LAB UPDATE

SOME UNCOMMON FEATURES IN A HEAT-TREATED FANCY SAPPHIRE

By GIT-Gem Testing Laboratory
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Introduction

In November 2015, the GIT-Gem Testing Laboratory (GIT-GTL) came across a fancy sapphire with prominent evidences of high-temperature treatment. However, some external and internal features appear to be somewhat different from what we have encountered previously in normal heat-treated corundum. We, therefore, prefer to document those uncommon features in this report.

Sample and Methods

The sample is a 9.68 ct dark brownish purple stone cut in oval-shaped brilliant facet style (Figure 1).

Figure 1. This 9.68 ct dark brownish purple sapphire (13.9 x 10.7 x 7.4 mm) was submitted to GIT-GTL for testing. Photo by S. Promwongnan

Basic gem instruments were used for the measurement of the stone's properties. Internal features were observed with both standard gem microscope and immersion scope in methylene iodide solution. All inclusions images were taken by using a gem microscope with Canon EOS 7D camera attached.

As for the advanced equipment, we used a Thermo-Nicolet 6700 Fourier-transform infrared (FTIR) spectrometer to obtain the IR transmittance spectra in the mid-IR range (4000–400 cm^{-1}) with a resolution of 4.0 cm–1 and 64 scans. UV-Vis-NIR absorption spectrum of the sample was taken with a PerkinElmer Lambda 950 spectrophotometer in the range 250–800 nm with a sampling interval of 3.0 nm and scan speed of 441 nm per minute. Raman spectrum was collected on the sample with a green laser 532 nm excitation. X-radiograph was recorded by a Softex SFX-100 instrument. The chemical analysis was carried out by an Energy-dispersive X-ray Fluorescence (EDXRF) spectroscopy of Eagle III system. In addition, any trace amount of beryllium, if present, in the stone was also detected by laser-induced breakdown spectroscopy (LIBS).

Results

General Properties

The gemological properties of this stone are generally consistent with natural corundum; i.e., refractive indices of 1.772-1.765, birefringence of 0.007 and uniaxial single crystal. The sample was inert to long- and short-wave UV radiation.

Microscopic Features

Microscopic examination with oblique fiber-optic illuminator revealed that this stone has undergone a relatively high temperature heating. Strong evidences for the heat treatment are numerous turbid 'snowball' crystal inclusions (possibly monazite and/or zircon, see Figure 2), uneven cloudy zones of minute inclusions just below the crown and pavilion facets throughout the whole stone (Figure 3a-c).

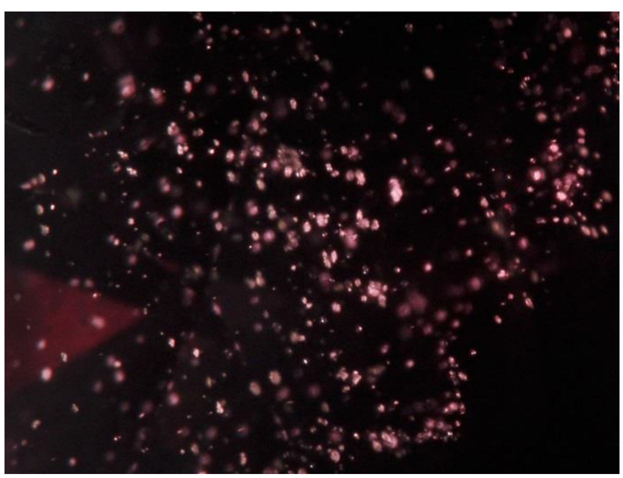

Figure 2. Numerous turbid 'snowball' crystal inclusions suggesting that this stone has subjected to a high temperature heating (field of view 4.8 mm). Dark field photomicrograph by S. Promwongnan

