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Heat treatment of basalt-related sapphire from Binh Thuan deposit, Southern Vietnam

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Abstract

Characteristics of basalt-related sapphires from Binh Thuan in Southern Vietnam were investigated before and after heat treatment. Heating at 700°C to 1000°C, caused blue hue to fade noticeably, while blue color was intensified when heated at 1650°C. Subsequently, these sapphire samples were subjected to beryllium (Be)-assisted heating by a local professional gem treater, which yielded yellow to yellowish-blue hues. Absorption spectra of blue sapphires indicated absorptions at 378 nm, 387 nm, 450 nm, 580 nm, and 880 nm. However, yellow sapphires, after Be-assisted heating, did not exhibit absorptions at 580 nm and 880 nm. In the FTIR spectra, bands associated with OH stretching disappeared after being heated to 1650°C as well as Be-assisted heating. Based on LA-ICP-MS analyses, an increase in Be concentration (5 ppma to 146 ppma) was detected following Be-assisted heating, which conclusively induces yellow coloration in sapphire.

1. Introduction

Sapphire is a variety of gem-quality corundum minerals that occur in wide color ranges, particularly red, blue, yellow, and green. Moreover, it should be notified that only red variety is called ruby. Combination of these main colors has been generally found in the natural stones which directly affect their commercial values. Both ruby and sapphire are very popular gemstones used in jewelry, primarily due to their beauty, durability, and rarity. Sapphires are found in several regions around the world, including Thailand, Cambodia, Myanmar, Vietnam, Laos, Sri Lanka, Australia, China, Africa, America, and several other regions. Aluminum oxide (Al_2O_3) is the main chemical component, whose pure phase is colorless. However, various colors observed in sapphires are caused by trace elements that substitute for Al^{3+} in the crystal lattice. For instance, Fe^{3+} may result in yellow sapphire whereas Fe^{2+}–Ti^{4+} intervalence charge transfer (IVCT) is responsible for blue sapphire. Additionally, V^{3+} may contribute to purplish or greenish hues [1–4]. High-quality natural sapphires with vivid colors have become increasingly very rare. As a result, lower-quality sapphires are often treated to improve their appearance and colors, consequently increasing their market values.

Gemstone enhancement can be achieved through a variety of methods, particularly heat treatment. Heat treatment has been the most widely used and accepted technique in the world gem market. Key factors influencing the outcome of heat treatment include temperature, duration, and atmospheric environment. Moreover, characteristics of sapphire, such as initial color, trace chemical composition, and inclusion, also play critical role of the final appearance after heat treatment [2,5,6]. Regarding sapphires from basaltic deposits, they naturally contain high amounts of Fe, giving them an inky dark blue appearance. To reduce intensity of blue color, oxidation heating is theoretically required. At lower temperatures (below 1200°C), iron is oxidized, which disrupts the Fe^{2+}–Ti^{4+} intervalence charge transfer, resulting in the lightening of blue color. However, when heated at 1200°C to 1350°C and above, rutile (TiO_2) micro inclusion in basaltic sapphire [7,8] potentially dissolves, introducing additional Ti^{4+} into the system. This promotes more formation of Fe^{2+}–Ti^{4+} pairs, intensifying blue coloration [6]. Consequently, basaltic sapphires are difficult to turn vivid yellow because their Fe content is much higher than Mg. This reduces the opportunity to isolate Mg^{2+} or Fe^{3+} for yellow colorations [9–12]. Therefore, beryllium-assisted heating is required to produce yellow coloration, as the small Be^{2+} ions can diffuse deeply into the corundum lattice and then create yellow color center (naturally caused by Mg^{2+}) in the sapphire [2].

Sapphires have been discovered in both Northern and Southern regions of Vietnam [13]. In Southern Vietnam, sapphire deposits have been known since the 1980s. They are geologically related to Cenozoic basalts which aged mainly from 17.6 Ma to 0.8 Ma (Neogene-Quaternary), following the end of the East Sea opening in the Middle Miocene [14–16]. Two main eruptive episodes have been recognized; the earlier episode produced mainly quartz, olivine tholeiite, and rare alkali basalt while the later episode yielded olivine tholeiite, alkali

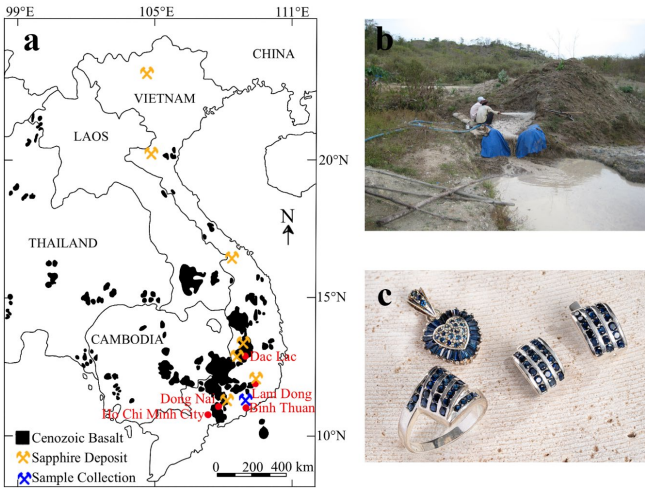

Figure 1. (a) Distribution of Cenozoic basalts in Southeast Asia and associated sapphire deposits in Vietnam modified after Barr and MacDonald [14], Hoang and Flower [15], Garnier, Ohnenstetter, Giuliani, Fallick, Trong, Quang, Van and Schwarz [16], Van Long, Quang Vinh, Garnier, Giuliani, Ohnenstetter, Lhomme, Schwarz, Fallick, Dubessy and Trong Trinh [19], Tri and Khuc [20], Huong, Häger, Hofmeister, Hauzenberger, Schwarz, Van Long, Wehmeister, Khoi and Nhung [21], Hoang, Choi, Yu, Pham, Nguyen and Ryu [22]. (b) Gem mining in Binh Thuan, agricultural equipment is usually used for shallow gem-bearing sediment within basaltic terrane. Photo by Doan Thi Anh Vu, and (c) Dark blue sapphires from Southern Vietnam placed in a pendant (total 1.25 ct), earrings (total 0.9 ct), and ring (total 1.3 ct). Photo by Doan Thi Anh Vu.

basalt, basanite, and rare nephelinite [17]. These basalts usually geographically form low plateaus [14,16]. Sapphire deposits are commonly hosted in alkali basalt, formed at depths of about 60 km to 120 km, and often associated with ultramafic xenoliths and xenocrysts [13]. Alluvial sapphire deposits related to basaltic exposures have been reported in four provinces of Southern Vietnam, i.e., Binh Thuan, Lam Dong, Dong Nai, and Dac Lac (Figure 1(a)).

Mining in Binh Thuan began in 1985 and has generally been small-scale mines, using agricultural equipment (Figure 1(b)). The sapphires found in this area exhibit a wide range of colors, dark blue (Figure 1(c)) in particular, bluish-green, greenish-blue, and yellowish-green [18]. However, many of these sapphires are of relatively low color quality, which significantly limits their commercial value. This study aims to enhance color quality of sapphires from the Binh Thuan deposit in Southern Vietnam, intending to increase their market values. The research focused on heat treatment at various temperatures under ambient atmospheric (oxidizing) condition and subsequently with beryllium-assisted heating.

