Sapphires Heated with *Pressure* – A Research Update

By Michael S. Krzemnicki, L. Cartier, R.W. Hughes, T. Leelawatanasuk, L. Kiefert, G. Choudhary, S. McClure, C. Milisenda, E. Gambini, S. Kim, D. Schwarz, C. Dunaigre, Y. Horikawa

Introduction

Sapphires heated with pressure reportedly entered the trade already about 10 years ago (Hughes et al. 2019), although in rather small quantities. Described in several gemological articles in the past few years (Choi et al. 2014a, 2014b, Song et al. 2015, Leelawatanasuk et al. 2016, Choi et al. 2018), this new variation of heat treatment came into the spotlight only recently, based on claims that sapphires heated with pressure have a stability issue (Peretti et al. 2018 and 2019). As a consequence, there have been extensive discussions about this topic among gem laboratories and within the gem trade, resulting in several press releases (e.g. LMHC 2018) and statements (AGTA 2018).

The following article is mainly based on a presentation (pdf file of presentation, LMHC 2019) given at the GILC Conference *(www.gemstone.org/events/gilc)* in Tucson 2019 summarizing the results of a joint research project and extensive discussion between the following laboratories and entities (in alphabetical order): CGL Central Gem Lab, Japan; CISGEM, Italy; German Gem Lab (DSEF), Germany; Dunaigre Consulting, Switzerland; Gemological Institute of America (GIA), USA; Gem and Jewelry Institute of Thailand (GIT); GJEPC-GTL, India; Gübelin Gem Lab, Switzerland; Hanmi Lab, South Korea; ICA GemLab, Thailand; Lotus Gemology, Thailand; Swiss Gemmological Institute (SSEF), Switzerland.

Historical Context of Heat Treatment and Other Treatments for Sapphires

The first account of heat treatment of rubies/sapphires dates back to circa 1045 A.D. by Al-Biruni, who described treatment at temperatures of up to 1100°C using a blowpipe, e.g. to remove the blue tint from rubies (Hughes et al., 2017). In 1916, heat treatment of dark blue (basaltic) sapphires from Queensland (Australia) was reportedly used to lighten their color (Anonymous 1916). This process was later adapted for heating all dark blue basaltic sapphires and continues to this day. It is difficult to detect heat treatment in these basaltic stones as they have already experienced a natural heating within the basaltic magma during their uplift to the Earth's surface.

As more ruby and sapphire deposits were discovered in recent decades, treatments were further developed to improve the appearance of the large spectrum of stones produced. This includes a wide range of equipment (e.g. electric muffle furnaces) and heating parameters (e.g. controlled atmosphere, temperature and treatment duration etc.). By the end of the 20th century and into the 21st century, this has led to two distinct types of treatment being applied to corundum:

A) Heating with no diffusion of coloring elements from an external source and with no addition of a flux to fill or even "heal" fissures. All variations of heating methods are commonly and since decades summarized and disclosed only as heated. *Examples: heat treatment of Geuda sapphires, low temperature heat treatment of pink sapphires, so-called "Punsiri" heat treated sapphires (Hughes et al. 2019).*

B) Heating with diffusion of coloring elements from an external source to produce color and/or assisted with a flux to fill or even "heal" fissures. In this case, each different method is specifically disclosed. *Examples: beryllium diffusion treated corundum, lead-glass filled rubies.*

Blue Sapphires Heated with Pressure

Sapphires heated with high temperatures and moderate pressures (~1kbar) first entered the market in 2009, and have become more common since 2016 (Figure 1) (Choi et al., 2014a and 2018). In late 2018, Gem Research Swisslab (GRS) issued a study claiming that such stones had durability issues (Peretti et al., 2018, 2019).

The study described in this present article sought to extensively test this material and determine how it could be gemologically characterized, review some of the stability claims that have been made and ultimately determine whether this treatment warrants specific disclosure.

