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Abstract: Blue sapphire has long been treated with heat to modify its blue color and attain greater value. However, the process of modifying the blue color in sapphire remains not well understood. The color-changing mechanism has traditionally been explained using the Intervalence Charge Transfer (IVCT) (Fe²⁺-Ti⁴⁺ and/or Fe²⁺-Fe³⁺) theory, wherein the blue color can be diminished by heat treatment in an oxidizing environment which alters Fe^{2+} (FeO) to Fe^{3+} (Fe₂O₃) and decreases the occurrence of the IVCT process. However, recently, the band gap theory has been proposed, suggesting that iron (Fe) in sapphire is always in the Fe³⁺ state, the blue color is caused by Fe³⁺-Ti⁴⁺ pair and the heat treatment does not affect Fe oxidation state. Therefore, in this study, eight magmatic sapphires from four localities were investigated for changes in blue color via color analysis, changes in spectra using XANES, and changes in chemical composition using PIXE both before and after heat treatment. The color analysis reveals a slight reduction in saturation (fading of blue) and a noticeable lightening after heat treatment, which corresponds with the high content of solid inclusions or trapiche samples. XANES data analysis using the LCF technique indicated insignificant changes in Fe oxidation state from 2+ to 3+ after heat treatment across all samples. However, when comparing the XANES data with color parameter L*a*b*, it is noted that the percentage of Fe oxidation state changes does not show a positive relationship with changes in blue based on color parameter b* (blue-yellow); rather, it shows a positive relationship with parameter L* (lightness). Microscopic observations also reveal the dissolution of clouds or minute particles around planes of ilmenite needles. It could be suggested that the changes in Fe oxidation state may not be directly related to changes in blue color but could be linked to the partial dissolution of Fe-bearing inclusions.

Keywords: blue sapphire; heat treatment; XANES; PIXE

1. Introduction

Gemstone treatment has a long history and has been implemented for thousands of years because naturally occurring high-quality gemstones are rare. Therefore, low-quality stones might have been treated to improve their appearance and, consequently, sell at better prices in the market [1]. The heat treatment of corundum (ruby and sapphire) is a popular method that is accepted and adopted by the gem trade. It is believed that the vast majority of the stones being sold in the market have been heat treated [2–4].



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Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Typically, corundum can be categorized into two major genetic types of deposits based on their geological origins, metamorphic deposits and magmatic (basaltic) deposits, distinguished by variations in the concentration of trace elements within the mineral. A significant factor in this classification is the presence of magma. In cases where the composition and conditions favor the recrystallization of corundum into a crystalline structure within basaltic rock, this type of deposit is referred to as "basaltic" or "magmatic", such as those from Australia, Thailand, China, Cambodia, Vietnam, and Nigeria.

Conversely, in metamorphic deposits such as those from Sri Lanka, Madagascar, Myanmar, and Kashmir, this transformation occurs when magma comes into thermal contact with adjacent rocks beneath the Earth's crust, leading to their heating, deformation, and recrystallization into a new form. Corundum found in metamorphic deposits may exhibit high levels of Ti and low levels of Fe, as the recrystallization process is indirectly influenced by magma, differing from the basaltic process [5–8].

Regarding the blue color in sapphire specifically, it has long been assumed that the substitution of Fe and/or Ti for Al in the crystal structure is primarily responsible for the blue color through the process of Intervalence Charge Transfer (IVCT) between $Fe^{2+}-Fe^{3+}$ and/or $Fe^{2+}-Ti^{4+}$ [9–13]. According to the IVCT theory, when the blue sapphire is heat-treated in oxidizing atmospheric conditions, the Fe^{2+} (FeO) is oxidized to Fe^{3+} (Fe_2O_3), resulting in a decreased interaction of IVCT between $Fe^{2+}-Fe^{3+}$ and/or $Fe^{2+}-Ti^{4+}$. As a result, the blue color is diminished.

Recently, the proposed presence of Fe³⁺-Ti⁴⁺ mixed acceptor states in the energy band gap has been proposed as the cause of the blue color in sapphire, suggesting that when blue sapphire is heat-treated in oxidizing conditions, electrons are added to holes on those mixed acceptors, the holes are filled up, and they require fewer electron transitions, resulting in the hindering/fading of the blue color. Therefore, the oxidation of Fe does not change in the process [14–19].

