Treated black sapphire

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Introduction

Since late 2013, a variety of gemstone sold as "black sapphire" has entered the market. The result of our preliminary investigation on those stones were quickly reported to the gem community (see GIT'S LAB INFO by Leelawatanasuk and Maneekrajangsaeng, January 2014; Leelawatanasuk et al., 2014). This article is the update of our detailed investigation on this material.

Material and methods

Four "black sapphire" samples (two obtained in late 2013 and the other two in mid 2014) were selected for this study. They were faceted stones come in mixed cut, oval shapes, weighing from 1.44 to 1.91 cts. (Figures 1 and 2). All stones were recorded for standard gemological properties. Some specific spectroscopic data were also collected by advanced instruments; UV-Vis-NIR, FTIR, EDXRF spectrometers, Soft X-Ray radiograph and DiamondView™.

Figure 1. *Two very dark blue (nearly black) stones weighing 1.44 ct. (left) and 1.91 ct. (right) obtained in late 2013. Photo: W. Krajaejan.*

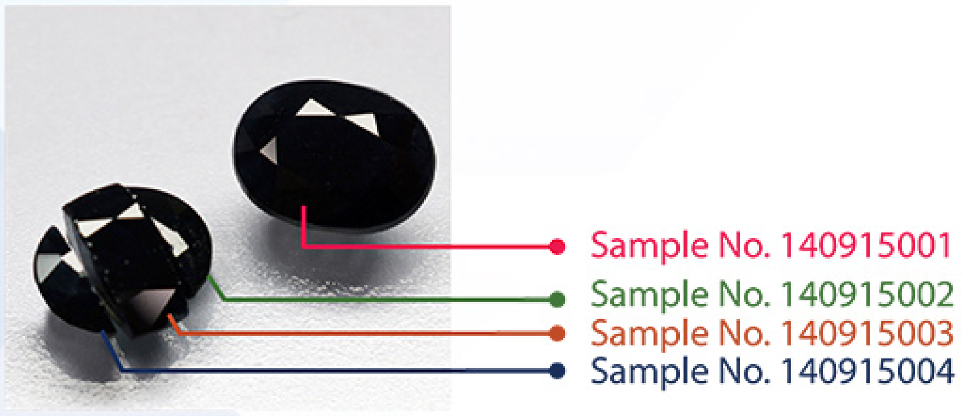

Figure 2. *The sliced stone on the left weighs 1.54 ct. altogether, and the one on the right weighs 1.80 ct. obtained in mid 2014. Photo: S. Saengbuangamlam.*

Results

General properties

The samples appear from extremely dark blue to almost black with low transparency under daylight (Figures 1 and 2). The stones standard gemological properties are generally consistent with natural sapphire. These four stones possess the RI values of 1.760 – 1.770 and SG values of 3.95 – 4.01. The stones show none to moderate dichroism from very dark blue to dark greenish blue through a dichroscope and inert under both LWUV and SWUV.

Microscopic features

Under magnification with normal illumination, the stones contain many healed fissures which made it difficult to find natural inclusions (Figures 3 and 4 left). However, fiber-optic lighting technique would be very helpful method to find blue to black color concentration along the healed fissures throughout the whole stones (Figures 3 and 4 right).

Due to the lack of transparency of mid 2014 stones, one sample (1.54 ct.) was cut into 3 pieces in order to see more inclusions and provide better results from advanced testing (Figure 2). The polished slabs (~1 mm thick) reveal many features indicating the natural origin of raw material, such as cloud of silk pattern (Figure 5) and repeated twinning (Figure 6).

