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 3047cm^{-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 1,200~1,800ºC 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).

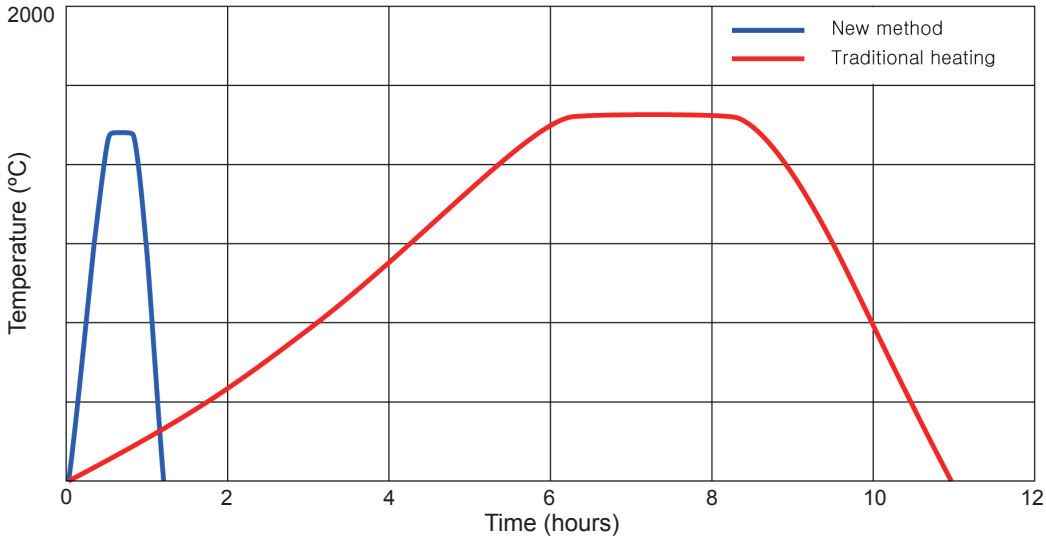

Fig. 2 Traditional heating takes a long time to reach a certain (or constant) temperature and treatment takes a long time (red line). Only a short time is needed to achieve a certain (or constant) temperature in the heat and pressure treatment so the treatment time is also short (blue line).
傳統加熱處理需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）。

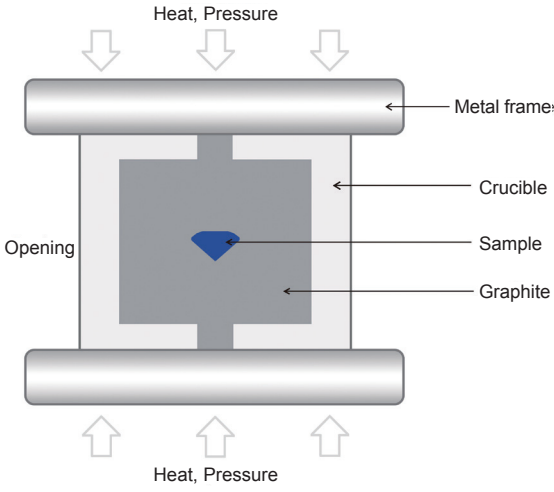

Fig. 3 Schematic diagram of heat and pressure treatment
高溫加壓力處理示意圖

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.

