https://doi.org/10.48048/tis.2024.8405

Beryllium Heat-Treated Blue Sapphire

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Received: 9 May 2024, Revised: 27 May 2024, Accepted: 3 June 2024, Published: 10 November 2024

Abstract

Since 2000, corundum heat-treated by beryllium (Be) has been successfully experimented to lighten the over-dark blue basaltic-related sapphire. In early 2006, advancements in heat treatment techniques in Chanthaburi revealed the ability to darken metamorphic-related blue sapphires using Be treatment, contrary to the previous lightening effect. The role of Be in corundum coloration obviously remains not well understood. Therefore, an experiment involving heat treatment was conducted to study changes in terms of physical, chemical, gemological, and spectroscopic properties of the blue sapphire after beryllium heat treatment, which has never been done before. Natural sapphires from Sri Lanka, varying in color and transparency, were subjected to Be heat treatment across a range of temperatures and in different types of furnaces (e.g. LPG gas, electric, and fuel oil), under both oxidizing and reducing atmospheres. The samples were studied after each heating step for gemological and spectroscopic properties using UV-Vis-NIR and infrared spectroscopy, as well as chemical composition using LA-ICP-MS. The combination of color appearance, absorption spectra, and chemical data suggests the role of beryllium in sapphire coloration. Be-trapped hole yellow color centers formed during oxidation heating can be deactivated through reduction heating. The resulting color is determined by the Mg to Ti ratio, with no influence from Be. However, most beryllium-treated blue sapphires had an Mg/Ti ratio greater than 1. The presence of higher energy level elements, such as Si, may facilitate the formation of blue color by allowing remaining titanium to pair with iron. Therefore, the blue coloration is mainly caused by strong broad absorption bands of Fe^{2+}/Ti^{4+} IVCT mechanism without Fe^{2+}/Fe^{3+} IVCT. The study highlights the complex interplay of elements within the crystal lattice and contributes to our understanding of color development mechanisms in beryllium-treated sapphires.

Keywords: Beryllium, Heat treatment, Corundum, Sri Lankan, Blue sapphire, Be-trapped hole color center

Introduction

Starting from 2002, gemstones with vibrant colors, such as yellow, orange, pink, and orangy red, have been appearing more frequently on the market. Of particular concern were the orangey pink to pinkish orange (padparadscha) sapphires that exhibited a colored surface-conformal layer that could not be attributed to traditional heat treatment. Multiple gemological laboratories confirmed that these sapphires had been applied to a new heating process, which involved the diffusion of the light element beryllium (Be) from an external source into corundum lattices by mixing ground chrysoberyl or beryllium compound into a crucible [1,4,7-14,17,20-23]. This new technique is more effective than traditional shallow blue diffusion treatment, which utilizes Ti or Cr, as the atomic size of Be is smaller and can penetrate much deeper into corundum lattices. This technique can create brown, yellow or orange color portions and can enhance the colors of corundum, turning light-colored or colorless sapphires into yellows and oranges, pink to pink-orange (padparadscha appearance), or vivid orange, as well as turning purplish rubies into purer red color. Additionally, it can lighten dark blue sapphires into a more pleasant color. This deeper color penetration depth can cover the entire stone, providing a more consistent appearance.

