

# Cobalt-doped glass-filled sapphires: An update

By Thanong Leelawatanasuk, Wilawan Atitchat, Visut Pisutha-Arnond, Pornsawat Wattanakul, Papawarin Ounorn, Wimon Manorotkul & Richard W. Hughes

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**Abstract:** The history of glass-infilling in blue sapphire is reviewed, along with a detailed description of the latest generation of this treatment, which was developed by Tanusorn Lethaisong in Chanthaburi, Thailand. Stones may be identified by reference to their inclusions, lack of pleochroism and red reaction in the Chelsea filter. Spectra and other advanced tests further characterize and separate these stones from natural and synthetic sapphire, as well as heated and bulk diffused sapphire.



Figure 1. Two blue stones weighing 7.57 ct (left) and 6.62 ct (right) submitted to GIT for testing in May 2012.

Photo by Warinthip Krajae-Jan.

## Introduction

In September of 2007, five faceted stones and a few rough samples were submitted to the Bangkok lab of the Gem & Jewelry Institute of Thailand (GIT) by a gem treater who informed the lab that they represented a new type of treatment. The name applied to this treatment at the time was *Super Diffusion Tanusorn*, named after Tanusorn Lethaisong, the Chanthaburi, Thailand treater who developed it (GIT, 2007). In reality this treatment did not involve diffusion, but was simply an infilling of cobalt-coloured glass into a highly fractured corundum, dyeing it blue. The starting material for this treatment was said to be low-grade near-colourless corundum from Madagascar or Sri Lanka (Abduriyim, 2007). Initial finished samples were of low quality, being semi-translucent.

Five years later, in May of 2012, GIT's lab received two unusual blue stones for identification (Leelawatanasuk, 2012). One was a 6.62-ct cabochon, with the other

being a 7.57-ct stone that was faceted on the crown and cabochon cut on the pavilion (Figure 1). It was said that the stones were blue sapphires heated in the conventional fashion.

Refractive index and specific gravity values were typical for sapphire within the degree of error. However microscopic examination revealed features that were decidedly not natural. While some features (included crystals, lamellar twinning) were typical of natural sapphire, the stones were riddled with fissures filled with a rich blue substance that stood out strongly against the otherwise near colourless sapphire. Indeed, so strong was the blue substance in the fissures that it strongly coloured what would otherwise be near colourless sapphires. In effect, the stones were dyed blue.

Since that time, a number of additional pieces have been examined. Effectively these stones represent a refinement of the original Tanusorn treatment.

What follows is a discussion of the general properties and key identifying features of this new type of treated sapphire.

## General properties

The gemological properties for these stones are generally consistent with natural sapphire, with a few important exceptions. Specific gravity values were slightly elevated in some specimens. But more importantly, all of the stones tested showed a strong red to orange-red when viewed with the Chelsea filter. Both natural and synthetic blue sapphires show no red.

In addition, examination with the dichroscope revealed a lack of pleochroism. This is because the rich colour of the stones comes from the cobalt colourant in the glass, rather than from the sapphire structure itself.

Together, the Chelsea filter reaction and lack of pleochroism allow easy separation from both natural and synthetic sapphire, including sapphire enhanced by both standard heating and titanium bulk diffusion.



Figure 2. Two first-generation cobalt-doped glass-filled sapphires (top row; 3.49 & 3.37 ct), along with eight latest-generation cobalt-doped glass-filled sapphires ranging from 1.50–2.25 ct each that were tested as part of this study. Note the far lower clarity of the first-generation stones. (Photo: Wimon Manorotkul)

