Luminescence and a New Approach for Detecting Heat Treatment of Geuda Sapphire

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Abstract. For decades, unravelling heat treatment of sapphire has been a challenging issue. The present study offers new aspects that support the detection of heat treatment of sapphire. Natural ~~unheated~~ geuda sapphire exhibits orange to red luminescence under long–wave ultraviolet (LWUV, 365 nm) light, while heated geuda sapphire shows blue luminescence under short–wave ultraviolet (SWUV, 225 nm) ~~Natural unheated sapphire is distinguishable from heated sapphire by its orange to red luminescence under long-wave ultraviolet (LWUV, 365 nm) light, whereas blue luminescence under short-wave ultraviolet (SWUV, 254 nm) light indicates their heated counterparts.~~ light. UV–excited photoluminescence reveals a connection between the broad emission spectrum of ~~natural~~ unheated sapphire, which appears orange to red under LWUV illumination, and the emission spectrum of heated sapphire, which appears blue under SWUV illumination. ~~UV-excited photoluminescence shows a linkage between a broad emission spectrum within the orange to red region and orange to red luminescence of natural unheated sapphire under LWUV illumination, as well as an emission spectrum around the green region and blue luminescence of heated sapphire under SWUV illumination.~~ The presence of melt inclusions in dissolved silks serves as an indicator of sapphire heat treatment. Fourier–transform infrared (FTIR) spectroscopy alone is insufficient for distinguishing unheated from heated sapphire. By combining orange to red luminescence with blue luminescence and melt inclusions, we provide a practical method for accurately differentiating natural gem–quality sapphire and heated gem–quality sapphire.~~Furthermore, the presence of melt inclusions within dissolved silks may be used as an indicator of heat treatment of sapphire. It seems that Fourier-transform infrared (FTIR) spectroscopy alone is inadequate for distinguishing unheated and heated sapphire. The application of orange to red, and blue luminescence together with melt inclusions offer a novel and practicable procedure for more precise differentiation of unheated versus heated sapphire.~~

Keywords: gem; sapphire; heat treatment; luminescence

1 Introduction

Since the 1970s, Sri Lanka has been renowned for its gemstone resources, particularly geuda sapphire, a milky or silky corundum variety that is frequently heat–treated to enhance color and clarity (Soysa and Fernando, 1992; Ediriweera and Perera, 1989; Perera et al., 1991). High–temperature treatment of corundum (including ruby and sapphire) can significantly alter its milkiness, asterism, color, and internal features such as mineral inclusions (Nassau, 1981; Ediriweera and Perera, 1989; Hughes, 1997, 2017; Kyi et al., 1999; Pisutha-Arnond, 2017; Themelis, 2018). Key factors in these transformations include the temperature, duration, and atmospheric conditions of the heating process (Nassau, 1981; Emmett and Douthit, 1993; Peiris, 1993; Emmett et al., 2003; Hughes, 2017; Pisutha-Arnond, 2017; Soonthorntantikul et al., 2019).

One of the first-rank challenges encountered by gemologists nowadays is the precise and reliable identification of heat-treated ruby and sapphire. Blue luminescence under SWUV light, observed in heated sapphire for over 50 years (Crowningshield 1966, 1970), can extend into the green region (Nassau, 1981) and has been extensively studied (Evans, 1994; Wong et al., 1995a; Wong et al., 1995b; Hughes 1997; McClure and Smith, 2000; Page et al., 2010; Alombert-Goget et al., 2016a; Alombert-Goget et al., 2016b; Hughes, 2017; Vigier et al., 2021a, b, 2023). ~~Since the 1970s, Sri Lanka has maintained an outstanding record for its rich supply of gemstones (Soysa and Fernando, 1992). Among diverse corundum varieties, the so-called geuda sapphire is noteworthy, as it has been often subjected to high-temperature heat treatment to increase its value by enhancement of color and clarity (Ediriweera and Perera, 1989; Perera et al., 1991). Geuda sapphire is characterized by milky and/or silky appearance. Heat treatment of corundum (ruby and sapphire) has the capacity to modify the appearance of milkiness and asterism, color, and even the internal features (including mineral inclusions) of the gemstones. Blue luminescence under SWUV light, observed in heated sapphire for over 50 years (Crowningshield 1966, 1970), can extend into the green region (Nassau, 1981) and has been extensively studied~~ (Evans, 1994; Wong et al., 1995a; Wong et al., 1995b; Hughes 1997; McClure and Smith, 2000; Page et al., 2010; Alombert-Goget et al., 2016a; Alombert-Goget et al., 2016b; Hughes, 2017; Vigier et al., 2021a, b, 2023). This luminescence may relate to rutile inclusions commonly found in natural blue sapphire (Hughes, 2017). During heating at around 1600 °C, rutile decomposes, incorporating Ti^{4+} ions into the sapphire structure (Sutthirat et al., 2006). Blue luminescence serves as a key indicator of heat treatment in sapphire (Crowningshield, 1966; McClure and Smith, 2000; Hughes, 2017; Hughes and Perkins, 2019). However, changes in original brown silk inclusions and orange luminescence in natural unheated sapphire, relative to blue luminescence in heated sapphire, have not been thoroughly explored. ~~Temperature and duration of the heating process, as well as reducing or oxidizing conditions, are the most significant factors influencing corundum's alterations (Nassau, 1981; Emmett and Douthit, 1993; Peiris, 1993; Emmett et al., 2003; Hughes, 2017; Pisutha-Arnond, 2017; Soonthorntantikul et al., 2019). Heat treatment can be classified as high- or low-temperature according to the decomposition of rutile silks in corundum (Nassau, 1981; Emmett and Douthit, 1993; Emmett et al., 2003; Hughes, 2017;~~

Hughes and Perkins, 2019). The term low-temperature heat treatment has been used (typically referred to as below 1000 °C) when rutile particles still reveal their original structures. On the other hand, temperatures beyond 1350 °C denote high-temperature heat treatment when rutile silks start to decompose and dissolve within the corundum host (Hughes, 2017; Themelis, 2018). Consequently, internal diffusion (indicated by a colored halo surrounding the crystal inclusion), molten or altered inclusions, and/or broken silk are strong indicators of high-temperature heat treatment. However, low-temperature heat treatment can also produce various altered mineral inclusions (Kammerling et al., 1990; McClure and Smith, 2000; McClure et al., 2010; Pisutha-Arnond, 2017; Soonthorntantikul et al., 2019).

The present~~is~~ study provides a novel approach by observing the transformations in silk inclusions and luminescence in sapphire before and after heating.~~One of the first-rank challenges encountered by gemologists nowadays is the precise and reliable identification of heat-treated ruby and sapphire.~~ ~~Blue luminescence under SWUV light has been observed in heated sapphire some 50 years ago (Crowningshield 1966, 1970). This luminescence may also extend into the green region (Nassau, 1981). It has been studied afterwards by numerous researchers (Evans, 1994; Wong et al., 1995a; Wong et al., 1995b; Hughes 1997; McClure and Smith, 2000; Page et al., 2010; Alombert-Goget et al., 2016a; Alombert-Goget et al., 2016b; Hughes, 2017; Vigier et al., 2021a, b, 2023). ~~—~~ ~~(~~This phenomenon may relate to rutile inclusions in sapphire (Hughes, 2017). It should be mentioned that most natural blue sapphires contain some exsolved rutile (TiO_2) in the form of silk and/or needle inclusions (Sutthirat et al., 2006; Hughes, 2017). When these sapphire samples are heated, rutile dissolves gradually at temperatures of about 1600 °C (Sutthirat et al., 2006), resulting in the incorporation of Ti^{4+} ions into the host sapphire structure. After Ti^{4+} being exposed to SWUV light, they yield luminescence. However, blue luminescence was not observed in both unheated and heated basaltic sapphire, possibly due to the abundant presence of Fe^{2+} of basaltic origin that may strongly quench such blue luminescence (Soonthorntantikul et al., 2019). More details will be discussed in this report. Furthermore, even though microscopic inclusions have been the distinguishing characteristics of heated sapphire, identifying heat-treated sapphire remains challenging (Crowningshield, 1966; Hughes, 2017). Spectroscopic techniques such as Fourier-transform infrared (FTIR) spectroscopy have also been applied to detect heated sapphire. In some cases, the presence or absence of specific FTIR features in the O-H absorption region (3100–3600 cm^{-1}) may serve as an indicator of heat treatment (Smith, 1995; Beran and Rossman, 2006; Saeseaw et al., 2018); however, it is probably not a conclusive evidence (Ediriweera and Perera, 1989; Perera, 1993; Sutthirat et al., 2006; Cartier, 2009; Jaliya et al., 2020). The most efficient technique and key evidence enabling to identify heat-treated sapphire is its blue luminescence (Crowningshield, 1966; McClure and Smith, 2000; Hughes, 2017; Hughes and Perkins, 2019). However, sequential research on original brown silk inclusions and orange luminescence in natural unheated sapphire in relation with blue luminescence in the heated counterparts has never been reported accordingly. Therefore, this study should be the first research that represents an innovative approach to observe both original silk inclusions and luminescence in sapphire and their change after heating experiments.~~

2 Materials and Methods

Natural unheated geuda sapphire (A–type) samples (types of samples, seeasas described by Vertriest et al., 2019) were separated based on the appearance of silk inclusions into three distinctive groups, i.e., high-density silk (HS), low-density silk (LS), and silk-free (SF) specimens Natural unheated geuda sapphire samples were separated into 3 groups:(Fig. 1 1) high-density silk group; 2) low-density silk group; and 3) silk-free group (Fig. 1).). Using an Enraf–Nonius Kappa single–crystal X–ray diffractometer (sXRD) with a charge–coupled device (CCD) area detector, these samples were oriented (based on 10 frames at a crystal detector distance of 35 mm), cut and polished into wafers with surfaces parallel to the *c*–axis. ForFor chemical analysis using an electron probe micro–analysiser (EPMA) system, slabs were coated with carbon for conductivity.