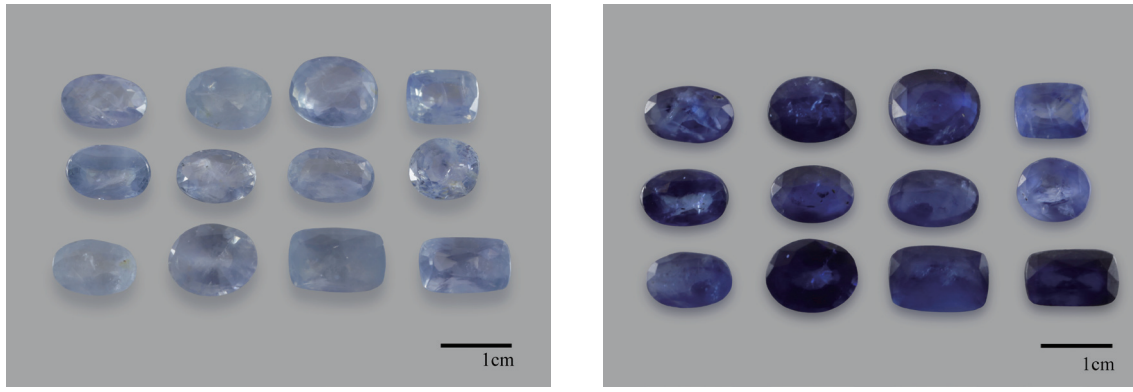

Fig. 4 A set of unheated sapphire samples (left) are obviously enhanced after heat and pressure treatment (right). *Photo by P. Ounorn*
一組未加熱的藍寶石樣品（左）在加熱加壓處理後（右）顏色明顯優化

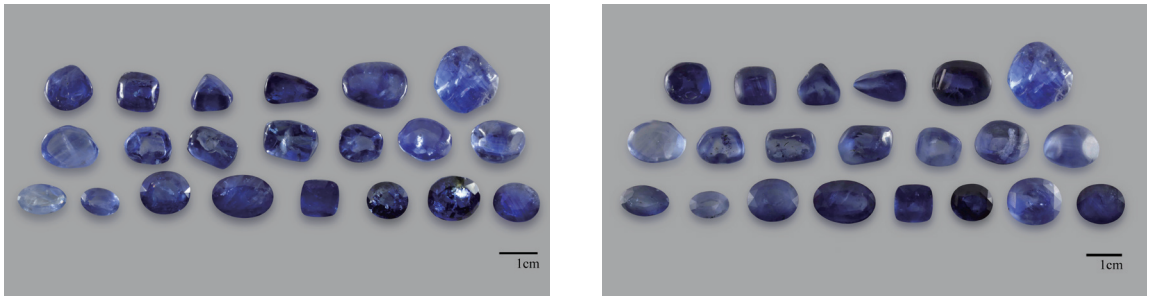

Fig. 5 Another set of previously heated sapphire samples (left) showing slight loss of colour in some samples and slightly improved colour and clarity in others after heat and pressure treatment (right). *Photo by P. Ounorn*
另一組預先加熱的藍寶石樣品（左）其中一些顏色不明顯，在熱和壓力處理後（右）顏色和透明度稍微改善。

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).

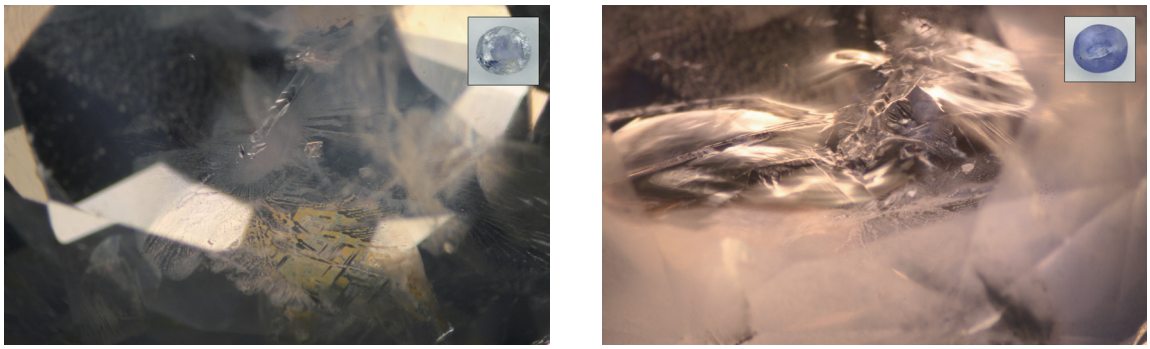

Fig. 6 The pale blue colour of a 6.75cts untreated sapphire (left) has obviously intensified after heat and pressure treatment (right). Notably, a big tension fracture has formed around elongated crystals following the treatment (magnified 12.5x).
Photo by N. Atsawatanapirom.
經加熱加壓處理後，一顆6.75cts未經處理的藍寶石（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）。