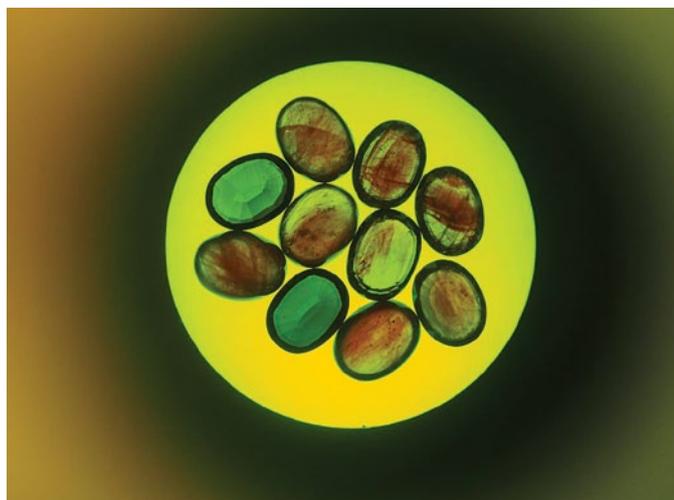


Figure 3. When viewed through the Chelsea filter, the new-generation cobalt-glass filled sapphires showed a strong red reaction. As the above photo demonstrates, the red colour is concentrated in the fissures filled with the cobalt-coloured glass. Natural, heat-treated, Ti-diffusion treated and synthetic sapphires will not show red through the Chelsea filter. The two stones in the above photo without red are Verneuil synthetic sapphires. Photo by Richard Hughes.

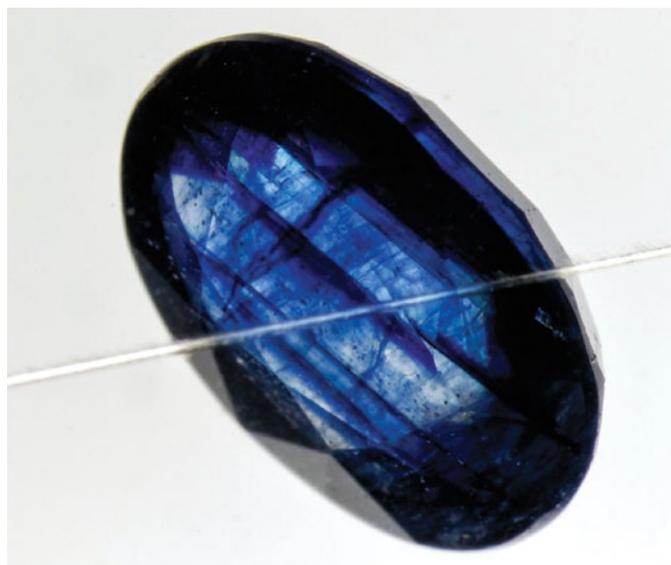


Figure 4. Testing with a London dichroscope revealed no pleochroism when inclined to the c-axis, as shown in the photo above. Natural, heat-treated, Ti-diffusion treated and synthetic sapphires will show obvious pleochroism in stones with this depth of colour. Photo by Wimon Manorotkul.

Table 1. Properties of cobalt-doped glass-filled sapphires

Property	Results: Old generation <sup>1</sup>	Results: New generation <sup>2</sup>
Refractive Index	1.762–1.770 (0.008); uniaxial (–)	1.762–1.770 (0.008); uniaxial (–)
Polariscope Reaction	None; semi-translucent	Doubly refractive; most stones too heavily twinned to resolve uniaxial figure
Specific Gravity (Hydrostatic)	3.95–3.96 ±0.06 <sup>3</sup>	4.05 ±0.12 <sup>3</sup>
UV Fluorescence	Weak red-orange in LW	Inert to weak red-orange in both LW & SW; red-orange fluorescence concentrated in the fissures
Visible Spectrum	Weak Fe spectrum from the sapphire, with lines at 450, 460, 471 nm; Co-glass spectrum from the glass, with broad absorption in the yellow at 591 and less at 544 and 625 nm	Weak Fe spectrum from the sapphire, with lines at 450, 460, 471 nm; Co-glass spectrum from the glass, with broad absorption in the yellow at 591 and less at 544 and 625 nm
Pleochroism	None visible; this is because the underlying sapphire has little colour and thus makes an excellent field-test	None visible; this is because the underlying sapphire has little colour and thus makes an excellent field-test
Chelsea Filter	Strong red to orange red; this test can be used to easily separate cobalt-doped glass-filled sapphires from both natural and synthetic sapphires	Strong red to orange-red; this test can be used to easily separate cobalt-doped glass-filled sapphires from both natural and synthetic sapphires
Inclusions	Natural inclusions such as crystals, healed fissures and polysynthetic twinning in the sapphire portion; pools of deep blue glass in surface-reaching cavities and fissures	Natural inclusions such as crystals and polysynthetic twinning in the sapphire portion; flash effect in the fissures from the glass filler; colour concentrations in the glass filler; undercutting of the glass filler at the surface; flattened gas bubbles trapped in the glass filler