2. Materials and methods

2.1 Sample collection

A total of 48 sapphire samples were collected by Dr. Doan Thi Anh Vu during fieldworks conducted in 2001, 2012, and 2017 in Binh Thuan province, Southern Vietnam. Each sample was polished using a faceting machine, with the cutting orientation aligned either perpendicular or parallel to the c-axis, depending on the shape and thickness of the sample, which ranged from approximately 1 mm to 4 mm. Based on their color and hue, the samples were grouped into dark blue (12 samples, weighing 0.39 ct. to 3.14 ct.), blue (12 samples, weighing 0.36 ct. to 1.83 ct.), greenish blue (12 samples, weighing 0.39 ct. to 3.14 ct.), and bluish green (12 samples, weighing 0.80 ct. to 3.08 ct.). All samples were subjected to standard gemological testing, e.g., measurements of refractive indices (RI), birefringence, and specific gravity (SG). In addition, their luminescence phenomena were also observed under both long-wave (365 nm) and short-wave (254 nm) ultraviolet (UV) lamps.

2.2 Heating experiments

Heating experiments were conducted using a Linh electric furnace (model HT1800 PlusVAC Bottom Loader) at the Department of Geology, Faculty of Science, Chulalongkorn University. All sapphire samples were initially heated in oxidizing atmosphere (ambient air) at 700°C and 1000°C for 10 h. Subsequently, 24 selected samples comprising 6 samples from each group were further heated at 1650°C for 5 h. A controlled heating rate of 5°C·min^{-1} was applied to reach the target temperatures. After each heating cycle, samples were gradually cooled to room temperature inside the furnace. Following these treatments, beryllium-assisted heating was provided by Mr. Pipop Thungjaipug, a local professional gem expert, who declared the heating at 1715°C for 168 h.

2.3 Spectroscopic analyses

A PerkinElmer Lambda 1050 spectrophotometer was used to collect ultraviolet-visible-near infrared (UV-Vis-NIR) spectra at a scan speed of 405.07 nm·min^{-1} and 3 nm spectral resolution. Fourier-transform infrared (FTIR) spectra were obtained using a Thermo Scientific Nicolet iN10 FTIR spectrometer at 4 cm^{-1} resolution with 128 scans. These measurements were performed at the Gem and Jewelry Institute of Thailand (Public Organization). All samples were analyzed by both UV-Vis-NIR spectrometer and FTIR spectrometer analyses before and after each step of heating experiments.

2.4 Trace chemical analyses

Laser Ablation-Inductively Coupled Plasma-Mass Spectrometer (LA-ICP-MS) was employed to measure natural trace compositions and additive beryllium contents in the sapphire samples before and after beryllium-assisted heating. Analyses were performed using a Thermo Scientific iCAP RQ series ICP-MS coupled with an Elemental Scientific Lasers NWR-213 Nd:YAG laser ablation system, at the Gem and Jewelry Institute of Thailand (Public Organization). The laser operated at 10 Hz with a 55 µm spot size and an energy density of ~10 J·cm^{-2}. Helium served as carrier gas at a flow rate of 0.75 L·min^{-1}, with argon plasma gas at 14 L·min^{-1}, and a plasma power of 1550 W. Laser energy was set to 85%, and each analysis had a dwell time of 60 s, with three spots analyzed per sample to ensure accuracy and consistency. Two NIST silicate glass standards (SRM 610 and 612) were used as external standards, while 27Al from pure corundum was used as internal standard.

3. Results

3.1 Gemological properties

All 24 sapphire samples are summarized in Table 1. Their refractive indices (R.I.) range from 1.769 to 1.772 for the ordinary ray (nω) and 1.760 to 1.764 for the extraordinary ray (nε), yielding a birefringence between 0.008 and 0.010. Specific gravity (S.G.) values ranged from 3.93 to 4.02. All samples were inert under both long-wave (365 nm) and short-wave (254 nm) ultraviolet lights. Pleochroism was observed in all color varieties, with dark blue and blue sapphires displaying strong pleochroism from blue to greenish blue, while greenish blue and bluish green sapphires exhibited strong pleochroism ranging from green-blue to yellow-green.

3.2 Color appearance

For dark blue sapphires, color changes observed after heat treatment between 700°C to 1650 °C followed a similar trend to that of the blue sapphire group (see Table 2). After heating at 700°C and 1000°C, the blue hue gradually diminished, subsequently at 1650°C, it intensified again. Following beryllium-assisted heating, a yellow hue developed around the rims of sapphires, while the centers remained blue. Notably, sample DB003 exhibited distinct color zoning between blue and yellow regions. Colorimetric changes were also analyzed using the CIE a* and b* coordinates (as shown in Figure 2), in which positive and negative a* values represent red and green hues whereas positive and negative b* values correspond to yellow and blue hues, respectively. Regarding a*, negative values were significantly observed throughout the heating experiments (Figure 2(a) and Figure 2(c)), these indicated the influence of green hue. Although positive a* values were recorded in some dark blue and blue samples after 1650°C heating, they might be an effect of dark color appearance (Figure 2(a)). On the other hand, b* values should play more important role for these studied sapphires. Although slightly positive b* values of a few dark blue and blue sapphires were recorded after 700°C, 1000°C, and Be-assisted heating which indicates an enhancement of the yellow hue and lightening the blue color. Shifts to negative b* values after 1650°C heating of both sample groups clearly reflects (Table 2 and Figure 2(b) and Figure 2(d)).

For greenish blue sapphires, the color response to heat treatment from 700°C to 1650°C exhibited a similar pattern to that observed in the dark blue and blue sapphire groups. The blue hue faded at lower temperatures and intensified at 1650°C. Following beryllium diffusion, three samples developed a yellow color (samples GB001, GB003, and GB005) whereas samples GB002 and GB004 exhibited distinct yellow and blue color zones (Table 3). As the negative a* values were observed nondirectionally (Figure 2(e)) throughout the experiment, the b* values clearly exhibited a positive trend increasing after 700°C, 1000°C and Be-assisted heating which indicates a fluctuating yellow hue, with the highest intensity after Be diffusion (Table 3 and Figure 2(f)).

Regarding bluish green sapphires, color modification behaved consistently with those observed in dark blue, blue, and greenish blue sapphires. However, after undergoing beryllium-assisted heating, four samples (BG001, BG002, BG005, and BG006) developed a distinct yellow coloration whereas samples BG003 and BG004 developed blue and yellow zones (Table 3). Similar to the other groups, the a* values yielded negative values throughout the experiment, signifying the green hue prominent (Figure 2(g)). The b* values increased from 700°C to 1000°C, indicating a stronger yellow hue. After Be-assisted heating, the b* values increased significantly (Figure 2(h)), showing clearly enhancement of the yellow hue.

3.3 UV-Vis-NIR spectroscopy

Ordinary ray (o ray) of UV-Vis-NIR spectra of the unheated sapphire samples exhibited characteristic absorption bands. These included Fe^{3+}–Fe^{3+} pair absorption peaks at 378 nm and 450 nm, Fe^{3+} absorption band around 387 nm, in which the latter band should respond to yellow coloration [23,24]. Moreover, Fe^{2+}–Ti^{4+} intervalence charge transfer (IVCT) absorption band at around 570 nm to 580 nm, is responsible for the blue coloration [25]. Additionally, a dominant broad band around 880 nm, attributed to Fe^{2+}–Fe^{3+} IVCT, is commonly associated with basaltic sapphire [6]. These specific absorptions are present in Figure 3.

