The Gem and Jewelry Institute of Thailand (Public Organization)

LAB ALERT

AN UPDATE ON TITANIUM-DIFFUSED SAPPHIRE

By Gem Testing Laboratory
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Introduction

While titanium-diffused sapphires may not be new, samples obtained last November by the GIT-GTL may be something worth looking a little closer. Figure 1 shows three faceted and 12 pre-forms, each with a foreign substance on the surface.

Figure 1: GIT's collection of surface diffusion sapphires. Cut stones are approximately 0.20 cts each and show different color intensities. Note the strong color rims and foreign materials coating the pre-formed stones. Photo: Wimon Manorotkul

Appearance and other features

Microscopic observation in the 3 faceted stones shows dotted lines and melted crystal inclusions that suggest they had been treated with very high heating temperatures (see Figures 2–4).

Under immersion, the samples show no angular blue color zoning as is commonly found in natural or traditionally heat-treated blue sapphire; instead they showed only blue patches of color, with faceted stones showing faint color concentrations along facet junctions (see Figure 5).

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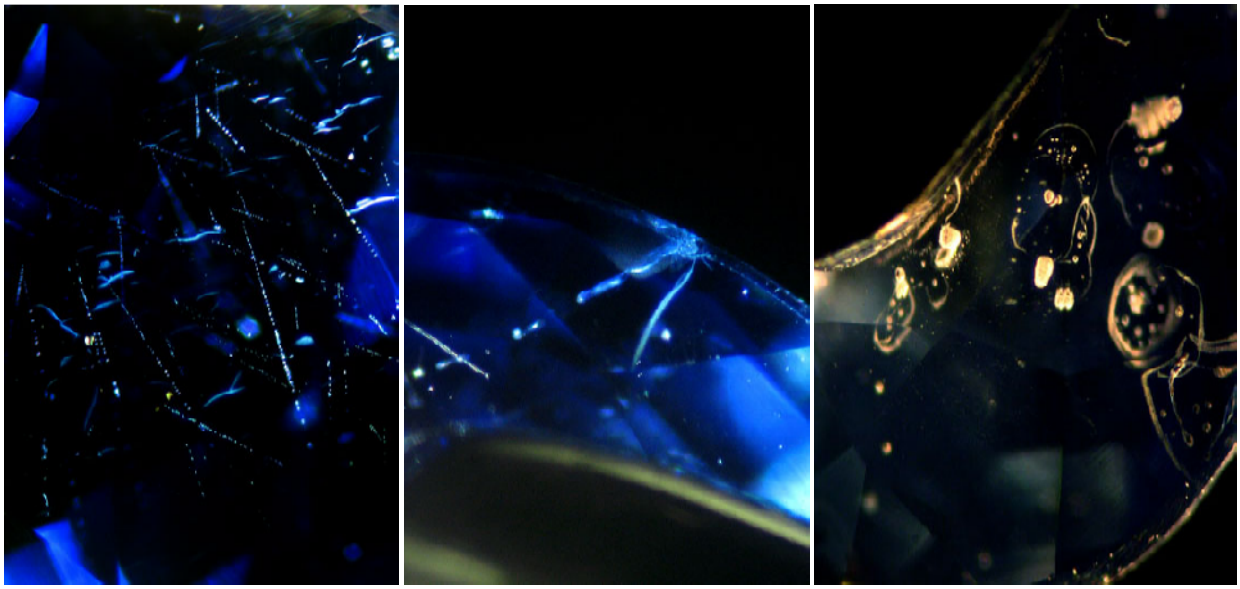

Figures 2–4: Partially resorbed needles, melted crystals and discoid fractures encircling melted crystals suggest stones had been exposed to high heat. Oblique fiber-optic illumination, 50x. Photos: Wimon Manorotkul