<sup>1</sup> Based on the testing of two stones weighing 3.49 and 3.36 ct. respectively, purchased by GIT in 2007

<sup>2</sup> Based on the testing of eight stones ranging in weight from 1.50–2.25 ct. each, purchased by RWH in Chanthaburi in December 2012

<sup>3</sup> Based on a potential error of ±0.01 ct in both the air and water weighing

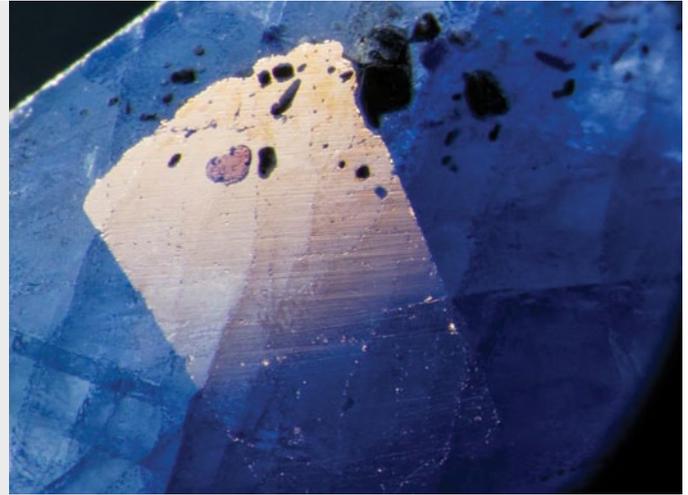
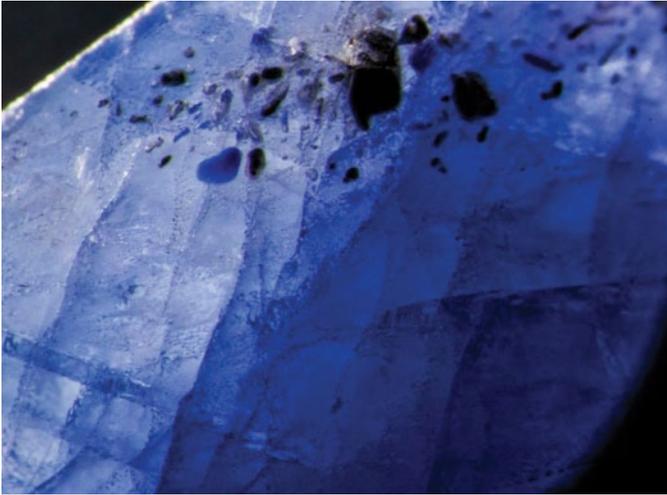


Figure 5. Left: Blue pool of cobalt-doped glass fills a surface cavity in this first-generation Tanusorn stone. Dark-field illumination. Right: The same inclusion in reflected light reveals the lower luster of the glass filler. Oblique fiber-optic illumination. Photos by Richard Hughes.



Figure 6. Blue cobalt-doped glass fills a surface-reaching fissure in this first-generation stone. Oblique fiber-optic illumination. Photo by Wimon Manorotkul.