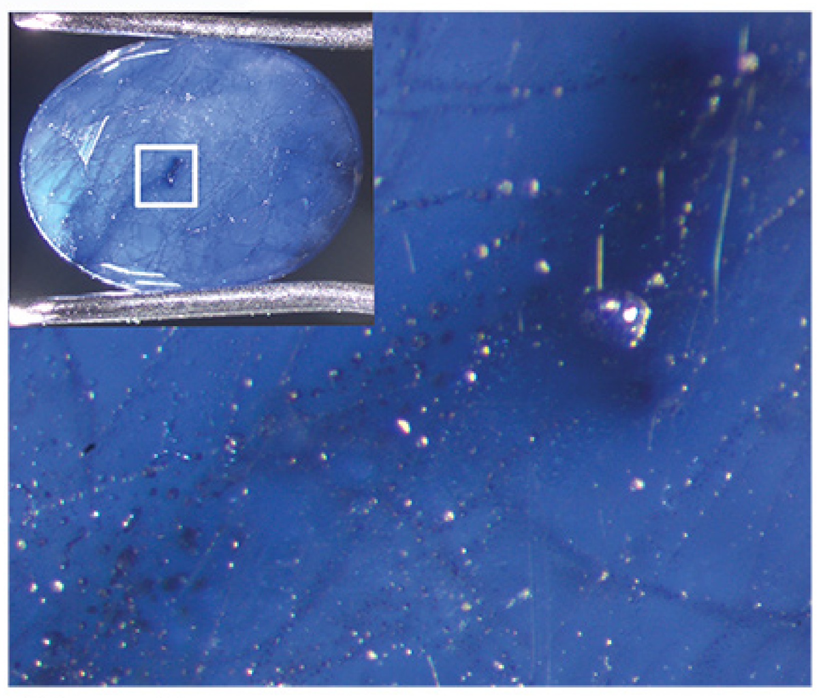

Figure 3. *The appearance of stone under a microscope with strong fiber optic light (left, 20x magnification) and a closed-up view of the surface showing dark blue coloration along those healed fissures (right, 40x magnification). photos: M. Maneekrajangsaeng.*

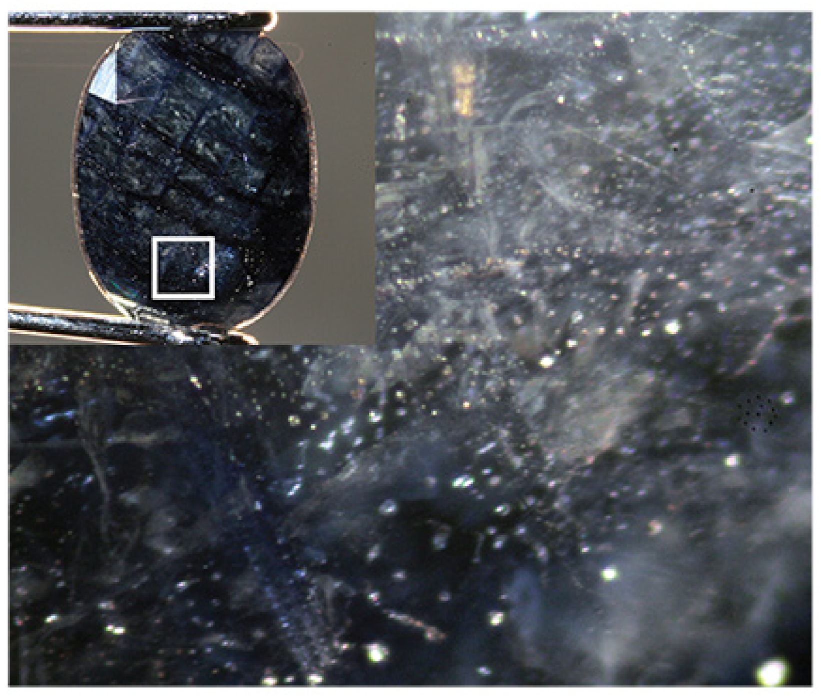

Figure 4. *Many healed fissures with color concentration throughout the whole stone, noted also the white spots of residue material left-over along healed fissures after treatment (Sample No. SAM14091500; left, 20x magnification; right, enlargement of the square area on the left, 40x magnification). Photos: S. Saengbuangamlam.*

