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Appearance of new treatment method on sapphire using HPHT apparatus

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Several treatment methods designed to change the appearance, and thus the perceived value, of sapphires have been practiced for decades. Historically, sapphires have been coated with substances to enhance their colour, or dipped in oil to improve apparent transparency. Although the coating of sapphire may not be as common today, the introduction of dyes into surface-reaching fissures is now a routine practice, particularly in low-end beads. More sophisticated treatments-particularly high-temperature, atmosphere controlled heating of corundum-are now commonplace. Heating became the stepping stone for two significant treatments that have radically altered the appearance of corundum and its perceived value over the last decade in particular: beryllium diffusion and lead-glass filling. Identification of Be diffusion treatment requires advanced instrumentation such as laser ablation-inductively coupled plasma-mass spectrometry to establish the presence of beryllium. The filled material also is readily identified with magnification or ED-XRF spectroscopy (Shor and Weldon, 2009).

Fig.1. Blue sapphires (1.30-3.94 ct) shown here are treated by using HPHT apparatus.

Recently, a Korean company has developed a technique to enhance colour of blue sapphire by applying with HPHT (high pressure and high temperature) apparatus, which is a unique process. Originally, the apparatus was designed to grow synthetic diamond. It took many attempts with thousands of conditions to finally get to the desired valuable blue colour from pale blue colour. The owner of the company explained that he had made certain changes in the HPHT apparatus and developed a mold for new treatment.

It is difficult to distinguish the new treated sapphires by HPHT apparatus from general heated sapphires with microscopic observation. They include stress fractures surrounding melted or heat altered inclusions; halos surrounding altered solid mineral inclusions; ruptured negative crystal and so on. Characteristically, however, they were found to possess a more localized concentration of absorption features in the infrared region from approximately 2500-3700 cm^{-1}. These consisted of a sharp band, with the primary band located at approximately 3047 cm^{-1} accompanied by a shoulder at approximately 2627 cm^{-1}. The sharp band observed here is similar to structural OH groups bonded within the corundum lattice. TG-DTA (thermogravimetry-differential thermal analysis) results, however, we found that the band is not associated with mineral phase as the aluminium oxyhydroxide diaspore.LA-ICP-MS (laser ablation-inductively coupled plasma-mass spectrometry) analysis revealed traces of Na, Mg, Ti, V, Cr, Fe, and Ga.

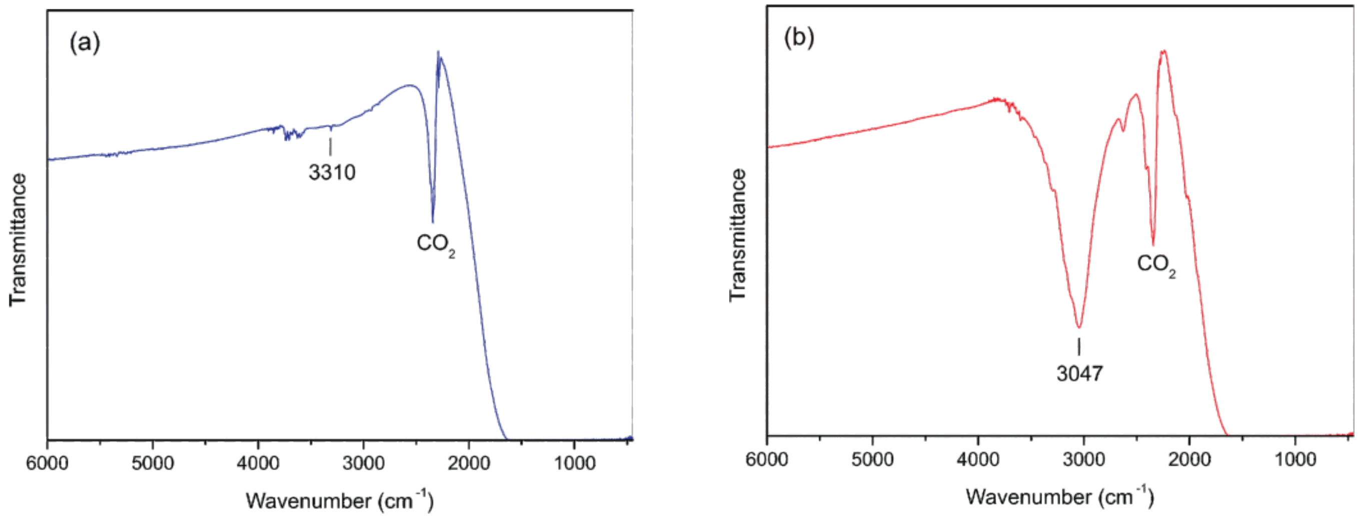

Fig.2a & Fig. 2b: Infrared spectra of a blue sapphire before (a) and after (b) new treatment process by HPHT apparatus. After treatment, a strong band is observed at approximately 3047cm^{-1}.