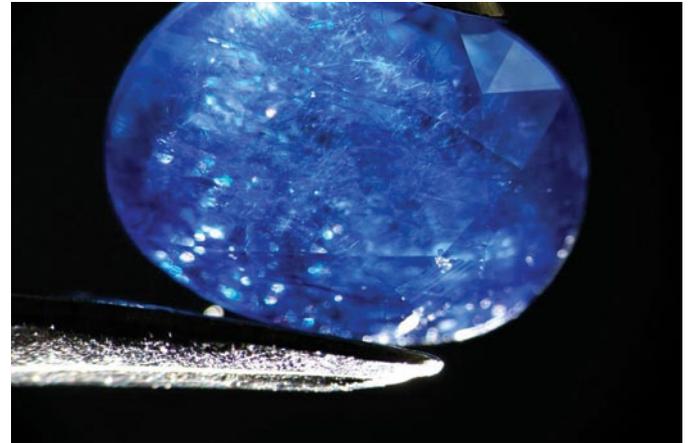


Figure 7. At low magnification the new generation stones display a roiled appearance caused by the network of glass-filled fissures. Dark-field illumination. Photo by Wimon Manorotkul.

## Microscopic features

Microscopic examination is also important for the identification of this treatment (Figures 5–12). The first generation Tanusorn stones (Figures 5–6) were heavily included, so much so that they were only semi-translucent. Stones were riddled with polysynthetic twinning and secondary healed fissures. Near the surface, cavities were filled with a rich blue cobalt-doped glass, while in other places the blue glass penetrated surface openings, such as fingerprints.

The new generation of stones (Figures 7–12) reveals features that are typical of glass-filled rubies. Fissure fillings show a luster much lower than the surrounding sapphire, and also showed serious undercutting, suggesting it was of far lower hardness. In addition, the fissures contained what appeared to be flattened gas bubbles that stood out in high relief from the surrounding glass filler.

The glass filler itself showed a deep blue colour, particularly if the gem was examined in diffused light-field illumination. When using oblique or dark-field illumination, a yellow/blue/pink flash effect from the fissures was seen, similar to what one encounters in glass-filled rubies.

## Advanced testing

### *DiamondView™*

Two cobalt-doped glass-filled sapphires were examined with the DeBeers DiamondView™. This is essentially a powerful short-wave UV light source. Both stones showed a strong chalky blue fluorescence concentrated in a spider-web like pattern of tiny fissures, corresponding to the areas of glass infilling (Figure 13).

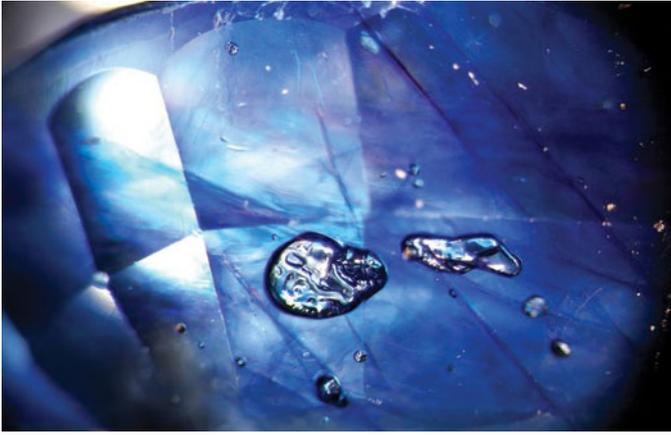


Figure 8. Flattened gas bubbles stand out in high relief in the glass filler of this cobalt-glass filled sapphire. Oblique fiber-optic illumination. Photo by Wimon Manorotkul.