To obtain a better understanding of the process behind blue coloration in sapphires, various sapphire samples from different sources were subjected to heat treatment in oxidizing atmospheric conditions. Proton—Induced X-ray Emission (PIXE) was used to analyze trace elements, and the CIE L*a*b* color space analysis and X-ray Absorption Near-Edge Structure (XANES) methods were utilized to observe the change in color and the absorption spectra features of Fe oxidation both before and after heat treatment.

2. Materials and Methods

2.1. Samples and Heat Treatment

In this study, a total of 8 dark-to-medium blue sapphire samples from various magmaticrelated sources were selected: Inverell, Australia (2); Pailin, Cambodia (2); Shandong, China (2); and Phrae, Thailand (2). Samples from Australia and China were obtained from a gem researcher who directly bought from local miners. Samples from Pailin, Cambodia and Phrae, Thailand were obtained directly from the local miners. Samples from Thailand and Shandong, China are relatively large compared with other sources. Samples from Cambodia contain a trapiche pattern, while samples from Inverell, Australia contain a dark blue hexagonal core. The samples' weight ranged from 3.42 to 4.75 carats with the diameter varying from 7.6 to 11.0 mm. To optimize the spectroscopic analysis, all samples were cut into slabs that were perpendicular to the optic (c) axis and polished. All the basic gemmological properties both before and after heat treatment were collected using gemmological instruments at the Gemmological Institute, China University of Geosciences (Wuhan).

The samples contain typical inclusions from magmatic-related origin, such as feldspars, zircons, rutile, ilmenite, and Fe-rich inclusions [20–28] as shown in Figure 1. The cloud or minute particles of inclusions are scattered across the samples, especially in the area around planes of ilmenite inclusions. A summary of Fe-bearing inclusions in this study compared with other reports is provided in Table 1.



Figure 1. Inclusions in sapphires found in this study: zircon (**top left**), columbite with comet tail (**top right**), planes of ilmenites inclusion needles (**bottom left**), clouds or minutes particles scattered across samples (**bottom right**).

Area	Inclusions	Sources
This study	Columbite, Ilmenite	
Thailand	Columbite, Ilmenite, Pyrrhotite, Chalcopyrite	Saeseaw, 2017 [22] Keller, 1982 [23] Khamloet, 2014 [24] Promwongnan, 2019 [25]
Vietnam	Columbite, Ilmenite, Pyrochlore	Vu, 2020 [21]
Australia	Columbite, Ilmenite	Promwongnan, 2019 [25] Palke, 2019 [8] Saeseaw, 2021 [26] Fang, 2021 [27]
Cambodia	Columbite, Pyrochlore	Saeseaw, 2017 [22]
Nigeria	Pyrochlore	Pardieu, 2014 [28]

The samples were subject to heat treatment to reduce the blue color using an electric furnace for better atmospheric conditions and to stabilize the heating temperature. The heat treatment was performed at a maximum temperature of 1000 °C for 5 h at the plateau temperature with a heating increase of 200 °C per hour. After the 5 h treatment at maximum temperature, the samples were cooled down at a rate of 200 °C per hour to room temperature to avoid tension cracking.

2.2. Color Analysis

Pictures were taken of all samples both before and after heat treatment under controlled conditions in a lightbox with 6500 K color temperature calibrated using a ColorChecker Gray Balance Card. The Adobe Photoshop program (Version 22.5, Adobe, San Jose, CA, USA) was used to determine the color parameters in L*a*b* color space [29] (defined by the International Commission on Illumination [CIE] in 1976) as depicted in Figure 2.



Figure 2. The CIE L*a*b* color system represents the quantitative relationship between colors on three axes: L* indicates lightness and a* and b* are chromaticity coordinates [30].

In the color space diagram, L* (lightness) is depicted vertically, ranging from 0 (representing black) to 100 (representing white). The a* value indicates the red–green component of a color, with positive values denoting red and negative values indicating green. Similarly, the b* axis represents the yellow–blue components, with positive values for yellow and negative values for blue. The central point on the plane signifies neutrality or achromatic coloration. The distance from this central axis reflects the color's saturation or chroma (C*). The angles of the chromaticity axes denote the hue (h°). The CIE (International Commission on Illumination) oversees standards in this color representation system.