After heating at 700°C and 1000°C, absorption band at 570 nm to 580 nm decreased, corresponding to a reduction in Fe^{2+}–Ti^{4+} IVCT and resulted in lightening of the blue color. Decreasing around 880 nm absorption varied depending on initial color of sapphires. Darker blue sapphires showed higher absorption after heating, while lighter blue sapphires exhibited decreasing absorption after such heating. Absorption peak at 450 nm, associated with Fe^{3+}–Fe^{3+} pair, exhibited negligible change, except for sample GB001 which showed a higher peak. Subsequently, after heating at 1650°C, absorptions at 450 nm, 580 nm, and 880 nm were mostly intensified. Regarding beryllium-assisted heating, some sapphire samples, greenish blue and bluish green in particular, turned completely yellow. On the other hand, dark blue and blue sapphires were partially modified and yielded yellow-blue zones in the same stone. Most of the treated yellow sapphires lacked absorptions at 580 nm to 585 nm and 880 nm but displayed sharp absorption peaks at 378 nm, 387 nm, and 450 nm (samples DB003 and GB001, Figure 3(a) and Figure 3(c)). The 450 nm absorption within the violet region of the visible spectrum should cause the complementary yellow color of sapphires. However, samples showing a mixture of yellow and blue zones still exhibited absorptions at 378 nm, 388 nm, 450 nm, 580 nm to 585 nm, and 880 nm (samples B005 and BG003, Figure 3(b) and Figure 3(d)).

3.4 Fourier-transform infrared (FTIR) spectroscopy

Representative FTIR spectra of all sapphire samples (Figure 4) prior to heat treatment exhibited characteristic absorption bands of the OH stretching region, with three prominent peaks at 3309 cm^{-1}, 3232 cm^{-1} to 3257 cm^{-1}, and 3183 cm^{-1} to 3193 cm^{-1}. The 3309 cm^{-1} peak is attributed to the stretching vibration of the OH bond. In dark blue sapphires, a distinct peak at approximately 3185 cm^{-1} was observed after heating at 700°C. Additionally, absorption features associated with C–H stretching were also detected at 2956 cm^{-1} to 2959 cm^{-1}, 2916 cm^{-1} to 2925 cm^{-1}, and 2848 cm^{-1} to 2854 cm^{-1}. After heating at 700°C and 1000°C, the intensity of the 3309 cm^{-1} peak decreased, whereas the 3232 cm^{-1} peak became more prominent. After heating at 1650°C as well as beryllium-assisted heating, OH–related peaks disappeared entirely, although C–H stretching pattern remained detectable (Figure 4).

Table 1. Summary of gemological properties of sapphire from Binh Thuan, Southern Vietnam.

Sample group	Refractive indices (R.I.)		Birefringence	Specific gravity	Fluorescence		Pleochroism
	n_ω	n_ε		(S.G.)	SWUV	LWUV	
Dark Blue	1.769 to 1.771	1.760 to 1.764	0.008 to 0.009	3.96 to 4.01	Inert	Inert	Blue/Greenish Blue
Blue	1.769 to 1.772	1.760 to 1.764	0.008 to 0.009	3.93 to 4.02	Inert	Inert	Blue/Greenish Blue
Greenish Blue	1.769 to 1.772	1.760 to 1.762	0.009 to 0.010	3.97 to 4.02	Inert	Inert	Green - Blue/Yellow Green
Bluish Green	1.769 to 1.770	1.760 to 1.762	0.009 to 0.010	3.94 to 4.01	Inert	Inert	Green - Blue/Yellow Green

Table 2. Color changes of dark blue and blue sapphires before and after heat treatments. After heating at 700°C to 1000°C, and following Be-assisted heating. Photos by Yuparat Kwangsawat.

Sample number	Unheated	Heat treatment				Sample number	Unheated	Heat treatment			
		700°C	1000°C	1650°C	Be-assisted heating			700°C	1000°C	1650°C	Be-assisted heating
	Dark blue sapphire						Blue sapphire				
DB001						B001					
DB002						B002					
DB003						B003					
DB004						B004					
DB005						B005					
DB006						B006					

3 mm

Table 3. Color changes of greenish blue and bluish green sapphires before and after heat treatments. After heating at 700-1000 °C, and Be-assisted heating. Photos by Yuparat Kwangsawat.

Sample number	Unheated	Heat treatment				Sample number	Unheated	Heat treatment			
		700°C	1000°C	1650°C	Be-assisted heating			700°C	1000°C	1650°C	Be-assisted heating
	Greenish blue sapphire						Bluish green sapphire				
GB001						BG001					
GB002						BG002					
GB003						BG003					
GB004						BG004					
GB005						BG005					
GB006						BG006					

3 mm

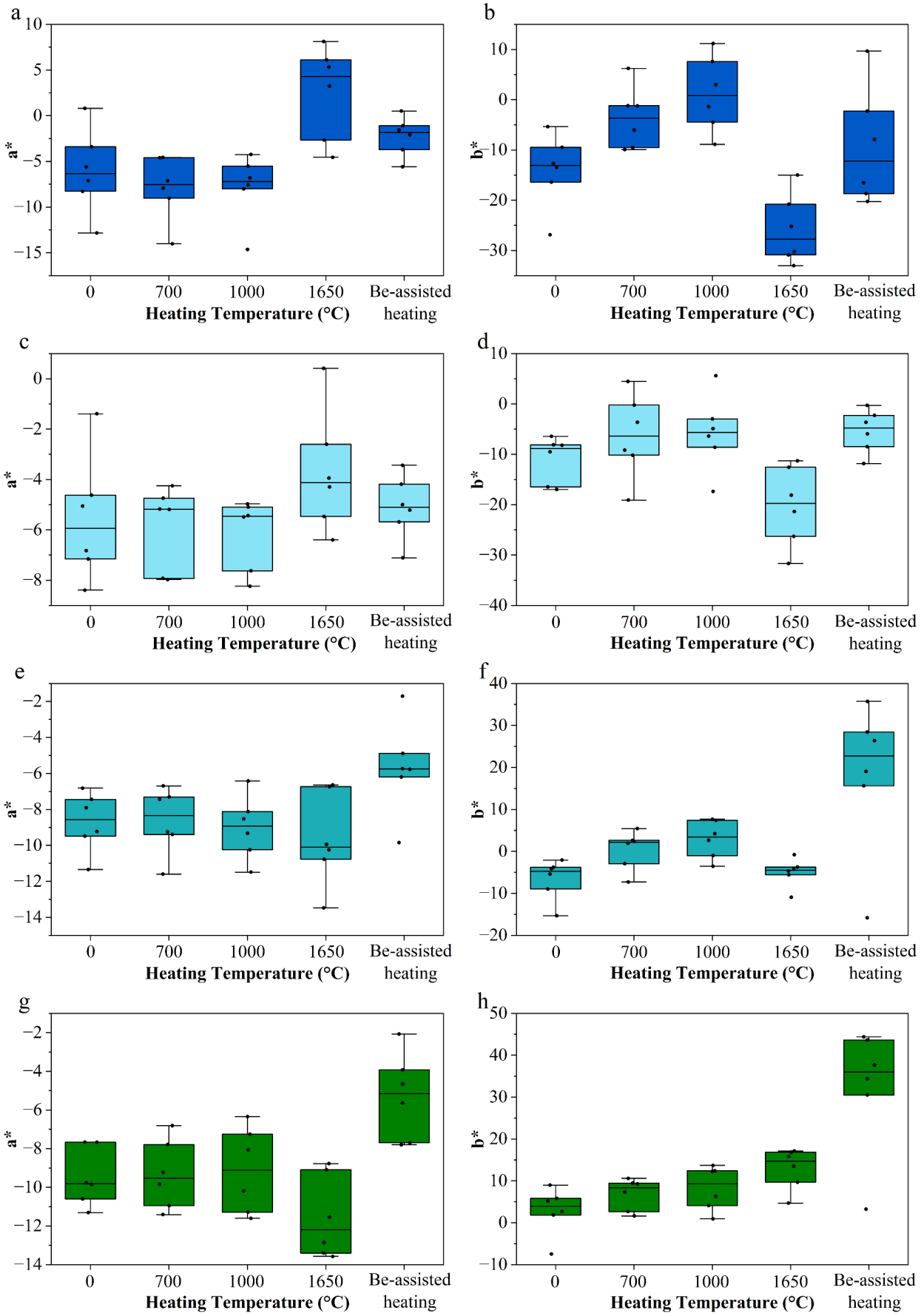

Figure 2. Correlation between a* and b* values after heating experiments observed in dark blue sapphires (a and b), blue sapphires (c and d), greenish blue sapphires (e and f), bluish green sapphires (g and h).