Emmett *et al*. (2003) discussed the effect of beryllium treatment on very dark blue basaltic-type sapphires, where $[Ti^{4+}] >> [Mg^{2+}]$. They suggested that the introduction of Be into very dark blue sapphire should produce the condition $[Ti^{4+}] > [Mg^{2+} + Be^{2+}]$, which would reduce or lighten the blue color saturation to a more commercial blue, since Ti will preferentially charge compensate Be^{2+} before Fe^{2+}. They stated in further research that the Be ppm range required for visible color alteration in blue sapphire is as little as between 0.5 and 1.5 ppma (1 ppma = 0.45 ppmw). In 2003 and 2004, the Gemmological Association of All Japan reported to members of the Laboratory Manual Harmonization Committee that they detected 10 to 35 ppmw (~ 22 to 79 ppma) concentrations of Be in some heated blue sapphires. Nevertheless, at the time, it was not certain if those sapphires were treated using the same process mentioned by Emmett *et al*. (2003). In 2006, Be-diffused blue sapphire posed a new threat to gem industry since its advent on the market in Bangkok. Many gem testing laboratories in Bangkok announced that they had detected significant amount of beryllium in a number of metamorphic-type blue sapphires, especially from Sri Lanka. All of them were Be-treated throughout the entire body of the stone, and with the same concentration levels known previously for other Be-treated fancy sapphires. However, the introduction of beryllium into corundum do not produce a blue color, and since relatively high Mg contents, compared with Ti, were detected in the Be-treated metamorphic-type blue sapphires, the $[Ti^{4+}] > [Mg^{2+}+ Be^{2+}]$ scenario for lightening dark blue sapphire presented by Emmett *et al*. (2003) is, therefore, contradicting. Because, as described by traders in Bangkok and heat treaters in Chanthaburi, the stones are intensified blue color rather than reduced by heat treatment with beryllium. It is evident that the role Be plays in corundum's color display is still not well understood and needs further investigation. Moreover, Emmett *et al*. (2017) showed the effect of silicon on the color range of corundum using secondary ion mass spectrometry (SIMS) on blue sapphire from Yogo Gulch, Montana. The color of natural corundum is determined by impurities of trace elements and their chemical reactions. Silicon, titanium, and magnesium reactions are especially important in producing various colors. The study emphasizes the importance of silicon as a trace element in gem corundum as it plays a significant role in determining the final color. They formulate a set of rules regarding impurity interactions based on defect chemical reactions and energy level positions. According to these rules, if corundum contains Ti, Mg, and Fe, Ti will pair with Mg before Fe. Similarly, if corundum contains Si, Mg, and Fe, Si will pair with Mg before Fe. If corundum contains Si, Ti, Mg, and Fe, Si will pair with both Mg and Fe before Ti. In cases where the concentration of Mg exceeds the combined amounts of Si and Ti, any excess Mg will be compensated for by trapped holes in oxidising conditions, by oxygen vacancies in reducing conditions, or by a combination of both. According to the SIMS analysis, a typical Yogo sapphire sample contains the following trace element concentrations in parts per million (ppma): Mg = 84.3, Si = 24.6, Ti = 79.7, V = 2.7, Cr = 2.2, Fe = 1130, and Ga = 10.4. Si, as the highest-lying donor, pairs with Mg first, leaving 59.7 ppma Mg^{2+} available for interaction with other trace elements. After that, Ti, as a donor, pairs with all remaining available Mg, leaving only 20.0 ppma Ti to combine with Fe and create the blue coloration. Notably, Yogo sapphire cannot be blue without silicon because Mg > Ti, and there would be no unpaired Ti to bond with Fe. This analysis is typical of all Yogo samples, highlighting the crucial role of silicon in determining the color of corundum. The objective of this study is to provide information on chemical characteristics, changes and comparison on the physical, chemical, gemological and spectroscopic properties of sapphires from Sri Lanka before and after beryllium heat treatment. This may help to understand the role of Be in influencing color display of corundum, particularly in heat-treated blue sapphire. The finding may also be useful for identification of beryllium-treated stones. The knowledge gained can be applied to other similar gemstones and are, ultimately, beneficial to gem and jewelry industry.

Materials and methods

A total of 92 natural sapphire samples from Sri Lanka underwent heat treatment with beryllium (Be) and were studied using standard gem testing equipment and spectroscopic instruments. They were categorized into 5 groups based on color and transparency, ranging from light blue, medium blue, light yellow, milky white, and violet-purple **(Figure 1)**.

Figure 1 The 5 groups of sapphires classified by color and appearance. Total weight of each group from left to right is 24.30, 23.79, 27.74, 25.77 and 24.28 ct respectively. (Photo by Sutas Singbamroong).

All groups of sapphire samples were subjected to heat treatment using gas, electric, and oil furnaces at various temperatures in both oxidizing and reducing atmospheres. These methods were based on successful practices by a professional heat treater named Mr. Thawatchai Somjaineuk from Chantaburi. The corundum samples were first heated in a traditional O_2/LPG mixed-gas furnace to about 1550 °C for 1.5 h soaking time in an oxidizing atmosphere. The second step of heating was done with Be in an electric furnace at about 1750 °C for 48 h in an oxidizing atmosphere. After this process, the stones were enhanced in the final step by reheating in a fuel furnace at about 1800 °C for 72 h soaking time in a reducing atmosphere. The samples were studied after each step of heating to determine gemological properties, characteristic spectra and the relationship between spectral pattern and chemical composition in term of electron transition associated with color spectroscopic properties using ultraviolet/visible/near-infrared (UV-Vis-NIR) and Fourier-transform infrared (FTIR) absorption spectroscopy. Chemical compositions of the samples were analyzed using Laser ablation-inductively coupled plasma-mass spectroscopy (LA-ICP-MS).

Results and discussion

After the first step of heating, the yellow and light to medium blue sapphires showed slightly reduction of their yellow and blue color turned to lighter tone or even colorless, whereas the purple to violet sapphires displayed reduction of their blue color to became pink. The milky white sapphire remains white or grey in light tone, while also displaying a slight increase in transparency. In the second step, this treatment aimed to improve clarity and enhance the quality of the samples. After this process, the samples that had initially exhibited very light yellow, blue, pink, or colorless tones during the first heating, transformed into displaying a yellow hue or distinct zones of yellow coloration. Furthermore, their transparency noticeably increased. Additionally, some samples that had a milky appearance prior to the treatment exhibited the development of blue color zoning. These stones were enhanced in the final step, all samples became blue with varying degrees of saturation and tone, ranging from light to strong. The results obtained from all the heating experiments conducted in this study indicate that among the groups of sapphire samples that develop a blue color after heating, the medium blue and violet-purple group exhibits the strongest saturation and tone, showing the most significant improvement in color. Following this group, the light blue group demonstrates a lesser degree of color improvement, followed by the milky white group and the yellow group, respectively (**Figure 2**).

Figure 2 The comparison of representative sapphire samples from light blue (LB), medium blue (MB), light yellow (LY), milky white (ML) and violet-purple (VP) group before and after each step of heating. (Photo by Sutas Singbamroong).