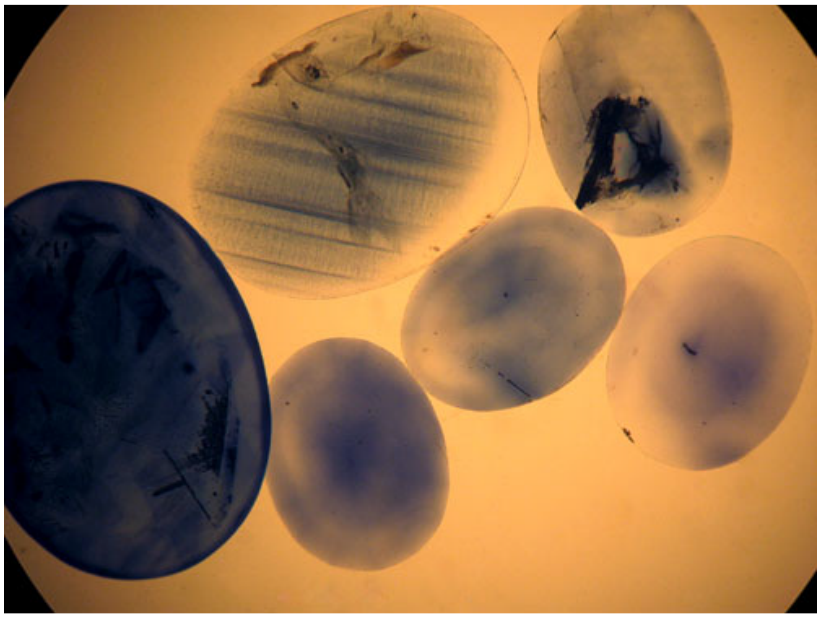

Figure 5: A traditionally heated sapphire (top left) compared with five titanium-diffused sapphires of varying penetration depths. Under immersion in diiodomethane (methylene iodide), the Ti-diffused sapphires reveal different levels of color concentrations at facet junctions, depending on the depths of penetration and how much surface material was removed during faceting and polishing after the treatment. Diffuse lightfield illumination, 12.5x. Photo: Wimon Manorotkul

The UV-VIS-NIR spectrum (see Figure 6) clearly reveals that cause of color is an intervalent charge transfer (IVCT) between iron and titanium (Fe^{2+}-Ti^{4+}) similar to those of blue sapphire of metamorphic origin. The FTIR spectrum (see Figure 7) shows patern that are often found in blue sapphire. Chemical analysis by EDXRF gives unusually high contents of

Ti and Fe (~1000-3000 ppm); in particular the Ti content is much higher than the normal range for natural or traditionally heat-treated blue sapphire of metamorphic origin. (less than 1000 ppm).

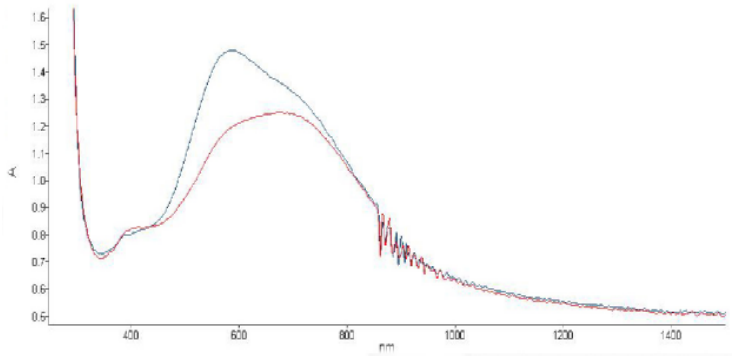

Figure 6: Represent UV-Vis-NIR spectrum of titanium-diffused sample shows cause of colour is Fe/Ti IVCT (blue line:O-ray,red line: E-ray)