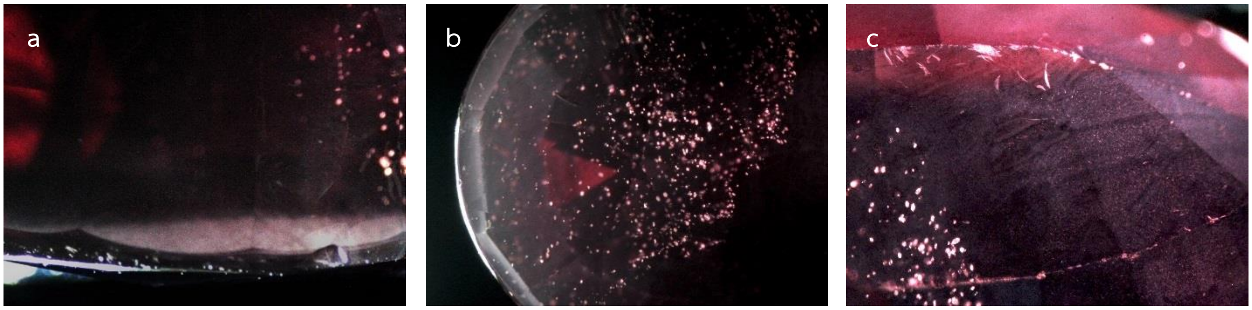

Figure 3. Uneven cloudy zones of minute inclusions just below the crown facet (a) and those just below the pavilion facets (b, c). Oblique fiber-optic light, photomicrographs by S. Promwongnan; field of view, 6.5, 9.0 and 4.5 mm for photos a–c, respectively

At higher magnification (Figure 4 left and right), the cloudy zones appear as circular clouds of pinpoint particles. This feature is not commonly encountered in heated sapphire but similar to what we have seen in diffusion-treated corundum.

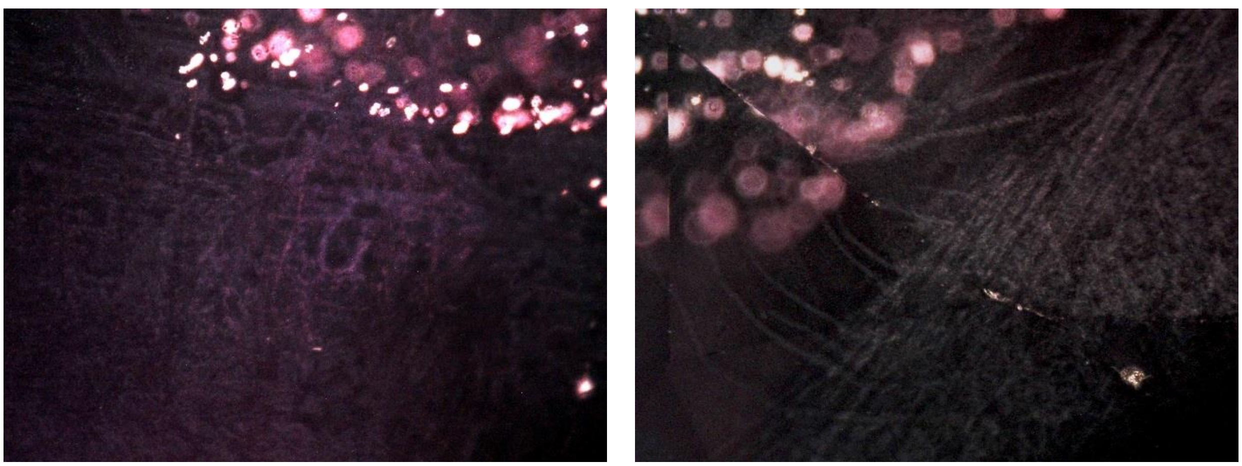

Figure 4. Circular clouds of minute particles seen at high magnification from the crown (left) and those from the pavilion (right). These clouds of pinpoint inclusions are uncommon for normal heat treatment. Photomicrographs by S. Promwongnan; field of view 3.5 mm for both photos

When viewing the stone under reflected light (at 20× magnification), many tiny pits and rounded droplets were seen on the surface (Figure 5a and b); while other facets showed irregular surface luster (Figure 5c) that could be visible even with unaided eye. In addition, glassy residue could be observed in several cavities (Figure 5d). These surface-damaged features are undoubtedly related to high temperature heating.