2.3. Proton-Induced X-ray Emission (PIXE)

Proton-Induced X-ray Emission (PIXE) was used to analyze trace elements in all samples, including TiO₂, V₂O₃, Cr₂O₃, FeO, and Ga₂O₃. The proton bean was collimated with a set of diaphragms that emitted a beam spot of 4 mm diameter to the sample. The preparation only required cleaning and mounting, and this method can simultaneously analyze multiple elements at the ppm level. PIXE, compared with Electron Probe Micro-Analyzer (EPMA), can provide lower detection limits for a larger element range, and it is non-destructive and can study the surface layers of the sample [31,32]. This analysis was conducted at the Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, using a 2 MeV proton beam generated by a 2.5 MV Van de Graaf accelerator and processed using GUPIX-WIN software (GUPIX-2). The measured accuracy of the experimental setup was approximately 8% [7].

2.4. X-ray Absorption Spectroscopy (XAS)

X-ray absorption spectroscopy (XAS) is a non-destructive analytical method utilized to determine the oxidation states, bond distances, and/or symmetrical arrangements of neighboring atoms [33]. The resulting spectra are categorized into two energy regions: the near-edge absorption (XANES) and the extended absorption fine structure (EXAFS).

In the fields of gemology and mineralogy, XANES spectroscopy has been employed to ascertain the oxidation states of Fe and Ti in heat-treated blue sapphire [14–18,34], the oxidation state of Fe in quartz [35,36], the Fe valence in beryl [37,38], and the Fe valence in heat treated spinel [39]. XANES spectroscopy is conducted using synchrotron radiation generated from a synchrotron light source radiation facility, as illustrated in Figure 3.





The Fe oxidation state of the samples before and after heat treatment was carried out using an X-ray Absorption Near-Edge Structure (XANES) at the XAS Beamline-5.2 station, Synchrotron Light Research Institute (SLRI), Nakhon Ratchasima, Thailand. Three scans were performed per sample and the mean value was calculated from these scans. The spectra were obtained using the high-purity 13-channel array Germanium (220) detector double-crystal monochromator. The beam size is 20 mm (width) by 1 mm (height) for the fluorescence mode and can study the surface layer of the sample. The measurement *K*-edge photon energy was calibrated according to the binding energy (E_0) using the Fe standard, including Fe foil (7112.02 eV), FeO (7121.19 eV), and Fe₂O₃ (7126.26 eV).

The analysis involves employing Linear Combination Fitting (LCF) between 30 eV below and 50 eV above the absorption edge, which can provide information on the symmetrical site of the absorbing atom and its oxidation state [40]. The LCF analysis was constructed using a combination of selected model spectra and reported goodness-of-fit parameters (R-factor and reduced χ^2). The data were compared with coordination environment chemical standards and known oxidation states. The XANES and LCF data were interpreted using the Athena XAS data processing program (Version 0.9.24, Demeter, Washington, DC, USA).

3. Results and Discussion

3.1. Heat Treatment

After heat treatment, all sapphire samples were slightly lightened. The two samples from Australia displayed a considerable reduction in blue color, and one sample (Australia_1) revealed a clearer edge of the dark blue core. The two samples from China exhibited a slight reduction in blue color, and one sample (China_1) showed clearer hexagonal zoning. The two samples from Cambodia revealed a reduction in blue and revealed a brown core or trapiche pattern, both of which were hardly seen before the treatment. The two samples from Thailand displayed a lighter color after treatment, as depicted in Figure 4.

For the internal features, all samples were noticeably lighter or clearer, especially the samples that contained many solid inclusions or a trapiche pattern, which might have been partially dissolved during the process of heat treatment. The clouds or minute particle inclusions around planes of ilmenite inclusions were obviously reduced, as shown in Figure 5.



Figure 4. Color comparison of samples before and after heat treatment at 1000 $^\circ \text{C}.$



Figure 5. Cont.



Figure 5. The clouds or minute particles were obviously reduced before (**left**) and after heat treatment (**right**).