Heating experiments were conducted using a high–temperature electric furnace, Linn–HT–1800–Vac. Heating was performed under ambient atmospheric conditions without any additional oxygen buffer. Experimental conditions involved the maximum temperature of 1650 °C, which was maintained for 10 hours, prior to natural cooling down in the furnace. A heating rate of 300 °C per hour was set to reach the maximum temperature. To minimize surface contamination, the samples were placed into a highly purified alumina (Al_2O_3) crucible.

Basic gemological data, such as The refractive index, of samples was measured by a gemological refractometer (KRUSS, model ER605) with 1.81 refractive index liquid. Specific gravity was determined by a hydrostatic weighing balance, by weighing samples in water (with a drop of dishwashing detergent added to reduce surface tension) and in air.

Micro–inclusions in all samples were investigated imaged using an Olympus BX–series microscope equipped with Olympus DP27 digital camera. The camera was operated using the Olympus Stream micro–imaging software. Raman spectra of inclusions were acquired using a confocal micro–Raman spectrometer Horiba Jobin Yvon LabRAM–HR Evolution. Using 473 nm laser excitation (15 mW at the sample) and a 50×/0.50 objective lens, a spectral range of 100–1350 cm^{-1} Raman shift was recorded. Wavenumber calibration was done using the Rayleigh line, resulting in wavenumber accuracy of better than 0.5 cm^{-1}. A spectral resolution of ca. 1.2 cm^{-1} resulted from 800 mm focal length and an 1800 grooves/mm optical grating in the monochromator system. For more details see Zeug et al. (2018).

Chemical compositions of the samples were determined using a JEOL JXA 8100 EPMA. Analytical conditions were set to 15 kV accelerating voltage and a probe current of about 2.5×10^{-8} A with electron beam focussed to <1 µm. Natural mineral and synthetic oxide references were selected suitably for calibration, including fayalite (Fe_2SiO_4) for Fe, wollastonite ($CaSiO_3$) for Ca, synthetic corundum (Al_2O_3) for Al, synthetic periclase (MgO) for Mg, synthetic quartz (SiO_2) for Si, potassium titanyl phosphate ($KTiOPO_4$) for K and Ti, synthetic manganosite (MnO) for Mn, synthetic eskolaite (Cr_2O_3) for Cr, synthetic gadolinium gallium garnet ($Gd_3Ga_5O_{12}$) for Ga, and synthetic lead vanadium germanium oxide for V. Counting times were 600 s peak and 300 s background for all elements. The K–α line was analysed for all elements except for Ga where the L–α line was measured. Analytical crystals were selected appropriately including thallium acid phthalate (TAP) crystal for Si and Al; pentaerythriol (PET) crystal for Ti, Mg, K, and Ca; lithium fluoride (LIF) crystal for V, Cr, Ga, Fe, and Mn. The detection limit

(estimated from threefold background noise) is approximated at 0.005 wt% or 50 ppm. Three ~~analytical~~ spots in each sample were ~~selected for further analysis~~analyzed.

Polarized optical absorption (UV–VIS–NIR) spectra of samples were recorded on double–sided polished crystal slabs in the spectral range of 35000–3500 cm^{-1}, covering the near ultraviolet (UV), the visible (VIS) and the near infrared (NIR) ranges. The measurements were performed in the sample chamber of a Bruker Vertex 80 FTIR spectrometer at 2 mm measuring spot, using a calcite Glan–prism polarizer and appropriate combinations of light sources (Xe or W lamp), beam splitters (CaF_2–~~Vis~~VIS~~is~~/UV or CaF_2–NIR), and detectors (GaP, Si or InGaAs diodes) to cover the desired spectral range. Hence, each full spectrum was combined from three partial spectra: 1) 35000–18000 cm^{-1} with 40 cm^{-1} spectral resolution and averaged from 256 scans; 2) 18000–9500 cm^{-1} with 20 cm^{-1} resolution and 256 scans; 3) 9500–3500 cm^{-1} with 10 cm^{-1} resolution and 128 scans.

Fourier–transform infrared ~~(FTIR)~~ spectra were acquired by means of a Bruker Tensor 27 FTIR spectrometer attached to a Bruker Hyperion microscope in the spectral range from 4000 cm^{-1} to 1600 cm^{-1}. A glowbar light source, a KBr beamsplitter, and a deuterated L–alanine doped triglycene sulphate (dLATGS; Tensor27) or Hg–Cd–telluride (MCT) detector (Hyperion) were employed. The spectral resolution was 4 cm^{-1}, sample and reference spectra were averaged from 128 scans.

Luminescence phenomena were observed and photo–captured both before and after heat treatment. The images were obtained under LWUV ~~(365 nm)~~ illumination using ZEISS microscope model stemi 508 with 0.63x magnification. The images were captured in a darkened room using CANON digital single lens reflex (DSLR) camera model EOS 80D (24.2 MP resolution), which was mounted on top of the microscope. The SUPERFIRE UV (365 nm) mini flashlight model S11–H, 3W (max), DC 3.7 V, was held approx. 15 cm above the samples. The camera settings involved an exposure time of 5 s~~econds~~, an exposure bias of 0 steps, and an ISO speed of 200. The aperture was adjusted to f/0, and the focal length of 0 nm.~~a commercial UV lamp, and~~ For ~~under~~ SWUV ~~(254 nm)~~ illumination (approximately 225 nm), ~~by means of~~ a DiamondView™ ~~device~~device ~~(approx. 225 .)~~ was used. The parameter settings for DiamondView™ were established as follows: Integration duration: 2.83 s~~econds~~; minimum excitation status: Off. Power settings ranged from 50% to 80%, contingent upon the intensity of luminescence. A gain of 13.85 dB is measured. ~~We set t~~The aperture was set to 80% and the field stop to 67%. Gamma was disabled. Photoluminescence (PL) spectra in the visible and ~~NIR~~ near–infrared ranges were acquired using a confocal Horiba Jobin Yvon LabRAM–HR 800 spectrometer. Spectra were excited using the 325 nm emission of a He–Cd laser (ca. 10 mW at the sample surface). The system was calibrated using emission lines of a Kr lamp. The spectral resolution was in the range 0.07 nm (violet) to 0.02 nm (NIR range).

All the spectra were acquired at the same position both before and after heating experiments.

3 Results

3.1 Heating–induced property changes and alteration

~~Natural unheated geuda sapphire samples were separated based on the appearance of silk inclusions into~~

three distinctive groups, i.e., high-density-silk, low-density-silk, and silk-free specimens. Representatives of natural unheated and their heated counterparts of all groups are shown in Fig. 1. All the samples ranged from a specific gravity of 3.83 to 4.08 g/cm^3, and refractive indices of 1.760 to 1.770 falling well within the field range of corundum's properties. Before heating, samples showed varying natural appearances based on inclusion density. Geuda samples with HS inclusions (e.g., G03HS and G04HS, Fig. 1) exhibited brown silk and brown color banding or zoning, while a few samples also displayed a natural blue color. Samples with LS inclusions (e.g., G18LS and G21LS, Fig. 1) generally appeared milky with yellowish or brownish tints. After heating, most samples turned blue, ranging from pale to dark shades, with the milky appearance and yellowish or brownish tints significantly reduced. After heating, most samples turned blue, varying from pale blue to dark blue. Alteration was clearly observed in the geuda samples with high-density-silk inclusions (G03 and G04, Fig. 1), which naturally showed brown silk and brown color banding/zoning. Moreover, a few samples in this group also showed a natural blue appearance (G02, Fig. 8). Regarding sapphire samples with low-density-silk inclusions, these stones (e.g., G18 and G21, Fig. 1) typically presented a milky appearance with yellowish or brownish tints, which were obviously diminished after heating. On the other hand, the silk-freeSF group usually showed a slightly yellowish appearance (Fig. 1, samples G11SF and G12SF). After the heating experiment, they had changed slightly to a very pale blue color.

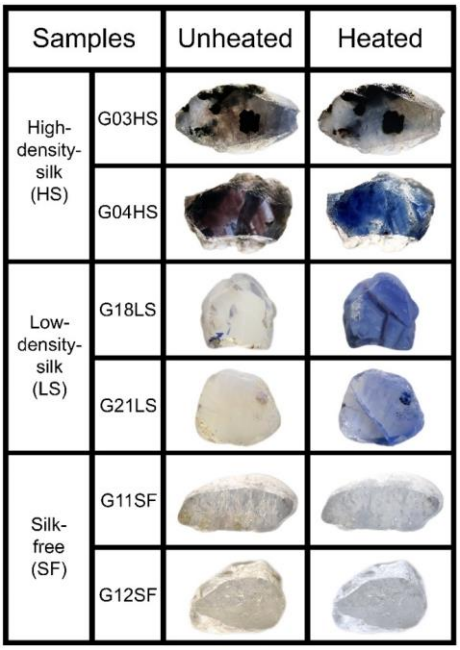

Figure 1. Representatives of natural unheated geuda sapphire samples within three separate groups, i.e., HS (G03HS, G04HS), LS (G18LS, G21LS), and SF (G11SF, G12SF) groups, and their appearances after heating. Sizes of stones range between 0.44 and 12 mm.