The treatment itself currently is applied only on a restricted number of sapphires, as it is commonly only possible to heat a single (cut) stone per treatment run (Hughes et al. 2019, Choi et al. 2018). This is very much in contrast to other treatments such as beryllium diffusion or lead-glass filling of corundum, being carried out in batches of rough or pre-shaped stones, and which have thus penetrated the market quickly and in huge quantities.

A detailed description of the treatment conditions is given by Choi et al. (2018). When compared to a more traditional approach, this new variation of a heating process differs

Figure 1: Series of sapphires heated with pressure. (Photo: SSEF)

Figure 2: This parcel of sapphires (mostly heated) before treatment reveals the wide color range of the starting material.
(Photo: Shane McClure, GIA)

mainly in the application of (moderate) pressure of approximately 1 kbar. The advantage in applying pressure is that the reaction kinetics are sharply accelerated, thus resulting in a treatment duration of 20-30 minutes compared to hours/days with more traditional heating.

Another aspect is that it may provide a positive color modification (i.e. a more attractive and saturated blue color) in cases that do not or only insufficiently react to other heat treatments. As a consequence, this new heating process is commonly applied only on heated sapphires of metamorphic origin (e.g. from Sri Lanka) as starting material (Figure 2), with the aim to further enhance and/or modify their blue color.

It is important to note that not all stones result in better colors after the treatment with pressure. Figure 3 shows the variability of resulting colors, with some stones with no color change or even a lighter color after the treatment. Clearly, original trace element concentrations in each individual stone greatly influences the result and the outcome in terms of color. As a result of the treatment in a graphite crucible, sapphires heated with pressure have to be re-polished after treatment, very similar to most heating processes.

The potential change in color (see Figure 3) is due to the creation or intensification of the Fe^{2+}-Ti^{4+} intervalence charge transfer (IVCT), which is the "classic" cause for the blue color of both unheated and heated blue sapphires. Detailed research on trace-element chemistry using LA-ICP-MS confirms that this form of treatment is not linked to any diffusion of color causing trace elements (e.g. Be, Li or Ti) that could induce a change in color (Hughes et al. 2019).

Gemological Characterization and Identification of Pressure Treated Sapphires

An extensive study of inclusions and specific features before and after pressure treatment on sapphire samples revealed that the studied samples showed (microscopic) features and properties very similar and even indistinguishable to those induced by more conventional heat treatments. Much as with conventional heat treatment, inclusions found within a stone can exhibit typical transformations from high temperature heat treatment (Figure 4). As an example, the treatment may induce expansion fissures in certain cases, but may also lead to improvement in clarity due to the healing of fissures. Subtle differences in surface granularity of healed fissures may occur (Hughes et al. 2019), but somewhat similar features can also be seen in conventionally heated sapphires. Sometimes graphite accumulations in fissures and cavities can be found in pressure treated sapphire samples close to the surface, but this is a result of the use of a graphite-filled crucible in the treatment process.

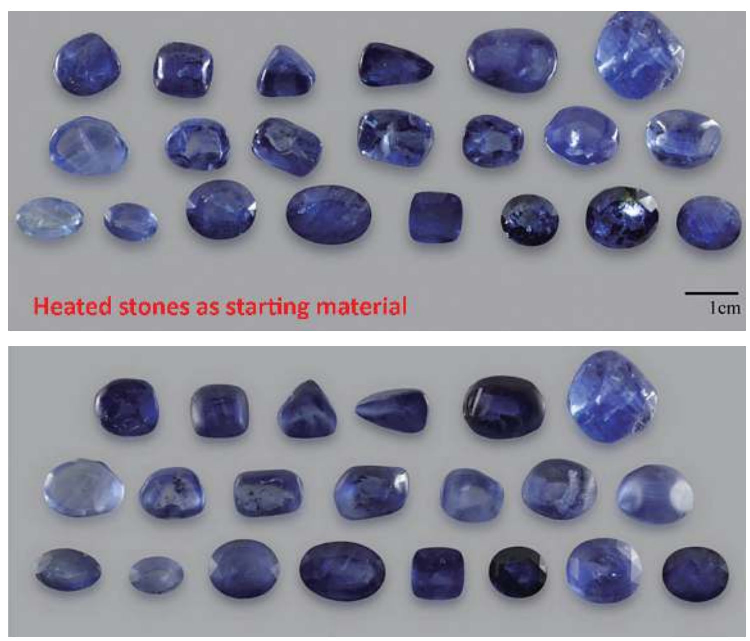


Figure 3: Top: before; Bottom: after treatment: variability of resulting colors, with some stones with no color change or even lighter color after the treatment. (Image from Choi et al. 2018.
(Photos: P. Ounorn)