According to the CIE L*a*b* color space data, samples with a higher change in parameter L* (lightness) are Cambodia_2, Cambodia_1, Australia_2, and Thailand_1, with changes of 25, 17, 14, and 10, respectively. According to parameter b* (blue–yellow), all samples were in the region of blue (b* < 0) and became less blue (yellower) after heat treatment with changes of 7 to 1 (avg. 3.4). The color analysis data of all samples both before and after heat treatment are presented in Table 2 and are plotted in the L*a*b* color space in Figure 6.

Table 2. L*a*b* color space data of samples both before and after heat treatment.

Sample	L* (Lightness)	Δ	a* (Green–Red)	Δ	b* (Blue–Yellow)	Δ
Australia_1	42 (48)	6	-3 (-3)	0	-47(-42)	5
Australia_2	18 (32)	14	3 (-3)	-6	-33 (-26)	7
Cambodia_1	14 (31)	17	3 (-4)	-7	-28 (-26)	2
Cambodia_2	8 (33)	25	2 (-4)	-6	-28 (-23)	5
China_1	35 (38)	3	24 (23)	-1	-42(-40)	2
China_2	30 (33)	3	-9 (-16)	-7	-21 (-20)	1
Thailand_1	15 (25)	10	4(-8)	-12	-23 (-21)	2
Thailand_2	43 (47)	4	-8 (-9)	-1	-10 (-7)	3

The post-heat treatment data are shown in parentheses.



Figure 6. L*a*b* color space of samples both before and after heat treatment (arrows indicate position before \rightarrow after heat treatment).

3.2. Proton-Induced X-ray Emission (PIXE)

The PIXE analysis results of eight samples from four magmatic-related origins (Australia, Cambodia, China, and Thailand) showed relatively high FeO (>0.1 wt.%; 0.5782–1.3228 wt.%) and relatively low TiO₂ (<0.1 wt.%; 0.0263–0.0498 wt.%). Insignificant amounts of other oxides such as V₂O₃ (avg. 0.01380 wt.%), Cr₂O₃ (avg. 0.01624 wt.%), and Ga₂O₃ (avg. 0.06038 wt.%) were also observed. The Cr₂O₃/Ga₂O₃ versus FeO/TiO₂ ratio ranged from 0.1372 to 1.0533 (avg. 0.3732). The FeO/TiO₂ concentration ratio of samples ranged from 20.6968 to 45.2473 (avg. 32.71788). These values are typical for sapphire from magmatic origin [7,31,34]. The data are presented in Table 3.

Table 3.	PIXE	trace	anal	lysis	results.
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Samples	TiO ₂ (wt.%)	V ₂ O ₃ (wt.%)	Cr ₂ O ₃ (wt.%)	FeO (wt.%)	Ga2O3 (wt.%)	Cr ₂ O ₃ /Ga ₂ O ₃ Ratio	FeO/TiO ₂ Ratio
Australia_1	0.0322	bdl	0.0132	1.3228	0.0897	0.1472	41.0807
Australia_2	0.0463	bdl	0.0221	1.0560	0.0453	0.4879	22.8078
Cambodia_1	0.0320	bdl	0.0128	0.5782	0.0933	0.1372	21.1938
Cambodia_2	0.0343	bdl	0.0230	0.8563	0.1056	0.2178	24.9650
China_1	0.0266	0.0149	0.0102	1.1023	0.0445	0.2292	41.4398
China_2	0.0263	0.0127	0.0114	1.1654	0.0304	0.3750	44.3118
Thailand_1	0.0498	bdl	0.0178	1.0307	0.0169	1.0533	20.6968
Thailand_2	0.0283	bdl	0.0194	1.2805	0.0574	0.3380	45.2473
Average	0.0345	0.0138	0.0162	1.0490	0.0604	0.3732	32.7179

The Cr_2O_3/Ga_2O_3 versus FeO/TiO₂ ratio of blue sapphires from this study is comparable with the magmatic-related-type blue sapphires studied by Saminpanya (2003) [41] using ED-XRF, PIXE, NAA, and LA-ICP–MS and Sutherland (1998) [20]. However, samples from Shandong, China in this study yielded different result from Abduriyim (2006) [42] using LA-ICP–MS, as depicted in Figure 7.