The gemological properties are consistent with the typical characteristics found in sapphires from various locations worldwide, with no significant variation observed before and after heat treatment (**Table 1**). This study also characterizes the presence of orange luminescence in Sri Lankan sapphires, which is attributed to a Mg-related defect or color center. After heating with beryllium, the sapphires displayed stronger orange fluorescence, possibly due to an increased concentration of defect centers induced by beryllium. Sapphires from Sri Lanka typically show internal rutile needle or particle inclusions, resulting in a cloudy appearance. After high-temperature heat treatment with beryllium, these inclusions undergo noticeable changes. Partially healed fissures become rounded with shiny fissures surrounding included crystals (**Figure 3**). Some included crystals exhibit frosty surfaces surrounded by discoid-like fissures (**Figure 4**). Clarity improves significantly as inclusions become less prominent or disappear entirely, including the breakdown of long needles into fine dot-like structures (**Figure 5**).

Table 1 Gemological properties of sapphire samples.

Sample (Number)	Refractive index (RI)		Birefringence	SG (average)	Fluorescence	
	n_e	n_o			LWUV	SWUV
LB sapphire (19)	1.761 - 1.763	1.769 - 1.771	0.008	3.89 - 4.06 (3.99)	weak orange	inert
LY sapphire (18)	1.761 - 1.763	1.769 - 1.771	0.008	3.87 - 4.04 (3.98)	weak orange	inert
MB sapphire (18)	1.760 - 1.764	1.768 - 1.772	0.008 - 0.009	3.90 - 4.06 (3.98)	weak orange	inert
ML sapphire (19)	1.760 - 1.762	1.768 - 1.770	0.008 - 0.009	3.89 - 4.05 (3.96)	weak orange	inert
VP sapphire (18)	1.760 - 1.764	1.768 - 1.772	0.008 - 0.009	3.90 - 4.06 (3.98)	weak orangy red	inert

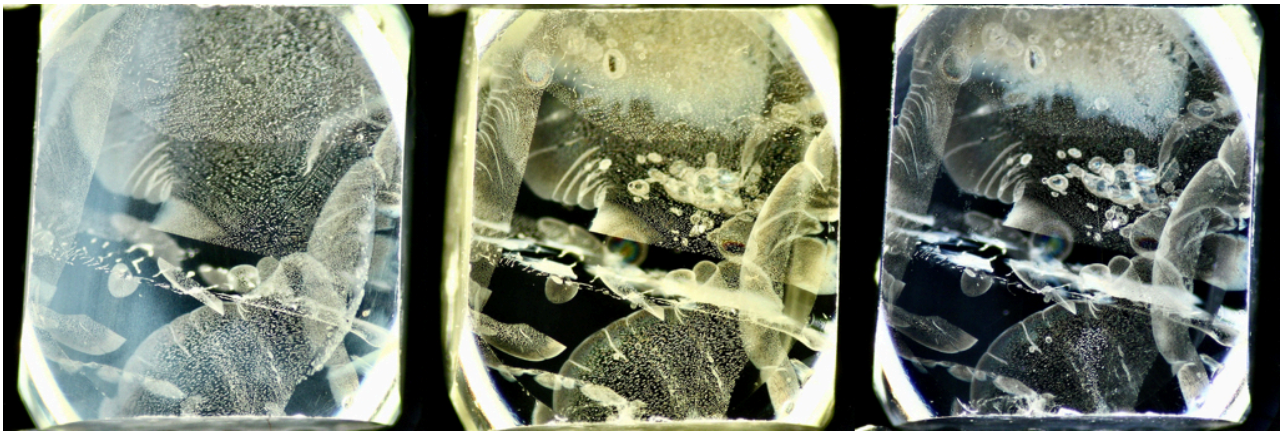

Figure 3 Partially healed fissures in light blue sample (LB08) before heating (left) displayed alteration and developed into rounded shapes (middle) after the second step of heating with beryllium, and fissures with a shiny appearance appeared around many of the included crystals after the last step of heating (right), field of view = 4.7 mm. (Photo by Sutas Singbamroong).

