Golden Sheen and Non-Sheen Sapphires from Kenya

Nalin Narudeesombat, Saengthip Saengbuangamlam, Thanapong Lhuaamporn and <u>Thanong Leelawatanasuk</u>

The Gem and Jewelry Institute of Thailand (Public Organization), Bangkok, 10500, Thailand

Abstract

A new variety of sapphire from Kenya with unique golden sheen \pm star phenomena, the so-called "Gold Sheen" sapphire has been introduced to the gem market in the last 6-7 years. This study was aimed at characterizing both the sheen sapphire and non-sheen sapphire from the same locality. It was found that both sheen and non-sheen samples shared somewhat similar inclusion assemblages, namely magnetite, goethite, hematite, short needles and zircon. The sheen stones, however, were apparently translucent to opaque with golden sheen \pm star effect caused by the reflection of the light from the combination of dense and well-oriented reddish brown platelets and short needle-like inclusions exsolved along three crystallographic directions in the basal pinacoid of sapphire. The transparent-to-semi-transparent non-sheen stones, in contrast, contained relatively much less amounts of platelets and needles. The advanced analyses revealed that both sheen and non-sheen sapphires contained high iron content, including boehmite, diaspore and kaolinite which were good indications of untreated stones.

Introduction

Gem corundum from Kenya is well known in the gem market for decades, especially ruby. However, 6-7 years ago, there was a new variety of corundum introduced to the gem market. These stones normally show yellow or yellow-blue body color and a unique glimmering golden sheen \pm star effects. This new variety of sapphire has been traded as "Gold Sheen" sapphire in the market.

Per the stone owner, this sapphire was discovered in 2009 in Kenya close to the border with Somalia (Figure 1). The mine was ostensibly depleted, yielding no good quality rough, for almost two years. In early 2013, the last production was only two to three percent of yielded materials that display the popular golden sheen effect. So far, the cut stone products are usually untreated and range in weight from 0.5 to 10 cts.



Figure 1: Location of Gold Sheen sapphire mining area in Kenya near the border with Somalia

Material and Methods

Gem Testing Laboratory of the Gem and Jewelry Institute of Thailand (GIT-GTL) received a parcel of untreated cabochon-cut sapphire from Mr. Tanzim Khan Malik. Out of that parcel, we selected 14 representative samples to be used in this study. The stones have been divided into two sets based on their transparency and phenomena. Set I (non-sheen) consists of 7 transparent-to-semi-transparent yellow-to-yellow-blue samples (weighing 0.35 to 0.65 cts.) without sheen \pm star phenomena (except one stone with star only). Set II (golden sheen) consists of 7 translucent-to-opaque yellow-to-yellow-blue samples (weighing 3.00 to 25.07 cts.) with golden sheen \pm star phenomena (Figure 2). Both sets were claimed to be from the same mine in Kenya.



Figure 2: Fourteen sapphire samples from Kenya used in this study, Set I (non-sheen) is 7 transparent-to-semi-transparent stones (left) and Set II (golden sheen) is translucent-to-opaque stones (right).

The standard gemological properties were collected by using basic gem instruments, namely refractometer, polariscope, longwave (LW) and shortwave (SW) UV lamps, hydrostatic balance and gemological microscope. Some unknown inclusions were identified by Renishaw inVia Raman microscope. The Mid-IR transmission spectrum (400-4000 cm⁻¹ range) of the stones was recorded by a Thermo Nicolet 6700 Fourier-transform infrared (FTIR) spectrometer. The chemical composition of the samples was analyzed by an energy dispersive x-ray fluorescence spectrometer (EDXRF- EDAX model Eagle III). The UV-Visible-NIR Spectrophotometer (PerkinElmer Lamda 950) was used for measuring the absorption spectra. All the analyses were carried out at the GIT-GTL.

Results and Discussion

Basic properties

Both sets of stones gave similar gemological properties, such as refractive indices (R.I.) of 1.760 - 1.773 and specific gravity (SG) values of 3.96-4.01. The samples were inert in both LWUV and SWUV lamps.