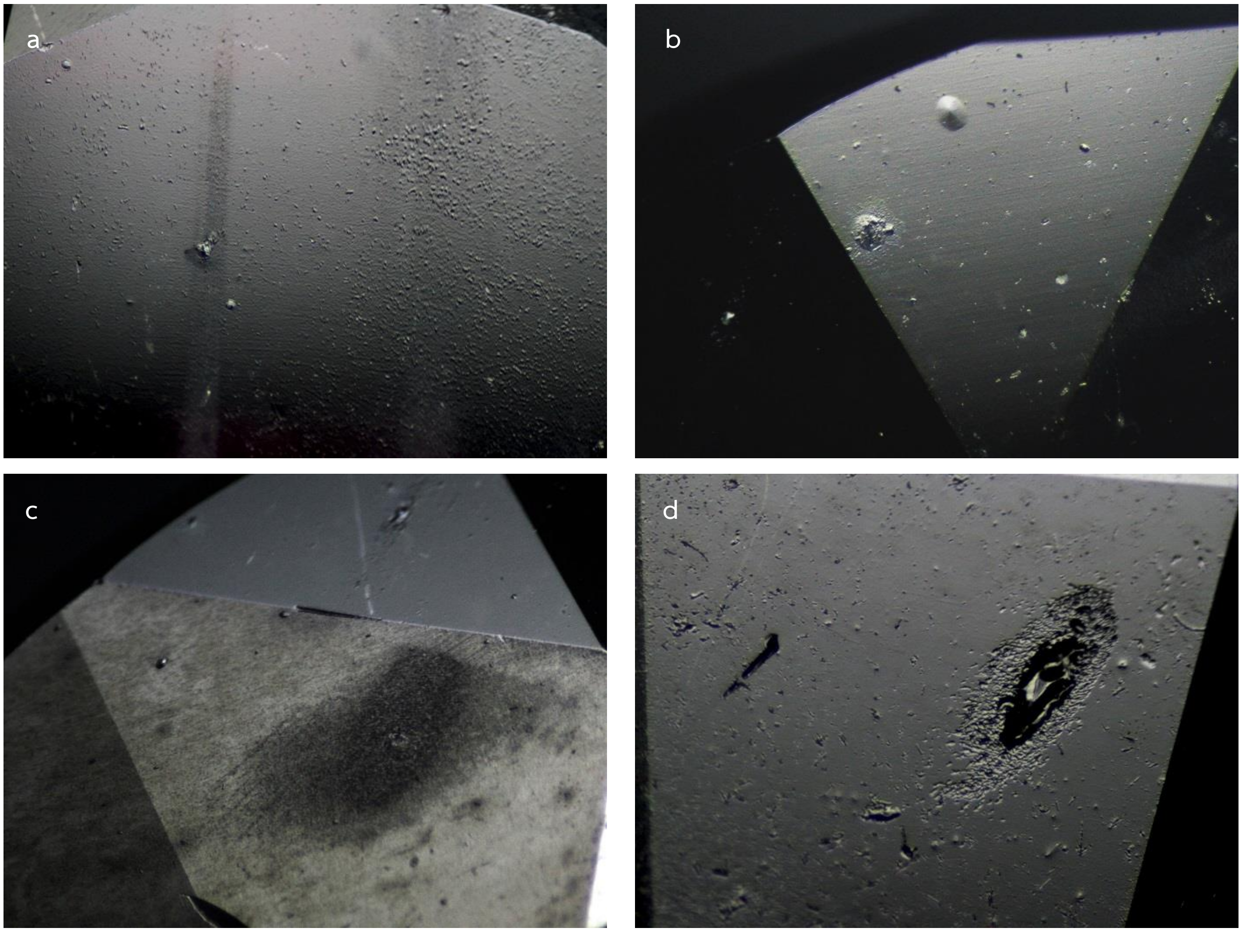

Figure 5. (a, b) numerous tiny pits and rounded droplets, (c) irregular surface luster and (d) glassy residue in cavities are clearly visible on the stone's surface with reflected overhead light. Photomicrographs by S. Promwongnan; field of view, 4.8, 2.8, 3.6, and 2.8 mm for photos a–d, respectively.

With immersion in methylene iodide solution under crossed polarized-light, Parallel color zoning (Figure 6 left) and numerous doubly-refractive crystal inclusions could be seen (Figure 6 right).