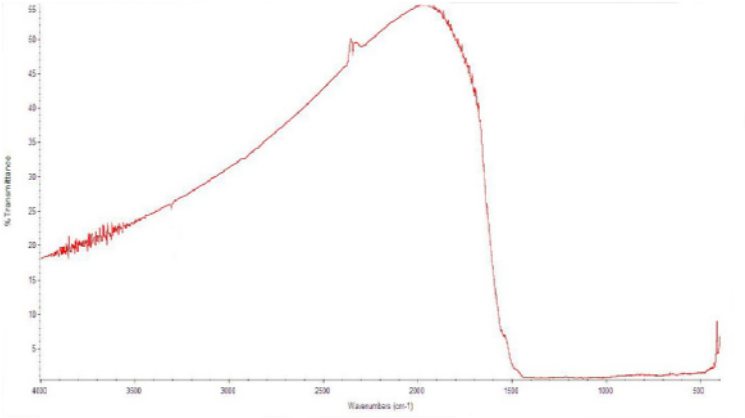

Figure 7: Represent FTIR spectrum of titanium-diffused sample shows normal pattern often found in blue sapphire

However, few treated pre-formed samples were cut and polished into thin-slabs, then analyzed on a traverse across the cut surface by LA-ICP-MS technique. The results show elevated titanium concentration from the core to the rims of every samples(see Figure 8), while the contents of iron and other elements (Mg, Be, B, etc.) are quite consistent throughout the stone. LIBS analysis shows no trace of beryllium in the samples .

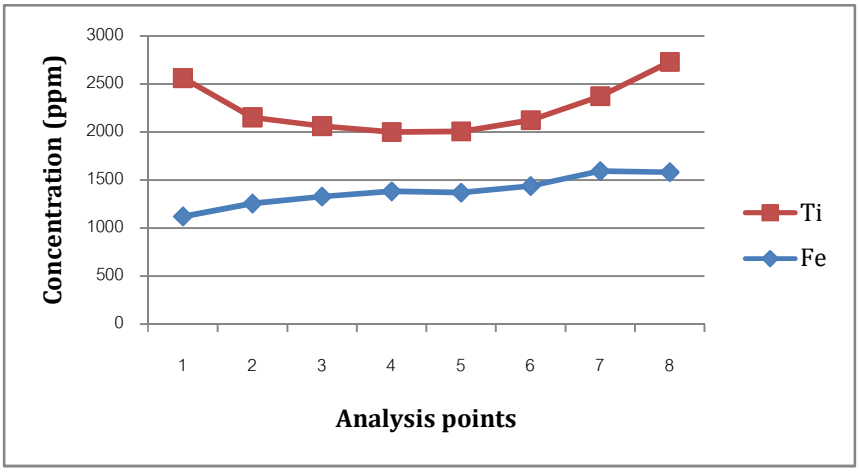

Figure 8: Slabs of titanium-diffused sample analyzed by LA-ICP-MS on a traverse across a thin-slab revealed higher titanium content normally shown in natural or heat-treated blue sapphire (less than 1000 ppm) and elevated from the core to the rim.

Based on the above observations, we believe these gem materials are the result of a treatment as follows:

- Raw materials were colorless or very light colored sapphires.
- The Ti coloring agent was applied to pre-forms instead of faceted stones.
- Stones were faceted and polished after the treatment.
- Like all lattice-diffusion treated stones, a thick color rim along the outline of pre-formed stones (varying from 0.20 to 0.50 mm) suggests a long and extremely high temperature heating. See Figure 9.

