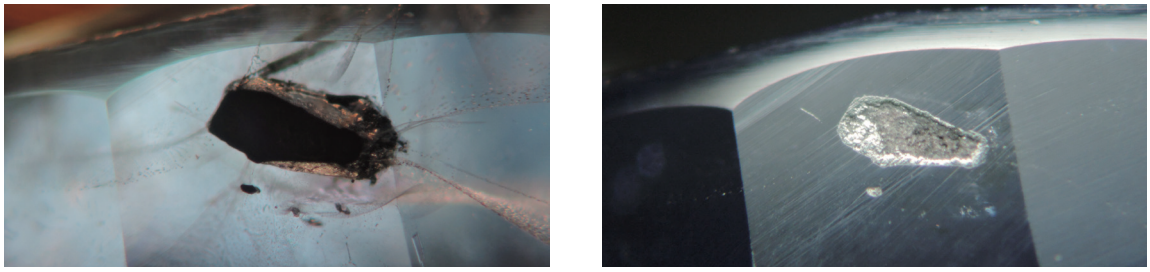

Fig. 17 Cavities filled with graphite appeared on the surface of this 8.30cts stone after heat and pressure treatment. Darkfield illumination (left) and overhead light (right) (magnified 15x). *Photo by Youngsoo Chung*
加熱加壓處理後，這8.30cts的寶石表面出現有石墨填充的空腔。暗域照明（左）和頂部照明（右）（放大15倍）。

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.

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).

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.

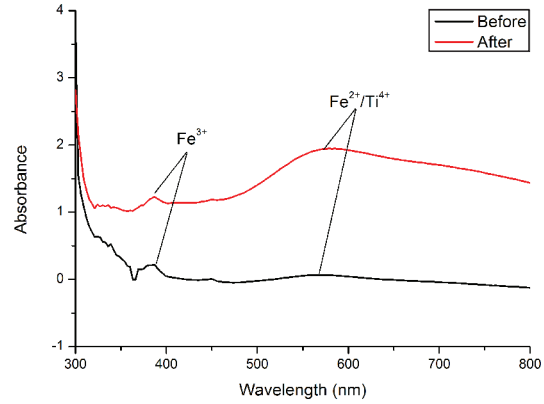

Fig. 18 The non-polarized Visible-UV absorption spectra of an untreated blue sapphire before (black) and after heat and pressure treatment (red).
未經處理的藍寶石之（黑線）和加熱加壓處理之後（紅線）的非偏振可見紫外吸收光譜。

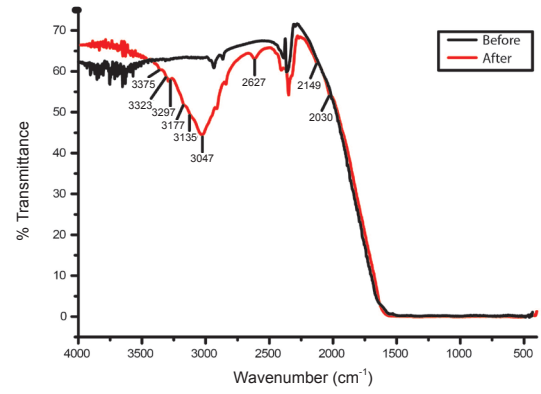

Fig. 19 After treatment, most of the OH bands produced were centered at 3047cm^{-1}.
經處理後，大部分產生的OH帶集中在3047cm^{-1}處。

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).

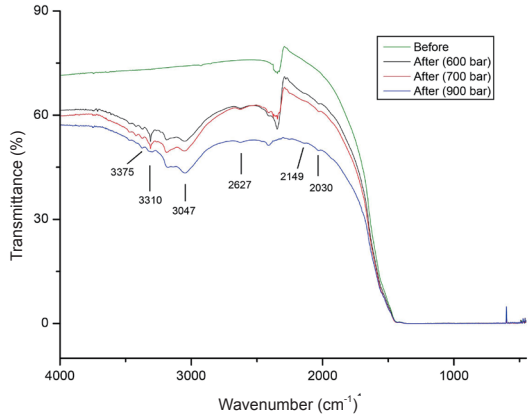

Fig. 20 Experiments with variable pressure at 600, 700 and 900 bars while the temperature and the amount of water were kept constant. The samples tested at 600 and 700 bars showed a peak at 3310cm^{-1} while that tested at 900 bars had no 3310cm^{-1} peak.
在溫度和水量保持不變的情況下，在600, 700和900 bars下進行可變壓力的實驗。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

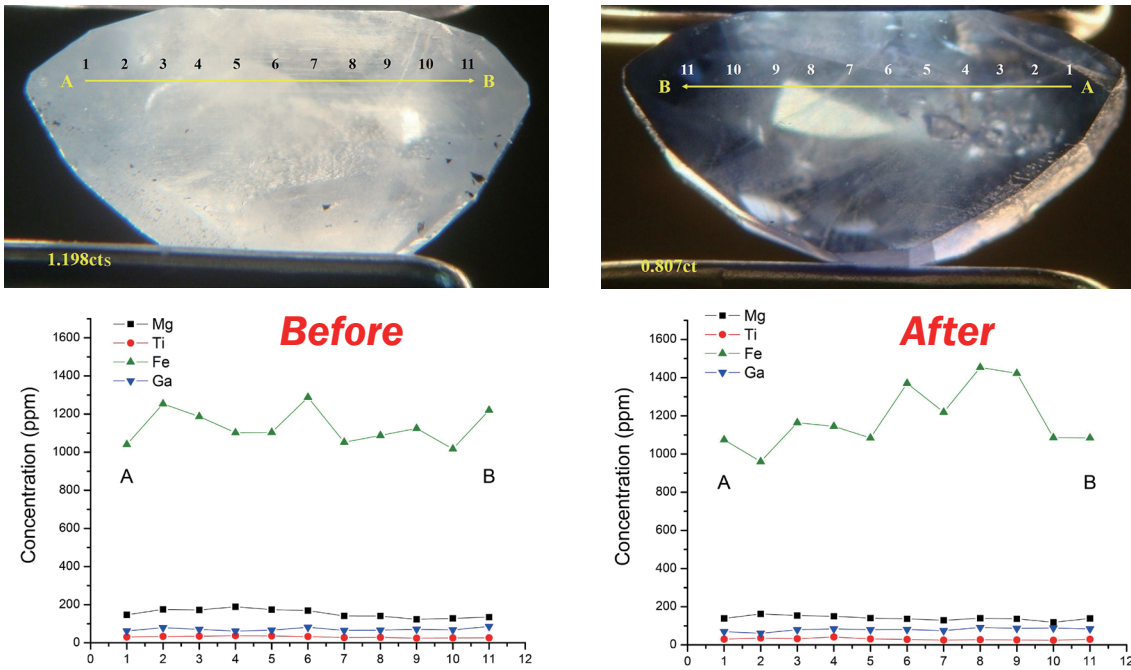

Fig. 21 Trace element contents by LA-ICP-MS of the untreated portion(1.19cts, left) and the treated portion (0.80ct, right)
未經處理藍寶石（1.19cts，左）和經處理藍寶石（0.80ct，右）的LA-ICP-MS的微量元素含量

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 <1800ºC) 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 2000ºC. (Forever Collections, Inc., n.d; and Reinitz *et al*., 2000).

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