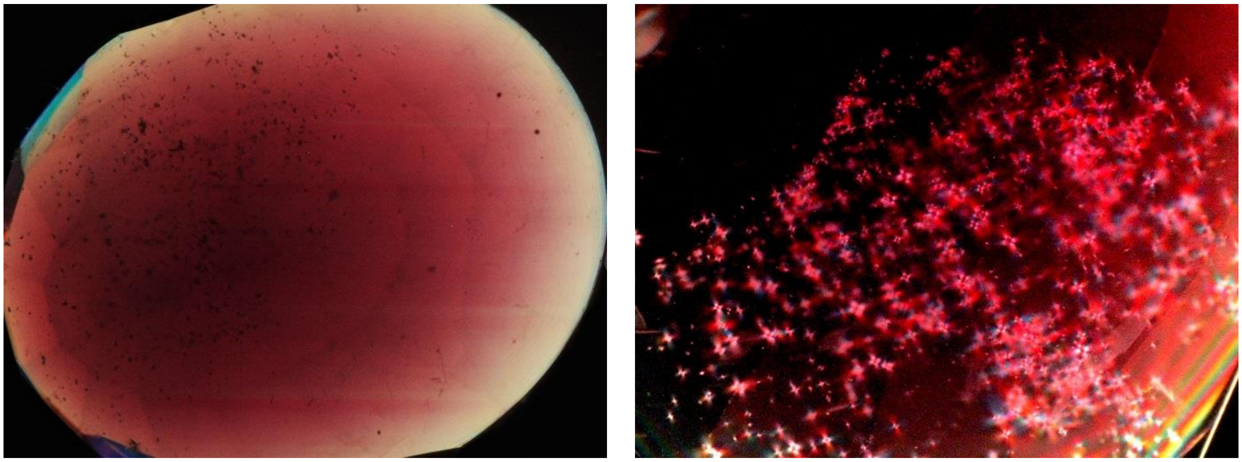

Figure 6. Horizontally-parallel color bands (left) and numerous doubly refractive crystal inclusions (right) are seen when the stone is viewing between crossed polarizers through (methylene iodide) immersion scope. Photomicrographs by S. Promwongnan; field of view, 12.4 and 10.5 mm from left to right

Advanced testing

The mid-infrared spectrum of the sample shows absorption pattern in the 4000–400 cm^{-1} range that is typical for corundum (Figure 7). The spectrum, however, does not give any absorption peaks between 3500 and 3000 cm^{-1} ,which can also give a hint whether the stone is untreated or heat-treated.

FTIR spectrum

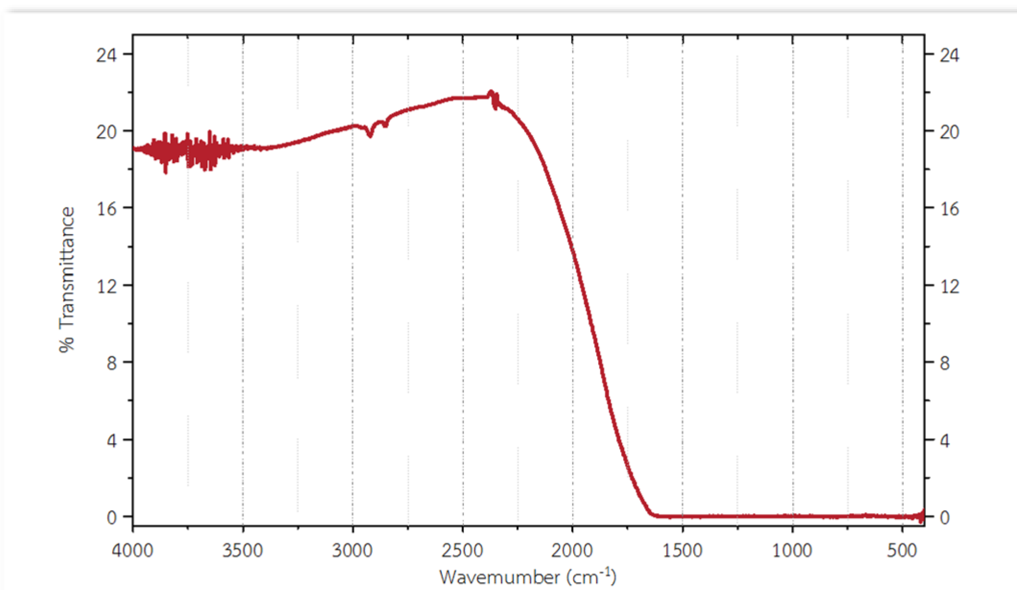

Figure 7. FTIR spectrum of the sample showing the absorption pattern commonly present in corundum.

