Sri Lankan Sapphire Enhanced by Heat with Pressure 高溫加壓優化處理的斯里蘭卡藍寶石

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數十年來，加熱加壓處理已成功地被採用作藍寶石的優化處理過程，特別是藍色藍寶石，並且在珠寶行業中被廣泛地接納及應用。優質藍寶石是經典的彩色寶石之一，需求量很大。加熱加壓處理的技術不單在泰國，而是在世界各地不斷發展，並日益採用上更精密的儀器和發展新的技術。在2013年一家韓國公司成功開發出一種優化藍寶石的新技術，並開始在寶石市場上推出該產品。

Abstract

For decades now heat treatment has been used successfully as an enhancement process for sapphires, particularly blue sapphires, and is both accepted and widely practiced in the jewellery industry. Considered one of the classic coloured gemstones, fine quality blue sapphire is always in great demand. The techniques used for heat treatment are constantly being developed, not only in Thailand, and seem to involve increasingly sophisticated instruments. For instance, the famous Sri Lankan heat treatment technique known as the "Punsiri method" that has been seen to improve the colour of blue sapphire from various deposits successfully (G. DuToit et al., 2009). In 2013, a Korean company successfully developed a new technique for enhancing blue sapphire and began to trade their product in the gem market.

This process involves the intentional application of pressure while heating the stone. This new technique significantly reduces the time needed to change the stone's colour and/or clarity compared with the traditional heat treatment where stones are simply heated in a furnace. So far, Sri Lankan sapphire, (the so called Geuda sapphires) is the only commercial product that this company claims to be treating successfully. The blue sapphire resulting from this treatment commonly shows a typical strong OH-related absorption in the Mid-IR spectrum. This and some characteristic inclusion features are important keys for identification of sapphire that has undergone heat and pressure treatment. Further study is required to increase our understanding of the change mechanism and also the exact role of pressure in this process.

Introduction

Since 2005, the first company to change the colour of blue sapphire using high-temperature and high-pressure equipment is Korea's Everfriend Co., Ltd. Its HPHT apparatus is very well known for the production of synthetic diamond and was imported from Russia to improve the colour of natural diamond. Finally, in August 2006, the company announced in a Korean newspaper that they succeeded in improving the colour of blue sapphire. However, the blue sapphire processed by the Everfriend Co., Ltd. was still very limited in availability and did not have any impact on the corundum market. By the end of the 2000s, the company had closed, since when they have produced no treated sapphire.

In 2009, another Korean company, HB Laboratory Co. Ltd., attempted to refine this technology by using a similar fundamental. They modified some important parts of the machine, such as the inner mold (crucible) and the outer mold (metal frame) and conducted various experiments to obtain optimum conditions for their treatment technique.

After three years of intense research, they had succeeded in finding optimal conditions for the quality of improving blue sapphire and the commercial product has been on the market since 2013. However, in November 2011 a client submitted a group of blue sapphires to Hanmi Gemological Laboratory with an unusual IR spectroscopic characteristic showing a strong absorption band centered around $3047 cm^{-1}$ in the InfraRed region. Further study by the Hanmi Lab using the TGA/DTA technique revealed that the strong band present in the InfraRed region was not related to hydroxyl-stretching modes of gibbsite, boehmite, and diaspore, which are commonly found as inclusions in sapphire.

Fig. 1 These 12 faceted Sri Lanka sapphires were all enhanced by heat and pressure treatment.
June 2016. Photo by Jaehak Ko
12顆經高溫加壓處理的斯里蘭卡藍寶石

In June 2016, the research team from Hanmi Lab were given their first chance to see the facilities and observe the treatment process at HB Laboratory Co. Ltd., in Hwasung City, Gyeonggi-do Province, Korea. They experimented on 12 blue sapphire samples shown in Fig. 1. Later, in 6th December 2016, the Hanmi research teamed up with researchers from The Gem and Jewelry Institute of Thailand (GIT). They paid another visit to the lab to witness the whole treatment process and did some experiments on known samples. (Figs. 4 and 5)

The Treatment Process in Brief

The apparatus used for this treatment is a modified mold press machine. The owner claimed that the temperature at which the treatment was carried out was in the range of 1,200~1,800°C and a mechanical pressure of slightly below 1 kilobar was applied during the process. This technique can, so far, only be carried out on one stone at a time (as shown in Fig. 3) but each treatment took less than 20 minutes. The very short processing time seems to be the big advantage of this technique as compared to traditional heat treatments, which usually take many hours to complete (Fig. 2).

