



Experimental Study on Heat Treatment of Semitranslucent-opaque Sapphire from Chanthaburi, Thailand

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Chanthaburi, eastern Thailand, is one of the world-renowned gemstones producers. It is designated as a “City of Gems” as most of the world’s gemstones pass through the city. Chanthaburi has long been known for high-quality gemstones derived from basalt-related deposits (e.g., Bang Ka Cha, Khao Wua, Khao Ploi Waen), especially natural yellow sapphire–Mekong Whisky color–which is unparalleledly unique. The important studies (e.g., Hughes, 2002; Emmett *et al.*, 2003) previously found that an application of lattice-diffusion heat treatment with beryllium could predominantly produce attractive colors, such as yellow, yellowish orange, in many types of sapphire. This made unmarketable sapphires could be modified to a characteristic golden-yellow color and used in fine jewelry (Figure 1). However, the supply of those raw materials has been substantially reduced and is presently deficient. The semitranslucent-opaque sapphires (Figure 1) have been discovered to substitute the original unmarketable ones, otherwise, they were often cut as a cabochon to exhibit dark color with asterism, aka black star sapphires. The dark body color, as well as almost opaque transparency, is characterized by high Fe-rich content and densely exsolved silks of hematite and/or in part other Fe-Ti oxides (Sampanya, 2001; Sripoonjan *et al.*, 2013, 2014) resulting in poor diaphaneity of these sapphires. In recent years, the proliferation of new treatments provided great potential for improving gemstone quality, the less valuable sapphire can potentially turn into intense and stable yellow sapphire applying beryllium-assisting treatment (Be-heating). This study aims to carry on an experiment of lower quality semitranslucent-opaque sapphires treatment and to investigate the cause of changes in color and clarity.



Figure 1 : The characteristic golden-yellow sapphire used in fine jewelry (left) and semitranslucent-opaque sapphires from basalt-related deposits in Chanthaburi (right)



Materials and methods

The semitranslucent-opaque sapphire samples (again, Figure 1) were obtained from Bang Ka Cha deposit in Chanthaburi. Their representative sample (weighing 1.78 ct) was cut into 3 pieces: bkc01-un (unheated), bkc01-h (heated), and bkc01-be (Be-heated) for comparison (Figure 2). Both heated and Be-heated samples had been subjected to traditional heating at 1650°C in an electric furnace (Linn HT-1800-Plus-Vac) with ambient air; however, the latter one was undergone further heating with beryllium under condition is unknown by Thai burner. Only the unheated sample has been remained unchanged for reference.

Internal features were documented using a gemological microscope attached to a capture device. For spectroscopic studies, PerkinElmer's LAMBDA 950 was employed to study absorption spectra and the cause of colors through oriented ordinary ray (O-ray). Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) was also applied to analyze the trace elements, using a Thermo Scientific iCAP RQ series ICP-MS coupled with an Elemental Scientific Lasers NWR213 laser ablation system.

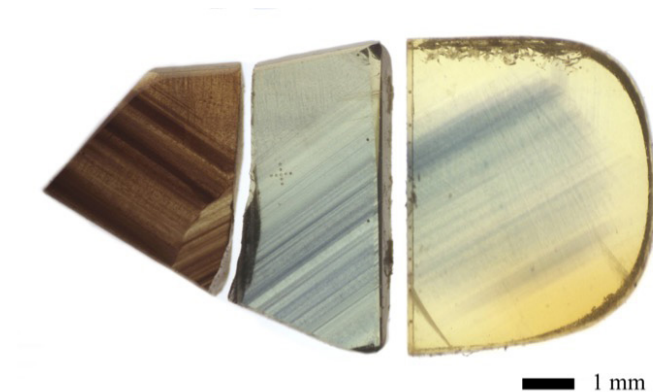


Figure 2 : The representative sample is split into three sections for heating experiments

Results and Discussion

In general, the initial material (Figure 2; left) displays brown body color, which is almost influenced by abundant arrays of exsolved hematite silks orienting along the crystallographic direction of the host sapphire. These inclusions can sometimes exhibit metallic luster when viewed at just the right angle.

The sample was changed to slightly green with a banded remnant of blue-colored zonings upon traditional heat treatment (Figure 2; middle). It was subsequently turned to yellow with a partial blue core once heated with beryllium (Figure 2; right). Microscopic observation revealed that the silky micro-inclusions were particulate measured approximately 1-5 microns each (Figure 3A), they were significantly destroyed after traditional heat treatment and remained either white- or blue-colored particles (Figure 3B) from being dissolved (Sripoonjan *et al.*, 2014). By the subsequent Be-heating, these inclusions were induced until creating dotted blue spots as a result of which the chromophore(s) from the particles incorporated into the host sapphire (Figure 3C). Consequently, these steps of treatment yield a more attractive color, as well as greater transparency.