The UV-Vis spectrum (Figure 8) shows strong absorption bands around 550, 410 nm and a small peak near 700 nm caused by chromium (Cr^{3+}) transition, resulting in stone's reddish coloration.

Also clearly visible in the spectrum is a relatively strong absorption peak around 450 nm due to iron (Fe^{3+}) transition.

UV-Vis-NIR Spectra

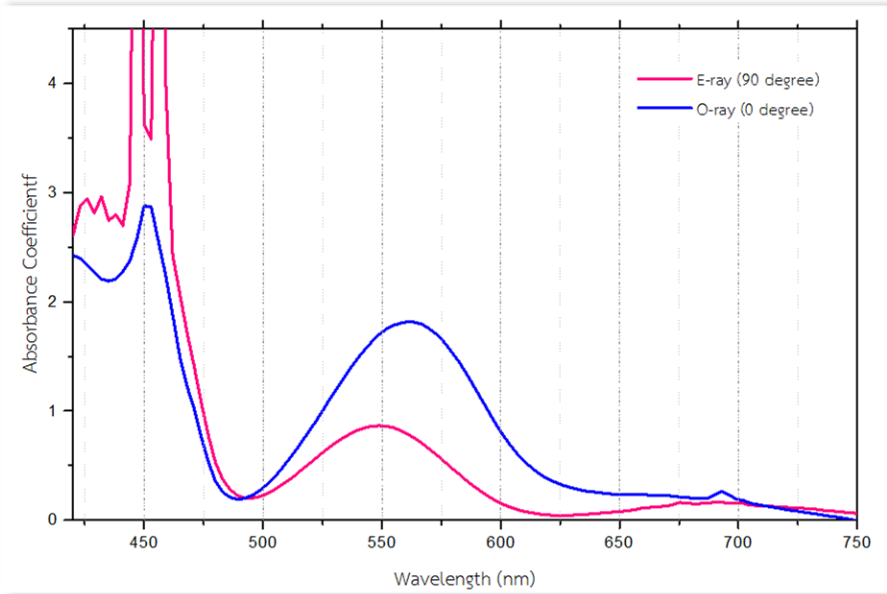

Figure 8. UV-Vis spectra of the sample show absorption bands at ~550, 410 nm and a small peak at ~700 nm due to Cr^{3+}, resulting in the reddish coloration and strong absorption related to Fe^{3+} at ~450 nm.

Chemical analysis

Trace element analysis of the sample by EDXRF gave rather high content of iron, moderate amounts of chromium, titanium and gallium (see Table 1). Such high iron content may be responsible for the stone's dark tone. Besides, a significant amount of silicon was also detected in glassy material in cavities in figure 5d. Additional test by LIBS showed no trace of beryllium, which could rule out the possibility of Be-diffusion treatment for this stone.

Table 1. Trace element contents of the sample obtained by EDXRF

Element Oxides (wt.%)	TiO_2	V_2O_5	Cr_2O_3	Fe_2O_3	Ga_2O_3	SiO_2
On the crown side	0.01	BDL	0.08	1.13	0.03	BDL
On the cavity (Figure 5d)	0.02	0.01	0.08	1.30	0.02	1.63

Discussions and Conclusions

In summary, the gemological properties, spectra and chemical composition of this sample are consistent with those of natural corundum and the stone's dark tone may be due to its high Fe content. The microscopic observation revealed many striking features, such as turbid 'snowball' crystal inclusions, unusual near-surface circular clouds of minute particles, several surface-damaged characteristics (i.e., numerous tiny-pits-and-round-droplets and glassy residue in cavities). All these features indicate that this stone was subjected to a relatively high-temperature heat treatment. In addition, chemical analyses of glassy residue in cavity gave a significant content of silicon. This can lead to the possibility of flux involved during the heating process. Furthermore, LIBS test has confirmed that there is no beryllium in this stone. In conclusion, this particular sample is a heat-treated fancy sapphire without subsequent re-polishing.

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