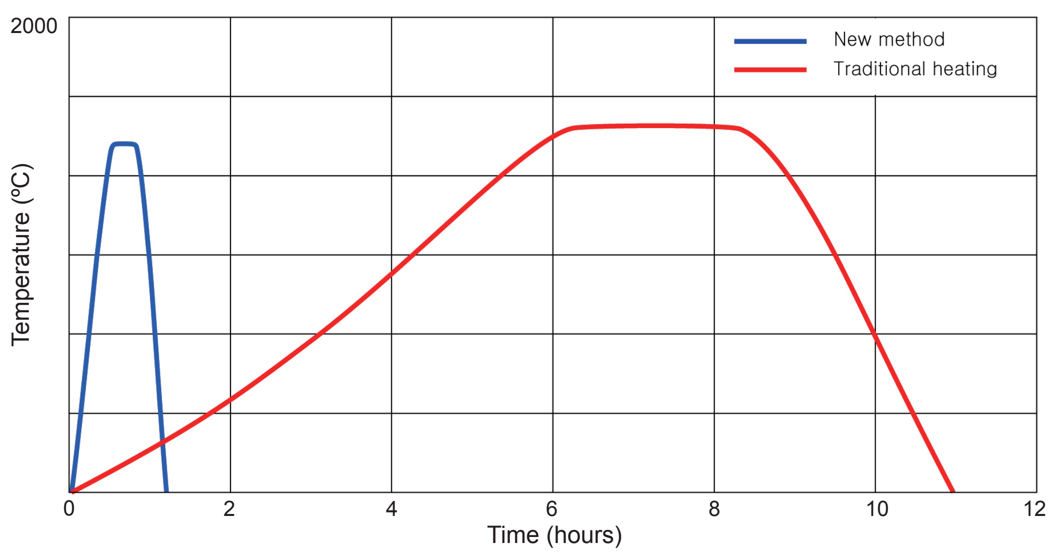


Fig. 2 Traditional heating takes a long time to reach a certain (or constant) temperature and treatment takes a long time (red line). Only a short time is needed to achieve a certain (or constant) temperature in the heat and pressure treatment so the treatment time is also short (blue line).
傳統加熱處理需要長時間才能達到一定（或恆溫的）的溫度，而且需時很長（紅線）。在高溫加壓處理中，只需要頗短的時間便能達到一定（或恆溫）的溫度，所需處理時間也短（藍線）。

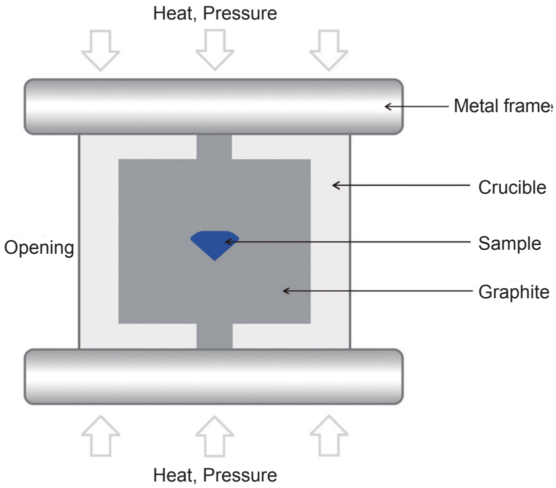


Fig. 3 Schematic diagram of heat and pressure treatment
高溫加壓力處理示意圖

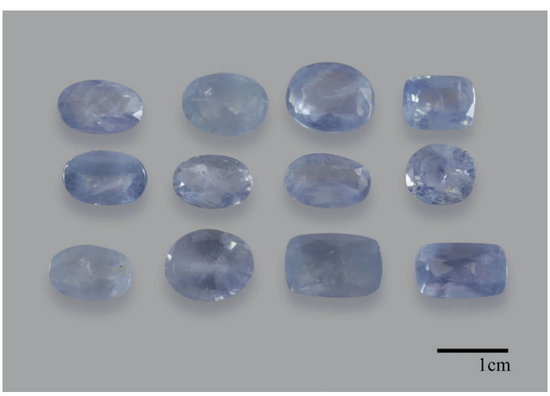
The stone was placed in the centre of a crucible made from refractory clay. Then the crucible was filled with graphite powder. Graphite was used because its good thermal conductivity can transfer heat directly from the electric heating element to the stone and it is also capable of producing a strong reducing atmosphere. Two different categories of sapphire have been successfully improved by this treatment method so far. The first category is pale blue, cloudy, unheated sapphire and the second is conventionally heated blue sapphire.

Materials and Methods

The first study was conducted by Hanmi's researchers in June 2016 on 12 faceted stones (0.82-19.02cts, Fig. 1), all of which it was claimed were Sri Lankan in origin. The stones were subjected to heat and pressure treatment and the data collected before and after treatment were compared based on standard gemmological testing and advanced analysis.

The absorption spectra of all samples were measured in the non-polarized range between 300-800nm using a UV-3101PC UV-Vis-NIR spectrometer. The FTIR spectra were scanned 64 times at 4cm^{-1} resolution using a PerkinElmer Spectrum One FTIR spectrometer. Two samples were analyzed by femtoseconds laser ablation-inductively coupled plasma mass spectrometry (fs LA-ICP-MS) for the analysis of chemical components before and after treatment.

A later experiment was conducted in December 2016 by the research teams from both Hanmi and GIT institutes. The intention was to run an experiment by preparing two sets of commercial quality sapphire specimens, the treatment of which would be witnessed by the researchers. The first set of samples consisted of 12 cloudy pale blue unheated sapphires (Fig. 4) while the second set consisted of 21 conventionally heated blue sapphires (Fig. 5). These stones ranged in weight from 4.73 to 44.85cts. The procedure followed in carrying out these experiments was reported to be similar to that in the June experiment and to the treatment carried out on other commercial products by the company.



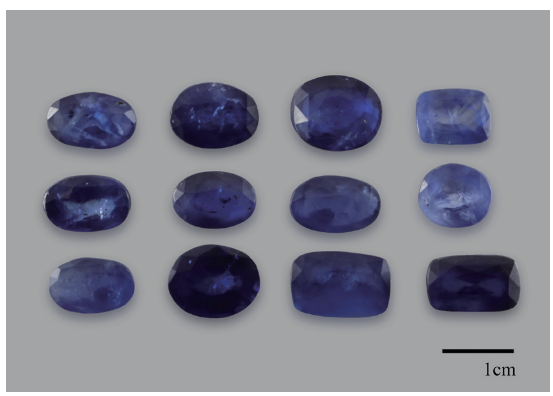


Fig. 4 A set of unheated sapphire samples (left) are obviously enhanced after heat and pressure treatment (right). *Photo by P. Ounorn*
一組未加熱的藍寶石樣品（左）在加熱加壓處理後（右）顏色明顯優化