3.2 Mineral chemistry

Chemical compositions of samples in the three distinct groups are summarized in Tables 1 to 3. The Al_2O_3 contents range between 98.2 and 99.5 wt%. Other elements are found as trace contents only, particularly Fe, Ti, and Ga. Fe and Ti are essential coloring elements in sapphire. The ~~high-density-silk~~HS group contained the highest Fe contents of 0.32–0.36 wt% FeO, together with 0.02–0.04 wt% TiO_2 and <0.7 wt% Ga_2O_3. The ~~low-density-silk~~LS group had a high Ti content of 0.02–0.51 wt% TiO_2 with ≤0.06 wt% FeO and ≤0.8 wt% Ga_2O_3. The ~~silk-free~~SF group contained 0.06–0.26 wt% FeO, ≤0.04 wt% TiO_2 and <1 wt% Ga_2O_3. ~~The general detection limits of major and minor analyses obtained from EPMA analyses are typicallyroughlyroughly estimate at 50 ppm.~~

227

Table 1. Representative chemical compositions (EPMA results) and calculated mineral formulae of ~~high-density silk~~HS~~HS~~ ~~sapphire samples~~sapphire samples.

Samples	**G01HS**	**G02HS**	**G03HS**	**G04HS**
Major oxides (wt%):				
SiO_2	0.00	0.00	0.45	0.40
TiO_2	0.02	0.02	0.04	0.03
Al_2O_3	99.0	98.7	98.9	98.7
V_2O_3	0.01	0.00	0.00	0.03
Cr_2O_3	0.00	0.02	0.03	0.00
Ga_2O_3	0.62	0.66	0.00	0.39
FeO_{total}*	0.32	0.33	0.36	0.36
MnO	0.02	0.00	0.00	0.02
MgO	0.00	0.00	0.01	0.01
K_2O	0.00	0.00	0.00	0.00
CaO	0.01	0.01	0.02	0.01
Total	100.0	99.8	99.8	100.0
Mineral formulae (apfu)**:				
Si	0.000	0.000	0.008	0.007
Ti	0.000	0.000	0.001	0.000
Al	1.990	1.989	1.985	1.982
V	0.000	0.000	0.000	0.000
Cr	0.000	0.001	0.000	0.000
Ga	0.007	0.007	0.000	0.004
Fe	0.013	0.014	0.005	0.005
Mn	0.000	0.000	0.000	0.000
Mg	0.000	0.000	0.000	0.000
K	0.000	0.000	0.000	0.000
Ca	0.000	0.000	0.000	0.000
Sum	2.010	2.011	1.999	2.000

* FeO_{total} = total Fe oxide, assuming all Fe to be ferrous

** Calculated based on 3 O atoms per formula unit

Table 2. Representative chemical compositions (EPMA results) and calculated mineral formulae of ~~low-density silk~~ sapphire samples.~~LS~~ sapphire samples.

Samples	**G06LS**	**G16LS**	**G18LS**	**G20LS**	**G21LS**
Major oxides (wt%):					
SiO_2	0.00	0.00	0.11	0.00	0.00
TiO_2	0.04	0.27	0.37	0.51	0.02
Al_2O_3	99.0	98.5	98.4	98.3	98.6
V_2O_3	0.02	0.03	0.01	0.02	0.01
Cr_2O_3	0.00	0.06	0.00	0.02	0.00
Ga_2O_3	0.10	0.37	0.58	0.81	0.59
FeO_{total}*	0.00	0.06	0.06	0.06	0.05
MnO	0.01	0.00	0.00	0.00	0.01
MgO	0.02	0.02	0.01	0.01	0.02
K_2O	0.00	0.00	0.00	0.00	0.00
CaO	0.00	0.00	0.01	0.01	0.00
Total	99.2	99.3	99.6	99.7	99.3
Mineral formulae (apfu)**:					
Si	0.000	0.000	0.002	0.000	0.000
Ti	0.001	0.003	0.005	0.007	0.000
Al	1.997	1.989	1.984	1.981	1.992
V	0.000	0.000	0.000	0.000	0.000
Cr	0.000	0.002	0.000	0.001	0.000
Ga	0.001	0.004	0.006	0.009	0.007
Fe	0.000	0.002	0.002	0.002	0.002
Mn	0.000	0.000	0.000	0.000	0.000
Mg	0.001	0.001	0.001	0.000	0.001
K	0.000	0.000	0.000	0.000	0.000
Ca	0.000	0.000	0.000	0.000	0.000
Sum	2.001	2.003	2.000	2.000	2.002

* FeO_{total} = total Fe oxide, assuming all Fe to be ferrous

** Calculated based on 3 O atoms per formula unit

238 **Table 3.** Representative chemical compositions (EPMA results) and calculated mineral formulae of ~~silk-~~
239 ~~free sapphire samples.~~SF sapphire samples.

Samples	**G07SF**	**G11SF**	**G12SF**	**G14SF**	**G22SF**	**G23SF**
Major oxides (wt%):						
SiO_2	0.01	0.13	0.06	0.00	0.00	0.00
TiO_2	0.03	0.04	0.03	0.00	0.04	0.01
Al_2O_3	98.7	98.7	98.8	99.5	98.2	98.7
V_2O_3	0.00	0.02	0.00	0.00	0.00	0.00
Cr_2O_3	0.00	0.00	0.01	0.00	0.00	0.00
Ga_2O_3	0.71	0.00	0.00	0.15	0.78	0.94
FeO_{total}*	0.06	0.26	0.08	0.10	0.22	0.13
MnO	0.01	0.02	0.00	0.01	0.02	0.00
MgO	0.00	0.02	0.00	0.00	0.00	0.00
K_2O	0.00	0.01	0.00	0.00	0.00	0.00
CaO	0.02	0.00	0.02	0.01	0.01	0.01
Total	99.6	99.2	99.0	99.8	99.3	99.8
Mineral formulae (apfu)**:						
Si	0.000	0.002	0.001	0.000	0.000	0.000
Ti	0.000	0.001	0.000	0.000	0.001	0.000
Al	1.991	1.993	1.997	1.997	1.988	1.988
V	0.000	0.000	0.000	0.000	0.000	0.000
Cr	0.000	0.000	0.001	0.000	0.000	0.000
Ga	0.008	0.000	0.000	0.002	0.009	0.010
Fe	0.002	0.011	0.003	0.004	0.009	0.005
Mn	0.000	0.000	0.000	0.000	0.000	0.000
Mg	0.000	0.001	0.000	0.000	0.000	0.000
K	0.000	0.000	0.000	0.000	0.000	0.000
Ca	0.000	0.000	0.000	0.000	0.000	0.000
Sum	2.002	2.009	2.003	2.003	2.007	2.004

240 * FeO_{total} = total Fe oxide, assuming all Fe to be ferrous

241 ** Calculated based on 3 O atoms per formula unit

242

3.3 Microscopic features

Negative crystals, with or without CO_2 gas bubbles, were commonly observed alongside mineral inclusions, such as oligoclase feldspar, calcite, and muscovite, in these sapphire samples. Brown silk inclusions were prominent in both HS and LS groups, as shown in Fig. 2 (G22SF, G18LS, and G04HS for Fig. 2a, Fig. 2b–c, and Fig. 2d–f, respectively). Micro–Raman spectroscopy was used to identify CO_2 and mineral inclusions. Although brown silk inclusions, typically needle–shaped and aligned with color banding (Fig. 3a), were often less than 1 µm in diameter and difficult to identify, irregular or flaky platelet forms (Fig. 3c) were also noted.~~Negative crystals with/without CO_2 gas bubble appeared to be the common internal feature as well as mineral inclusions (e.g., oligoclase feldspar, calcite, and muscovite) that were usually found in these sapphire samples. Additionally, brown silk inclusions were clearly recognized in high-density silk and low-density silk groups. Fig. 2 presents the most common micro-inclusions found in these samples. Micro-Raman spectroscopy was applied for identification of CO_2 and mineral inclusions. However, brown silk inclusions, usually oriented along the color banding/zoning (Fig. 3a), were very tiny (less than 1 µm in diameter) and rather difficult to be identified by any technique. These silk inclusions were typically needle shaped, however, thin, irregular, or flaky platelets of silk inclusions (Fig. 3c) also appeared in these sapphire samples.~~

3c) were also noted.

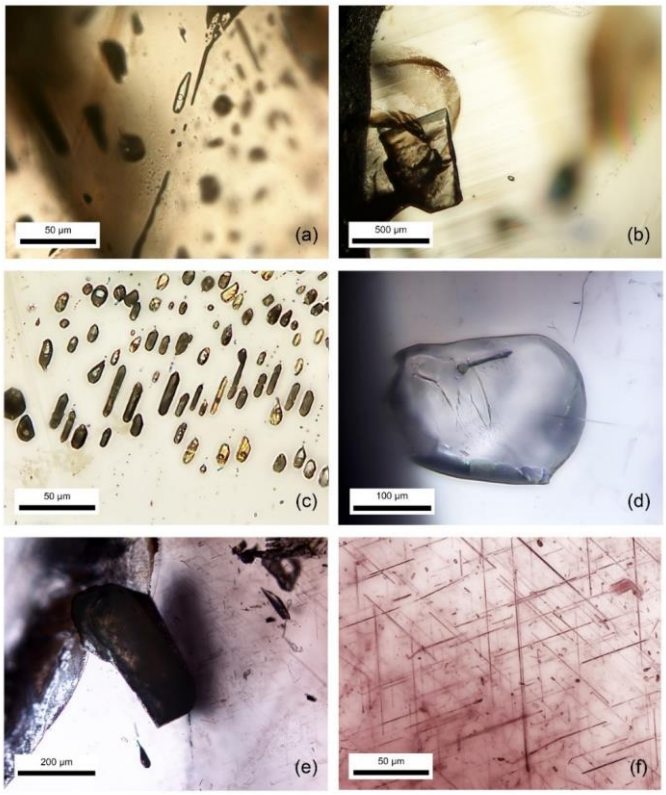

Figure 2. ~~Photomicrographs~~Transmitted–light p~~P~~hotomicrographs of inclusions including CO_2~~-~~ containing negative crystals **(a)**, calcite **(b)**, cluster of negative crystals **(c)**, oligoclase **(d)**, muscovite **(e)**, and brown silks **(f)** in natural unheated sapphire.