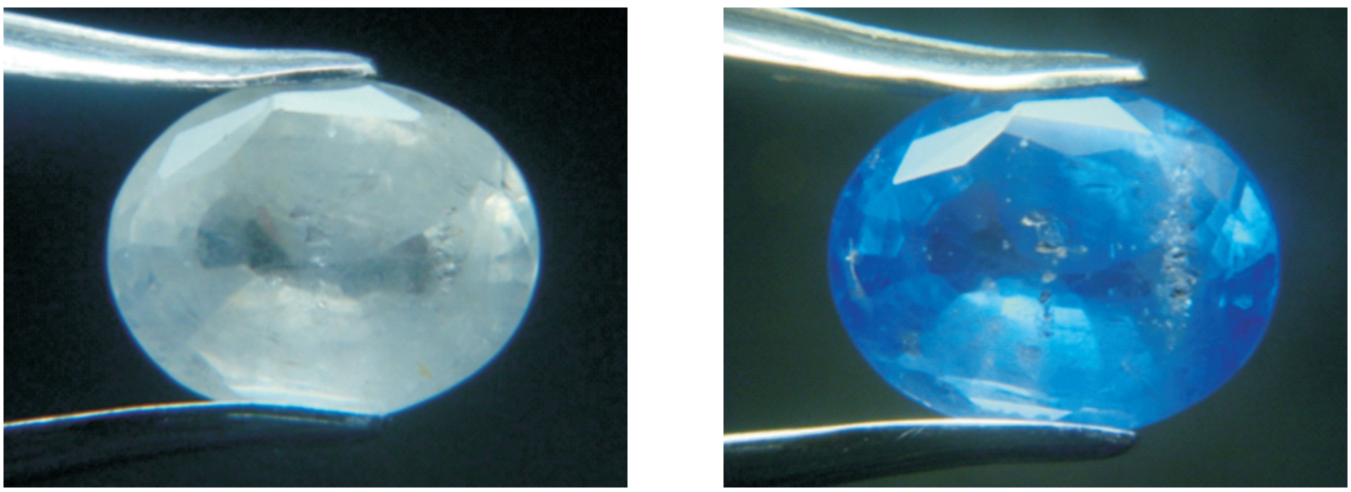

Fig.3a & Fig3b: These two illustrations show how the 5.97ct, pale blue colour sapphire changed to a bright blue colour after treatment using HPHT apparatus.

Reference:

Shor R., Weldon R. (2009): Ruby and sapphire production and distribution: A quarter century of change, G&G, Vol. 45, No. 4, pp. 236-529.

"BLUE SILK"
Color change-like effect in pink sapphire from Batakundi

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Can the mechanism of the beauty of Kashmir sapphire be seen in other corundum? The pink to purple sapphire from Batakundi in Pakistan controlled Azad Kashmir area has the same feature in it. The finding of sapphire from depositwas reported in 2009 by Mr. V. Pardieu et al. with description of its strong color zoning and cloud inclusion. And recently the color change like effect caused by this cloud inclusion is focused. When it is lighted with daylight or white LED from the side, it shows bluish over tone on pink stonelike Photo.1) and 2).

Video) http://www.icglabs.org/video/colorchange.wmv

Its mechanism is same as blue moonstone like its cloud inclusion causes the Rayleigh scattering. The cloud inclusion over the stone consists of a lot of minute particles. And these particlesare implied to be smaller than wavelength of visible light and when it is lighted from the side, it causes scattering of light to give blue overtone on the pink stone. And this blue adularescence is also seen in Kashmir sapphire to give it a hazy blue appearance on it.

This inclusion is also called as "blue silk" in the market because of its silky appearance. Actually, it has high Ti content and often this sapphire is heated in reducing atmosphere to change to deep blue color. But when it is heated over 1300^{0}C, the inclusion can be dissolved and this effect is also lost.

As far as we know, this effect is also seen in some Sri Lankan pink sapphire and Tajik and Afghani ruby. But it is the most eminent in pink sapphire from Batakundi.

When this effect gives blue adularescence to the blue stone like Kashmir sapphire, it is considered as a part of its beauty. In pink stone, it can give an attraction like a color change effect.