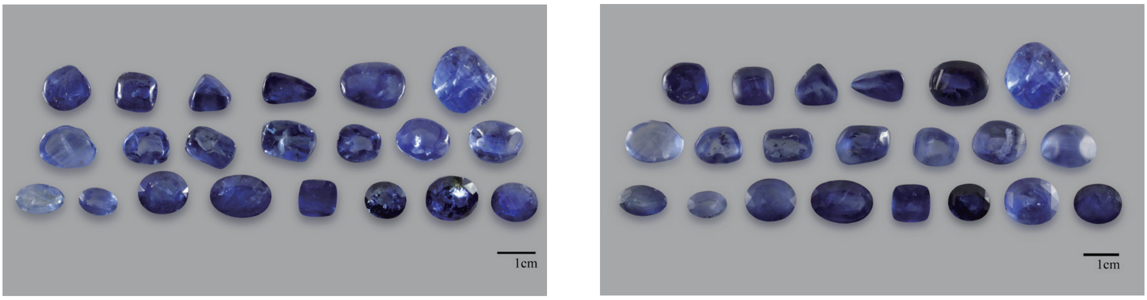


Fig. 5 Another set of previously heated sapphire samples (left) showing slight loss of colour in some samples and slightly improved colour and clarity in others after heat and pressure treatment (right). *Photo by P. Ounorn*
另一組預先加熱的藍寶石樣品（左）其中一些顏色不明顯，在熱和壓力處理後（右）顏色和透明度稍微改善。

Results

The results of the experiments in both June and December 2016 revealed that in the first set, where unheated sapphires were used as the start material, the colour of all the stones became visibly less cloudy and the colour improved to a quite intense blue even after the first trial (Fig. 4). However, many unexpected cracks had clearly developed from negative crystals and healed fissures. Some of these had a tendency to break the stone apart and certainly had a negative impact on the clarity of the stones.

As for the second set, using conventionally heated blue sapphires as the start material, the results of the treatment were quite varied and it remained difficult to predict the outcome. Some stones were observed to lose their colour dramatically while others gained colour to various degrees under the same treatment conditions (Fig. 5). Nevertheless, many of the tension cracks and fractures formerly produced from the conventional heat treatment seemed to have been healed and certainly became less visible or actually invisible even under microscopic observation resulting in a significant improvement in clarity. This outcome was consistent with the information given by the owner. Hence, it is apparent that this treatment can turn previously unheated pale blue sapphire into intense blue material but with obviously reduced clarity. In contrast, while conventionally heated blue sapphires tend to show an improvement in clarity after the treatment, their colour might not be improved as expected.

Comparison - before and after

Microscopic features

Observation under gem microscope revealed many interesting external and internal features as follows:-

In the first set, the pale blue colour of previously unheated sapphires deepened to an intense blue after heat and pressure treatment and the milky cloudy appearance observed before treatment was removed. However, many fissures and cracks developed from internal inclusions such as crystals and negative crystals. (Figs. 6, 7, 8 and 9).

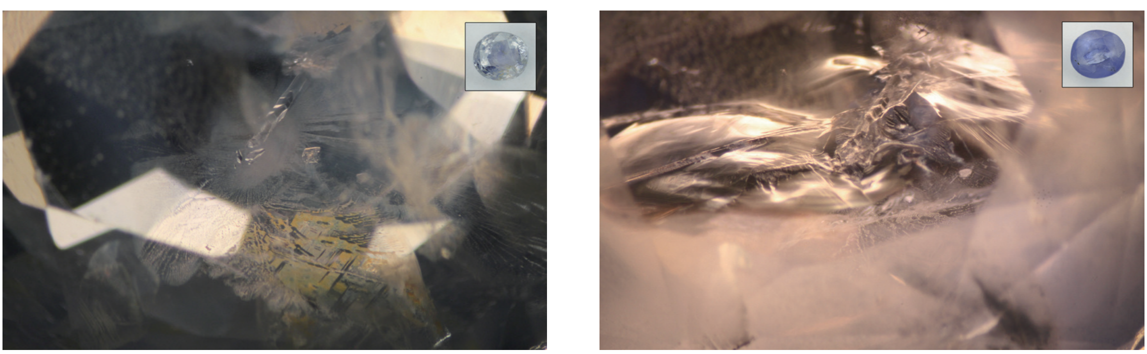


Fig. 6 The pale blue colour of a 6.75cts untreated sapphire (left) has obviously intensified after heat and pressure treatment (right). Notably, a big tension fracture has formed around elongated crystals following the treatment (magnified 12.5x).
Photo by N. Atsawatanapirom.
經加熱加壓處理後，一顆6.75cts未經處理的藍寶石（左）的淡藍色明顯增強（右）。值得注意的是，經處理後的拉長晶體周圍形成了一個張力斷口（放大12.5倍）。