After high~~–~~temperature heating, molten surfaces (Fig. 3e) and decomposed crystal inclusions were commonly observed in these ~~sapphire~~ samples. The most notable alteration was also detected in the initial area of brown silks (Fig. 3a), which exhibited distinct bluish color banding/zoning (Fig. 3b) after heating.

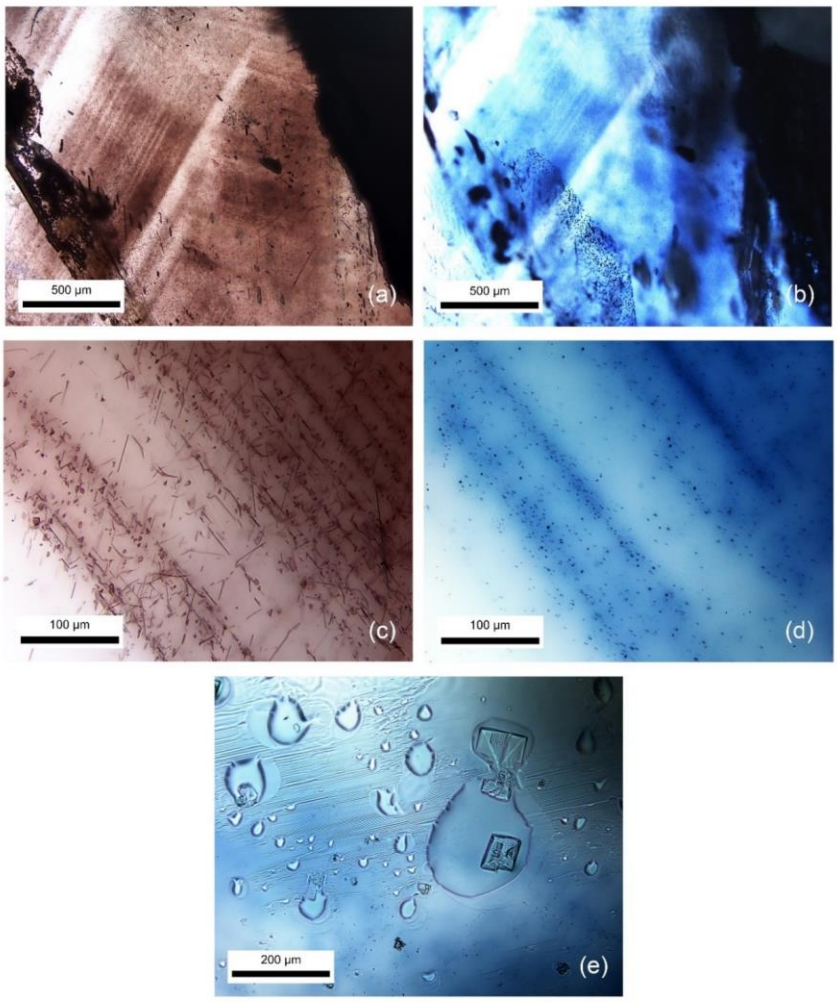

Figure 3. Transmitted ~~—~~light photomicrographs showing ~~that~~that b~~B~~rown banding **(a)** with irregular platy brownish flakes and tiny needles **(c)** in natural unheated sapphire ~~samples~~samplesample G04HS turned into blue color banding **(b)** with blue dots **(d)** ~~after~~ upon heating. Melted surface **(e)** was also observed after heat treatment.

The brown silks (Fig. 3c) experienced a transformation upon heating into blue dots (Fig. 3d). Additionally, melt inclusions among blue dots were likely developed by melting of brown silks with collaborative reaction of the sapphire host, which have never been reported elsewhere, becoming significantly noticeable and useful for indicating heat treatment of sapphire (Fig. 4).

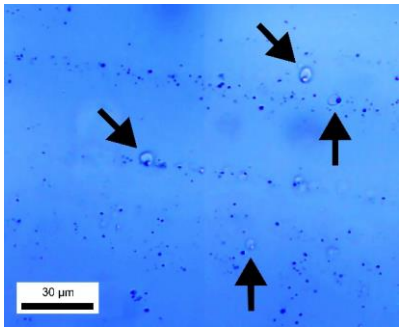

Figure 4. ~~Melt~~M~~T~~ransmitted light photomicrograph showing melt inclusions (arrows) among blue dots transformed from silk inclusions in sapphire after heating (sample G04HS).

3.4 Optical (UV–VIS–NIR) spectroscopy

The optical spectra of representative sapphire samples are presented in Fig. 5. Absorption peaks at 374, 388, and 450 nm, as well as bands around 580 and 880 nm, were observed. Optical spectra have been studied on unheated and heated sapphire by numerous previous researchers (e.g., Ediriweera and Perera, 1989; Perera et al., 1991; Emmett and Douthit, 1993; Hughes, 1997; Kyi et al., 1999; Emmett et al., 2003; Sripoonjan et al., 2014; Hughes, 2017; Pisutha-Arnond, 2017; Themelis, 2018; Palke et al., 2019; Soonthorntantikul et al., 2019; Dubinsky et al., 2020). The 374, 388, and 450 nm peaks as well as the 880 nm band were proposed to be attributed to Fe, the 580 nm band to the Fe–Ti pair. After heating, all samples showed a significant increase in the main Fe–Ti pair related absorption band at around 580 nm (Figs. 5a–c), whereas Fe–Fe related absorption at around 880 nm was obviously increased in some samples (i.e., Figs. 5a and 5c). The intensified absorption of the 580 nm band in these samples is referred to an increase of Fe–Ti pairs after heating which leads to enhanced blue coloration in heated sapphires.

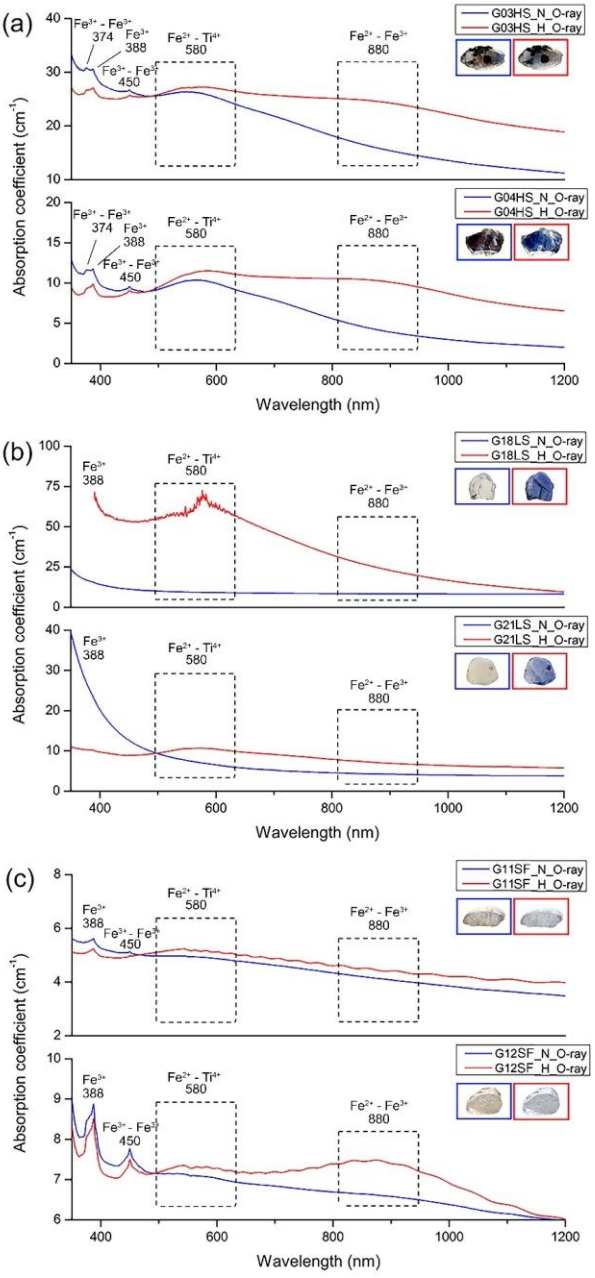

Figure 5. Optical absorption spectra of untreated (blue lines) and heated (red lines) samples: **(a)** ~~high-density silk~~HS group (G03HS, G04HS); **(b)** LS group (G18LS, G21LS); **(c)** ~~silk-free~~SF group (G11SF, G12SF). Sizes of stones range between ~~0.~~4 and 12 mm.

Spectral characteristics of corundum containing Fe^{3+} ions exhibit a high degree of complexity. It is noteworthy that Fe^{3+} has electron configuration d^5 resulting in a crystal field spectrum with ground state $^6A_1$ (Ferguson and Fielding, 1972). Small peaks at 374 nm ($^4E^b$) and 450 nm ($^4A_1$,$^4E^a$) should be attributed to the enhanced absorption of Fe^{3+}–Fe^{3+} pairs (McClure, 1962; Ferguson and Fielding, 1971; Krebs and Maisch, 1971; Ferguson and Fielding, 1972) as well as a weak broadband absorption at 540 nm ($^4T_2$) which could not be seen in this work. The distinct peak observed at a wavelength of 388 nm ($^4T_2{}^b$) (Krebs and Maisch, 1971) is linked to the individual Fe^{3+} ions. This, however, does not rule out the possibility of a higher-order cluster with extra ions or other point defects (Emmett et al., 2003). Additionally, there is also a broad band at a wavelength of 330 nm ($^4T_1{}^b$) which is interpreted as a Fe^{3+}–Fe^{3+} pair absorption (Ferguson and Fielding, 1972). This is also present in the spectra of heated samples G03HS and G04HS, as well as in all spectra of sample G12SF in this study. In trace contents both Fe^{2+} (d^6) and Ti^{4+} (d^0) ions alone do not exhibit any absorption in corundum in the visible range (Townsend, 1968); on the other hand, Fe^{2+}–Ti^{4+} pairs ($t_2 \rightarrow {}^2E$) (Ferguson and Fielding, 1971) may yield a broad band absorption around 580 nm (E⊥c), or 700 nm (E∥c) (Dubinsky et al., 2020). The Fe^{2+}–Fe^{3+} pair gives rise to the broad absorption band at ca. 880 nm (Fig. 5; Ferguson and Fielding, 1972).