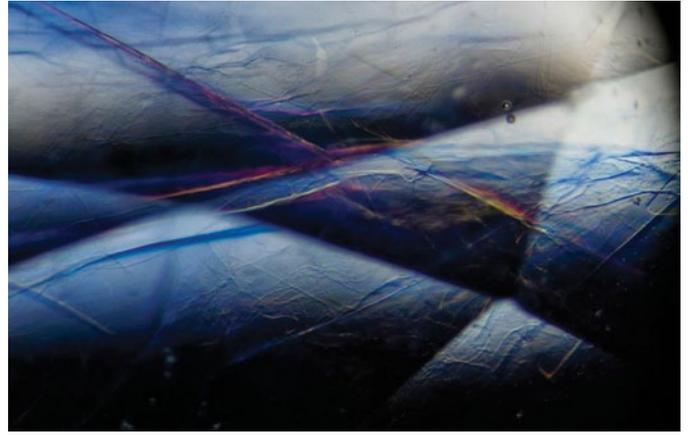


Figure 9. The lead-glass filler often produced a yellow/blue/pink flash effect as the stone was rotated in the microscope. Oblique fiber-optic illumination. Photo by Wimon Manorotkul.

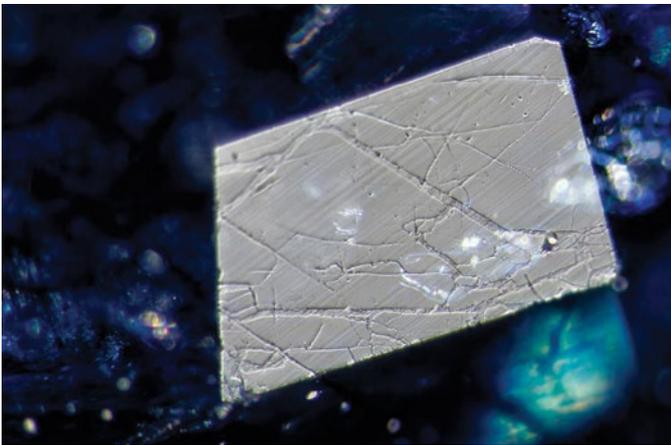


Figure 10. A small facet viewed in reflected light reveals a network of fissures filled with glass. The low hardness of the glass shows serious undercutting compared with the surrounding sapphire. Surface-incident fiber-optic illumination. Photo by Wimon Manorotkul.

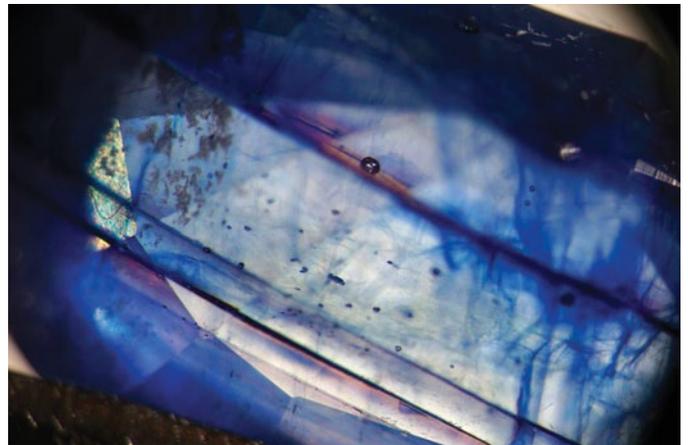


Figure 11. When viewed with transmitted light field illumination, rich blue colour concentrations are found in the fissures. Photo by Wimon Manorotkul.



Figure 12: Immersion in di-iodomethane (methylene iodide) in diffuse light-field illumination quickly reveals the blue colour concentrations in the cobalt-glass filled sapphires (top two stones), whereas natural sapphires show angular colour zoning (lower two stones). Image corrected to remove yellow colour of liquid. Photo by Wimon Manorotkul.