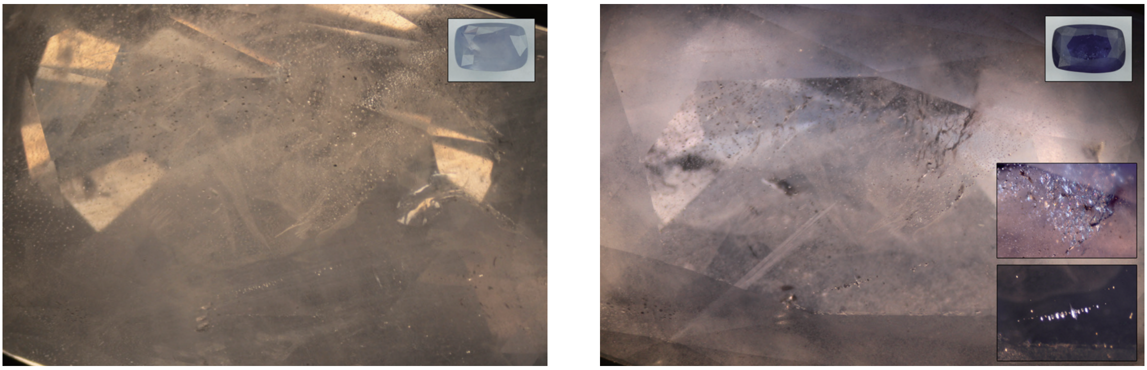


Fig. 7 The pale blue colour of a 10.16cts untreated sapphire (left) has been improved to vivid blue after heat and pressure treatment (right) but shiny tension fractures have also formed around crystals/negative crystals after treatment (magnified 6.5x). *Photo by N. Atsawatanapirom*
經加熱加壓處理（右）後，一顆10.16cts未經處理的藍寶石（左）的淡藍色得到了改善，呈鮮藍色；但處理後也形成了晶體/負晶體周圍出現了明亮的壓力斷口（放大6.5倍）。

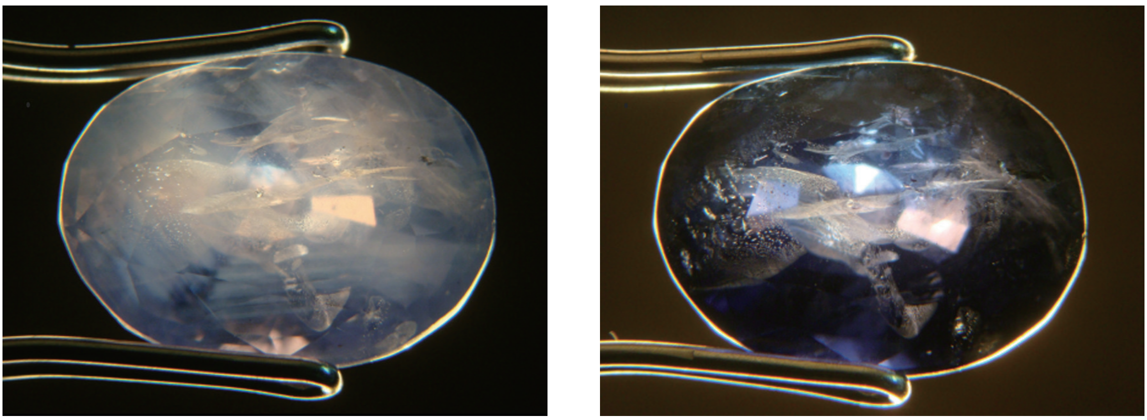


Fig. 8 The colour of a 5.91cts untreated, pale blue sapphire (left) improved to an intense blue after heat and pressure treatment (right). Also, milky, cloudy inclusions were removed by the treatment (magnified 3x). *Photo by Youngsoo Chung*
5.91cts未經處理的淡藍色藍寶石（左）經過加熱加壓處理後（右）顏色改善為強烈的藍色。此外，通過處理亦去除了乳白色的混濁內含物（放大3倍）。

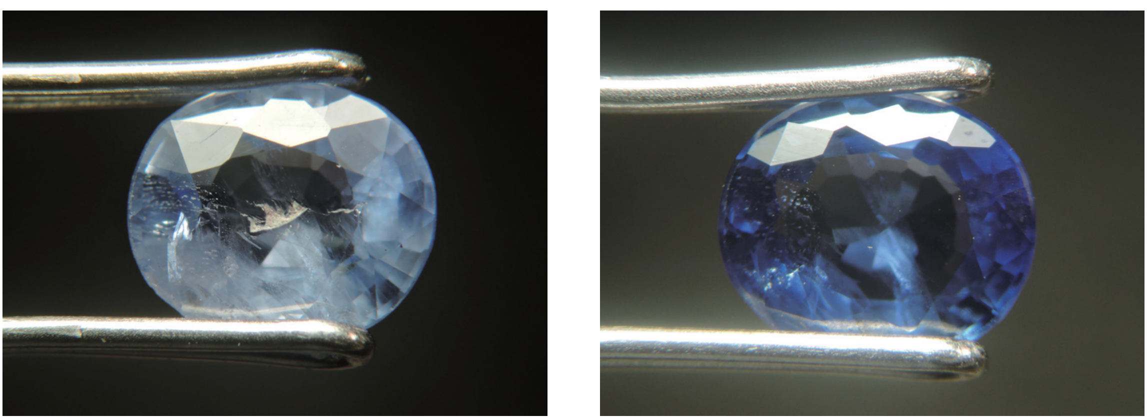


Fig. 9 The colour of a 0.82ct untreated, pale blue sapphire (left) improved to an intense blue (right) after heat and pressure treatment Milky, cloudy inclusions were also removed (magnified 2x). *Photo by Youngsoo Chung*
0.82ct未經處理的淡藍色藍寶石（左）在加熱加壓處理後顏色改善為強烈的藍色（右）。白色混濁的包裹體也被去除（放大2倍）。

In the second set, using traditionally heated sapphires as the start material (as shown in Figs. 10-15), short and long rutile needles that were still present after conventional heating were seen to have been completely removed following this treatment (Fig. 10). Also, many thermally induced tension cracks still remaining after the earlier treatment tended to have healed and were