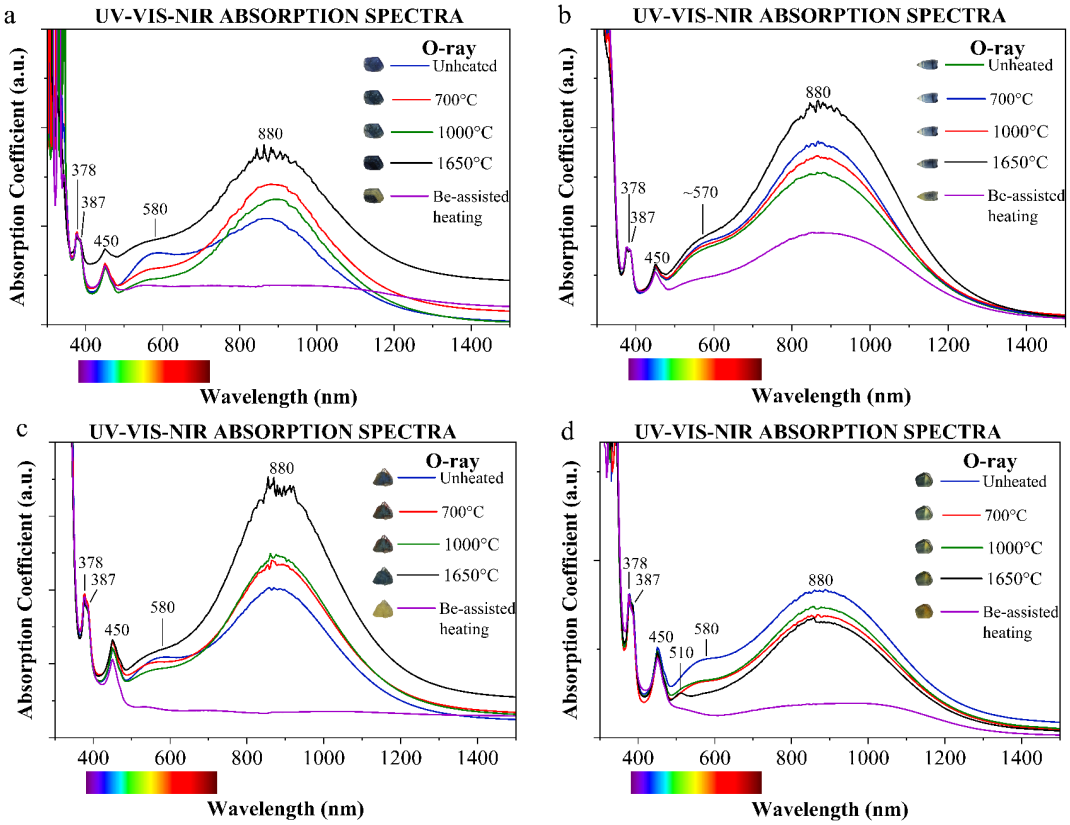

Figure 3. Representative UV-Vis-NIR absorption spectra within the range of 300-1500 nm of sapphire samples before and after each heating experiment, 3a) sample DB003 of dark blue sapphire, 3b) sample B005 of blue sapphire, 3c) sample GB001 of greenish blue sapphire, 3d) sample BG003 of bluish green sapphire.

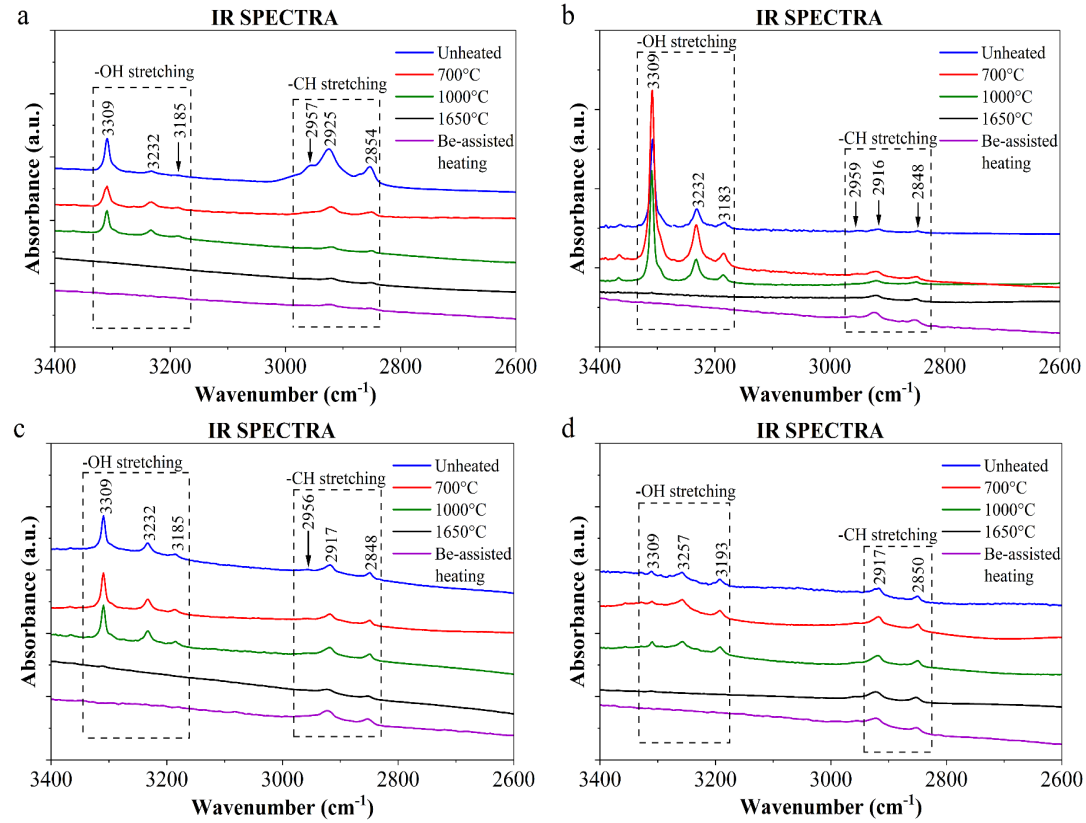

Figure 4. Representative FTIR spectra ranged from 3400-2600 cm^{-1} of sapphire samples before and after treatments, 4a) dark blue sample DB003, 4b) blue sapphire sample B001, 4c) greenish blue sapphire sample GB006, 4d) bluish green sapphire sample BG003.