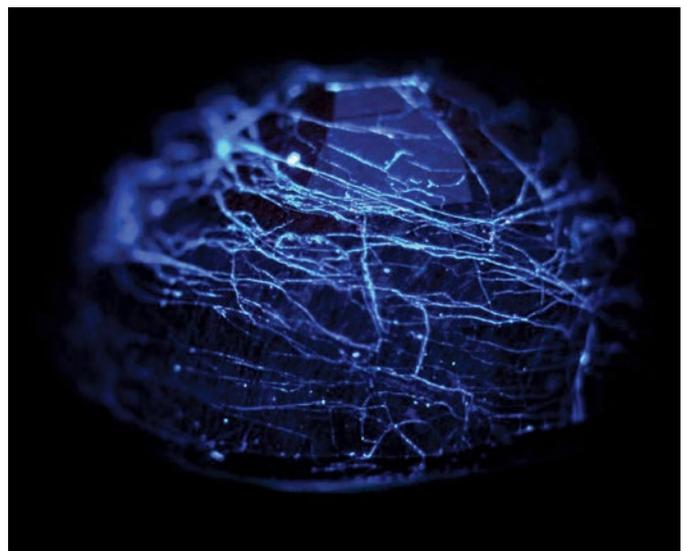
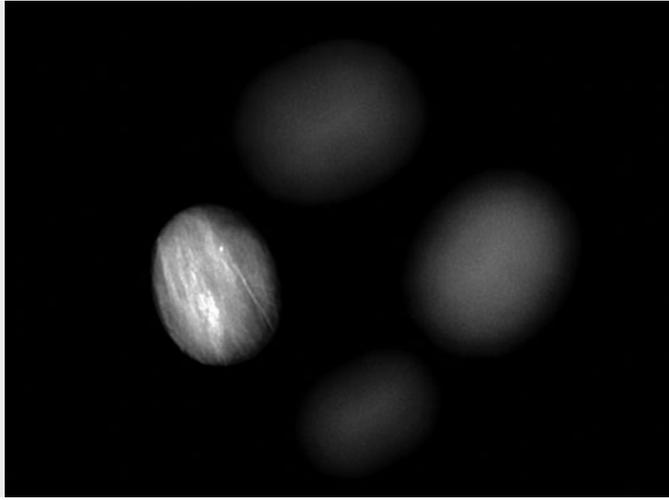


Figure 13: DiamondView™ image of a cobalt-doped glass-filled sapphire, showing chalky blue fluorescence from the glass-filled fissures. Image by GIT.

Figure 14. X-ray image of the new generation cobalt-doped glass-filled sapphire (left), showing opaque areas along the fractures. In contrast, a natural sapphire (top), an original Tanusorn-treated sapphire (right) and a Verneuil synthetic sapphire show no such x-ray opacity in the fissures. Image by GIT.



### Chemistry

In order to determine the identity of the filler, energy dispersive x-ray fluorescence (ED-XRF) analysis was carried out. As expected, cobalt (Co) and lead (Pb) in the blue glass filler were detected. Further analysis by X-radiography also revealed opaque areas in the X-ray images; these coincided with the positions of glass-filled fractures and cavities (Figure 14).

### Spectra

The UV-Vis-NIR spectra shows clear cobalt-related absorption bands peaked at 544, 591 and 625 nm (Figure 15) that perfectly matched our reference spectra for "cobalt-blue glass". The Mid-IR spectra also show absorption humps at around 3500, 2597 and 2256  $\text{cm}^{-1}$  (Figure 16), which are commonly found in the normal glass-filled ruby.

Figure 15. Non-polarized UV-Vis-NIR spectra of a new generation Tanusorn-treated sapphire showing cobalt-related absorption bands peaked at 544 and 591 nm. An additional peak at 625 nm is sometimes seen. Spectrum by GIT.