Figure 7. Cr_2O_3/Ga_2O_3 versus FeO/TiO₂ ratio of blue sapphires in this study (red) compared with other basaltic type blue sapphires from [20,41,42].

3.3. X-ray Absorption Near-Edge Structure (XANES)

The measurement of Fe *K*-edge photon energy is classified by the rising edge position referring to the binding energy (E_0) using an Fe standard chemical compound, including Fe foil (7112.02 eV), FeO (7121.19 eV), and Fe₂O₃ (7126.26 eV), as depicted in Figure 8a.





The Fe *K*-edge XANES spectra of sapphire samples of four different origins suggested that Fe in all samples is a mixture of Fe^{2+} and Fe^{3+} (mostly Fe^{3+}), with an average rising energy position of 7125.8 eV. After heat treatment, the rising edge position slightly shifted toward higher energy, with an average of 7126.1 eV and an average change of 0.3 eV (Figure 8b). The photon energy positions were calculated for the percentage of Fe^{2+} and Fe^{3+} through Equations (1) and (2). When comparing XANES with the PIXE data, it is noted that samples with a higher change in eV are the samples with a lower Fe/Ti ratio, vice versa. The XANES analysis data are presented in Table 4.

% of
$$Fe^{2+} = \left(1 - \frac{\Delta E \text{ of sample}}{\Delta E \text{ of } Fe^{2+} \text{ and } Fe^{3+}}\right) \times 100$$
 (1)

% of Fe³⁺ =
$$\left(\frac{\Delta E \text{ of sample}}{\Delta E \text{ of Fe}^{2+} \text{ and Fe}^{3+}}\right) \times 100$$
 (2)

Table 4. XANES analysis result.

Samples	E0 (eV)	$\Delta \ eV$	% Fe ²⁺	% Fe ³⁺	%Δ	Fe/Ti
Australia_1	7125.9 (7126.1)	0.2	7.47 (3.54)	92.53 (96.46)	3.93	41.0807
Australia_2	7125.8 (7126.2)	0.4	9.43 (1.57)	90.57 (98.43)	7.86	22.8078
Cambodia_1	7125.7 (7126.0)	0.3	11.39 (5.50)	88.61 (94.50)	5.89	21.1938
Cambodia_2	7125.8 (7126.1)	0.3	9.43 (3.54)	90.57 (96.46)	5.89	24.9650
China_1	7126.0 (7126.2)	0.2	5.50 (1.57)	94.50 (98.43)	3.93	41.4398
China_2	7126.0 (7126.2)	0.2	5.50 (1.57)	94.50 (98.43)	3.93	44.3118
Thailand_1	7125.5 (7126.0)	0.5	15.32 (5.50)	84.68 (94.50)	9.82	20.6968
Thailand_2	7126.0 (7126.2)	0.2	5.50 (1.57)	94.50 (98.43)	3.93	45.2473
Average	7125.8 (7126.1)	0.3	8.69 (3.05)	91.45 (97.08)	5.65	32.7179

The after-heat treatment data are shown in parentheses. These values were determined through experimental resolution.

The fractional weight (%) of the Fe²⁺ oxidation state before heat treatment ranged from 5.50 to 15.32 (average 8.69) and, in all samples, lowered to 1.57 to 5.50 (average 3.05) after heat treatment with the change in Fe oxidation (Δ %) from 2+ to 3+ ranging from 3.93 to 9.82 (average 5.65). The change in oxidation state was classified into two groups: the higher change (9.82%–5.89%), and the lower change (3.93%). The higher change group consists of Thailand_1 (9.82%), Australia_2 (7.86%), Cambodia_1, and Cambodia_2 (5.89%). The lower change group (all 3.93%) consists of Australia_1, China_1, China_2, and Thailand_2. The Fe *K*-edge energies (eV) both before and after heat treatment in both groups are plotted using a linear regression compared with Fe chemical standards, as depicted in Figure 9a,b.



Figure 9. Cont.



Figure 9. Linear regression plots of Fe *K*-edge energies (eV) of samples before and after heating at 1000 °C of the higher change group (**a**) and the lower change group (**b**) compared with Fe chemical standards.