3.5 FTIR spectroscopy

FTIR spectra of most samples yielded identical patterns within the range of 1600–4000 cm^{-1} (Fig. 6). They usually showed CO_2 peaks (at 2339 and 2360 cm^{-1}), as well as C–H stretching related peaks ((at 2856 and 2925 cm^{-1}), likely from artefacts ~~turbidity ((~~Fig. 6, blue lines), in accordance with Hughes ~~(2017)~~(2017) and Soonthorntantikul et al. (2021). However, O–H stretching of boehmite/diaspore peaks ((at 1975 and 2105 cm^{-1}) (Delattre et al., 2012; Sun et al., 2015; Choi et al., 2017; Filatova et al., 2021; Soonthorntantikul et al., 2021) was only observed in sample G03HS ~~from the high-density silk group ((~~Fig. 7a, blue line). Weak absorption features of O–H stretching from H_2O (broad band at ca. 3400 cm^{-1}) and OH groups (ca. 3600–3700 cm^{-1}) were only found in the untreated samples (blue lines), see Fig. 6a.

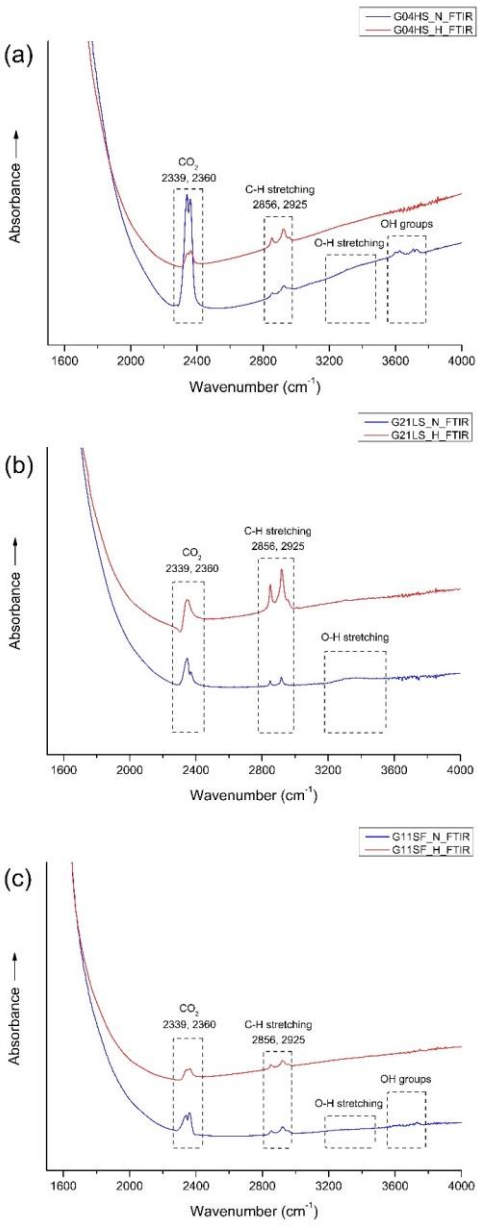

Figure 6. FTIR spectra obtained before ~~(~~(blue lines) and after ~~(~~(red lines) heating experiments of representative samples G04HS **(a)**, G21LS **(b)**, and G11SF **(c)** ~~of the high-density silk group **(a)**, low-density silk group **(b)**, and silk-free group **(c)**.~~, respectively.

After heating, boehmite/diaspore–related absorption peaks (only observed in sample G03HS ~~of the high-density silk group~~, Fig. 7a) at 1975 and 2105 cm^{-1} disappeared. In contrast, the 3309 cm^{-1} hydroxyl (O–H) absorption, which was not present in any natural sample before heating, appeared only in sample G18LS ~~of the low-density silk group~~ after heating (Fig. 7b, red line). ~~It should also be mentioned that the presence of CO_2 peaks at 2339 and 2360 cm^{-1}, as well as the C-H stretching related peaks at 2856 and 2925 cm^{-1} of all samples remained the same after heating. In contrast, their intensities vary dramatically (see Figs. 6 and 7).~~

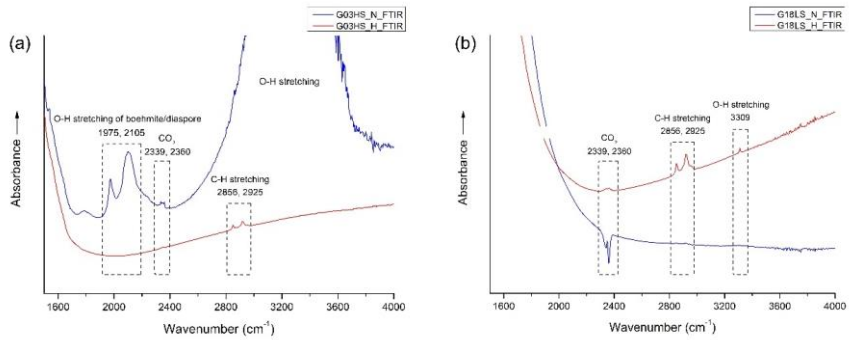

Figure 7. FTIR spectra obtained before (blue lines) and after (red lines) heat treatment of samples G03HS ~~of high-density silk group~~ **(a)** and G18LS ~~of low-density silk group~~ **(b)**.

~~To detect the heat treatment in corundum, FTIR spectroscopy is a recommended tool. In some circumstances, the presence or absence of certain FTIR features in the O-H absorption region (3100-3600 cm^{-1}) could be used as an indicator of heat treatment (Smith, 1995; Beran and Rossman, 2006; Saeseaw et al., 2018; Saeseaw et al., 2020). For example, the presence of the 3309 cm^{-1} FTIR absorption peak was used as an indicator of heated corundum (Hughes and Perkins, 2019; Saeseaw et al., 2020; Soonthorntantikul et al., 2021). However, there were some inconsistencies presented recently: in some cases the 3309 cm^{-1} peak was also found in unheated sapphire, thus it is not a reliable indicator of heat treatment (Hughes, 1997, 2017; Hughes and Perkins, 2019; Saeseaw et al., 2020; Soonthorntantikul et al., 2021).~~

In this study, an absence of O–H absorption in the 3100–3600 cm^{-1} range in all natural geuda sapphire samples, together with the development of a weak absorption at 3309 cm^{-1} upon heating in only one of the samples (see Fig. 7b, red line), address the limitation to differentiate unheated and heated sapphire by FTIR spectroscopy. Furthermore, heat treatment employed in this study did not involve the use of any additional gases, such as hydrogen, to create a reducing atmosphere within the furnace. Despite this, the 3309 cm^{-1} absorption band was seen after the heating process. This might be in accordance with an explanation proposed earlier by Notari et al. (2018).

The controversy of the presence of an O–H peak in the FTIR spectrum in unheated and heated sapphire could be attributed to an inherent hydrogen content of the corundum. Hydrogen was found in corundum, primarily in the form of alumina hydrates (Notari et al., 2018). These hydrates could release

hydrogen through de-hydroxylation at temperatures as low as ~~approximately~~approx.approx. 450 °C. Additionally, hydrogen was present in the air as H_2O, which can be split at temperatures around 900 °C to produce hydrogen gas (H_2) and oxygen gas (O_2) through the reaction $2H_2O \rightarrow 2H_2 + O_2$ (Notari et al., 2018).

3.6 Photoluminescence imaging and spectroscopy

Photos presenting luminescence of some samples both before and after heat treatment are shown in Fig. 8. Before heating, all natural sapphire samples were inert to SWUV light; moreover, all ~~low-density-silk~~LS and ~~silk-free~~SF samples exhibited orange to red luminescence under LWUV light (Fig. 8). After heating, all ~~low-density-silk~~LS and ~~silk-free~~SF samples, exhibited intense blue luminescence under SWUV light whereas their initial orange to red luminescence under LWUV light turned into a strong purplish red luminescence (Fig. 8, samples G06LS and G20LS in particular). In summary, the ~~high-density-silk~~HS~~HS~~ samples were all inert to SWUV and LWUV light both before and after heating. Notably under LWUV light, an initial orange to red luminescence of a few samples from the ~~silk-free~~SF group was drastically reduced after heating (e.g., G23SF in Fig.8).

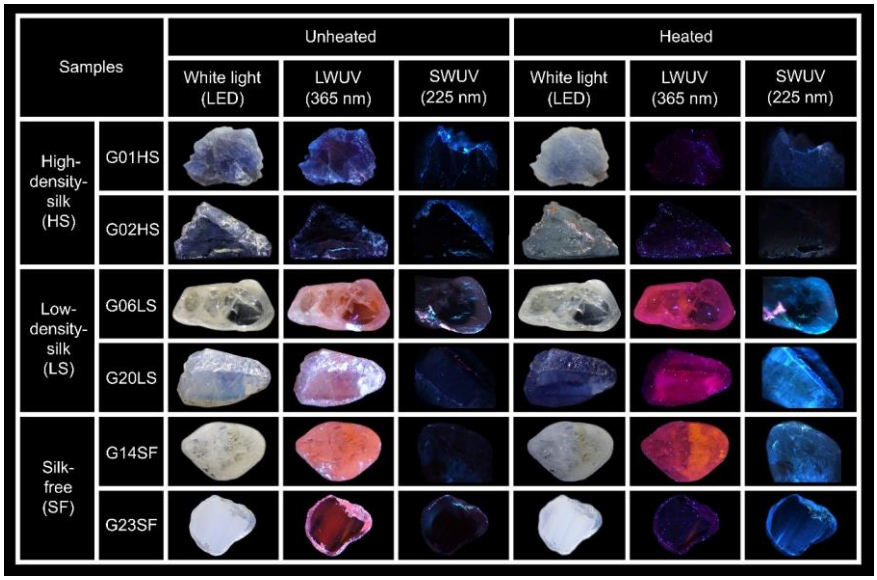

Figure 8. ~~Representatives~~Representative images of ~~high-density-silk~~HS (G01HS, G02HS), ~~low-density-silk~~LS (G06LS, G20LS), and ~~silk-free~~SF (G14SF, G23SF) groups obtained under LWUV and SWUV illumination before and after heating. Sizes of stones range between ~~0.~~4 mm and 12 mm.