3.5 Trace composition

Representative trace element analyses were recalculated and reported in parts per million atomic (ppma) contents as presented in Table 4. In general, these results are similar to those obtained from basalt-related sapphires from other localities which are typically characterized by high Fe concentration along with Ti. For instance, averages of each element are reported here

Dark blue sapphires contained Fe concentration of about 3522 ppma, with Ti and Ga contents of approximately 55 ppma and 30 ppma, respectively. Mg and V were present at lower concentrations, averaging 3 ppma and 2 ppma. Blue sapphires contained approximately 2615 ppma Fe, with Ti and Ga contents of about 25 ppma and 33 ppma, respectively. V and Mg were both present at about 3 ppma. Greenish blue sapphires showed the highest Fe concentration (average 7670 ppma) among all color groups, with Ti and Ga contents of about 31 ppma and 40 ppma, respectively. Mg and V were present at average 8 ppma and 4 ppma. In contrast, bluish green sapphires had a lower average Fe concentration of 1255 ppma, with Ti and Ga contents of about 6 ppma and 26 ppma, Mg and V at average 3 ppma and 1 ppma. In addition, Cr and Be in most samples were below the detection limit. However, after beryllium-assisted heating, Be concentrations increased across all color groups, ranging from 11 ppma to 146 ppma in dark blue sapphire, 27 ppma to 62 ppma in blue sapphire, 5 ppma to 111 ppma in greenish blue sapphire,and 19 ppma to 48 ppma in bluish green sapphire.

4. Discussion

4.1 Color modification

The UV-Vis-NIR spectra show that sapphires from the Binh Thuan deposits exhibit blue coloration primarily due to Fe^{2+}–Fe^{3+} IVCT (peaked at 880 nm) and Fe^{2+}–Ti^{4+} IVCT (around 580 nm) (see Figure 3). In addition, the chemical composition is not entirely homogeneous, and chemical zoning in some samples may cause unequal distribution of chromophoric elements, resulting in uneven color within the same stone. Some sapphire samples show partly green appearance because of the combined effects with additional Fe^{3+}–Fe^{3+} pair (peaked at 450 nm). After heating at 700°C and 1000°C, the blue coloration diminishes as a result of oxidizing from Fe^{2+} to Fe^{3+}, leading to a reduction of the 580 nm absorption band in particular, consistent with Hughes and Perkins [26]. When heated at 1650°C, the blue color intensifies again due to the dissolution of rutile (TiO_2) inclusions. Then, released Ti^{4+} ions likely combine with Fe^{2+} within the sapphire lattice to form Fe^{2+}–Ti^{4+} IVCT, as reported by Kwansirikul, Thanasuthipitak and Thanasuthipitak [27], Rossi, Biondi, Rizzi, Corriero, Sequino and Vergara [28]. For Be-assisted heating, most modified yellow sapphires show the disappearance of Fe^{2+}–Fe^{3+} IVCT and Fe^{2+}–Ti^{4+} IVCT because beryllium preferentially bonds with Ti rather than Fe, forming Be^{2+}–Ti^{4+} pairs that do not absorb in the visible region [2]. Oxidation of Fe^{2+} to Fe^{3+} further eliminates Fe^{2+}–Fe^{3+} IVCT and Fe^{2+}–Ti^{4+} IVCT, but potentially form Fe^{3+}–Fe^{3+}, which is responsible for the yellow coloration.

Table 4. Representative LA-ICP-MS analyses in ppma of sapphires before heating from Binh Thuan, Southern Vietnam.

Dark blue sapphire							
Sample number	**Be**	**Mg**	**Ti**	**V**	**Cr**	**Fe**	**Ga**
DB001	bdl	3	23	4	1	3477	30
DB002	bdl	4	73	4	bdl	3675	34
DB003	bdl	3	28	1	bdl	3761	32
DB004	bdl	4	34	2	bdl	4052	26
DB005	bdl	3	67	4	bdl	3220	33
DB006	bdl	1	47	bdl	1	2947	27
Blue sapphire							
No.	**Be**	**Mg**	**Ti**	**V**	**Cr**	**Fe**	**Ga**
B001	bdl	3	28	3	bdl	2610	30
B002	bdl	3	28	3	bdl	3111	32
B003	bdl	3	26	3	bdl	2379	38
B004	bdl	3	29	2	bdl	2118	33
B005	bdl	3	35	4	bdl	2470	36
B006	bdl	2	18	3	bdl	3051	30
Greenish blue sapphire							
No.	**Be**	**Mg**	**Ti**	**V**	**Cr**	**Fe**	**Ga**
GB001	bdl	20	26	3	bdl	10111	45
GB002	bdl	5	23	3	bdl	7704	41
GB003	bdl	2	11	2	bdl	6975	32
GB004	bdl	17	13	2	bdl	8842	40
GB005	bdl	5	14	3	3	5586	48
GB006	bdl	3	72	6	1	6799	37
Bluish green sapphire							
No.	**Be**	**Mg**	**Ti**	**V**	**Cr**	**Fe**	**Ga**
BG001	bdl	8	7	2	bdl	1290	27
BG002	bdl	2	5	bdl	2	1430	20
BG003	bdl	1	3	bdl	1	1057	27
BG004	bdl	3	5	2	bdl	1244	29
BG005	bdl	2	3	2	bdl	1217	26
BG006	bdl	3	3	2	bdl	1292	25

Note: bdl = below detection limit

The Häger [29] diagram (Figure 5) is modified for discussion under this study because the original diagram was developed for metamorphic deposits and is based on the concentrations of titanium (Ti), total iron (Fe_{tot}), and magnesium (Mg). In contrast, these studied sapphires originated from basaltic deposit and contained high Fe content as reported earlier. Accordingly, we found that enlarging the Fe_{tot} and adding Be^{2+} to Mg component provide a more appropriate framework for predicting the color after heat treatment, as shown in the revised diagram (Figure 6–9). Be-assisted heating increases the (Mg + Be)/Ti ratio in the sapphires which the modified yellow sapphires (from greenish blue and bluish green samples in particular, Table 3) after such treatment show $(Mg^{2+} + Be^{2+})/Ti^{4+} > 1$ (Figure 8–9). As a result, Be^{2+} may bond with Ti^{4+} prior to Fe^{2+}, then prevents Fe^{2+} from pairing with Ti^{4+} to form $FeTiO_3$ cluster (potential cause of blue coloration). Instead, Be^{2+} and Mg^{2+} pair with Ti^{4+} to form $BeTiO_3$ and $MgTiO_3$ clusters which are colorless. Due to the similar ionic size and energy level of Be and Mg, they can substitute for each other. Moreover, the excess Mg^{2+} or Be^{2+} may stabilize the trapped-hole color centers produced by high temperature heating that in turn enhance the yellow hue of Be-treated sapphire [2,9–12,30–32]. In contrast, most dark blue and blue sapphires remained blue after Be-assisted heating (Table 2) still contain $(Mg^{2+} + Be^{2+})/Ti^{4+} < 1$ (Figure 6–7). Excess Ti^{4+}, remaining after the formation of $MgTiO_3$ clusters, combined with Fe^{2+} to produce $FeTiO_3$ clusters. Consequently, Fe^{2+}–Ti^{4+} IVCT is responsible for the blue coloration.

In basaltic sapphires, Fe^{3+} is typically present in relatively high concentrations and plays an important role in the overall coloration of the stone. During Be-assisted heating, Be^{2+} may preferentially associate with Fe^{3+} rather than Fe^{2+} because of the energy level and charge-compensation [2]. This preferential association reduces the number of Fe^{2+}-Fe^{3+} IVCT, thereby decreasing the absorption responsible for the blue component of the color. However, some sapphires under this study, contain exceptionally high total iron (Fe_{tot}) concentrations, Fe-related absorption remains sufficiently strong to dominate the visible spectrum. Consequently, the suppression of Fe^{2+}–Fe^{3+} IVCT does not affect color modification, therefore, the overall appearance of the sapphire may remain relatively unchanged after Be-assisted treatment.