Microscopic features

Under magnification, both sets shared somewhat similar inclusion features, such as black (magnetite -as identified by Raman spectroscopy, see below) platelets (Figure 3a), brownish red (goethite---ditto) inclusions (Figure 3b), reddish brown to brownish red (hematite---ditto) well-oriented platelets (Figure 3c) plus yellowish brown short needle(silk)-like inclusions intersecting in three crystallographic directions

(Figure 3d), brown (zircon---ditto) crystals (Figures 3e and 3f), including angular banding, and hexagonal zoning.



Figure 3: Inclusions in both sets of sample: (a) black (magnetite) platelets in a non-sheen yellow sapphire (50X, field of view 1.8 mm); (b) brownish red (goethite) inclusions in a none-sheen yellow stone (50X, field of view 1.8 mm); (c) reddish brown (hematite) platelets in a golden sheen sapphire (100X, field of view 0.9 mm); (d) yellowish brown short needle-like inclusions intersecting in three directions in a golden sheen stone (100X, field of view 0.9 mm); (e) a cut-open brown zircon crystal under fiber optic light (40X, field of view 2.3 mm) and (f) the cut-open zircon fluorescing greenish blue under SWUV light (ditto as e) in a golden sheen sample.

Comparatively, however, the golden sheen (set II) stones seemed to contain much higher amounts of platelets and needles intersecting in three crystallographic directions than those in the non-sheen (set I) samples. Thus, the combination of plentiful occurrence of exsolved reddish brown platelets plus short needles in three crystallographic directions in the basal pinacoid of sapphire is responsible for golden sheen \pm star effects found in the set II samples.

Advanced Analyses

We used the Raman spectroscope to identify the mineral inclusions as shown in Figure 3 as follows. The black platelets in (3a) were magnetite in a non-sheen yellow sapphire, and the brownish red inclusions in (3b) were goethite in a non-sheen yellow stone which is a good indication of no heat treatment (Sripoonjan *et al.*, 2016). The reddish brown platelets in (3c) were hematite in a golden sheen sapphire. However, Bui *et al.* (2015) previously confirmed that both the platelets and short needles were Fe-Ti oxides (exsolved intergrowth phases of hematite and ilmenite). The cut-open brown crystal in (3e) was zircon in a gold sheen stone and this zircon inclusion gave greenish blue fluorescence under SWUV light source (3f). The Raman spectra are displayed in Figure 4.

Semi-quantitative Energy Dispersive X-Ray Fluorescence analyses on both sets of samples revealed that the stones contained relatively high Fe concentration but rather low contents of Ti, V, Cr and Ga (see Table 1). We, however, were not be able to find any trace amounts of Nb, Ta, S, Ba, Cu, K and Na that were previously mentioned by Bui *et al.* (2015).

285



Figure 4: The Raman spectra of magnetite, goethite, hematite and zircon inclusions in golden sheen and non-sheen sapphires from Kenya.

Fable 1: Trace element contents of the samples determined	ected by EDXRF
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Element (Wt.% oxide)	Set I (non-sheen)	Set II (golden sheen)
TiO ₂	0.02 - 0.07	0.01 - 0.02
V ₂ O ₅	0.01 - 0.04	0.00 - 0.01
Cr ₂ O ₃	0.01 - 0.03	0.00 - 0.01
Fe ₂ O ₃	1.19 - 1.58	1.00 - 1.50
Ga ₂ O ₃	0.02 - 0.04	0.02 - 0.05

Both non-sheen and golden sheen samples gave a similar Mid-IR pattern with absorption bands at ~1988, 2120cm⁻¹ and 3620, 3696 cm⁻¹ which may represent OH-structural stretching of boehmite and kaolinite impurities in the stones (Smith, 1995; Beran and Rossman, 2006) as shown in Figures 5 and 6(a). The presence of boehmite and/or kaolinite in a sapphire is a useful criterion to indicate that the stone is unheated (Smith, 1995). Furthermore, the peaks at 2850, 2925 related to C-H structure that probably causes by grease or cutting residues (Cartier, 2009). Some golden sheen stones also gave the peaks at 1826, 1976, 2111 cm⁻¹ which may relate to the OH-structural stretching of diaspore (Smith, 1995; Beran and Rossman, 2006) as shown in Figure 6(b). The boehmite and diaspore were also detected by Raman spectroscopy in the previous study (Bui *et al.*, 2015).