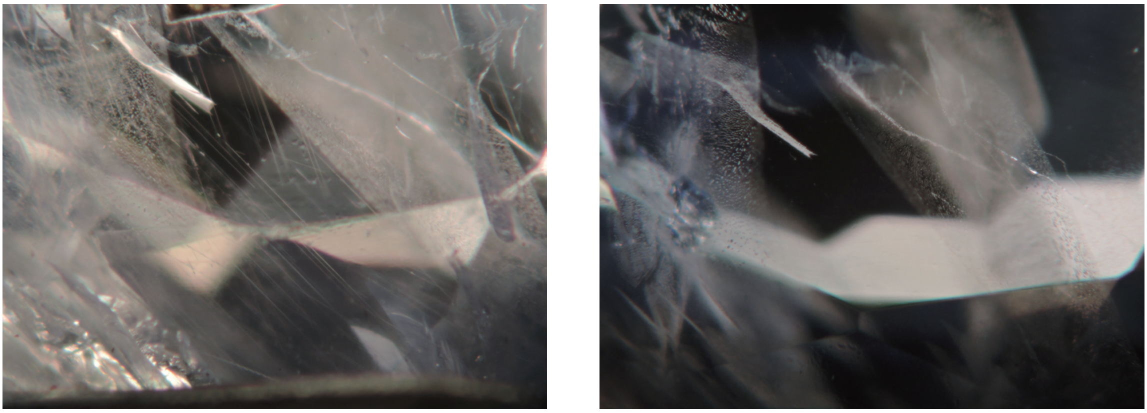


Fig. 10 A 0.82ct sapphire that had already received conventional heat-treatment before (left) and after heat and pressure treatment (right). Notably, previously visible short and long rutile needles could be seen to have been removed during this treatment (magnified 15x). *Photo by Youngsoo Chung*
經常規熱處理的0.82ct藍寶石（左）和經加熱加壓處理之後（右）的比較。值得注意的是，在處理過程中，短而長的金紅針已被移除（放大15倍）。

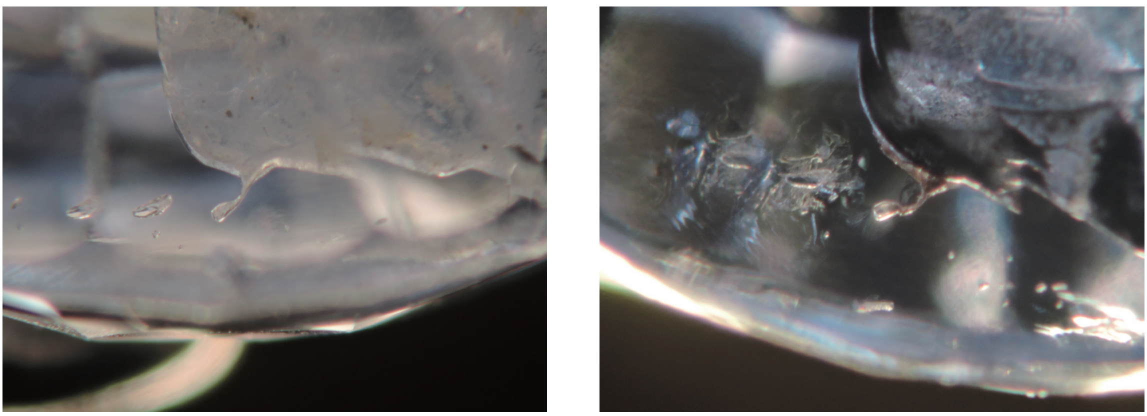


Fig. 11 A 0.89ct sapphire before and after heat and pressure treatment. Fuzzy looking tension fractures formed around negative crystals after this treatment (magnified 13x). *Photo by Youngsoo Chung*
加熱加壓處理前後的0.89ct藍寶石。經處理後負晶體周圍形成了模糊的張力斷口（放大13倍）。

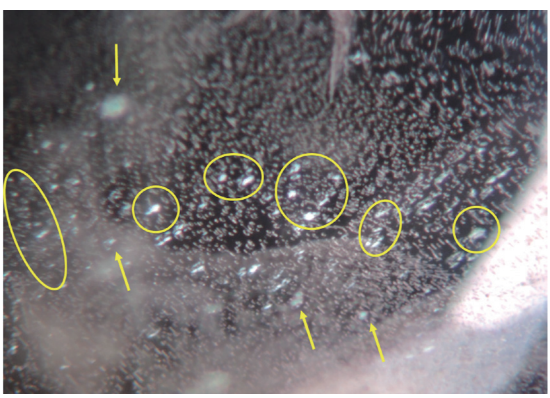


Fig. 12 Heating with pressure can show some unique characteristics, such as a shiny internal feather between liquid inclusions in the stone. This feature is rarely seen in traditionally heat-treated sapphire (magnified 20x). *Photo by Hyunmin Choi*
壓力和熱力可以顯示出一些獨特的特徵，例如寶石中液相包裹體之間具光澤的內部羽毛狀物。在傳統熱處理藍寶石中很少發現這種特徵（放大20倍）。

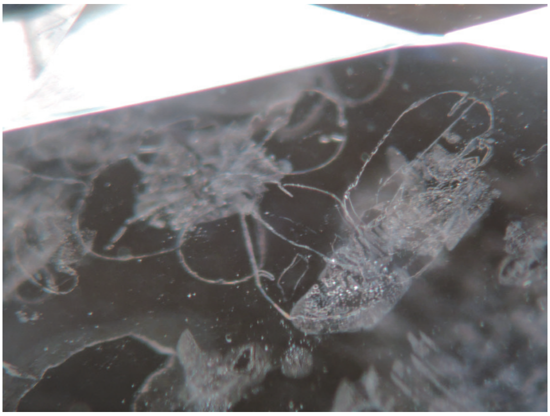


Fig. 13 Another unique feature is that partly healed thin-film tension cracks often appear in stones that have undergone heat and pressure treatment (magnified 20x).
Photo by Hyunmin Choi
另一個獨特的特徵是經過加熱加壓處理的寶石（放大20倍）經常出現部分癒合的張力裂紋薄膜。