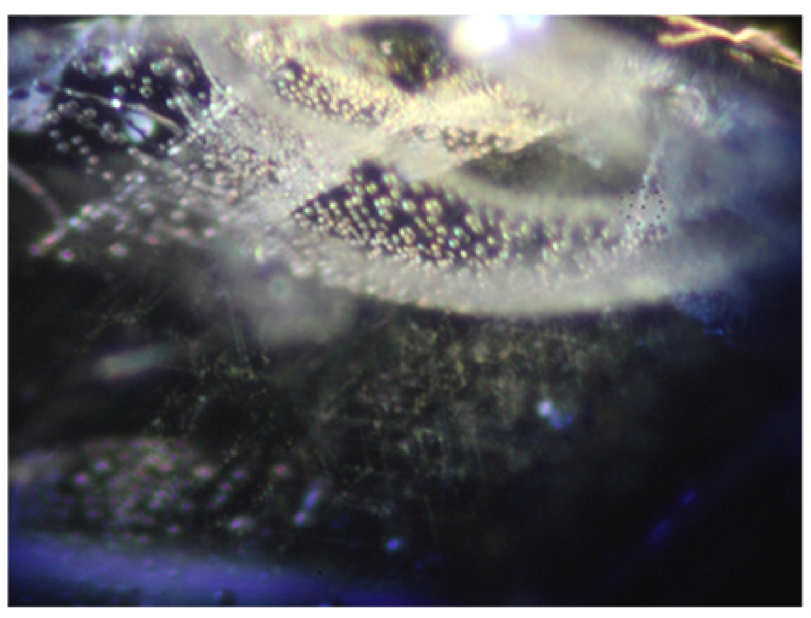

Figure 5. *Cloud of silk pattern under dark field illumination of the mid 2014 stone (50x magnification). Photo: N. Atsawatanapirom*

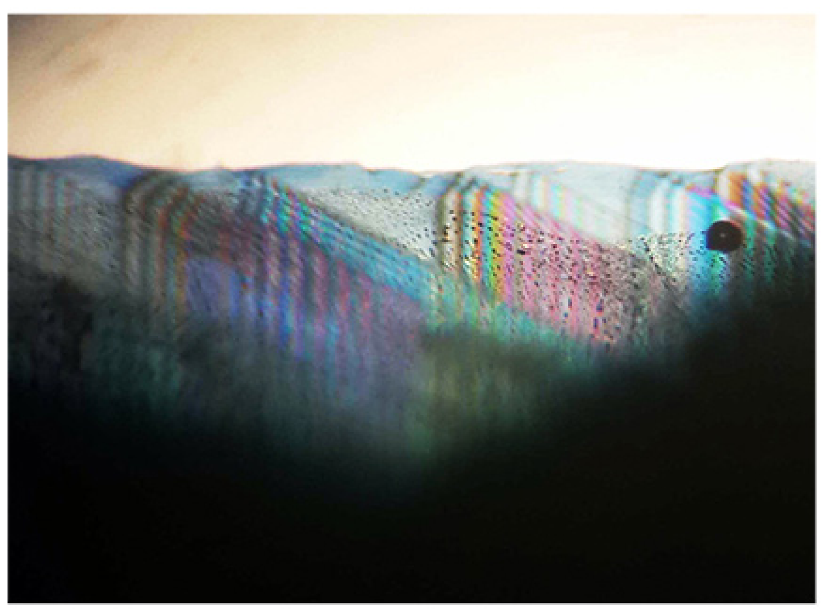

Figure 6. *Repeated twinning of the mid 2014 stone seen under immersion in di-iodomethane solution. Photo: S. Saengbuangamlam*

Immersion in di-iodomethane (methylene iodide) reveals the unusual color concentration along healed fissures due to diffusion of color-causing element(s) outward from the fissures into the host sapphire. A blue color rim was also observed along the stone surface outline indicating color penetration inward from outside of the stone (Figure 7). With high-intensity ultra-shortwave UV radiation of the DiamondView™ (~225 nm), all samples show strong chalky blue fluorescence along the healed fissures (Figures 8 and 9).