In contrast, some greenish blue and bluish green sapphires from this deposit can be completely transformed into yellow sapphires following Be-assisted heating. Their coloration is controlled by a combination of Fe^{3+} and Fe^{2+}–Fe^{3+} IVCT. During Be-assisted heating, Be^{2+} may preferentially associate with Fe^{3+}, reducing the occurrence of Fe^{2+}–Fe^{3+} IVCT, thereby causing the yellow color to become visible. The remaining Fe^{2+} is present in such a small amount that it does not contribute to the appearance of a blue color [2,6,33].

Dark Blue Sapphire: showed the deepest blue coloration, which typically leads to low market value and necessitates quality improvement through heat treatment. Experimental results suggest that the most effective heating condition is 700°C in an oxidizing atmosphere which the intense blue color becomes noticeably paler. After beryllium-assisted heating, the stones typically exhibit bicolor dark blue and yellow, which results in less vibrant appearance. As shown in Figure 6, the Mg + Be–Fe–Ti ternary diagram indicates that $Ti^{4+} >> Mg^{2+} + Be^{2+}$, and thus the samples (DB003, DB005, and DB006) plotted within the blue region of the diagram. This occurs because excess Ti^{4+}, remaining after the formation of $MgTiO_3$ clusters, combined with Fe^{2+} to produce $FeTiO_3$ clusters. Then Fe^{2+}–Ti^{4+} IVCT is significantly responsible for the blue coloration [2,9–12,30–32].

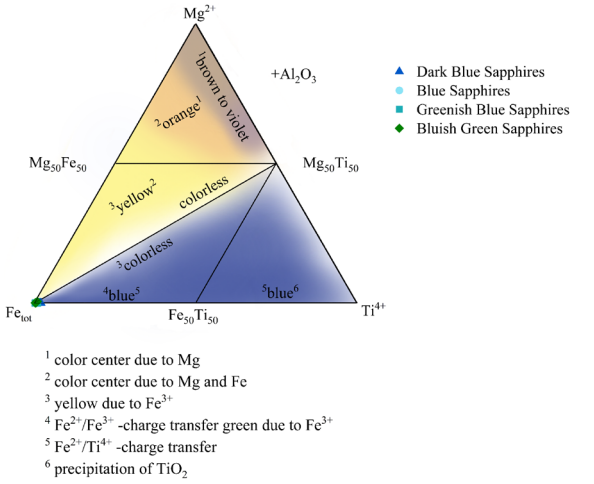

Figure 5. Ternary diagram showing the compositional relationship between Fe_{tot}, Ti^{4+}, and $Mg^{2+}$of sapphire samples before Be-assisted heating. The diagram was modified from Häger [29].

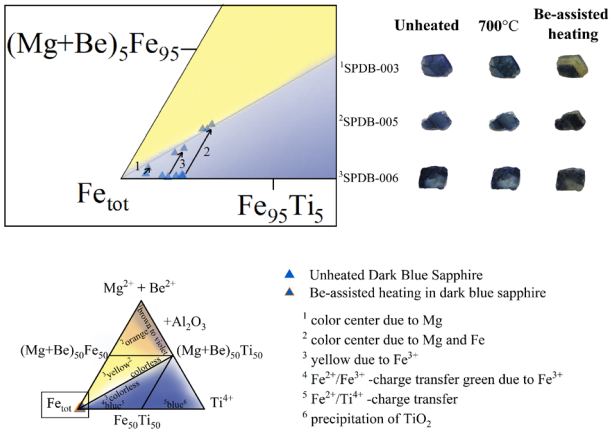

Figure 6. Mg + Be–Fe–Ti triangular diagram modified from Häger [29] showing compositional change and modified color of dark blue sapphire before and after Be-assisted heating.

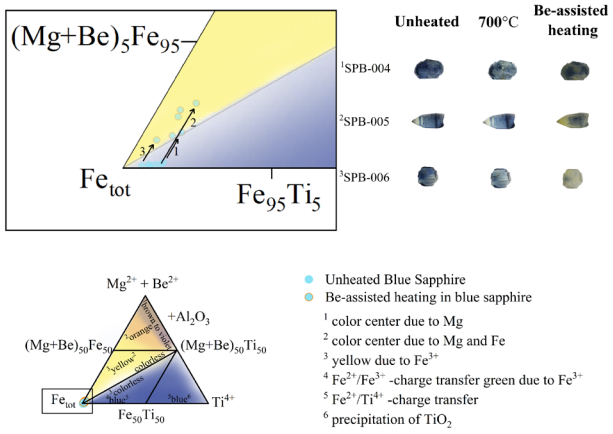

Figure 7. Mg + Be–Fe–Ti triangular diagram modified from Häger [29] showing compositional change and modified color of blue sapphire before and after Be-assisted heating.

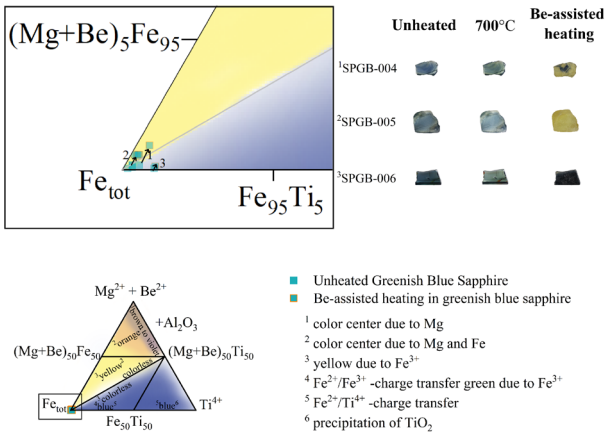

Figure 8. Mg + Be–Fe–Ti triangular diagram modified from Häger [29] showing compositional change and modified color of greenish blue sapphire before and after Be-assisted heating.

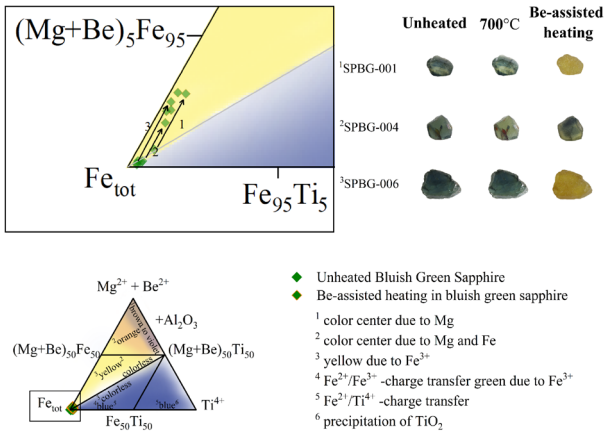

Figure 9. Mg + Be–Fe–Ti triangular diagram modified from Häger [29] showing compositional change and modified color of bluish green sapphire before and after Be-assisted heating.

Blue Sapphire: became paler blue when heated at 700°C to 1000°C. After beryllium-assisted heating, the stones typically exhibited bicolor dark blue and yellow, similar to the dark blue group. As shown in Figure 7, the Mg + Be–Fe–Ti ternary diagram indicates that Ti^{4+} >> Mg^{2+} + Be^{2+}, and thus the sample (B004) plotted within the blue region of the diagram. In contrast, B005 and B006 shows the ratio Mg^{2+} + Be^{2+} > Ti^{4+}, causing the plotted positions close to the field of yellow coloration [2,9–12,30–32].

