000 ± 0.021	7122.95
	Fe ₂ O ₃ (Fe ³⁺)	1.000 ± 0.021	
Heated at 1650 °C	FeO (Fe ²⁺)	0.000 ± 0.021	7122.94
	Fe ₂ O ₃ (Fe ³⁺)	1.000 ± 0.021	

The XAS spectra revealed that the Fe oxidation state in the host structure of blue sapphire through the heating process is mainly Fe³⁺. Meanwhile, the Ti oxidation state before and after heat treatment is Ti⁴⁺ confirmed by the other researches [6-7]. In contrast, the intensity of the 3309, 3232, and 3185 cm⁻¹ peak is constantly changed all over the heating process. Therefore, it is highly possible that the Fe and Ti oxidation state does not affect to the appearance of those significant peaks in FTIR spectra particularly in blue sapphire samples regarding to the basaltic origins.

4. Conclusion

The Fe and Ti oxidation state of blue sapphire samples from basaltic origins are mainly Fe³⁺ and Ti⁴⁺ through the heat-treated. Therefore, the alteration of the 3309 cm⁻¹ peak in FTIR spectra and its side peaks at 3232 cm⁻¹ and 3185 cm⁻¹ does not depend on the Fe and/or Ti oxidation state.

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