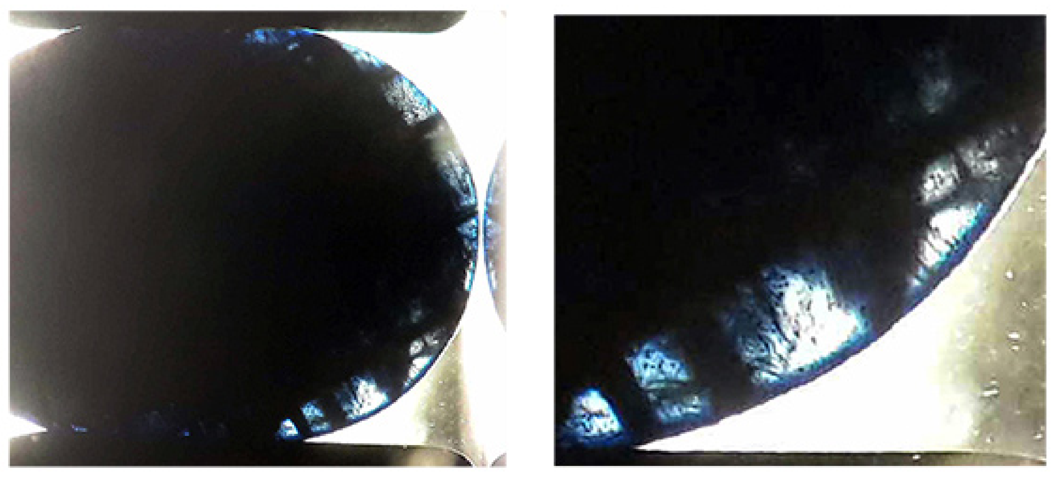

Figure 7. *Color concentration along healed fissures and blue color rim along the mid 2014 stone surface outline seen under immersion in di-iodomethane solution. Photos: S. Saengbuangamlam.*

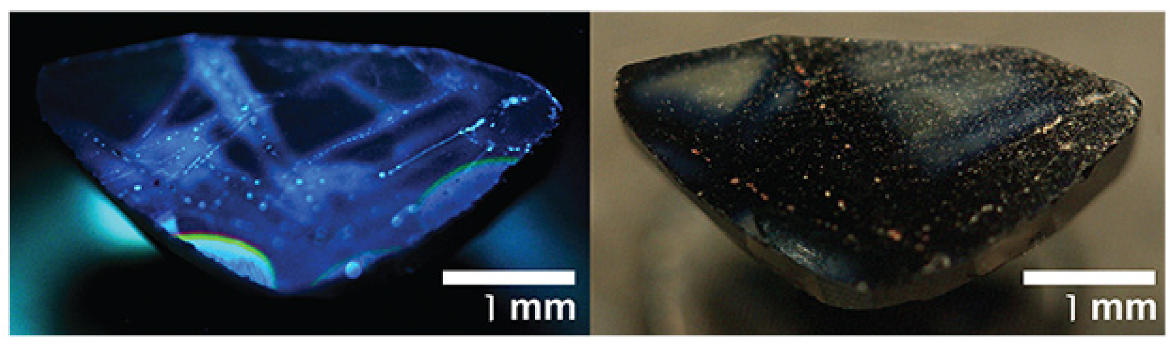

Figure 8. *DiamondView™ images showing strong chalky blue fluorescence zones and bright dots in the mid 2014 slab sample no. SAM140915003 (left, SWUV light) that correspond to the dark blue diffusion bands and dots of residue material along the healed fissures (right, normal light). Photos: S. Promwongnan.*

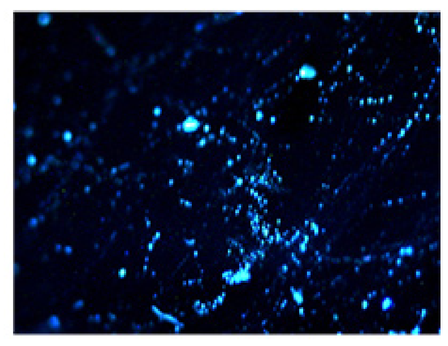

Figure 9. *The DiamondView™ image showing chalky bluish glow along the healed fractures of late 2013 stone. Photo: M. Maneekrajangsaeng.*

Absorption spectra

The UV-Vis-NIR spectra of the late 2013 samples reveal iron-related absorption peaks at 377, 388, 450 nm, and Fe^{2+}/Ti^{4+} Intervalent charge transfer (IVCT) band at ~580 nm indicating the stone's 'metamorphic origin' (Figure 10). By contrast, the UV-Vis-NIR spectra of the mid 2014 samples clearly give not only the Fe-related peaks at 377, 388, 450 nm and Fe^{2+}/Ti^{4+} IVCT band at ~580 nm, but also the Fe^{2+}/Fe^{3+} IVCT absorption bands at ~900 nm indicating the stone's 'basaltic origin' (Figure 11). Notably the absorption spectrum of the blue zone shows higher intensity of Fe^{2+}/Ti^{4+} IVCT absorption band near 580 nm than that found in the paler color zone of the same slab sample.