The UV-excited ~~photoluminescence~~ PL ~~(PL)~~PL spectra showed that all the unheated and heated sapphire samples have an identical feature of two narrow peaks of trace Cr^{3+} lines at around 692.8 and 694.2 nm (Fig. 9) that are assigned to the spin-forbidden $^2E \rightarrow {}^4A_2$ relaxation of trace Cr^{3+} (Nelson and Sturge, 1965). However, the Cr^{3+} lines of some samples (Fig. 9c) are too weak to be visible

within the noise of a broad and strong emission band. All unheated sapphire samples showed a similar emission band in the orange to red region centered around 630–650 nm (Fig. 9a–c, blue line). Remarkably, this appears to be associated with orange to red luminescence under LWUV light, as noted by (Segura, 2013; Vigier et al., 2021a, b, c; Vigier and Fritsch, 2022). Despite having the emission band around 630–650 nm, only unheated sapphire from HS group ~~s with high-density silk~~ appeared inert under LWUV illumination while the others revealed orange to red luminescence.

After heating, significant alteration in the emission band was observed, as depicted by the red lines in Fig. 9a–c. The photoluminescence spectra of sample G03HS ~~from the high-density silk group~~ exhibited a notable reduction in the emission band through the visible region (Fig. 9a, red line). This went along with a lack of luminescence both under SWUV and LWUV excitation, whereas sample G12SF ~~(silk-free group)~~ demonstrated a slight increase of the emission band in the orange to red region (Fig. 9c, red line). More details are given in the discussion part below.

In contrast to the other groups, after heating, sample G21LS ~~of the low-density silk group~~ (Fig. 9b, red line) exhibited a significant emission band in the green region at around 525 nm. Note that this broad emission is excited with the 325 nm laser (Fig. 9) but does not seem to affect significantly the emission colors observed under SWUV (~~254~~225~~54~~ nm) and LWUV (365 nm) excitation (Fig. 8). For a discussion of the possibly strong dependence of emission intensity (and color) on the excitation wavelength see for instance Zeug et al. (2022). Likewise heated sapphire has been proposed to have an emission band in the blue region, which corresponds to blue luminescence under SWUV light (Nassau, 1981; Hughes, 2017; Vigier et al., 2023).

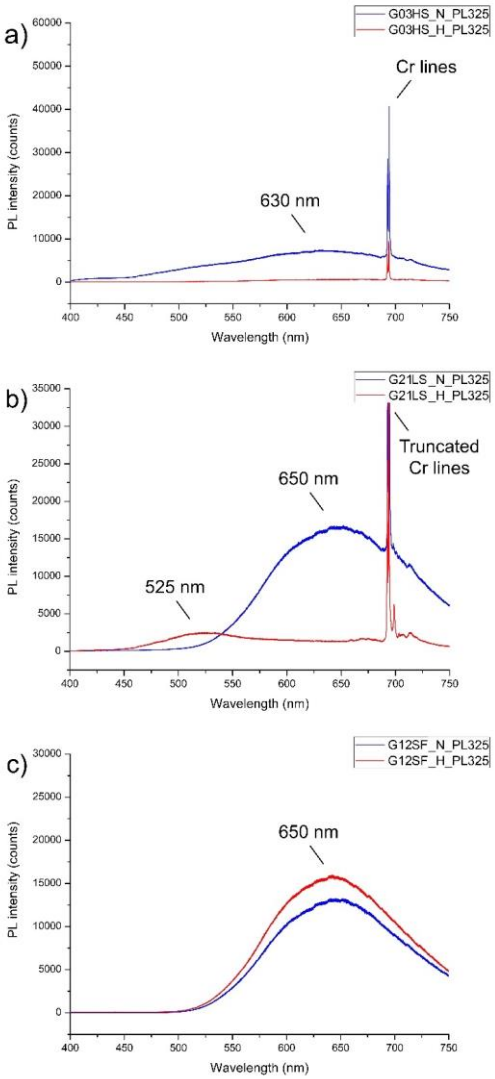

Figure 9. Representative photoluminescence (UV–excited) spectra obtained before (blue lines) and after (red lines) heating of sample G03HS ~~of high-density silk group~~ **(a)**, sample ~~G21 of low-density silk group~~G21LS **(b)**, and sample ~~G12 of silk-free group~~G12SF **(c)**.

4 Discussion

4.1 Generalities

After Ti^{4+} being exposed to SWUV light, they yield luminescence (Nasdala and Fritsch, 2024). However, blue luminescence was not observed in both unheated and heated basaltic sapphire, possibly due to the abundant presence of Fe^{2+} of basaltic origin that may strongly quench such blue luminescence (Soonthorntantikul et al., 2019). More details will be discussed in this report. Furthermore, even though microscopic inclusions have been the distinguishing characteristics of heated sapphire, identifying heat–treated sapphire remains challenging (Crowningshield, 1966; Hughes, 2017). FTIR spectroscopy ~~have~~has also been applied to detect heated sapphire. In some cases, the presence or absence of specific FTIR features in the O–H absorption region (3100–3600 cm^{-1}) may serve as an indicator of heat treatment (Smith, 1995; Beran and Rossman, 2006; Saeseaw et al., 2018); however, it is probably not a conclusive evidence (Ediriweera and Perera, 1989; Perera, 1993; Sutthirat et al., 2006; Cartier, 2009; Jaliya et al., 2020). For example, the presence of the 3309 cm^{-1} FTIR absorption peak was used as an indicator of heated corundum (Hughes and Perkins, 2019; Soonthorntantikul et al., 2021). However, recent discoveries show that this peak may also be found in unheated sapphire, suggesting that it is not a reliable indication of heat treatment ~~indication~~ (Hughes, 1997, 2017; Hughes and Perkins, 2019; Soonthorntantikul et al., 2021).

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4.2~~1~~ Silk inclusions and coloration of sapphire

Studies addressing brown silk inclusions in corundum are scarce. Soonthorntantikul et al. (2021) reported a mix of whitish silk and irregular/flaky/platelet-like brownish silk inclusions in corundum from Mogok. Brown silk was ascribed as presumable ilmenite ($FeTiO_3$) which is noticeable in high-Fe sapphire, whereas white silk was suggested to consist of rutile (TiO_2). The brown silks seen in our sapphire samples are likely ilmenite, which is supported by their irregular/flaky/platelet-like brownish appearance and their high Fe and Ti contents (note that the highest quantity of Fe was found in the HS group). Ilmenite decomposition upon heat treatment does result in Fe and Ti migration into the host sapphire and subsequently causes blue coloration. In particular, the decomposition of brown silks during heat treatment induces the formation of blue dots, which is a result of the Fe^{2+}–Ti^{4+} pairing formation. Upon closer inspection using a high-resolution microscope, these blue dots reveal distinct micro-inclusions as melt inclusions (with size of ≤1 μm, see Fig. 4), which have never been documented before. However, it should be noted that these melt inclusions are possibly derived from the decomposition of silks.

This work focuses only on blue coloration in sapphire which mainly relates to the Fe^{2+}–Ti^{4+} pair, as initially noted by Townsend (1968), followed by Mattson and Rossman (1988), Moon and Phillips (1994), and Emmett et al. (2003). Ti exhibits electron-donor properties, whereas Fe may function as an electron acceptor. When occupying neighboring Al^{3+} positions, absorption due to intervalence charge transfer between such donor-acceptor pairs may occur (details reported by Emmett et al., 2003 and Monarumit et al., 2023).

It should also be mentioned that Ti^{4+} ions do not exhibit any absorption characteristics in the visible spectrum when considered individually. The Ti^{4+} ion has a closed-shell electron configuration, whereas the Fe^{2+} ion mainly absorbs wavelengths within the near infrared and low-energy visible regions. In contrast, when Fe^{2+} and Ti^{4+} ions are situated on neighboring structural sites, notable absorption bands

develop across the visible and near-infrared spectral regions. These Fe^{2+}–Ti^{4+} pairs exhibit a band center at around 580 nm (see Fig. 5) when the electric field vector E is perpendicular to the crystallographic c-axis (E⊥c), but a peak at 700 nm is seen when the electric field vector E is parallel to the crystallographic c-axis (E||c) (Dubinsky et al., 2020). Although the theory of the energy levels of an individual transition metal ion inside a crystal has been extensively explored, the corresponding theory for ion pairs or clusters within a crystal remains underdeveloped (Dubinsky et al., 2020).