From the data, the samples with high amounts of solid inclusions or trapiche patterns are in the higher change in Fe oxidation state group, and the samples with fewer inclusions are in the lower change in oxidation state group. This change could be related to the dissolution of Fe-bearing solid inclusions in samples after the heat treatment, as observed in internal features.

When comparing the CIE L*a*b* color space results with the percent of change (Δ) in the Fe oxidation state, it is noted that both color parameters a* and b* do not show a positive relationship with the change in Fe oxidation state. However, parameter L* (lightness) shows a noticeably positive trend of increase with the changes in Fe oxidation state, wherein the lightness obviously increases as the differences in oxidation state increase (Table 5).

Sample	L* (Lightness)	Δ	a* (Green-Red)	Δ	b* (Blue–Yellow)	Δ	Fe Oxidation %Δ
Australia_1	42 (48)	6	-3 (-3)	0	-47 (-42)	5	3.93
Australia_2	18 (32)	14	3 (-3)	-6	-33 (-26)	7	7.86
Cambodia_1	14 (31)	17	3 (-4)	-7	-28 (-26)	2	5.89
Cambodia_2	8 (33)	25	2 (-4)	-6	-28 (-23)	5	5.89
China_1	35 (38)	3	24 (23)	-1	-42 (-40)	2	3.93
China_2	30 (33)	3	-9 (-16)	-7	-21 (-20)	1	3.93
Thailand_1	15 (25)	10	4 (-8)	-12	-23 (-21)	2	9.82
Thailand_2	43 (47)	4	-8 (-9)	-1	-10 (-7)	3	3.93

Table 5. CIE L*a*b* color space compared with the percentage change in Fe oxidation state.

Considering the parameter b* (blue–yellow) specifically, the changes in blue color do not show a positive relationship with the changes in Fe oxidation state. The highest change in Fe oxidation state (9.82) is among the lowest changes in blue color (Δ b* = 2), while the lowest changes in Fe oxidation state (3.93) are varied from 1 to 5 in Δ b*.

The results from the parameter b* compared with Fe oxidation state changes in this study suggest that the change in blue color might not be directly related to the change of

Fe oxidation but rather related to the reduction in partially dissolved clouds or minute Febearing inclusions during the process. The inclusions are possibly the following: ilmenite (FeTiO₃), in which Ti can be separated at 900–1200 °C; pyrrhotite (Fe₇S₈); or chalcopyrite (CuFeS₂), which breaks down at less than 1000 °C [43] and is commonly found in sapphires from these localities [15,23,25,44–46]. These inclusions might be partially dissolved during the process of heat treatment, providing a clearer appearance of the stones and causing changes in Fe oxidation state after heat treatment.

Fe³⁺ is also responsible for the yellow color in sapphire [9,13,47,48], and the excessive Fe³⁺ that was supplied from the partial melting during the process of heat treatment might be related to the changes in parameters a* and b*, which cause samples to be greener and yellower.

4. Conclusions

After heat treatment, the blue color of all the studied natural sapphire samples of magmatic origin were slightly reduced in saturation (fading of blue) and lightened, especially samples with a high number of solid inclusions or a trapiche appearance. The Fe oxidation state from XANES analysis shows a slight change from Fe^{2+} to Fe^{3+} in all samples (avg. 5.65%). However, when comparing percentages of changes in Fe oxidation state data with the color parameter L*a*b*, it is noted that the percentage of Fe oxidation state change does not show a positive relationship with changes in blue color (parameter b*; blue–yellow). The sample with higher changes in Fe oxidation state rather show a positive relationship with parameter L* (lightness), which could also be observed from the reduction in clouds or minute inclusions in samples; inverse results were observed in samples with lower changes in oxidation states. This could suggest that the changes in Fe oxidation state may not be directly related to a change in blue color but could be linked to the partial dissolution of clouds or minute Fe-bearing inclusions, such as ilmenite (FeTiO₃), pyrrhotite (Fe₇S₈), or chalcopyrite (CuFeS₂), which are commonly found in sapphires from these localities. The further study of these clouds or minute Fe-bearing inclusions might be of genetic and practical significance.

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