In summary, in most cases there is no evident microscopic feature to detect this treatment apart from common heating features.

The UV reaction of the studied samples showed very similar features to those of "traditionally" heated sapphires. They showed partly no reaction under long and short-wave ultraviolet and partly chalky white zones at the surface under short-wave ultraviolet. As such, there is no specific ultraviolet reaction that would enable detection of this treatment.

UV-Vis absorption spectroscopy showed spectra that were very similar to any metamorphic sapphire, whether heated or unheated. Absorption spectra are dominated by Fe^{2+}-Ti^{4+} IVCT absorption band (culminating at approximately 560 nm), optionally with additional absorption peaks by Fe^{3+} and Cr^{3+} and there is no additional specific absorption feature to detect this treatment specifically.

Trace element chemistry (ED-XRF and LA-ICP-MS) measurements showed that the trace element composition is similar to other sapphires, whether heated or unheated, and is rather linked to their formation and origin (geological setting). No diffusion of beryllium or other coloring element could be detected (Choi et al. 2018, Peretti et al. 2018, Hughes 2019). Residues of the crucible filling are removed after treatment from the surface by repolishing the samples and thus not accessible anymore to chemical testing.

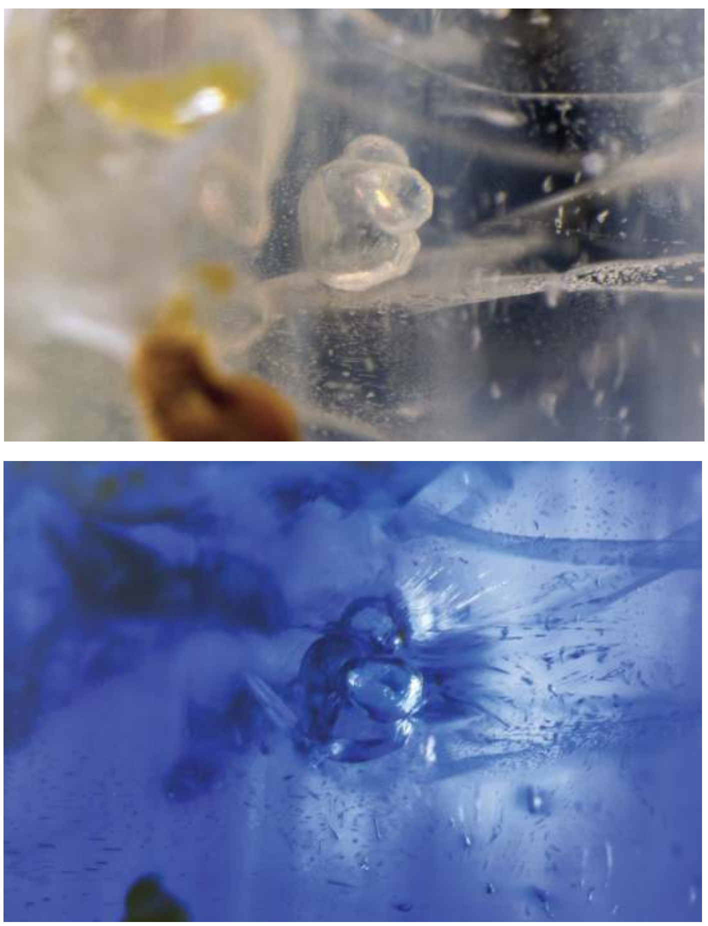


Figure 4: Sample before (top) and after (bottom) heating with pressure, showing an inclusion with a fairly typical transformation as can be expected from any high temperature heat treatment. (Photo: S. McClure, GIA)

