# URGENT LAB INFO A TREATED STONE SOLD AS 'BLACK SAPPHIRE'

By GIT Gem Testing Laboratory January 17, 2014

#### INTRODUCTION

One of the GIT's main duties as the national gem institute is to provide a highly standard gemstone testing service to the country's gem and jewelry industry. Our gem-testing laboratory (GIT-GTL) has constantly monitoring any new gem material or treatment that comes in the market. Once it was found, we then make a preliminary investigation, and quickly disclose its intrinsic properties and proper name of such material to the gem community.

# **MATERIAL**

Recently, our GIT-GTL received a parcel of gems sold as "black sapphire" in the market for identification. All of them look very similar in their quality and cutting style. We selected two representative pieces that came in mixed cut oval shapes weighing 1.44 and 1.91 cts for a preliminary study (Figure 1) reported hereafter.

On a first glance these two stones appear black but when we observed closely they actually are very dark blue stones. As such the next question that came to our minds was whether these stones genuine or treated. They can be a very dark blue sapphire reportedly found in several localities worldwide, such as those in Shandong province of China or the very deep blue variety of Australian sapphire. These gem materials are usually sold as "Black Sapphire" in the market. On the other hand they can be a newly treated stones as well.



Figure 1: Two very dark blue (nearly black) stones weighing 1.44 ct (left) and 1.91 ct (right) submitted to the GIT-GTL for testing. (Photo: Warinthip K.)

## **GEMOLOGICAL PROPERTIES**

Microscopic observation can reveal very prominent features of these sapphires. The stones contain abundant healed fissures with dark blue color concentration along those fissures running throughout the whole stones.(Figure 2) The blue coloration seems to gradually fade away from the fissures toward the host sapphire. The stones show no fluorescence under LWUV but glow weak chalky blue mainly along the healed fracture areas under SWUV. The fluorescent images obtained by Diamond View<sup>TM</sup> clearly reveal such texture. (Figure 3)

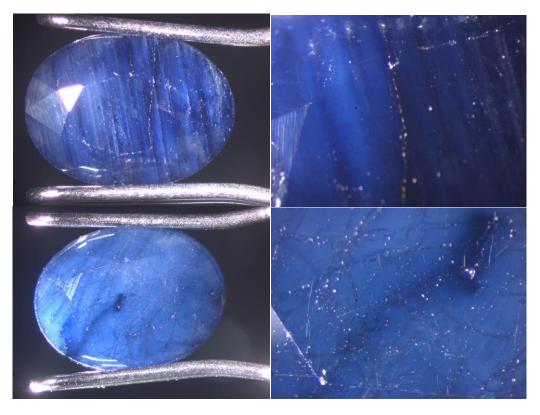


Figure 2: The appearance of stone under a microscope with strong fiber optic light (two images on the left) and a closed-up view of the surface showing dark blue coloration along those healed fissures (two on the right). (photo: Marisa M.)

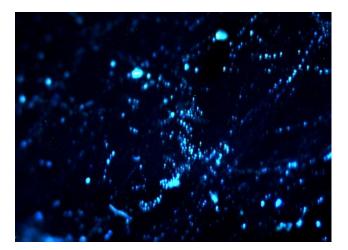


Figure 3: The Diamond View<sup>TM</sup> image showing chalky bluish glow along the healed fractures of the stone. (Photo: Marisa M.)

The standard gem testing gives RI values of 1.76 - 1.77 and SG values of approximately 3.95-3.97 which is expected for corundum. The dichroic colors varying from very dark to dark bluecan be observed through a dichroscope

#### ADVANCED INSTRUMENTAL ANALYSIS

The advanced testing can also give more details on this material. The Raman spectroscopic analyses did confirm that the stones are corundum with distorted structure (Figure 4). As also expected the bulk semi-quantitative chemical analyses by EDXRF reveal alumina (AI) as its major constitute with rather high content of titanium (0.18-0.37 %wt  $TiO_2$ ) and iron (0.39 – 1.71 %wt  $Fe_2O_3$ ). Notably the content of both minor elements seem to be higher in dark blue area of healed fissures than in the lighter color area of host corundum. Hence, the presence of both Ti and Fe is the first clue to suggest that they are responsible for blue coloration in these stones. The X-ray image shows no high contrast area—that are consistent with the chemical analysis result (Figure 5). This implies that no heavy elements (such as lead) were added during the treatment.