Reference:
V. Pardieu et al. (2009) GAI Thailand Website "Sapphires Reportedly from Batakundi/Basil area"

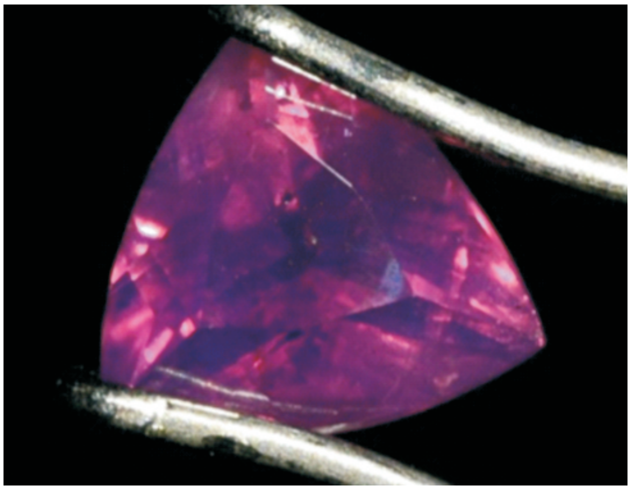

Photo 1) Lighted with white LED from above

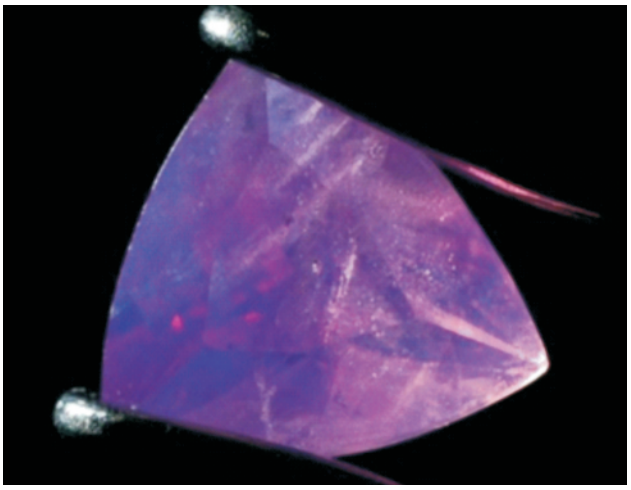

Photo 2) Lighted with same white LED from the side

Cobalt-doped glass-filled treated blue sapphire

By TayThye Sun and Loke Hui Ying

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An oval shape cabochon cut blue sapphire set in man's ring was brought in for identification and was found to be cobalt-doped glass-filled treated sapphire. The cabochon sapphire measured 12.99 x 10.71 x 6.61mm and weighed approximately 10 ct and was surrounded by a single row of small round faceted cubic zirconia set in silver (Fig.1).

Fig.1. Cobalt treated sapphire set in man's ring (photo by TayThye Sun)

Results: Gemmological testing was carried out, R.I. of 1.76 was determined by spot reading and the prism spectroscope showed 460nm absorption and under ultraviolet lighting the stone remained inert both under long and short waves. Under microscopic observation, artificial blue colouring, pink flashes and gas bubbles were found in fissures. Some natural included crystals with straight growth colour zoning were observed (Fig.2). Under reflected light, the surface showed dull lustre with glassy filled surface compared to the surface of the harder corundum showing bright vitreous lustre (Fig.3).

Infrared spectrometer results showed the presence of wax peak at 2916 and 2848 cm-^{1} (top spectrum 2014) and also previously mentioned 2579cm-^{1} and 2256 cm-^{1} as cobalt-doped glass-filled sapphire (Thanong et al, 2013).

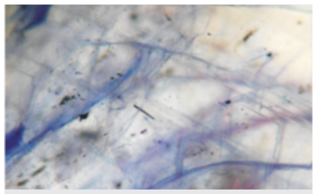

Fig.2. Cobalt treated sapphire set in man's ring (photo by TayThye Sun)

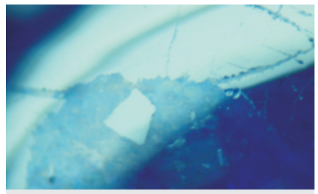

Fig.3. Cobalt treated sapphire set in man's ring (photo by TayThye Sun)