Extensive study of FTIR spectra on pressure treated sapphire samples generally showed a distinct pattern of hydroxyl (OH^-) related absorption bands in the range of 2800-3500 cm^{-1} (Figures 5a and 5b). This might be the consequence of the few drops of water which are commonly added to the graphite crucible before treatment (Leelawatanasuk et al., 2016). However, this and further studies also revealed a great variability of infrared spectra of sapphires heated with pressure, with some samples showing only a series of OH^- peaks (3307, 3230, 3185 cm^{-1} see Figure 5c) well-known for traditionally heated sapphires (Smith 1995). Samples heated even with higher pressure (5 kbar), but no water addition did not show any OH^-- related FTIR absorption (Song et al. 2015).

Furthermore, it has to be stated that similar OH^--related patterns have been reported for beryllium treated sapphires (DuToit et al. 2009), "Punsiri-type" heated sapphires (Scarratt 2003, Saeseaw 2017) and even from unheated basaltic corundum (Sangsawong et al. 2016) and Mg-doped synthetic corundum (Fukatsu et al. 2003).

In summary, although the FTIR spectrum may be indicative of a heating with pressure, it cannot be unanimously considered a diagnostic criterion for this treatment. The situation is further complicated in that, if a sapphire heated with pressure is subsequently heated again, the above mentioned complex OH^--absorption band may disappear, resulting finally in a FTIR spectrum equal to those of traditionally heated sapphires (series of OH^- peaks at 3307, 3230, 3185 cm^{-1}).

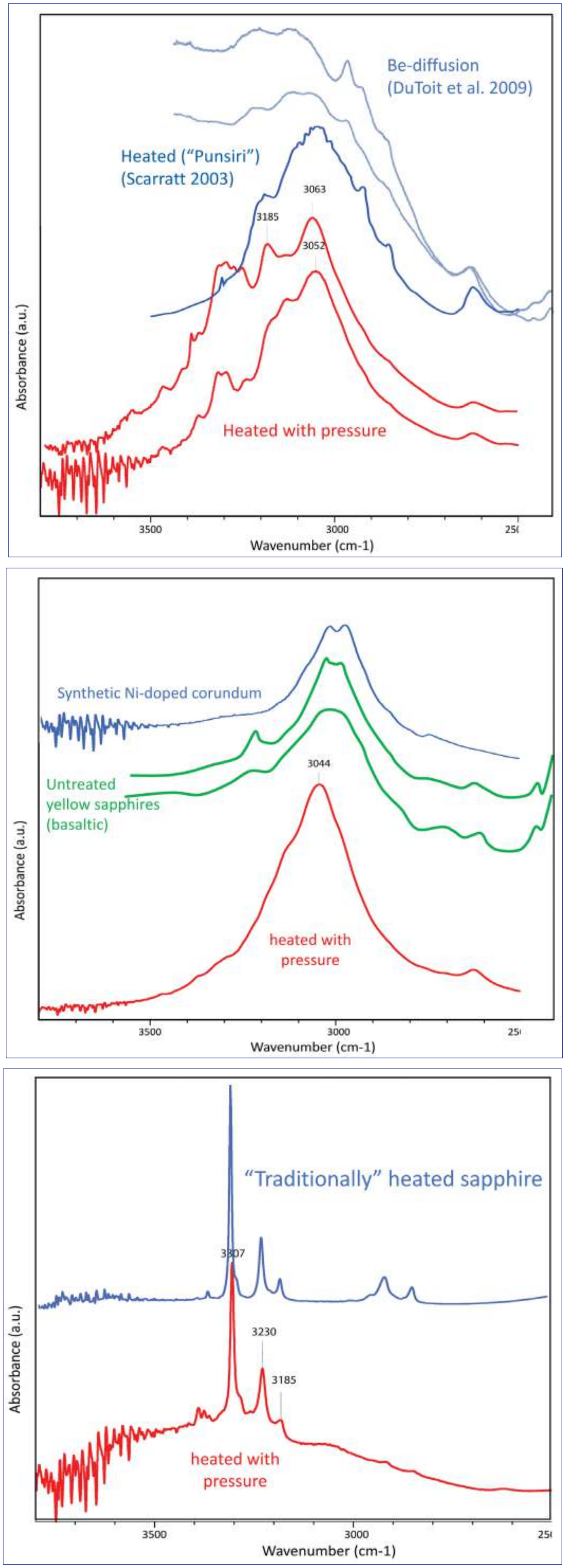
Durability Study of Sapphires Treated with Pressure