Figure 5: Representative FTIR spectrum of a non-sheen sapphire (Set I samples) showing O-H stretching of kaolinite and boehmite.



Figure 6: Representative FTIR spectra of a golden sheen sapphire (Set II samples) showing the O-H stretching of kaolinite, boehmite (**a**) and diaspore (**b**).

Due to the lack of transparency of the golden sheen (set II) samples, the UV-Vis Spectra of sapphire can be obtained from the non-sheen (set I) samples only. The spectrum of yellow non-sheen sapphires showed dominant Fe^{3+} absorption peaks at 450, 377 and 388 nm that could have been attributed to its yellow coloration (Nassau, 2001; Pisutha-Arnond *et al.*, 2010). This result is consistent with the fact that the stones contain relatively high iron but rather low titanium contents. The spectrum of some yellow-blue sapphires, however, displayed not only the peaks at 450, 377 and 388 nm but also a broad Fe^{2+}/Ti^{4+} IVCT absorption band at 565 nm which was responsible for the stones' blue tint (Nassau, 2001; Monaruemit, 2012; Wongrawang *et al.*, 2016) (Figure 7).



Figure 7: Non-polarized UV-Vis-NIR absorption spectra indicating the different causes of color in yellow and yellow-blue sapphire of set I due to Fe^{3+} and Fe^{2+}/Ti^{4+} IVCT.

Conclusions

As this study was aimed at characterizing the gem properties of both golden-sheen and non-sheen sapphires from the same mine in Kenya, it was found that both the non-sheen (set I) and golden sheen (set II) samples were quite similarly in terms of their basic gem properties, i.e., RI (1.760-1.773), SG (3.96 - 4.01), inert in both LWUV and SWUV radiation. Both sets of samples also shared a similar inclusion assemblage, namely reddish brown platelets plus yellowish brown short needles of hematite-ilmenite intergrowth, magnetite platelets, brownish red goethite and zircon. It was also found that the numbers of (hematite-ilmenite) platelets and needles, which have been responsible for the golden sheen \pm star effects, were much higher in the golden sheen (set II) stones than those in the non-sheen (set I) stones. The cause of yellow color could have been contributed from its high iron content (Fe³⁺) with additional blue hue from Fe²⁺/Ti⁴⁺ IVCT. Moreover, the IR peaks of both sets similarly exhibited the OH-structural stretching of boehmite, diaspore and kaolinite, which are good indications that both non-sheen (set I) and golden sheen (set II) sapphires have not been heated.

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References

- Beran, A., and Rossman, G. R., 2006, OH in naturally occurring corundum, European Journal of Mineralogy, Vol.18, No.4, p.441-447.
- Bui, T. N., Deliousi K., Malik T.K., and Corte K. D., 2015, From exsolution to 'Gold Sheen': A new variety of corundum, The Journal of Gemmology, Vol.34, No.8, p.678-691.
- Cartier, L.E., 2009, Ruby and sapphire from Marosely, Madagascar, Journal of Gemmology, Vol.31, No.5-8, p.171-179.
- Monaruemit N., 2011, Applications of advanced techniques for identifying geological environments of blue sapphire samples, M.S. Thesis, Kasetsart University, 156 p.
- Nassau, K., 2001, The physics and chemistry of color, 2nd ed. (New York: Wiley-Interscience), 496 p.
- Pisutha-Arnond, V., Wathanakul, P., Sutthirat, C., Boonchai, A., and Somboon, C., 2010, Role of trace elements in causing color in corundum, The Gem and Jewelry Institute of Thailand's Internal Report, p.122-128.
- Smith, C. P., 1995, A contribution to understanding the infrared spectra of rubies from Mong Hsu, Myanmar, Journal of Gemmology, Vol.24, No.5, p.321-335.
- Sripoonjan T., Wanthanachaisaeng B. and Leelawatanasuk T., 2016, Phase transformation of epigenetic iron staining: indication of Low-temperature heat treatment in Mozambique ruby, Journal of Gemmology, Vol.35, No.2, p.156-161.
- Wongrawang P., Monarumit N., Thammajak N., Wathanakul W. and Wongkokua W., 2016, Oxidation states of Fe and Ti in blue sapphire, Materials research Express, Vol.3.No.2, p.026201.