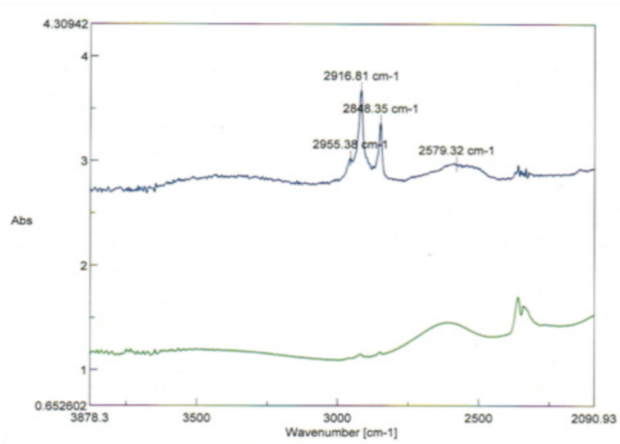

Fig.4. Infrared spectrum shows the presence of strong wax peak 2919 and 2848cm-^{1} (2014) compared to (2012) when the cobalt-doped glass-filled sapphire first appeared (in green) by Tay Thye Sun.

Conclusions – Cobalt-doped glass-filled treated sapphire is quite easily identified by the artificial blue colouring, pink flashes and some gas bubbles in fissures. One interesting information about the infrared spectrum is that the presence of strong wax peak at 2919 and 2948cm-^{1} (2014) which was not previous reported and the double hump at 2579cm-^{1} but 2256cm-^{1} previously reported by Thanong 2013, is not seen now (Fig. 4).

References:

Thanong Leelawatanasuk, Wilawan Atichat, VisutPisutha-Arnond, Pornsawat Wattanakul, Papawarin Ounorn, Wimon Manorotkul and Richard Hughes:
"Cobalt-doped glass-filled sapphire: An update", The Australian Gemmologist, Jan-Mar 2013, Vol.25, No.1. pp 14-20.

Punsiri type heat treatment of sapphire done in Khambat, India

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Many gemmologists may be familiar with the Punsiri heat treatment of sapphires, those exceptional blue sapphires which had absolute "colourless rims" – when immersed in methylene iodide and viewed. Those days the treatment had raised speculation as the sapphires might be subjected to a hitherto unknown lattice diffusion technique. Months later, the American Gem Trade Association's Gem Trade Laboratory noted it had not discovered any form of lattice diffusion in the sapphires, but concluded the stones showed diagnostic characteristics of heat treatment.

Fig. 1: 3.02 carats treated blue sapphire

In fact some may even recall that GIA researchers visited Punsiri Tennakoon, of Punsiri Gems in Ratnapura, Sri Lanka, the proprietor of the heat treatment facility. In analyzing his heat treatment process, it is said that the researchers discovered no evidence of intentional or inadvertent diffusion of elements from an outside source. Colour concentrations inside the stones, as well as the near-colourless boundaries were subjected to various forms of infrared spectroscopy, as well as highly sensitive chemical analysis using LA-ICP-MS and SIMS machines. Several hundreds of non-heated and heated blue sapphires were investigated also involving different types of geuda, the colourless to white or pale blue starting material. Finally, the conclusion drawn was that the colour concentrations of these treated blue sapphires were the cause of a "specific heating regimen used by Mr. Punsiri Tennakoon of Punsiri Gems, Ratnapura, Sri Lanka."

In Khambat, a treatment on blue sapphire is being done which involves heat. The process gives rise to dark blue sapphires and the stones do show characteristic inclusions of heat treated sapphires. The stone gives a colourless rim when immersed in methylene-iodide.

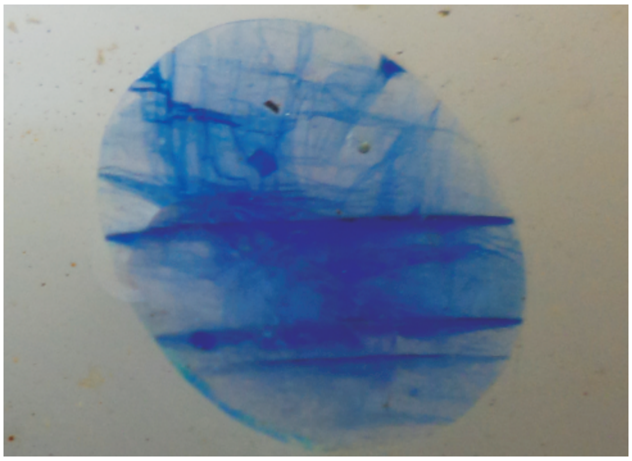

Fig.2: 3.02 ct treated blue sapphire when immersed in methylene-iodide

The technique as explained uses not very high temperature (below 1000^{0}C) and prolonged heating almost for three months on intermittent basis. The final heating is done by coating the stones with slurry of aluminium oxide – this may be responsible for the colourless rim. With UV-Vis spectrophotometer it had a similar spectrum as most metamorphic heated blue sapphires from Ilakaka in Madagascar.