To better confirm the cause of its coloration, the UV-Vis absorption spectrum was recorded and clearly reveal the dominant Fe<sup>2+</sup>/Ti<sup>4+</sup> intervalent charge transfer (IVCT) absorption band maximized at around 575 nm (Figure 6). However small Fe-related absorption peaks around 450 and 377/387 nm can also be detected. It is interesting to note that the Fe<sup>2+</sup>/Fe<sup>3+</sup> IVCT absorption band commonly peaked at around 900 nm has not been observed in those spectra. This may suggest that the treater could use a low-iron metamorphic-type sapphire as the starting material. The Mid-IR spectrum show absorption pattern usually found for a corundum with strong CO<sub>2</sub>-related absorption peaks around 2345 cm<sup>-1</sup> and two OH-related peaks at 3602 and 3702cm<sup>-1</sup>. (Figure 7)

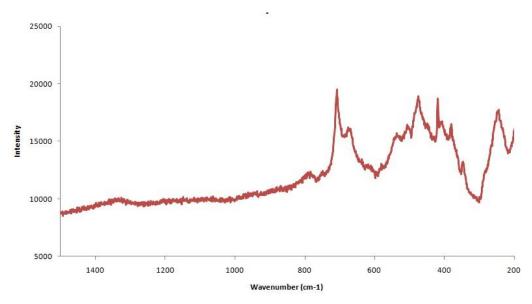


Figure 4: A representative Raman spectrum of the stone revealing that it is a distorted corumdum structure

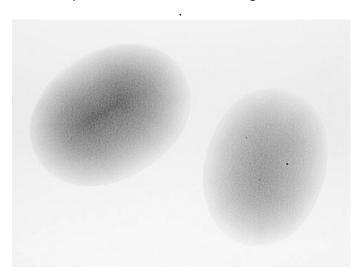


Figure 5: X-ray images of the two blue stones showing no high contrast area.

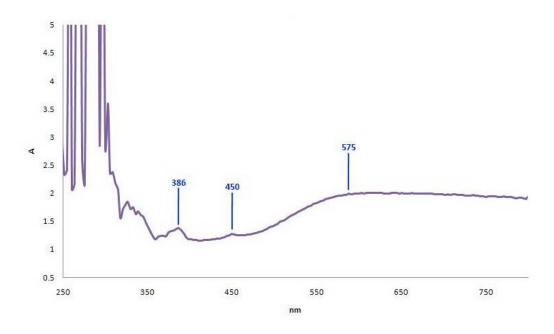


Figure 6: A representative non-polarized UV-Vis spectrum of the stone showing small Fe-related absorption peaks at 377/387 and 450 nm and dominant Fe<sup>2+</sup>/Ti<sup>4+</sup> IVCT absorption band maximized at around 575 nm.

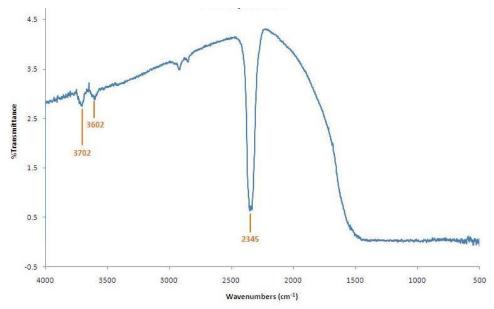


Figure 7: A representive Mid-IR spectrum of the stone showing strong  $CO_2$ -related absorption peaks around 2345 cm<sup>-1</sup> and two OH-related peaks at 3602 and 3702cm<sup>-1</sup>.

#### **DISCUSSION AND CONCLUSIONS**

Based on above preliminary testing, it seems to suggest that these stones were subjected to a common type of Ti diffusion treatment. Generally in the ordinary surface diffusion sapphires, the treatment was carried out on a transparent-colorless or pale-colored facetted sapphire that was unable to be treated by normal heating due to the lack of its intrinsic chromophoric elements. In such diffused treated stone, the diffusion took place only at or very near stone surface. Owing to the low diffusion rate of titanium the treatment allows to create only very thin color layer along the outer surface of the stone. But in this treated material, it is likely that the starting raw materials could be a very low quality colorless to pale color sapphire with abundant open fissures. Then the material could be treated by a usual Ti-diffusion technique. Having been a heavily fractured material to begin with, the Ti compound could enter into the stone via open fissures and the Ti-diffusion could possibly take place from the fissures outward into the host corundum while those fissures were also healed during high temperature treatment. Hence we recommend to call this new product as "diffusion-treated black sapphire".

Finally, because of the booming of black fashion trend in last several years, the use of black as the mainstream color in jewelry design has created a strong demand for black gemstones such as black diamond, black spinel, black chalcedony or onyx and, of course, the "black sapphire" as well. Among those except diamond, the black sapphire seems to be more favorable due to its superior hardness. Consequently, strong demand of such stones certainly led to the innovation of new products.

For the practical purpose, we strongly recommend traders and jewelers to carefully observe this type of gem material not to mixed-up with and/or miss-identified from the recently cobalt-glass treated sapphire or newly composite sapphire. However, the simple microscopic observation together with the use of dichroscope and UV-fluorescence can be the efficient tools for separate these three different types of treated sapphire recently available in the market.

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