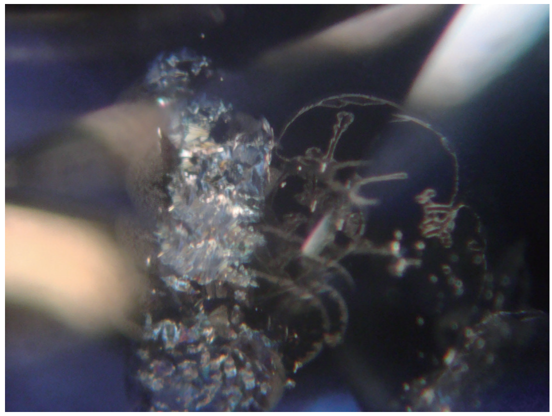


Fig. 14 Partially healed thin-film tension cracks are sometimes observed along with irregular tension fractures around the negative crystals (magnified 30x). *Photo by Hyunmin Choi*
部分癒合的薄膜張力裂紋及負晶體周圍的不規則張力斷裂（放大30倍）。

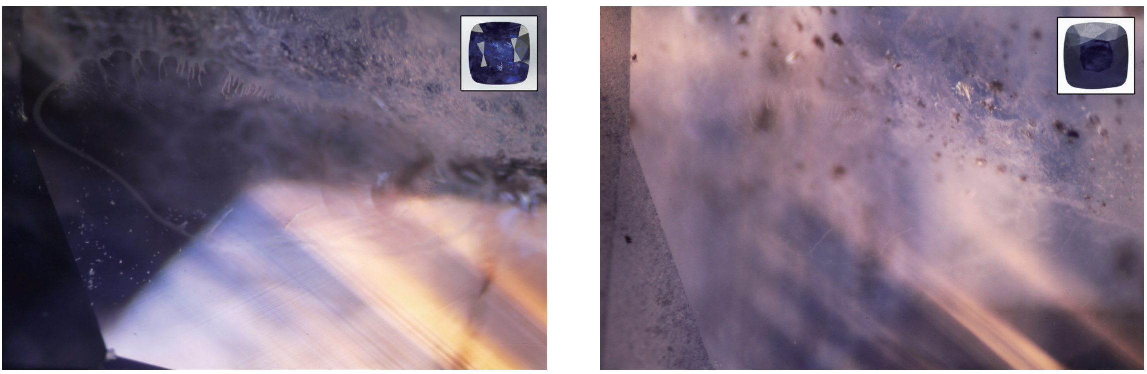


Fig. 15 An 8.09cts sapphire before (left) and after heat and pressure treatment (right). It is noteworthy that formerly partially healed fissures tend to have healed completely after this treatment (magnified 25x). *Photo by N. Atsawatanapirom*
加熱加壓處理前（左）和後（右）後的8.09cts藍寶石。值得注意的是，其部分裂隙在處理後趨向完全癒合（放大25倍）。

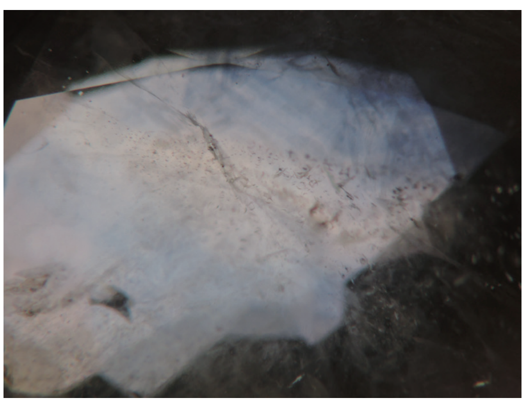


Fig. 16 Changes to colour banding and zoning are not clear after heat and pressure treatment (magnified 15x).
Photo by Youngsoo Chung
經加熱加壓處理後的斯里蘭卡藍寶石的色帶和顏色分區變得模糊不清（放大15倍）。

certainly less visible after heat and pressure treatment. Pronounced colour bands and zoning usually also became less prominent (Fig. 16). However, the stones often showed an obviously corroded surface after treatment and graphite residues were commonly seen at un-polished girdles and in the cavities even after re-polishing (Fig. 17).

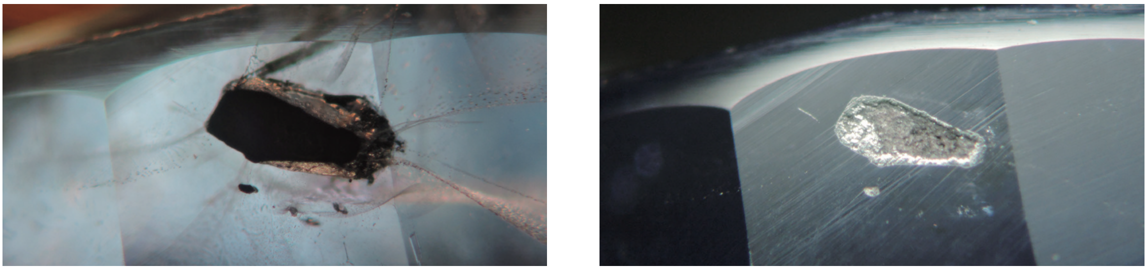


Fig. 17 Cavities filled with graphite appeared on the surface of this 8.30cts stone after heat and pressure treatment. Darkfield illumination (left) and overhead light (right) (magnified 15x). *Photo by Youngsoo Chung*
加熱加壓處理後，這8.30cts的寶石表面出現有石墨填充的空腔。暗域照明（左）和頂部照明（右）（放大15倍）。

Advanced Analysis

UV-Vis-NIR spectroscopy

UV-Visible spectrum of originally unheated pale blue sapphire sample showed a small absorption band due to Fe^{2+}-Ti^{4+} intervalence charge transfer (IVCT) and Fe^{3+}-related peaks at 388 and 450nm (Fig. 18). The Fe^{2+}-Ti^{4+} IVCT band responsible for the blue colouration has been obviously enhanced after heat and pressure treatment. A cutoff is observed in the region where the energy is higher than 300nm.