In ~~this~~the present~~is~~ study, the natural unheated geuda sapphire samples were placed in atmospheric conditions and subjected to a maximum temperature of 1650 °C for a duration of 10 h. According to the exsamples presented in Fig. 1, samples G03HS and G04HS ~~with high-density silk inclusions~~ exhibited a noticeable increase in blue coloration, particularly around the area of brown silks and brown color banding/zoning, after heating. On the other hand, the initial blue patch (e.g. samples G01HS and G02HS) became paler blue after heating, which might be due to the breakage of initial Fe–Ti pairs in those areas. The other groups, which have yellowish and/or milky appearances, revealed an increase in blue color after heating (samples G12SF and G18LS, Fig. 1). This blue coloration is attributed to two distinct factors, notably the ~~dissolving~~ decomposition of silk inclusions and a subsequent charge transfer mechanism (Emmett and Douthit, 1993; Hughes, 1997, 2017; Nassau, 1980, 1981; Themelis, 2018). The process of charge transfer (Ferguson and Fielding, 1972; Nassau, 1981) is described as:

$$Fe^{2+} + Ti^{4+} \rightleftarrows Fe^{3+} + Ti^{3+} \quad (1)$$

It is important to note that the blue color observed in sapphire could also be produced with the application of heat in oxidizing conditions at high temperature. Heat treatment can be classified as high– or low–temperature according to the decomposition of rutile silks in corundum (Nassau, 1981; Emmett and Douthit, 1993; Emmett et al., 2003; Hughes, 2017; Hughes and Perkins, 2019). The term low–temperature heat treatment has been used (typically referred to as below 1000 °C) when rutile particles still reveal their original structures. On the other hand, temperatures beyond 1350 °C denote high–temperature heat treatment when rutile silks start to decompose and dissolve within the corundum host (Hughes, 2017; Themelis, 2018). Consequently, internal diffusion (indicated by a colored halo surrounding the crystal inclusion), molten or altered inclusions, and/or broken silk are strong indicators of high–temperature heat treatment. However, low–temperature heat treatment can also produce various altered mineral inclusions (Kammerling et al., 1990; McClure and Smith, 2000; McClure et al., 2010; Pisutha–Arnond, 2017; Soonthorntantikul et al., 2019).

In recent studies, the possibility of employing Fe^{2+}–Fe^{3+} charge transfer as an alternate method for blue coloration has also been mentioned (Nikolskaya et al., 1978; Schmetzer and Kiefert, 1990; Häger, 1992, 2001; Sripoonjan et al., 2014; Pisutha–Arnond, 2017). However, it is necessary to emphasize that this approach was considered highly improbable (Nassau, 1981). Nevertheless, previous studies have indicated that a minor proportion of geuda sapphire from Sri Lanka and geuda-like sapphire from Mogok in Burma revealed an alteration in color to blue when subjected to heating in an oxidizing environment (Hughes, 1997, 2017; Kyi et al., 1999), which is in complete contradiction to the treatment method employed for the geuda sapphire in a reducing condition. The appearance of certain stones displaying a blue coloration under oxidizing conditions might be attributed to the presence of ilmenite silks, which is composed of Fe and Ti, with Fe in its reduced Fe^{2+} state (Hughes, 1997). Therefore, it is unnecessary to

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reduce Fe^{3+} to Fe^{2+} ions to generate the Fe^{2+}–Ti^{4+} pairs that are responsible for the manifestation of the blue color. Hence, the blue areas have a substantial concentration of Fe ions in form of Fe–Ti pairs, derived from the decomposed ilmenite silk inclusions.

According to Nassau (1981) and Koivula (1987), the presence of blue dots in heated sapphire is attributed to remains of dissolved silk inclusions and internal cation diffusion. The diffusion process is positively correlated with temperature and duration of heat treatment (Nassau, 1981). Despite the slow diffusion rates of Fe and Ti, the distances across are extremely short, i.e., just a few micrometers (Nassau, 1981). Consequently, a potential Fe–Ti combination within the corundum's lattice may generate the blue dots.

The presence of melt inclusions among the blue dots after high-temperature heating might be due to the decomposition of brown silk and its solubility into the host sapphire as demonstrated by Jung et al. (2009). They predicted a phase relationship within the Al_2O_3–Ti_2O_3–TiO_2 system based on experimental data and thermodynamic calculation. Consequently, they suggested that a liquid phase (the composition of the liquid inclusion phase varies significantly between Al_2O_3 and Ti_3O_5) could possibly be present at a temperature of 1600 °C and slightly below, which is close to the heating temperature (1650 °C) of our experiment. Silk inclusions as represented by Ti_2O_3–TiO_2 components may have dissolved into the host sapphire (Al_2O_3 component), and produced a proper composition of solution which could be melted partially at ≤ 1650 °C. Some of these melts can be preserved as inclusions after cooling down.

4.32 Luminescence of sapphire

Luminescence of corundum may be assigned to two types, namely (a) emissions of impurity-related centers such as Ti^{4+} (commonly known) and (b) emissions of defect-related centers, which typically involve either vacancies, such as oxygen (O) or aluminum (Al) vacancies known as F center (color center; from the German "*Farbzentrum*"), or interstitials (Al_i and O_i), possibly trapped at impurities (less known), or both (Viger et al., 2021a–c). This means that defect-related emission centers in corundum refer to an inconsistency in the atomic arrangement limited to one or a few atoms (often called color-centers). O vacancies (or electron holes) are sometimes called hole centers, because the holes simply designate the absence of an electron. The holes are sometimes filled with one or two electrons in order to maintain electroneutrality (Vigier et al., 2021a).

As presented in Fig. 8, a notable orange to red luminescence is easily noticeable under LWUV excitation in most unheated sapphire samples, except for those of the ~~high-density-silk~~HS group, which appear inert. After heat treatment, the orange to red luminescence that is initially observed in all samples of the ~~low-density-silk~~LS group and many samples of the ~~silk-free~~SF group turns into a purplish-red luminescence. In contrast, no orange to red or purplish red luminescence is observed in any sample of the ~~high-density-silk~~HS group both before and after heating.

The origin of orange to red luminescence in sapphire remained controversial, with varying ideas among researchers (Vigier et al., 2021a, b, 2023). The occurrence of orange luminescence has been documented in some previous studies (e.g. Spencer, 1927; Kane, 1982; Emmett et al., 2003; Fritsch et al., 2003; Nasdala and Fritsch, 2024). In the beginning, it was hypothesized that this luminescence is associated with the geographic origin of yellow sapphire from Sri Lanka (Webster, 1984). Subsequently,

Segura ~~(2013)~~(2013) presented an alternative argument to this notion, suggesting the presence of orange luminescence in various colors of corundum, regardless of treatment or synthetic origin, might be attributed to the existence of some defects. However, the orange to red luminescence observed in our study (characterized by a broad emission band) seems to be associated with complex defect–related centers. ~~As previously stated, orange to red luminescence was proposed to be attributed with an F center or defect characterized by the occurrence of two O vacancies (Vigier et al., 2021a, b). An O vacancy refers to the absence of an O atom in the structure. It has the potential to remain an empty vacancy or to incorporate one or two unpaired electrons (Vigier et al., 2021a, b).~~

~~However, it is possible that these defects may originate from boehmite/diaspore, which undergo oxidation (Strange et al., 2022), dehydration (Gog, 2021), or dehydroxylation (Ananthakumar et al., 1998) at temperatures exceeding 400 °C (Vlaskin et al., 2016). This process occurs through the decomposition of $2AlO(OH) \rightarrow Al_2O_3 + H_2O$ (Kloprogge et al., 2002; Sifontes et al., 2019). Therefore, when subjected to heating, these hydrated aluminas decompose and expell water (Samadhi et al., 2011). This could result in the development of defects related to dehydration (Gog, 2021), which may be linked to the F center as mentioned above.~~

Orange to red luminescence in sapphire is not due to impurities (Vigier et al., 2021a, b). HS sapphire (e.g., with ilmenite, $FeTiO_3$) lack noticeable luminescence, likely because Fe^{2+} suppresses luminescence, contrasting with LS and SF sapphire, which display stronger luminescence both before and after heating. While sample G23SF shows decreased purplish–red luminescence after heating, most display increased purplish–red luminescence, potentially due to complex, defect–related centers in the sapphire lattice. Observations suggested that Fe^{2+} acts as a luminescence quencher in the orange to red range (Andrade et al., 2008; Norrbo et al., 2016; Vigier et al., 2021a, b, c; Vigier and Fritsch, 2022); Orange luminescence generally appears in colorless, low–Fe areas (Segura, 2013; Notari et al., 2003). However, a definitive explanation remains unresolved. ~~Furthermore, it is important to note that the orange to red luminescence is not attributed to any impurities (Vigier et al., 2021a, b). In addition, the absence of noticeable luminescence in high-density silk sapphire samples (see Fig. 8), both before and after heat treatment, can be attributed to the presence of significant amounts of brown silks (ilmenite, $FeTiO_3$), where Fe^{2+} is suggested to play an important role to suppress luminescence. This contrasts with samples of the low-density silk and silk-free groups, which exhibit more distinct orange to red luminescence both before and after heating. Even though an orange to red luminescence of a few samples (e.g., G23) decreases after heating, increasing of orange to red luminescence to a purplish red luminescence in most samples upon heating is generally observed (Fig. 8). This might be due to the remaining of altered, complex defect-related centers in the sapphire lattice as mentioned earlier whereas the disappearance of orange to red luminescence in a few samples (see Fig. 8, sample G23) might be due to the disappearance of defects after heating. Moreover, the orange luminescence was proposed to be seen generally in colorless areas (Segura, 2013), which were described later on as low Fe-containing areas (Notari et al., 2003). Therefore, Fe^{2+} serves as a quencher of luminescence for emissions in the orange and red spectral range (Andrade et al., 2008; Norrbo et al., 2016; Vigier et al., 2021a, b, c, 2023; Vigier and Fritsch, 2022). However, an exact clarification has never been established.~~