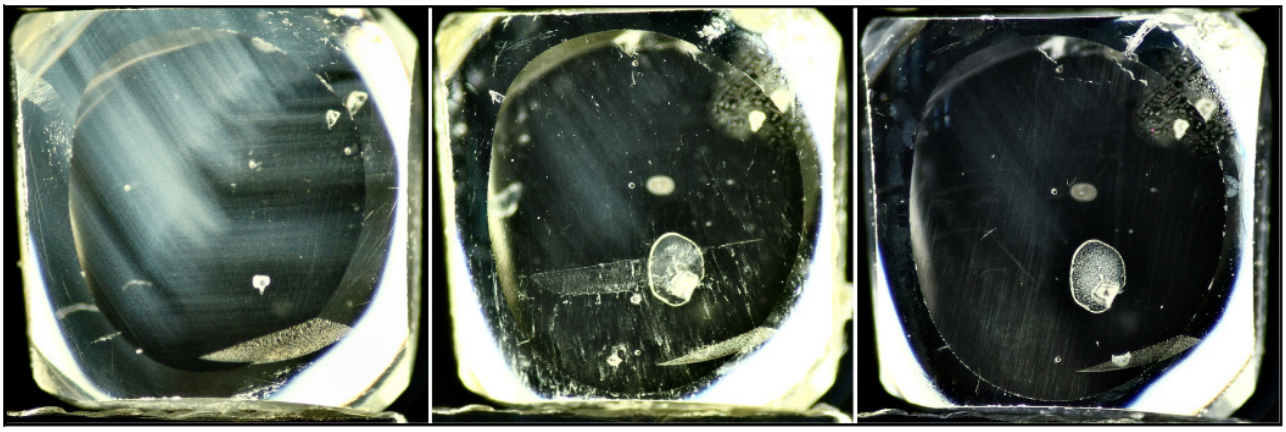

Figure 4 Transparent colorless included crystals in sample ML04 (left) developing a "frosty" appearance with rough surfaces and surrounded by discoid-like fissures (middle and right), field of view = 4.5 mm. (Photo by Sutas Singbamroong).

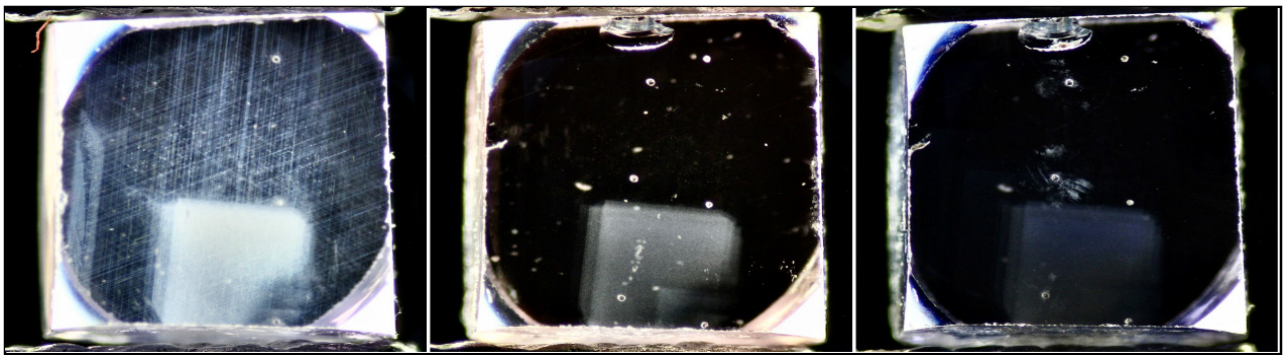

Figure 5 Long rutile (?) needles and whitish cloud inclusion in sample VP05 (left) became less noticeable or disappeared entirely (middle and right), field of view = 3.73 mm. (Photo by Sutas Singbamroong).

UV-Vis-NIR absorption spectra of the heated sample correspond well with the color modification of samples. Absorption spectra of the light and medium blue group samples (see example **Figure 6**) before heating, show broad uplifting absorption band increase continuously from around 500 nm toward the visible border and ultraviolet (UV) region and exhibited Fe^{3+} and Fe^{3+}-Fe^{3+} peaks at 388 and 450 nm, respectively, along with a small broad Fe^{2+}/ Ti^{4+} band with a maximum at approximately 580 nm, responsible for the light to medium blue color. After the first heating step in an oxidizing environment using a gas furnace, the intensity of the small broad Fe^{2+}/ Ti^{4+} band decreases. As a result, the blue color of the samples turns to a lighter tone or even becomes colorless. This change occurs because heating in an oxidizing atmosphere promotes the oxidation state of Fe^{2+} to Fe^{3+}, causing the sapphire to appear lighter blue [16,19,21]. In the second heating step, which involves the use of an electric furnace and beryllium compound in an oxidizing environment, the absorption spectra show a prominent continuously increasing broad uplifting absorption band that extends from around 500 nm towards the visible border and the UV region. This band overlaps with the absorption peaks at 388 and 450 nm. Consequently, the samples that initially exhibited very light blue or colorless tones during the first heating transform into displaying a yellow hue or distinct zones of yellow coloration. This change is attributed to the activation of elevated Be and/or Mg trapped hole color centers or yellow color centers through oxidizing heating [15]. Finally, after the third heating step in a reducing environment using an oil furnace, a strong broad Fe^{2+}/ Ti^{4+} absorption band centered at 580 nm develops. As a result, the samples acquire a blue color with varying degrees of saturation and tone. The previously increased broad absorption band from around 500 nm towards the visible border and the UV region decreases significantly. This change is attributed to the inactivation of Be and/or Mg trapped hole color centers through reducing heating [15].