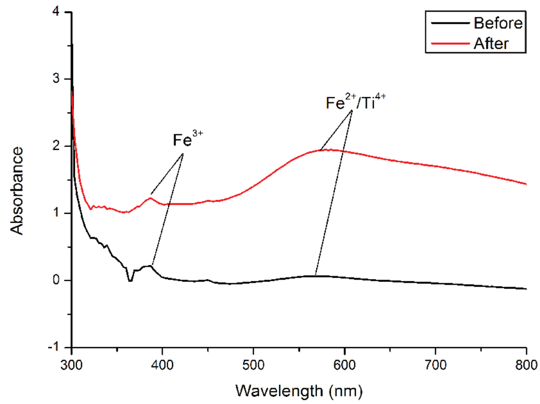


Fig. 18 The non-polarized Visible-UV absorption spectra of an untreated blue sapphire before (black) and after heat and pressure treatment (red).
未經處理的藍寶石之（黑線）和加熱加壓處理之後（紅線）的非偏振可見紫外吸收光譜。

Infrared spectroscopy

All stones that have undergone heat and pressure treatment clearly display a strong absorption band centre around 3050-3040cm^{-1} in the Mid-Infrared region, regardless of whether the stones have been previously heat-treated or not. After heat and pressure treatment, most of the OH bands produced were centered at 3047cm^{-1}. The band centre was formed in the 3050-3040cm^{-1} range, although the centre of the band had shifted slightly in some samples. In addition to the 3047cm^{-1} centre band, side bands appeared at 1933, 2030, 2149, 2412, 2627, 3135, 3177, 3297, 3323, 3375, 3421 and 3471cm^{-1} (Fig. 19).

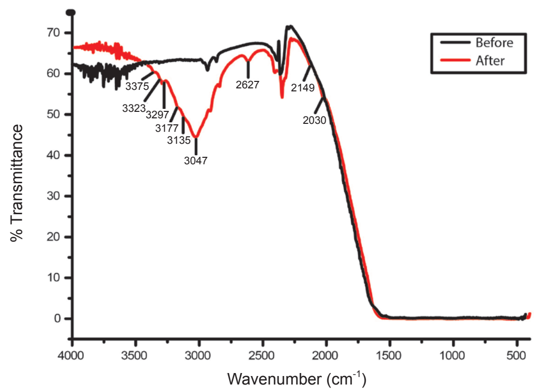


Fig. 19 After treatment, most of the OH bands produced were centered at 3047cm^{-1}.
經處理後，大部分產生的OH帶集中在3047cm^{-1}處。

Effect of pressure on IR spectrum

The strong OH bands near 3047cm^{-1} and side bands in the infrared region, which were not present before treatment, have occurred after heating with pressure. However, the sidebands appearing in each sample after treatment have slightly different positions.

How does pressure affect the OH band of sapphire?

First, in order to create the same starting conditions for the samples used in the experiment, one sapphire crystal was cut at regular intervals. For this experiment, the temperature and the amount of water used were kept constant, but the pressure was varied at 600, 700, and 900 bars.

The results of the experiments with different pressures showed that a strong band near 3047cm^{-1} and side band were commonly seen at approximately 2030, 2149, 2412, 2627, 3177, 3375, 3421, and 3471cm^{-1} in all the infrared regions of all samples. The peak of 2149cm^{-1} in the infrared region did not appear from the samples tested at 600 and 700 bars. And the peak of 2149cm^{-1} was found only in the samples tested at 900 bars. The peak at 3310cm^{-1} was found in the samples tested at 600 and 700 bars but disappeared at 900 bars (Fig. 20).

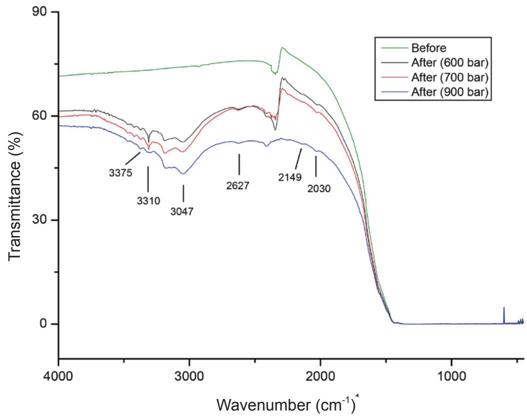


Fig. 20 Experiments with variable pressure at 600, 700 and 900 bars while the temperature and the amount of water were kept constant. The samples tested at 600 and 700 bars showed a peak at 3310cm^{-1} while that tested at 900 bars had no 3310cm^{-1} peak.
在溫度和水量保持不變的情況下，在600, 700和900 bars下進行可變壓力的實驗。在600和700 bars測試的樣品在3310cm^{-1}處顯示吸收峰，而在900 bars測試的樣品沒有3310cm^{-1}吸收峰。

LA-ICP-MS spectroscopy

In order to test whether there had been any change of trace element composition after the heat and pressure treatment, a sample was cut into two pieces (1.19cts and 0.80ct). The 0.80ct piece was subjected to heat and pressure treatment. Then both pieces were measured for their trace element contents using the LA-ICP-MS technique.