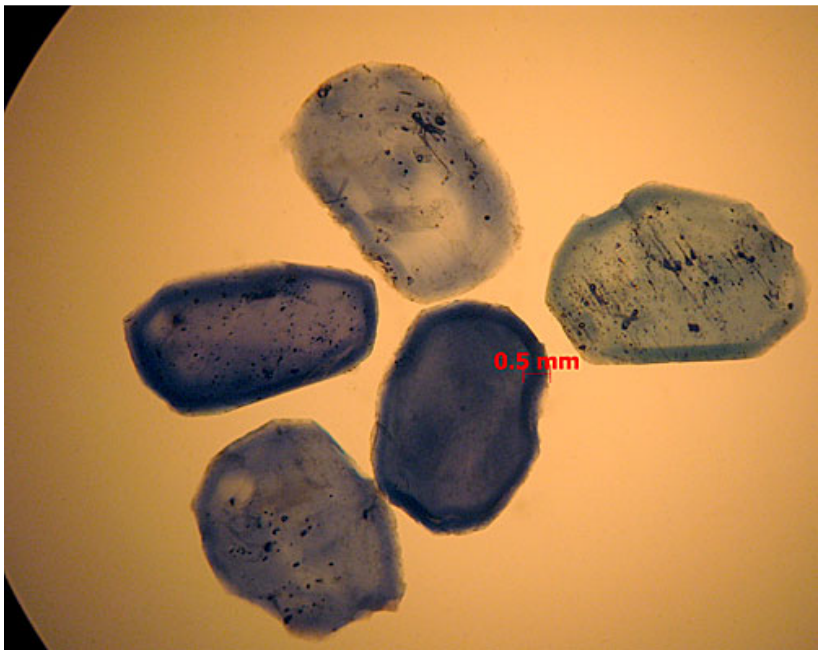

Figure 9: Depth of color penetration measures on uncut lattice-diffusion treated sapphires under immersion in diiodomethane. Diffuse lightfield illumination, 9x. Photos: Wimon Manorotkul

Conclusions

Because the treatment was done on pre-formed stones, subsequent faceting and polishing greatly reduces or even eliminates the evidence of treatment typically seen in titanium-diffused sapphires. Color concentrations at facet edges and stone edges are greatly reduced. This is similar to what was reported by Hughes in 1988 and 1991. In order to avoid mistakes in identification, gemologists must take great care, particularly with small stones or mounted pieces. If necessary, chemical analysis is strongly recommended.

References

Carr, R.R. and Nisevich, S.D. (1975) *Altering the appearance of corundum crystals.* US Patent No. 3,897,529. <http://www.patentstorm.us/patents/6635309/claims.html>

Carr, R.R. and Nisevich, S.D. (1976) *Altering the appearance of corundum crystals.* US Patent No. 3,950,596.

Carr, R.R. and Nisevich, S.D. (1977) *Altering the appearance of corundum crystals.* US Patent No. 4,039,726.

Crowningshield, R. (1979) Developments and Highlights at GIA's Lab in New York: Some sapphire problems. *Gems & Gemology,* Vol. 16, No. 7, pp. 194–196.

Crowningshield, R. and Nassau, K. (1981) The heat and diffusion treatment of natural and synthetic sapphires. *Journal of Gemmology,* Vol. 17, No. 8, Oct., pp. 528–541.

Hughes, R.W. (1988) Reappearance of surface-diffusion treated sapphires in Bangkok. *ICA Lab Alert,* No. 12, 2 pp.

Hughes, R.W. (1991) There's a rumble in the jungle—The sapphire face-lift face-off. *Gemological Digest,* Vol. 3, No. 2, pp. 17-31. <http://www.ruby-sapphire.com/blue_surface_diffusion.htm>

Hughes, R.W. (1992) Devil's Advocate: Vampire blues: deep-diffusion treated sapphires. *JewelSiam,* No. 3, May-June, pp. 83–86. <http://www.ruby-sapphire.com/vampire_blues.htm>

Kane, R.E., Kammerling, R.C. *et al.* (1990) The identification of blue diffusion-treated sapphires. *Gems & Gemology,* Vol. 26, No. 2, Summer, pp. 115–133.

McClure, S.F., Kammerling, R.C. *et al.* (1993) Update on diffusion-treated corundum: red and other colors. *Gems & Gemology,* Vol. 29, No. 1, pp. 16–28.

Yaverbaum, L.H., ed. (1980) *Synthetic Gems Production Techniques.* Park Ridge, NJ, Noyes Data Corp., 353 pp.