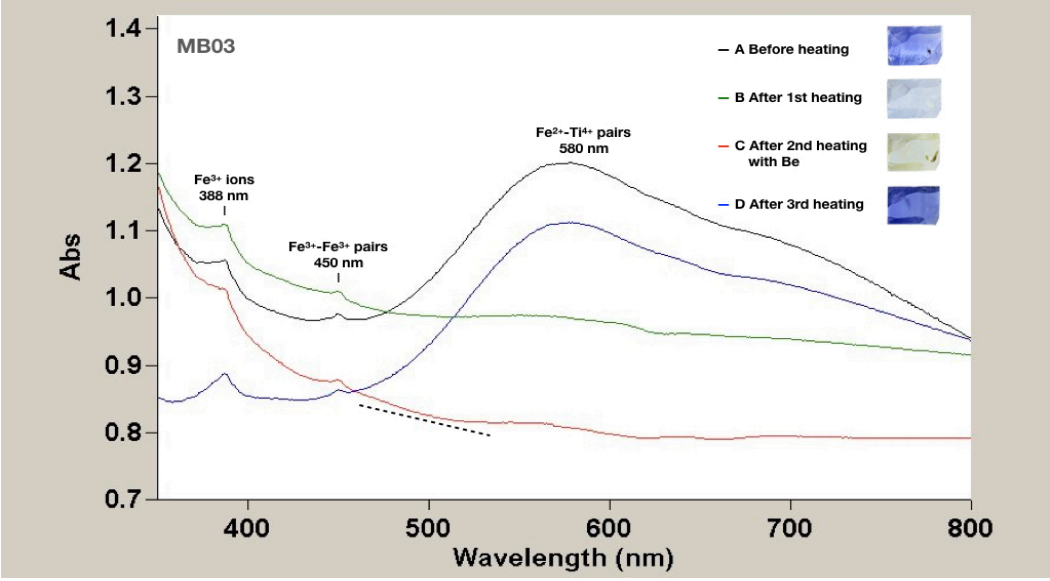

Figure 6 Representative UV-Vis-NIR absorption spectra of medium blue group (MB03) before and after 3 steps of heating. The thickness of sample is 2.59 mm.

The absorption spectra of the light yellow and milky white group samples (see example **Figure 7**) before heating are dominated by a broad uplifting absorption band that extends from around 500 nm towards the visible border and the ultraviolet (UV) region. This band is related to the presence of Mg trapped hole color centers or yellow color centers, which are responsible for yellow coloration. The band also

includes small peaks at 388 and 450 nm. After the first heating step, the broad band is slightly reduced. However, during the second heating step, it regains its strength, indicating the activation of elevated Be and/or Mg trapped hole color centers or yellow color centers through oxidizing heating. In the final heating step, the initial band is completely destroyed due to the inactivation of Be and/or Mg trapped hole color centers through reducing heating. Instead, a new strong broad absorption band emerges, centered at 580 nm, accompanied by distinct absorption peaks at 388 and 450 nm, resulting in the appearance of blue coloration.

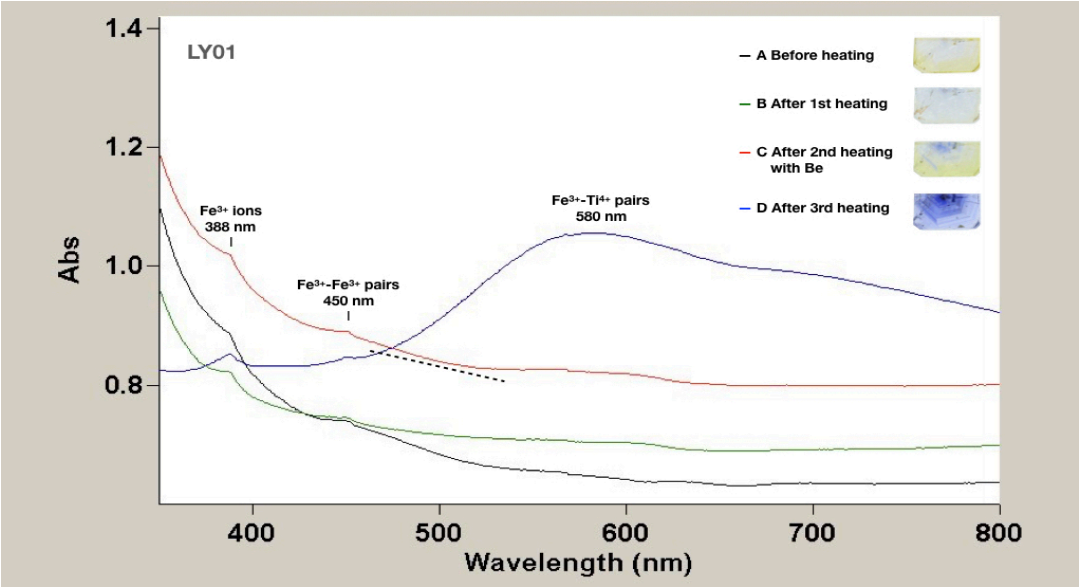

Figure 7 Representative UV-Vis-NIR absorption spectra of light yellow group (LY01) before and after 3 steps of heating. The thickness of sample is 2.98 mm.

The absorption spectra of the violet-purple group reveal absorption bands at approximately 410 and 555 nm, along with overlapping peaks at 377, 388, and 450 nm (**Figure 8**). The intensities of these absorption bands vary among the samples, with purple sapphires showing stronger absorption at 410 nm compared to 555 nm, while violet samples exhibit the opposite pattern. After the first heating step, the absorption band at 410 nm increases, while the absorption band at 555 nm slightly decreases due to the reduced intensity of the Fe^{2+}/ Ti^{4+} band that overlapped before heating, resulting in a pink color. However, the absorption band at 555 nm decreases again after the second heating step, accompanied by a broad uplifting absorption band extending towards the ultraviolet (UV) region. This change is attributed to the activation of elevated Be and/or Mg trapped hole color centers or yellow color centers through oxidizing heating, resulting in some sapphires displaying an orange-pink color. During the final heating step, the initial broad UV absorption band is completely destroyed due to the inactivation of Be and/or Mg trapped hole color centers through reducing heating. Instead, a new strong and broad absorption band emerges, centered at 580 nm, along with an absorption band at 410 nm and distinct peaks at 388 and 450 nm. These changes contribute to the appearance of a strong blue coloration in the sapphires.