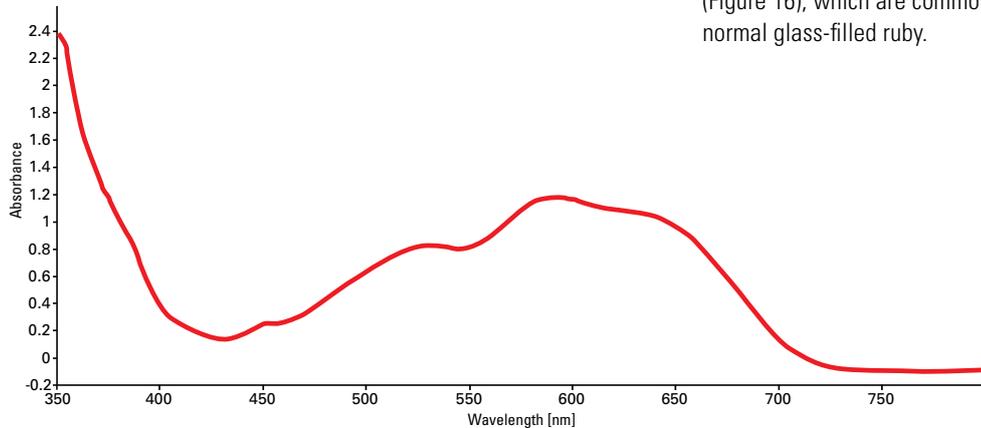


Figure 16. Mid-IR spectrum of a new generation Tanusorn-treated sapphire showing absorption bands at 2,597 and 2,256  $\text{cm}^{-1}$ ; these bands are often present in glass-filled stones. Spectrum by GIT.

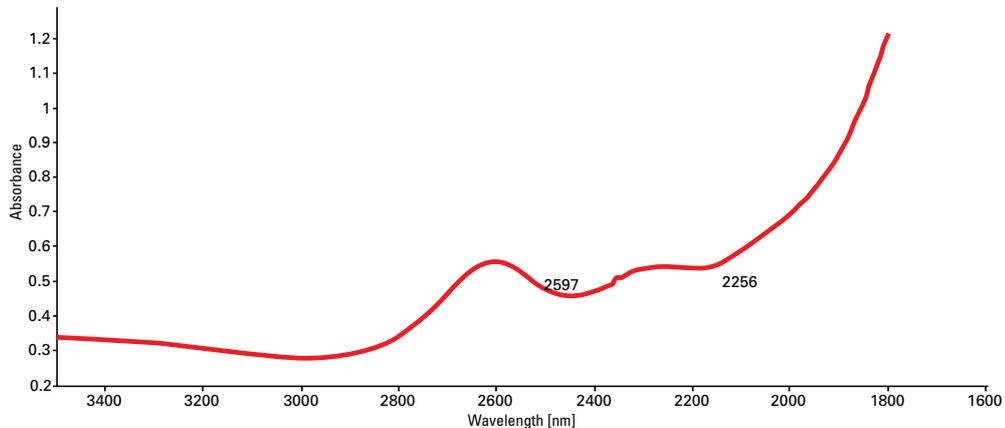


Figure 17. Boiling in a strongly basic solution (sodium hydroxide) for ten minutes caused the glass filler to quickly deteriorate. Photo by Thanong Leelawatanasuk.

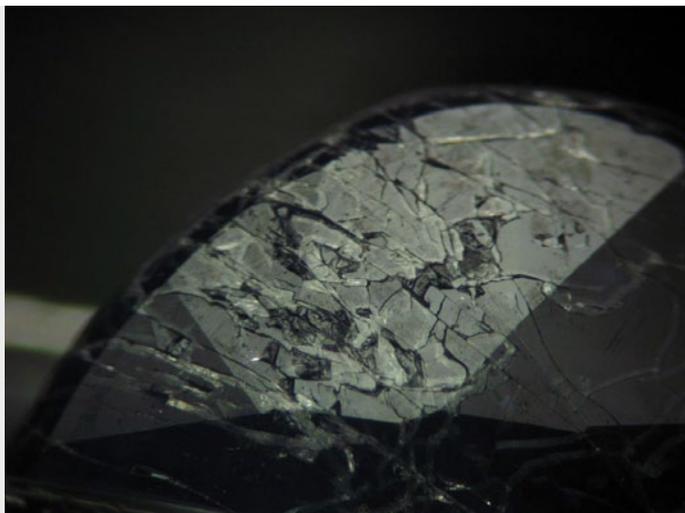


Table 2. Stability testing of latest generation cobalt-doped glass-filled sapphire