Greenish Blue Sapphire: Heating at 700°C and 1000°C generally causes fading of blue tone and then making more greenish appearance. After Be-assisted heating, these sapphires displayed both yellow and blue colors. As shown in Figure 8, the Mg + Be–Fe–Ti ternary diagram indicates that GB005 and GB006 samples show Mg^{2+} + Be^{2+} > Ti^{4+} which is plotted in the yellow coloration region. On the other hand, sample GB004 contains Ti^{4+} >> Mg^{2+} + Be^{2+} and consequently is still within the blue coloration area [2,9–12,30–32].

Bluish Green Sapphire: When heated at 700°C to 1000°C, the blue component faded while the green hue remained visible. After Be-assisted heating, most samples (e.g., BG001, BG004, and BG006) changed to yellow. These samples clearly exhibit Mg^{2+} + Be^{2+} > Ti^{4+} ratios after Be-assisted heating and therefore plot within the yellow coloration region (Figure 9).

The optimal treatment conditions for this study can be categorized according to the initial color groups. However, sapphires in all color groups can ultimately be converted to yellow with sufficiently extended heating durations. Dark blue sapphires should be heated at 700°C. Blue sapphires should not be undergone any heat treatment whereas greenish blue and bluish green sapphires are suitable for beryllium-assisted heating.

4.2 Indicator of heating

Chemical analysis using LA-ICP-MS provided valuable information on the beryllium concentrations in sapphires from Binh Thuan, Southern Vietnam. Before beryllium-assisted heating, the Be contents were below the detection limit. After the beryllium-assisted heating, measurable Be levels increased to 5 ppma to146 ppma. These values are comparable to those previously reported for beryllium-treated blue sapphires (11 ppma to 45 ppma) [34] and for beryllium-treated blue sapphires from Sri Lanka (11 ppma to 26 ppma) [35].

Moreover, infrared absorption (FTIR) spectra can be used to assess the thermal enhancement of sapphires. After heating at 1650°C and during beryllium-assisted treatment, the OH-stretching absorption bands at all positions (i.e., 3309 cm^{-1}, 3232 cm^{-1}, and 3186 cm^{-1}) disappeared completely. In contrast, the CH–stretching absorption bands at 2850 cm^{-1} to 2950 cm^{-1} remained unchanged after all steps of heating. The reduction of 3309 cm^{-1} in basaltic sapphires after heat treatment occurs because the Ti–OH stretching bond is broken during heating under the specific thermal conditions of this experiment and subsequently re-formed in a different orientation within the corundum structure. Moreover, during Be-assisted heating, Be preferentially bonds with Ti rather than Fe due to its electron energy, resulting in the absence of the Ti–OH stretching peak. This observation is consistent with Hughes, Manorotkul and Hughes [6], Phlayrahan, Monarumit, Lhuaamporn, Satitkune and Wathanakul [36], Soonthorntantikul, Khowpong, Atikarnsakul, Saeseaw, Sangsawong, Vertriest and Palke [37].

4.3 Commercial value

The market value of sapphire is primarily determined by color, clarity, cut, and carat. Since this study focuses specifically on color modification, the suitability of treatment was evaluated mainly based on the resulting color appearance and relative commercial value. For the dark blue group, low-moderated temperature in oxidizing condition can improve the appearance by reducing overly dark tones and increasing brightness, resulting in a more attractive blue color. In contrast, further high temperature heating is not recommended because it may produce excessively dark blue coloration, which lowers visual appeal and market value.

For the blue group, heat treatment is generally not recommended because the natural blue color already represents the most commercially desirable category. Heating may reduce color saturation or shift the color away from the preferable blue appearance, thereby decreasing value compared to natural unheated stones.

For the greenish blue and bluish green groups, high temperature heat treatment and beryllium-assisted heating can modify the color toward yellowish or more blue hues. Although these treatments may improve visual appearance and higher market value compared to

the original greenish tones, the proper treatments should be selected carefully because color modification clearly depends on the original trace Mg–Fe–Ti composition.

5. Conclusions

Color enhancement through heat treatment significantly influences the appearance of sapphire samples from Binh Thuan, Southern Vietnam. Heating at 700°C and 1000°C in an oxidizing atmosphere can lighten the blue color, as shown by UV-Vis-NIR spectra that reveal a decrease in Fe^{2+}–Ti^{4+} intervalence charge transfer (IVCT) absorption. Intensity of 450 nm peak, which is associated with Fe^{3+}–Fe^{3+} pair, did not exhibit a significant change. In contrast, heating at 1650°C causes the blue color to deepen due to the dissolution of rutile and hematite inclusions, leading to increased absorption in both the Fe^{2+}–Ti^{4+} IVCT and Fe^{2+}–Fe^{3+} IVCT bands. When beryllium is introduced during heating, some sapphires, especially greenish blue and bluish green stones, change to a yellow color, associated with the formation of color center which depends on the Ti and Mg + Be ratio.

FTIR can be used for supportive determination of heat treatment because after heating at 1650°C and Be-assisted heating the absorption peak at 3309 cm^{-1}, which is characteristic of basaltic sapphire, disappears due to the dissolution of hematite and rutile inclusions.

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References

[1] K. Nassau, "The origins of color in minerals," *American Mineralogist,* vol. 63, no. 3–4, pp. 219–229, 1978.

[2] J. L. Emmett, K. Scarratt, S. F. McClure, T. Moses, T. R. Douthit, R. Hughes, S. Novak, J. E. Shigley, W. Wang, and O. Bordelon, "Beryllium diffusion of ruby and sapphire," *Gems & Gemology,* vol. 39, no. 2, pp. 84–135, 2003.

[3] P. Wongrawang, N. Monarumit, N. Thammajak, P. Wathanakul, and W. Wongkokua, "Oxidation states of Fe and Ti in blue sapphire," *Materials Research Express,* vol. 3, no. 2, p. 026201, 2016.

[4] E. V. Dubinsky, J. Stone-Sundberg, and J. L. Emmett, "A quantitative description of the causes of color in corundum," *Gems & Gemology,* vol. 56, no. 1, pp. 1–27, 2020.

[5] K. Nassau, "Heat treating ruby and sapphire: Technical aspects," *Gems & Gemology,* vol. 17, no. 3, pp. 121–131, 1981.

[6] R. W. Hughes, W. Manorotkul, and E. B. Hughes, *Ruby & Sapphire: A Gemologist's Guide*. Bangkok, Thailand: RWH Publishing, 2017.

[7] J. Mogmued, N. Monarumit, K. Won-In, and S. Satitkune, "Spectroscopic properties for identifying sapphire samples from Ban Bo Kaew, Phrae Province, Thailand," *Journal of Physics: Conference Series*, vol. 901, no. 1, p. 012075, 2017.

[8] S. Saeseaw, S. Sangsawong, W. Vertriest, U. Atikarnsakul, V. Raynaud-Flattot, C. Khowpong, and V. Weeramonkhonlert, "A study of sapphire from Chanthaburi, Thailand and its gemological characteristics," *GIA Research News,* pp. 1–42, 2017.

[9] V. Pisutha-Arnond, T. Hager, P. Wathanakul, and W. Aticha, "A brief summary on a cause of colour in pink-orange, orange and yellow sapphires produced by the "new" heating technique," *Journal of Gem and Jewelry,* vol. 3, pp. 11–12, 2002.