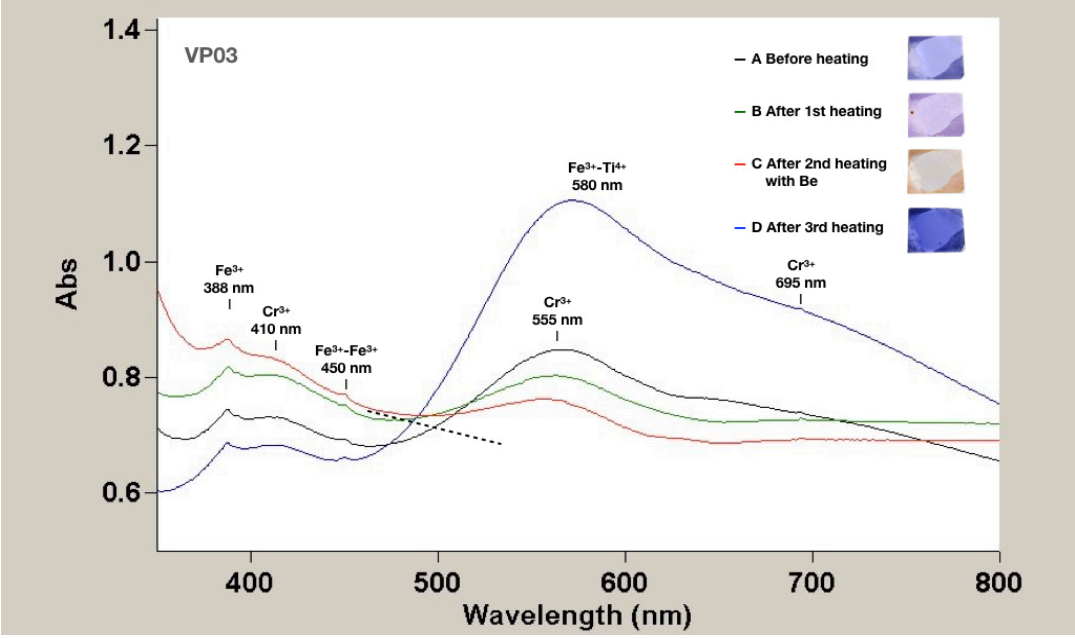

Figure 8 Representative UV-Vis-NIR absorption spectra of purple-violet group (VP03) before and after 3 steps of heating. The thickness of sample is 2.63 mm.

The infrared absorption spectra patterns of milky white, blue, purple/violet, yellow sapphires from Sri Lanka have been recorded to compare the changes both before and after undergoing a 3-step heat treatment. Infrared absorption peaks presented in all samples at 2925 and 2855 cm^{-1} are assigned to $^{-}$CH and at 2345 cm^{-1} is CO_2. The majority of the infrared spectra show sharp absorption bands within the 2500 - 4000 cm^{-1} region. Most samples exhibit a small sharp band of OH-stretching at 3309 cm^{-1}, with some samples displaying a combination of 3185, 3232, and 3391 cm^{-1}, while others lack infrared absorption entirely. All natural unheated yellow sapphires from Sri Lanka, including those in this study, typically display infrared absorption bands of Mg-related OH-stretching at 3160 cm^{-1} with a combination of 3240 and 3355 cm^{-1} related to trapped-hole defects [18] (**Figure 9**).

Upon the first step of heating, the 3309 cm^{-1} band is removed in most samples, except for some blue and violet/purple samples. After the second heating, most samples show 2 broad absorption bands centered at around 2493 and 3055 cm^{-1} which is consistent to those reported as typical characteristics for Be-diffusion treated corundum [2]. After the final step of heating, these 2 absorption bands are mostly eliminated in all samples, with only a few samples still show 2 broad absorption bands centered at 2628 and 3055 cm^{-1}. These infrared absorption band may be used as an indicator for heat-treated blue sapphires with beryllium if they are present.