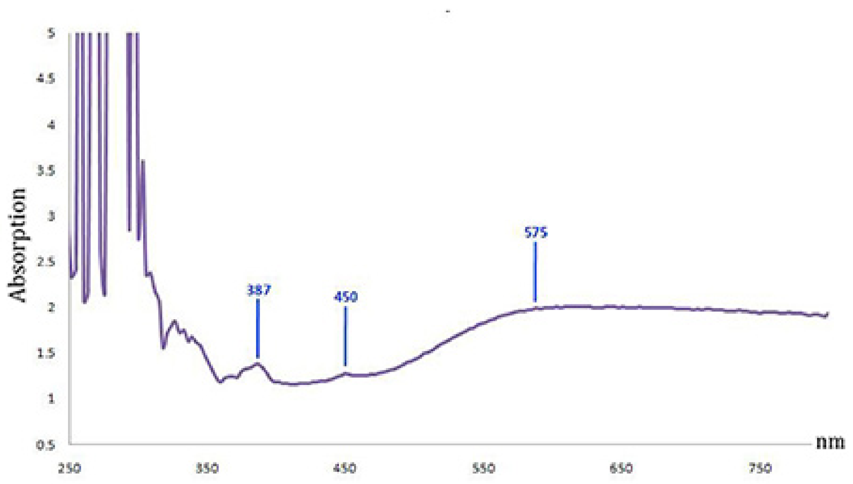

Figure 10. *. Non-polarized UV-Vis spectrum of late 2013 stone showing small Fe-related absorption peaks at 377/387 and 450 nm and dominant Fe^{2+}/Ti^{4+} IVCT absorption band maximized at around 575 nm.*

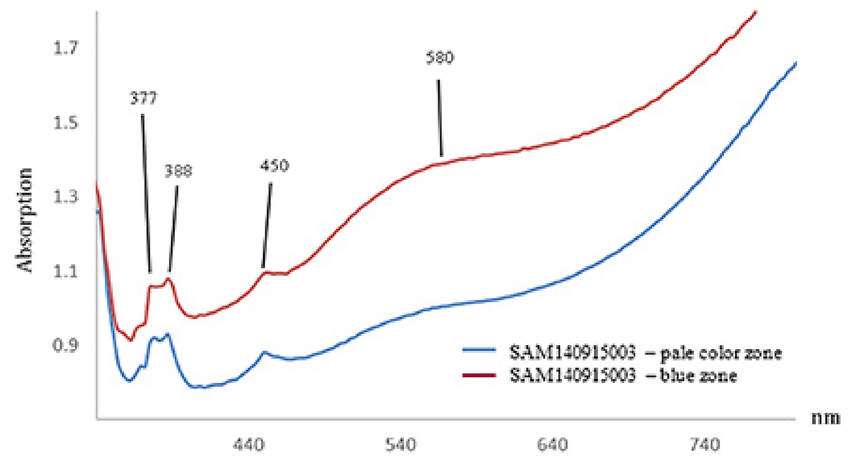

Figure 11. *Non-polarized UV-Vis absorption spectra illustrating the differences in the blue and paler color zones of the mid 2014 slab sample no. SAM140915003, the spectra merely displayed up to 800 nm due to signal error at higher nm region.*

Discussion and conclusion

The late 2013 samples are blue to dark blue stones that were treated from starting raw material of metamorphic origin. By contrast, the mid 2014 samples apparently look much darker blue to almost black stones that were treated from starting raw materials of basaltic origin. The starting raw materials could be low-quality, near colorless to pale colored sapphire with abundant open fissures from both types of origins that were treated by a usual Ti-diffusion technique. Having been heavily fractured materials to begin with, the Ti compound could enter into the stone via open fissures and the Ti-diffusion could have been taken place from the fissures outward into the host corundum while those fissures were also healed during high temperature treatment. Hence, Ti-diffusion technique could create dark blue color zones extending outward from the fissures inside the stone and make them look very similar to a black sapphire. As such, these new products should to be called "diffusion-treated black sapphire", rather than 'black sapphire' in the markett

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