[10] V. Pisutha-Arnond, P. Wathanakul, W. Atichat, T. Haeger, T. Win, T. Leelawatanasuk, and C. Somboon, "Beryllium-treated vietnamese and mong hsu rubies," in *Proceedings of the 2 nd International Workshop on Geo-and Material-Science on Gem-Minerals of Vietnam*, Hanoi, Vietnam, 1–8 October 2003, pp. 171–175.

[11] V. Pisutha-Arnond, T. Haeger, P. Wathanakul, W. Atichat, T. Win, T. Leelawatanasuk, C. Somboon, and C. Sutthirat, "Chemical characteristic of "Classical" versus "Beryllium" heat-treated ruby and sapphire," in *Proceedings of the 29th International Gemmological Conference*, Wuhan, China, 12–21 September 2004, pp. 4–92.

[12] V. Pisutha-Arnond, T. Häger, P. Wathanakul, and W. Atichat, "Yellow and brown coloration in beryllium treated sapphires," *The Journal of Gemmology,* vol. 29, no. 2, pp. 77–103, 2004.

[13] C. P. Smith, R. C. Kammerling, A. S. Keller, A. Peretti, K. Scarratt, N. D. Khoa, and S. Repetto, "Sapphires from southern Vietnam," *Gems & Gemology,* vol. 31, no. 3, pp. 168–180, 1995.

[14] S. Barr, and A. MacDonald, "Geochemistry and geochronology of late Cenozoic basalts of Southeast Asia," *Geological Society of America Bulletin,* vol. 92, no. 8 Part II, pp. 1069–1142, 1981.

[15] N. Hoang, and M. Flower, "Petrogenesis of Cenozoic basalts from Vietnam: Implication for origins of a 'diffuse igneous province'," *Journal of Petrology,* vol. 39, no. 3, pp. 369–395, 1998.

[16] V. Garnier, D. Ohnenstetter, G. Giuliani, A. E. Fallick, T. P. Trong, V. H. Quang, L. P. Van, and D. Schwarz, "Basalt petrology, zircon ages and sapphire genesis from Dak Nong, southern Vietnam," *Mineralogical Magazine,* vol. 69, no. 1, pp. 21–38, 2005.

[17] H. Nguyen, M. Fower, X. B. Nguyen, and T. Y. Nguyen, "Trace element and isotopic compositions of Vietnamese basalts: implications for mantle dynamics in the southeast Asian region; Compositions isotopiques et en elements en trace des basaltes vietnamiens: implications pour la dynamique du manteau en Asie du Sud-Est," *Bulletin de la Societé géologique de France,* vol. 167, no. 6, pp. 785–795, 1996.

[18] D. T. A. Vu, A. Salam, A. Fanka, E. Belousova, and C. Sutthirat, "Mineral inclusions in sapphire from basaltic terranes in southern

Vietnam: Indicator of formation model," *Gems & Gemology,* vol. 56, no. 4, pp. 498–515, 2020.

[19] P. Van Long, H. Quang Vinh, V. Garnier, G. Giuliani, D. Ohnenstetter, T. Lhomme, D. Schwarz, A. Fallick, J. Dubessy, and P. Trong Trinh, "Gem corundum deposits in Vietnam," *Journal of Gemmology,* vol. 29, no. 3, pp. 129–147, 2004.

[20] T. Tri, and V. Khuc, *Geology and earth resources of Việt Nam* (General department of geology and minerals of Vietnam). Hanoi, Vietnam: House for Science and Technology, 2011.

[21] L. T. T. Huong, T. Häger, W. Hofmeister, C. Hauzenberger, D. Schwarz, P. Van Long, U. Wehmeister, N. N. Khoi, and N. T. Nhung, "Gemstones from Vietnam: An update," *Gems & Gemology,* vol. 48, no. 3, pp. 158–176, 2012.

[22] T. H. A. Hoang, S. H. Choi, Y. Yu, T. H. Pham, K. H. Nguyen, and J.-S. Ryu, "Geochemical constraints on the spatial distribution of recycled oceanic crust in the mantle source of late Cenozoic basalts, Vietnam," *Lithos,* vol. 296, pp. 382–395, 2018.

[23] J. Krebs, and W. Maisch, "Exchange effects in the optical-absorption spectrum of Fe^{3+} in Al_2O_3," *Physical Review B,* vol. 4, no. 3, p. 757, 1971.

[24] J. Ferguson, and P. Fielding, "The origins of the colours of natural yellow, blue, and green sapphires," *Australian Journal of Chemistry,* vol. 25, no. 7, pp. 1371–1385, 1972.

[25] E. Dubinsky, and J. Emmett, "The colors of corundum," *The GemGuide,* vol. 32, no. 1, pp. 1–11, 2013.

[26] E. B. Hughes and R. Perkins, "Madagascar sapphire: Low-temperature heat treatment experiments," *Gems & Gemology,* vol. 55, pp. 184–197, 2019.

[27] K. Kwansirikul, P. Thanasuthipitak, and T. Thanasuthipitak, "Experimental heat treating of trapichelike blue sapphire of southern Vietnam," *Suranaree Journal of Science & Technology,* vol. 23, no. 4, pp. 409–419, 2016.

[28] M. Rossi, R. Biondi, R. Rizzi, N. Corriero, F. Sequino, and A. Vergara, "Mechanism of be-thermodiffusion in rutile inclusions of fancy sapphires," *Crystal Growth & Design,* vol. 22, no. 11, pp. 6493–6503, 2022.

[29] T. Häger, "High temperature treatment of natural corundum," in *International Workshop on Material Characterization by Solid State Spectroscopy: The Minerals of Vietnam*, Hanoi, Vietnam, 4–10 April 2001, pp. 4–10.

[30] W. Atichat, B. Sriprasert, P. Wathanakul, V. Pisutha-Arnond, T. Sun, T. Puttarat, and T. Leelawatanasuk, "Characteristics of "beryllium" heat-treated yellow sapphires," in *Proceedings of the 29th International Gemmological Conference, Wuhan, China*, 12-21 September 2004, pp. 14-207.

[31] K. Schmetzer and D. Schwarz, "The causes of colour in untreated, heat treated and diffusion treated orange and pinkish-orange sapphires-a review," *Journal of Gemmology,* vol. 29, no. 3, pp. 149–182, 2004.

[32] T. Themelis, *The Heat Treatment of Ruby & Sapphire: Experiments & Observations*. Florida, USA: Gemlab, 1992.

[33] E. Fritsch, and G. R. Rossman, "An update on color in gems. Part 2: Colors involving multiple atoms and color centers," *Gems & Gemology,* vol. 24, no. 1, pp. 3–15, 1988.

[34] G. DuToit, J. Thanachakaphad, and K. Scarratt, "Beryllium treated blue sapphires: Continuing market observations and update including the emergence of larger size stones," *GIA Research News,* pp. 1–25, 2009.

[35] S. Singbamroong, P. Limtrakun, and T. Somjaineuk, "Beryllium heat-treated blue sapphire," *Trends in Sciences,* vol. 22, no. 1, pp. 8405–8405, 2025.

[36] A. Phlayrahan, N. Monarumit, T. Lhuaamporn, S. Satitkune, and P. Wathanakul, "Spectroscopic investigation of properties of blue sapphire samples depending on heating conditions," *Journal of Applied Spectroscopy,* vol. 86, pp. 810–816, 2019.

[37] W. Soonthorntantikul, C. Khowpong, U. Atikarnsakul, S. Saeseaw, S. Sangsawong, W. Vertriest, and A. Palke, "Observations on the heat treatment of basalt-related blue sapphires," *Gemological Institute of America Report,* pp. 1–60, 2019.