Regarding blue luminescence, it has been observed that upon exposure to SWUV light, all natural unheated ~~sapphire~~ samples appeared inert. After heating, apart from ~~high-density-silk~~HS sapphire, a distinct blue luminescence has been detected throughout most heated sapphire samples (Fig. 8). Previous studies suggest that luminescence in sapphire becomes noticeable only at heating temperatures of 1000 °C ~~It was previously suggested that luminescence in sapphire is not noticed until they are heated up to a temperature of 1000 °C~~ (Hughes and Perkins, 2019), at which point blue luminescence is linked to heat treatment detection. This luminescence is believed to arise from silk inclusions composed of TiO_2, commonly found in natural blue sapphire. ~~. At this point, the discernible blue luminescence observed in sapphire has been linked to the detection of heat treatment. This blue luminescence was proposed to be attributed to the presence of silk (Hughes and Perkins, 2019) since the majority of natural blue sapphire usually show the exsolved silk, which is composed of TiO_2.~~ Notably, despite the relatively low Ti concentration (0.02–0.03 wt% oxide) in comparison to Fe (0.05–0.08 wt% oxide) in some samples (e.g., G12SF and G21LS ~~of the silk-free and low-density-silk groups, respectively~~), blue luminescence remains ~~this blue luminescence is still detected.~~detectable. In contrast, HS samples (e.g., G02HS) show an absence of blue luminescence, likely due to the presence of ilmenite, supporting findings by ~~Moreover, the absence of blue luminescence in high-density-silk samples (Fig. 8, sample G02) is likely attributed to the presence of ilmenite. This corresponds to previous studies conducted by Norrbo et al.~~Norrbo et al. (2016), Andrade et al. (2008), as well as Vigier et al. (2021a–c; 2023) that Fe^{2+} acts as a luminescence quencher. Blue luminescence has been associated with the interaction between O^{2-} and Ti^{4+} ions (Evans, 1994; Wong et al., 1995b; Nasdala and Fritsch, 2024), followed by a later hypothesis of a charge transfer process involving Ti^{4+} ions and certain defect–related centers (Lacovara et al., 1985; Mikhailik et al., 2005). However, it was widely accepted that the blue luminescence (characterized by a broad emission band at blue to green region) observed in sapphire under SWUV illumination is associated with the presence of Ti impurities, which are classified as element–related defects (Vigier et al., 2021a, b). Thus, it is likely that the blue luminescence reported in this work is associated with Ti impurities, whereas orange to red luminescence seems to be associated with complex defect–related emission centers.

The correlation between the orange to red PL emission band (approx. 650 nm, Fig. 9 blue lines) and orange to red luminescence in unheated sapphire (Fig. 8), as well as the emission band (approx. 525 nm, Fig. 9 red lines) and blue luminescence in heated sapphire (Fig. 8), is particularly evident in the LS group (Fig. 9b). In contrast, the HS group shows a reduction in emission across the visible spectrum after heating, indicating inertness under LWUV and SWUV excitation (Fig. 9a). The SF group exhibits a notable increase in the red emission band (Fig. 9c) and intense purplish–red luminescence under LWUV excitation after heating. Interestingly, this group also displays strong blue luminescence under SWUV excitation despite the absence of a corresponding blue emission band, likely due to the 325 nm excitation laser used in our PL investigation. Variations in excitation wavelengths significantly affect observed emissions, as noted by Wong et al. ~~The correlation between the orange to red PL emission band (approx. 650 nm, Fig. 9 blue lines) and orange to red luminescence in unheated sapphire (Fig. 8), as well as the blue emission band (approximately 525 nm, Fig. 9, red lines) and blue luminescence in heated sapphire (Fig. 8), seem to correspond with each other only in samples from the low-density-silk group (Fig. 9b). The high-density-silk group exhibits a reduction in the emission band throughout the whole visible spectrum after~~

~~heating, corresponding to an inertness under LWUV and SWUV excitation (Fig. 9a). The significant increase in the red emission band (Fig. 9c) of the silk-free group corresponds to an intense purplish-red luminescence under LWUV excitation after heating. Notably it also displays a strong blue luminescence under SWUV excitation after heating despite the lack of a blue emission band; this is possibly due to the 325 nm excitation laser used in our PL investigation. Due to absorption-emission conditions, it is obvious that changing excitation wavelengths have substantial impact on the observed emission. Even in the narrow range of 254, 325, or 365 nm UV excitation, significant differences in emission are expected. This was presented by Wong et al.~~(1995a) and Vigier et al. (2023), who showed that their sapphire emission band at 425 nm was only visible with a 254 nm excitation laser. Utilizing distinct SWUV (225~~5~~4 nm) and LWUV (365 nm) lasers, or conducting excitation spectroscopy, may yield more accurate results compared to relying solely on a 325 nm laser. Thus, the presence of orange to red luminescence at approx. 650 nm and blue luminescence at around 525 nm are vital indicators for differentiating unheated and heated sapphire. ~~whose sapphire emission band at 425 nm was obviously seen only with a 254 nm excitation laser. By employing distinct SWUV (254 nm) and LWUV (365 nm) excitation lasers, or even by conducting excitation spectroscopy, we may obtain more accurate results compared to using a 325 nm laser only. Hence, the presence of orange to red luminescence and a broad emission band at approximately 650 nm, along with blue luminescence and a broad emission band at around 525 nm, may serve as crucial indicators for distinguishing unheated and heated sapphire.~~

5 Conclusions

The present~~is~~ study demonstrates that melt inclusions (~1 µm) serve as indicators of heat treatment in sapphires and highlights the critical role of luminescence in distinguishing unheated from heated geuda sapphire. Under LWUV light, orange luminescence may arise from defect–related F centers, while blue luminescence under SWUV light likely correlates with Ti impurities. Geuda sapphires with low Fe concentrations exhibit distinct luminescence, whereas those with HS inclusions show minimal luminescence due to Fe^{2+} quenching effects. The presence of orange luminescence may be a helpful indicator for unheated geuda sapphires, while blue luminescence is generally absent in unheated samples, confirming its utility for identifying heated geuda sapphire. Although the 3309 cm^{-1} O–H stretching band from FTIR analysis alone is insufficient for differentiation, increased intensity around the 580 nm of an optical spectra effectively indicates heat treatment, as it corresponds to higher Fe–Ti pair concentrations from silk inclusion decomposition. Combining blue and/or purplish–red luminescence with additional analytical techniques provides a promising strategy for accurately distinguishing between unheated and heated geuda sapphires (Fig. 10). Future research should acquire emission and excitation spectra on the samples before and after heat treatment. Further investigation of luminescence characteristics from various sapphire origins (and colors) and clarify the specific Fe and Ti concentrations impacting luminescence is also recommended. Finally, using as low as 200–254 nm laser excitation may enhance the detection of emission shifts towards the blue region in heated sapphires, improving gemological identification criteria.

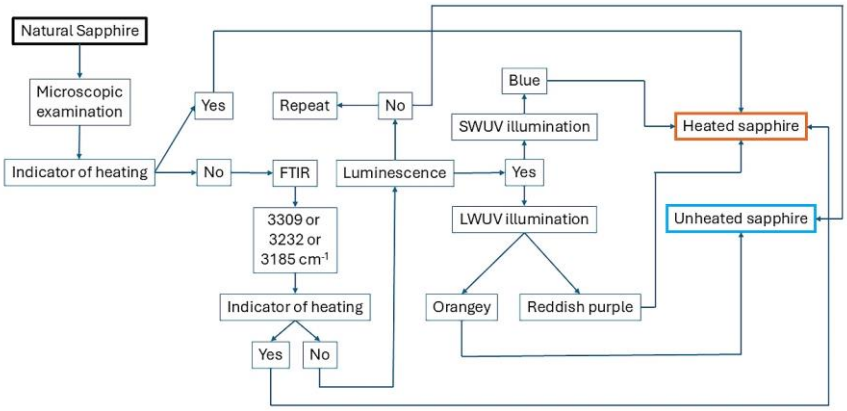

Figure 10. Flowchart proposinges the combined strategy for heated sapphire identification criteria.

~~Overall, this work presents empirical evidence of the presence of melt inclusions (~ 1 µm in size) among blue dots serving as new hint of heat treatment. Additionally, the study highlights the significance of luminescence in distinguishing unheated sapphire from their heated counterparts.~~

~~Although the occurrence or disappearance of orange to red and blue luminescence has not been conclusively elucidated, the F center (defect related center) may be responsible for orange to red luminescence, whereas the blue one may be attributed to Ti impurities. Luminescence under SWUV and LWUV excitation is likely seen only in sapphire with low Fe concentration (as supported by chemical analysis), since we barely see luminescence in the group of high density silk sapphire samples. However, the presence of orange to red luminescence under LWUV excitation may help in identifying unheated sapphire. Blue luminescence under SWUV light can also serve as a useful indicator for identifying heated sapphire since this luminescence, except for the high density silk group, is absent in all unheated sapphires studied. This may be due to the interference quenching effect of Fe^{2+}. In addition to blue, the presence of purplish red luminescence under LWUV light may also facilitate the identification of heated sapphire. For the FTIR spectra, the 3309 cm^{-1} O H stretching band alone seems to be insufficient to identify unheated or heated sapphire since the effect of additional gas used during the heat treatment as well as the internal diffusion may influence the appearance or absence of such an O H feature. Also, an increase or elevated intensity of the optical spectra at an absorption around 580 nm may indicate heated sapphire, as the majority of heated sapphire samples exhibit a greater intensity in this band due to a higher number of Fe Ti pairs, derived from a decomposition of silk inclusions after heating.~~

~~Thus, combining blue luminescence (and/or purplish red luminescence) with additional analytical techniques represents a promising strategy for distinguishing unheated and heated sapphire. Further studies should be conducted to explore the luminescence properties of sapphire originating from different origins. This will contribute to a better understanding of the factors influencing the orange to red and blue luminescence observed in these sapphire samples. It is also essential to turn attention on comparing the luminescence characteristics shown by unheated and heated colored sapphire, as well as determining the~~

~~precise Fe and Ti concentration required to affect orange to red and blue luminescence. Furthermore, to optimize the emission spectrum, it is recommended to utilize 254 nm laser excitation to obviously see a shift of the emission band towards the blue region of heated sapphire.~~

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