References:

McClure S., Kane R.E. and Sturman N. (2010): Gemstone Enhancement and its detection in the 2000s, Gems & Gemology, Vol. 46, pp218-240

Current Trends within the Thai Gemstone Industry

Dietmar Schwarz and Yadhunath Ramakrishnan

Asian Institute of Gemological Sciences Thailand

2014 has been an eventful year for the Thai gem industry, with the following notable event occurring within these past ten months:

Nigeria-Cameroon Basaltic Sapphire Deposits

New basaltic sapphire deposits have been discovered on the Cameroon side of the Nigeria-Cameroon border, in the form of silky, milky blue-green corundum crystals. This is a welcome occurrence for Thai gem industry, as there had recently been limited production from similar sources in Thailand, Cambodia and Australia.

Thai gemstone-treaters have been able transform most of this Nigerian-Cameroonian material into intense blue stones - and thus helped to restore the supply of blue sapphire within the Thai marketplace - using a heat treatment process which is quite different from that of other basaltic sapphires, with reduced temperatures and the unprecedented use of oil furnaces.

The stones are first heated - in an oxy-propane gas furnace - to a temperature between 1400 ºC and 1500 ºC, as temperatures in excess of this produce an undesired dark blue color. The next step is to re-heat the gems to a temperature of 1300 ºC -again, in an oil furnace - in order to further improve their color. Finally, the sapphires are annealed at a temperature below 800 ºC for a period of 200 to 240 hours, before being slowly cooled and removed from the furnace. The stones with a sufficiently intense color are withdrawn, and the process is then repeated three or four times, with those that remain until 80% have obtained the desired color.

Fig. 1a

Fig. 1b

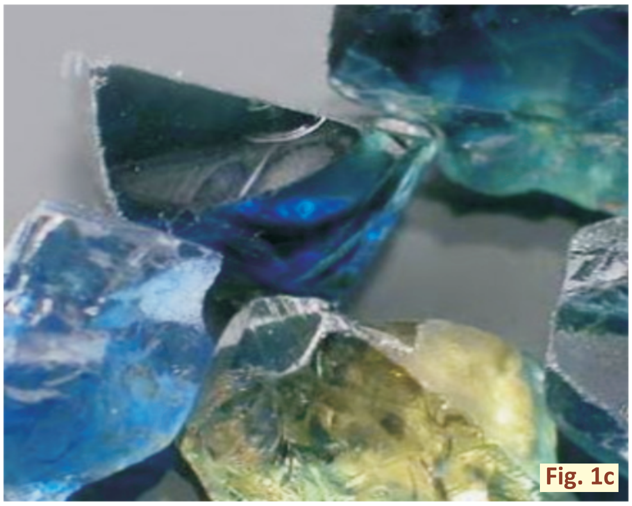

Fig. 1c

Fig 1a, Fig. 1b and Fig. 1c: Nigerian-Cameroonian rough sapphire material before treatment

The opinion of the experts in the heat treatment industry is that these sapphires do not require beryllium-based treatment, as the color after regular heat treatment is sufficiently intense. Furthermore, it is said that Be-treating the stones in a reducing atmosphere produces an undesired dark blue color - similar to that seen in Australian stones - while a dark green hue occurs when heating in an oxidizing atmosphere.

The primary goal of the Thai gemstone-treaters is to now improve the transparency and clarity of material from this deposit, without sacrificing the intensity of its post-treatment color. At present, these sapphires have a mild silky appearance, which diffuses light entering the gemstone and produces the gentle, velvety effect seen in intense blue varieties. However, upon further inspection, grey and green secondary hues are observed, which have been intentionally disguised through the specific orientation and cutting of the stones.

Fig. 2a

Fig. 2b

Fig 2a and Fig 2b: After new type of heat treatment on blue sapphire from Cameroon

Since the second week of June 2014, the above deposit and enhancement process have combined to produce a considerable amount of intense blue sapphire in Chanthaburi gem market. However, as the source has started to deplete, the value of this material has already increased ten-fold from the prices originally observed in June.

Note:
The exact conditions used in this process - including the specific temperatures, atmospheric conditions and associated chemicals - are a proprietary technology of professionals within Thailand's heat treatment industry, and as such are not disclosed in this paper at their request.

Acknowledgements:
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