The chemical result given by LA-ICP-MS, of the untreated piece (1.19cts) and the treated piece (0.80ct) showed iron contents of 1,017-1,253ppm, magnesium 123-175ppm, titanium 24-36ppm, and gallium 62-86ppm without any unusual light elements in either piece (Fig. 21). It could thus be seen that there was no significant difference in the trace element contents of the two pieces.

Discussion and Conclusion

The advantage of applying the heat and pressure treatment to sapphires is that it can improve the colour and clarity of the stones in a very short time. When previously heated sapphires are used as the start material, the technique has the advantage of being able to heal any shiny tension cracks and fractures caused by the earlier heating process, thus improving the stone's clarity. Even though most inclusions observed in sapphires that

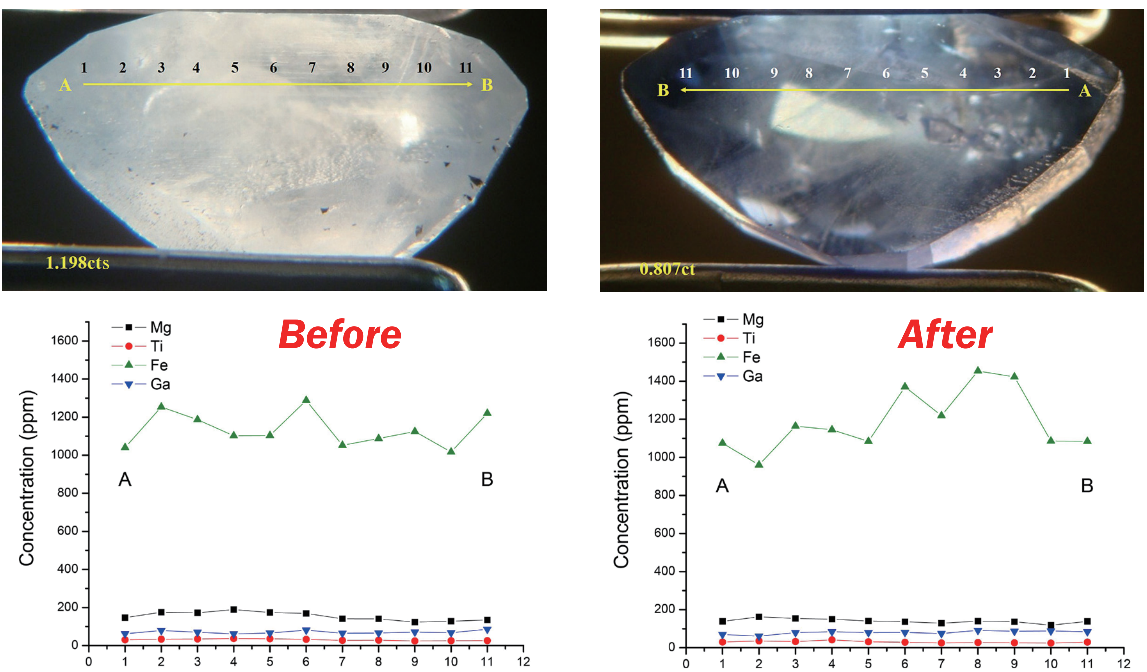


Fig. 21 Trace element contents by LA-ICP-MS of the untreated portion(1.19cts, left) and the treated portion (0.80ct, right)
未經處理藍寶石（1.19cts，左）和經處理藍寶石（0.80ct，右）的LA-ICP-MS的微量元素含量

have undergone heat and pressure treatment are similar to those in stones that have undergone traditional heating, some unique inclusion characteristics appear in heat and pressure treated sapphires. For example, shiny internal feathers appearing between liquid inclusions (see Fig. 12) and irregular tension fractures around negative crystals (see Fig. 14) are diagnostic and are not usually seen in the traditionally heat-treated sapphire.

In general, non-heated Sri-Lankan sapphires do not have an OH-associated absorption peak at $3310cm^{-1}$ or, if it does exist, the peak intensity is very weak. On the other hand, most samples of heated Sri-Lankan sapphires do have strong absorption peaks associated with OH at $3310cm^{-1}$ as well as at $3232cm^{-1}$. The OH peak of $3310cm^{-1}$ is known to be affected by heating and transitional metal ions such as Ti, Fe, etc (Emmett, 2009). It is noteworthy that the crucible is surrounded by the outer frame located at the centre of the apparatus. The frame can transfer and maintain mechanical pressure to the sample inside the crucible packed with graphite powder.

Since graphite is directly in contact with the sample, it can act as a powerful reducing agent as well as transfer heat supplied from the outside. Therefore, even though the treatment time is short, the absorption band due to Fe^{2+}-Ti^{4+} IVCT (responsible for the blue colouration) can be enhanced.

In addition, based on the characteristic IR spectrum, more than 100 specimens of commercial-quality blue sapphire were submitted to both labs by our customers during the period 2011 to 2016.

Hence, based on the aforementioned results, we suggest that the term “high pressure and high temperature or HPHT” is not a suitable name for this new technique and might mislead consumers’ perception of the product. This is because the pressure and temperature used in this process (e.g. <1 Kbar and <1800°C) are much lower than those used in the HPHT treatment for diamond which commonly applies pressure of more than 50 Kbar and temperatures up to 2000°C. (Forever Collections, Inc., n.d; and Reinitz *et al*., 2000).

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