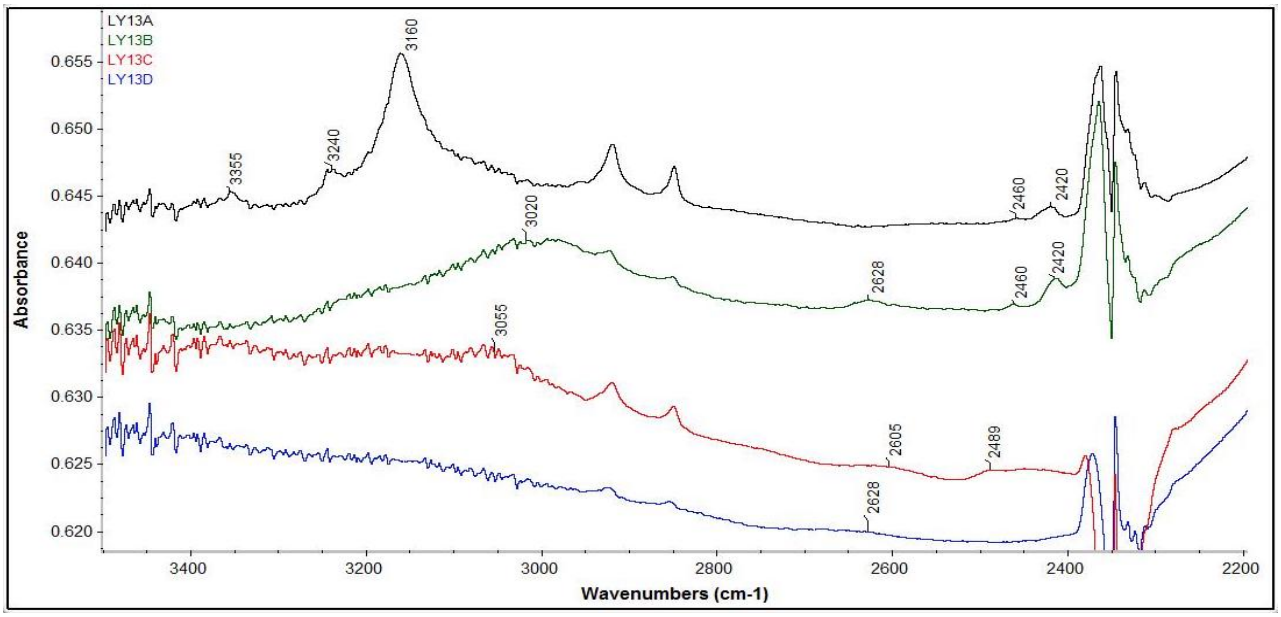

Figure 9 Representative infrared absorption spectra of light yellow group (LY13) before (black line) and after 3 steps of heating, first heating (green line), second heating (red line) and final heating (blue line). The thickness of sample is 1.95 mm.

The chemical analysis using LA-ICP-MS has provided valuable characteristic information about the presence of various minor and trace elements in the Sri Lanka sapphire samples (**Table 2**). Among these elements, iron (Fe) was found to have an average highest content ranging from 97 to 421 ppma, playing a crucial role in the mechanism responsible for the blue color in sapphires. Titanium (Ti) and magnesium (Mg) were detected as significant trace elements, with average contents of 38 to 141 ppma and 39 to 137 ppma, respectively. Gallium (Ga) was also present in measurable amounts, with an average content of 4 to 40 ppma. Trace amounts of vanadium (V) and chromium (Cr) were detected, with average contents below the detection limit to 11 ppma and below the detection limit to 26 ppma, respectively. However, their quantities were considered insignificant, except for the violet-purple sample group, which exhibited an average Cr content of 17 to 109 ppma. These minor and trace elements are consistent with the reported values for natural sapphires from Sri Lanka in general, with average Fe ranging from 75 to 728, Ti from 14 to 216, Ga from 5 to 24, V from 6 to 20, and Cr below the detection limit to 3 ppma [6]. It is noteworthy that the concentrations of trace elements in all samples were detected similarly before and after heat treatment, except for the presence of beryllium (Be) which ranged from an average content of 11 to 26 ppma after the heat treatment. These values are comparable to those reported for beryllium-treated blue sapphires, ranging from 11 to 45 ppma [3].

Table 2 LA-ICP-MS analysis results in ppma concentration showing minimum and maximum values along with the average value in parenthesis of 8 sapphire samples from different groups before and after Be heating.