For the purpose of this study, treated samples were chosen from three categories: A) eye clean, B) included, and C) heavily included. The samples were subjected to a series of tests (Hughes et al. 2019) by different laboratories to investigate if there is any specific durability issue with this material.

In a first test, the samples were placed in an ultrasonic bath commonly used for cleaning. The ultrasonic bath was filled with slightly warm water. All the samples were placed on a wire bucket and soaked in an ultrasonic bath for 5, 10, and 30 minutes, respectively. The test at GIT revealed no damage on any of the stones. A similar setup was chosen at GGL for four sapphires revealing, by microscopic inspection, no additional damage after the ultrasonic bath on top of preexisting abrasions.

A second test involved testing the resistance of the treated materials to acids. Three sapphire samples (one of each category) were selected for: a) soaking in strong nitric acid (HNO_3) for six hours and b) strong hydrofluoric acid (70% HF) for two minutes. In both cases, no etching whatsoever occurred.

A third test examined the brittleness of the samples when subject to a paper clip and metal blade. Three stones (one



of each category) were selected to be scratched by a paper clip (A) and scalpel blade (B). No damage to the stones could be observed, only flakes of metal that came off the paper clip and ended up accumulating on the surface of the stone.

The fourth test was to drop the samples as a basic durability test. Three stones (one of each category) were selected and dropped onto a hard concrete floor from approximately one meter height. This procedure was repeated three times for each stone. No damage (cracking) was observed in any of the samples.

The fifth test involved testing the pressure treated sapphire samples for their resistance to thermal shock. Three stones (one of each category) were selected and heated with a jewelry torch burner for five seconds until each of them started to glow red. No change of color occurred due to the testing. One stone from category C (highly included!) developed additional tension cracks extending from internal inclusions. The same would have been expected of a heated (no pressure) stone full of inclusions.

Re-polishing of a stone is not expected to have an impact either. A Montana sapphire from the GIA reference collection was heated with pressure in Korea and subsequently faceted. No damage occurred during polishing and cutting.

In summary, the claim of specific brittleness of sapphires heated with pressure (Peretti et al. 2018, 2019) could not be substantiated by our tests, which were carried out by several laboratories simultaneously (see also LMHC 2019). However, it is clear that heavily included starting material (low quality) may produce fissures and cracks (durability issue) regardless of which heating method ("traditional" or "new") is applied.

Outlook

This treatment has not significantly increased the supply of sapphire in the market. Based on our studies, it is thought that the treatment does not produce significant advantages in terms of improvements in clarity (fissure healing, etc.). The differences are generally slight and not unlike sapphires conventionally heated at high temperatures.

Important to note is that there is no flux nor diffusion of coloring elements from an external source involved. And most importantly, our study could not substantiate any specific durability issue of this material after treatment.

In summary, based on current information and research of the involved laboratories and organizations, this treatment does not, at present, warrant separate disclosure and rather fits with normal heating disclosure practices (CIBJO, LMHC) used since decades for a wide range of heating processes. Further research is underway to better understand the mechanisms involved with applying pressure to sapphires for treatment.

Figures 5a (top), 5b (center), 5c (bottom): Variability of FTIR spectra observed in sapphires heated with pressure compared to spectra documented in literature of corundum (unheated and heated with different methods). (Figures: M.S. Krzemnicki, SSEF)

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