Tools and reagents	Time/Temperature	Results	Conclusion	Remarks
Ultrasonic cleaner for 10 minutes	10 minutes in water at room temperature	No change	Possibly safe; needs further testing	–
Exposure to flame of jeweler's torch for one minute	1 minute at approx. 1000 °C	Glass filler showed obvious decay	Avoid heat of any kind	–
Immersion in strongly acidic solution sulfuric acid H <sub>2</sub> SO <sub>4</sub> at 98% concentration	30 minutes at room temperature	Glass filler slightly dissolved	Avoid any and all contact with strong acids particularly hydrofluoric acid, which is known to quickly dissolve silica-based glasses	This acid in dilute form (20%) is commonly used to clean jewellery surfaces before plating
Immersion in strongly basic solution sodium hydroxide NaOH	10 minutes/boiling	Glass filler strongly dissolved; open fractures clearly observed	Avoid any and all contact with strong bases	Test performed by treater in Chanthaburi

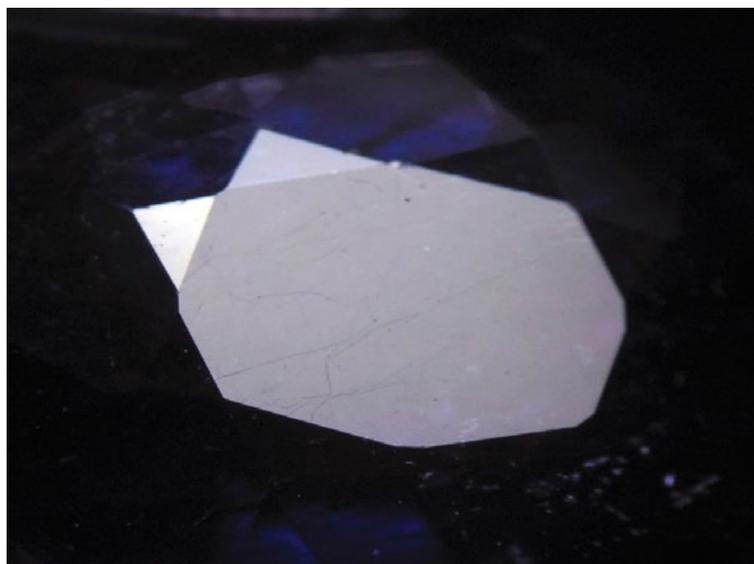


Figure 18. Table facet of one cobalt-doped glass-filled sapphire before (top) and after (below) heating with a jeweler's torch. Photos by Thanong Leelawatanasuk.

### Stability testing

Because glass-filled rubies are known to be extremely unstable (Scarratt, 2012; LMHC, 2012), the authors conducted stability testing on some of the stones. These tests included ultrasonic cleaning, heating with a jeweler's torch and immersion in strongly basic and strongly acidic solutions. The results are contained in Table 2.

### Conclusions

Glass-filled (a.k.a. 'composite) rubies have become ubiquitous since their appearance in late 2004 (Pardieu, 2005; GIT, 2008). It is very possible that this scenario will be repeated with cobalt-doped glass-filled sapphires, since the treatment allows a near-colourless sapphire of poor clarity to mimic the appearance of a blue sapphire of higher value. Thus it is important for traders, jewelers and gemologists to be familiar with the material and the methods of identification.

A simple Chelsea filter screening test can easily separate the latest generation of stones seen thus far from both natural, heated (including titanium diffused) and synthetic sapphires. This preliminary identification can be confirmed by the lack of pleochroism and particularly the distinctive internal and surface features visible under magnification. Advanced testing can also be used, but is not necessary in most cases.

### Acknowledgements

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