Sample	Heating	Be	Mg	Ti	V	Cr	Fe	Ga
LB04	before	bdl	71 - 101 (91)	68 - 104 (91)	3 - 4 (4)	7 - 8 (8)	135 - 142 (138)	15 - 17 (16)
	After	16 - 19 (17)	89 - 145 (121)	69 - 110 (85)	3 - 4 (4)	6 - 8 (7)	148 - 167 (155)	17 - 19 (18)
LB05	before	bdl	63 - 104 (81)	52 - 115 (76)	1 - 2 (2)	2 - 3 (3)	147 - 174 (160)	21 - 23 (22)
	After	12 - 14 (13)	55 - 77 (62)	40 - 62 (47)	1 - 2 (1)	2 - 4 (3)	157 - 189 (172)	24 - 28 (26)
LY05	before	bdl	35 - 80 (62)	17 - 68 (48)	1 - 9 (6)	bdl	99 - 202 (154)	11 - 14 (13)
	After	16 - 24 (19)	22 - 105 (61)	9 - 81 (42)	3 - 8 (5)	bdl	91 - 226 (158)	10 - 14 (12)
LY06	before	bdl	27 - 159 (94)	1 - 8 (5)	1 - 5 (3)	bdl	43 - 241 (153)	2 - 5 (4)
	After	15 - 26 (19)	9 - 54 (29)	bdl - 3 (1)	1 - 2 (1)	bdl	35 - 88 (56)	2 - 3 (2)
MB04	before	bdl	67 - 85 (74)	63 - 78 (69)	3 - 4 (4)	bdl	409 - 444 (421)	27 - 30 (28)
	After	18 - 34 (24)	78 - 106 (90)	72 - 143 (96)	3 - 4 (4)	bdl	446 - 478 (462)	26 - 28 (27)
MB05	before	bdl	130 - 151 (137)	127 - 143 (134)	2 - 3 (3)	bdl	221 - 250 (238)	17 - 18 (18)
	After	12 - 13 (13)	117 - 124 (121)	113 - 119 (114)	2 - 3 (2)	bdl	246 - 268 (257)	17 - 18 (17)
ML05	before	bdl	40 - 52 (45)	36 - 127 (71)	1 - 2 (2)	bdl	95 - 96 (96)	15 - 16 (16)
	After	10 - 12 (11)	31 - 41 (36)	28 - 33 (30)	1 - 2 (2)	bdl	115 - 118 (116)	14 - 15 (15)
ML06	before	bdl	81 - 174 (124)	56 - 219 (121)	3 - 5 (4)	1 - 2 (1)	364 - 480 (404)	14 - 15 (14)
	After	14 - 34 (26)	121 - 173 (140)	107 - 152 (124)	4 - 5 (5)	1 - 2 (1)	440 - 484 (460)	14 - 15 (14)
VP07	before	bdl	53 - 83 (64)	80 - 119 (93)	15 - 16 (15)	88 - 125 (109)	385 - 395 (390)	11 - 12 (12)
	After	18 - 27 (23)	52 - 95 (70)	70 - 97 (88)	15 - 16 (15)	94 - 131 (107)	492 - 540 (516)	11 - 12 (12)
VP08	before	bdl	100 - 131 (111)	122 - 153 (141)	22 - 24 (23)	23 - 24 (24)	162 - 174 (168)	39 - 40 (40)
	After	15 - 21 (19)	134 - 146 (140)	157 - 167 (164)	23 - 29 (25)	20 - 33 (25)	230 - 248 (237)	38 - 43 (40)

*bdl = below detection limit.

The combination of color appearance and absorption spectra recorded after reduction and oxidation heating, along with the chemical data, suggests the role of beryllium (Be) in causing color in sapphires. The results of these heating experiments clearly demonstrate that the active Be-trapped hole yellow color centers, which are formed during oxidation heating and Be diffusion, can be rendered inactive through reduction heating. Consequently, the resulting color after reduction heating is solely determined by the ratio of magnesium (Mg) to titanium (Ti), with no influence from Be. Specifically, the stone will exhibit a blue color when the Mg/Ti ratio is less than 1, or a colorless appearance when the Mg/Ti ratio is greater than 1 and when subjected to re-heating in oxidation conditions, the role of Be becomes active once again [15]. However, most of beryllium heat-treated blue sapphires analyzed in this study exhibited a Mg/Ti ratio greater than 1. According to the impurity interaction rules in corundum [5], titanium tends to form pairs with magnesium before iron. In this study, the atomic content of the magnesium is higher than that of titanium. If all the titanium were to pair with magnesium, the stone would theoretically display no blue color, and there would be no absorption observed at 580 nm. Therefore, it is likely that elements with higher energy levels than titanium, such as silicon (Si), exist in the crystal lattice and preferentially pair with magnesium. This allows the remaining titanium to form pairs with iron, resulting in the generation of a blue color. Although silicon is commonly found in corundum [5], its detection was beyond the scope of this study due to the limited sensitivity of LA-ICP-MS caused by mass interference.

Conclusions

The results obtained from all the heating experiments conducted in this study indicate that the medium blue and violet-purple groups exhibit the strongest saturation and tone among the sapphire samples that developed a blue color after heating, showing the most significant improvement in color. The combination of color appearance, absorption spectra, and chemical data suggests the role of beryllium in the coloration of sapphires. Heating experiments demonstrated that Be-trapped hole yellow color centers formed during oxidation heating and Be diffusion can be deactivated through reduction heating. The resulting color after reduction heating is solely determined by the Mg to Ti ratio, with no influence from Be. However, most beryllium-treated blue sapphires analyzed in this study had a Mg/Ti ratio greater than 1. The presence of higher energy level elements such as silicon (Si), which preferentially pair with magnesium, may play a role in allowing remaining titanium to form pairs with iron, resulting in the generation of a blue color. The detection of silicon was not possible in this study due to limitations in sensitivity. These findings contribute to our understanding of the mechanisms behind color development in sapphires treated with beryllium and highlight the complex interplay of elements within the crystal lattice.

Acknowledgements

Deep gratitude is extended to Mr. Thawatchai Somjaineuk for his generous conduct of the heat treatment in this study experiment. Appreciation is also extended to Mr. Han Meng Kwang, Associate Professor Dr. Theerapongs Thanasuthipitak and Associate Professor Dr. Panjawan Thanasuthipitak for their invaluable assistance, hospitality, encouragement, and support in various aspects. Grateful acknowledgment is owed to Mr. Sombat lekkarn for the donation of samples. Additionally, thanks are extended to all personnel of the Gem and Jewelry Institute of Thailand (Public Organization) for their assistance and hospitality.

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