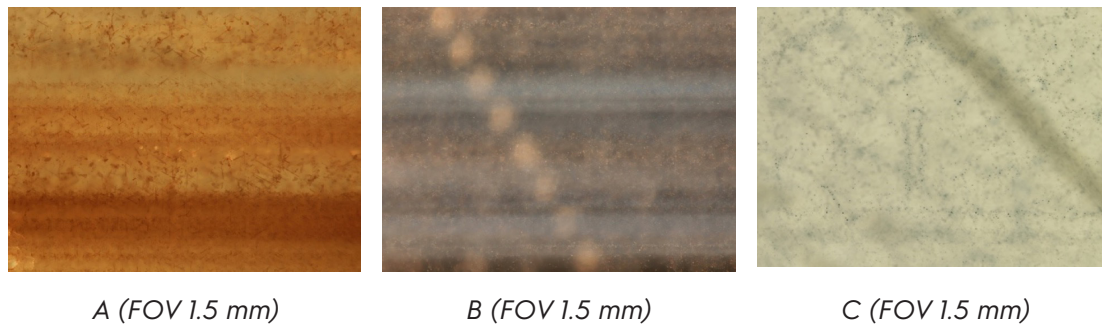


Figure 3 : Exsolved hematite silks commonly observed in the semitranslucent-opaque sapphires from Bang Ka Cha deposit of Chanthaburi (A). After traditional heating at 1650 °C, these inclusions were decomposed into minute particles (B). After Be-heating, silk inclusions were mostly dissolved and internally diffused into the lattice creating bluish dots.

As shown in Figure 4, the UV-Vis-NIR spectra of unheated sapphires always display absorption peaks mainly due to Fe^{3+} at 377, 388 and 450 nm (red line) which are typically seen in those sapphires from basalt-related origins (Ferguson and Fielding 1972; Sripoonjan *et al.*, 2014). Although these Fe^{3+} -related peaks tend to be reduced when heated at 1650°C in ambient air, this produces broad absorption bands around 910 and 565 nm respectively caused by $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Fe}^{2+}/\text{Ti}^{4+}$ intervalence charge transfer (IVCT) (Burns, 1993) that responsible for blue coloration along zonings (blue line). However, the absorption pattern is slightly decreased when heated with beryllium to become typical spectra of high iron concentration yellow sapphire (orange line), the resultant spectra may be correlated with Be and/or Mg trapped color centers as suggested by Pisutha-Armond *et al.* (2006, 2015).

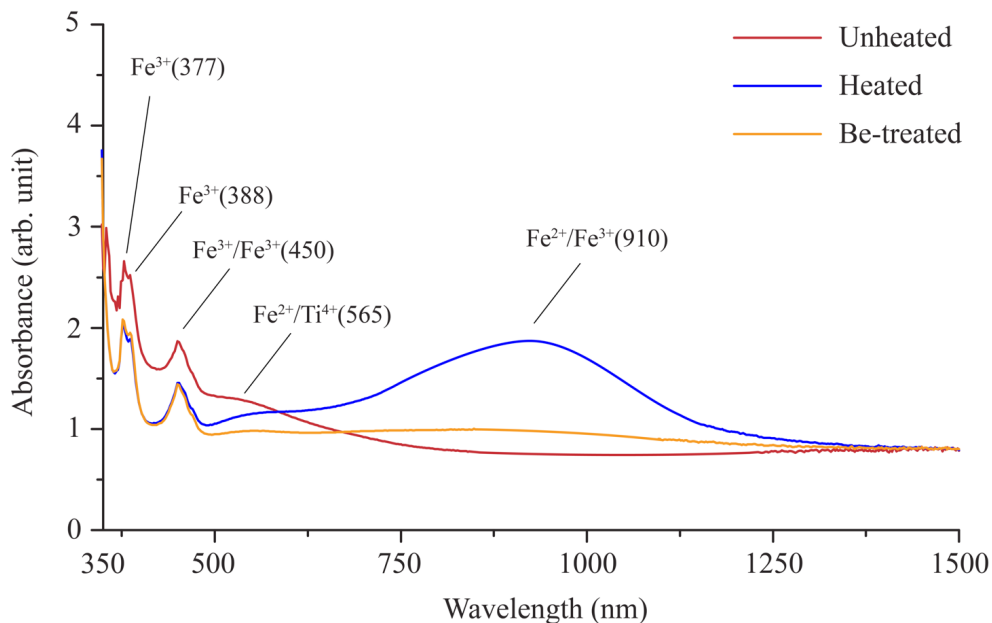


Figure 4 : Comparison between UV-Vis absorption spectra (O-ray) of an unheated sample (in red), a heated sample at 1650°C (in blue), and a be-heated sample (in orange).



The crossed 46-points traverse analysis (Figure 3A) across yellow edge and blue core of a cut-open cross section (Figure 5A) reveals that the stone contains relatively high Fe (~ 3100-3600 atom mole ppm or ppma) (Figure 5B), low Be (~ 1-93 ppma), Ti (~ 20-81 ppma) and Mg (~ 10-57 ppma). All points in the outer yellow edge (spot 1-9, 25-34 and 45-46) give $(\text{Be}+\text{Mg})>\text{Ti}$ (~ 9-130 ppma), whereas almost all of the points in the blue core (spot 10-24 and 35-44), illustrate $(\text{Be}+\text{Mg})<\text{Ti}$ (~ -1 to -62 ppma). Note that only very few points, especially transitional areas still showed slightly residue Ti, resulting in green color (e.g., spot 41-44). Trace elements analysis indicates that Be was introduced into the stone from an external source. These chemical data are also consistent with the assumption that the excess Be and/or Mg together with Fe atoms, remained from the formation of colorless BeTiO_3 and/or MgTiO_3 clusters, could form stable yellow color centers (Pisutha-Arnond *et al.*, 2006, 2015) in the outer edge area. Vice versa, Be could not be sufficiently diffused and exceeded Ti to form yellow color centers in the core area where contains intense blue zoning (Figure 5C). However, the study cannot measure accurate concentration of silicon (Si) due to limitation of analytical capability, it may otherwise provide more information on the reaction role among trace elements to cause color(s) as suggested by Emmett *et al.* (2017).

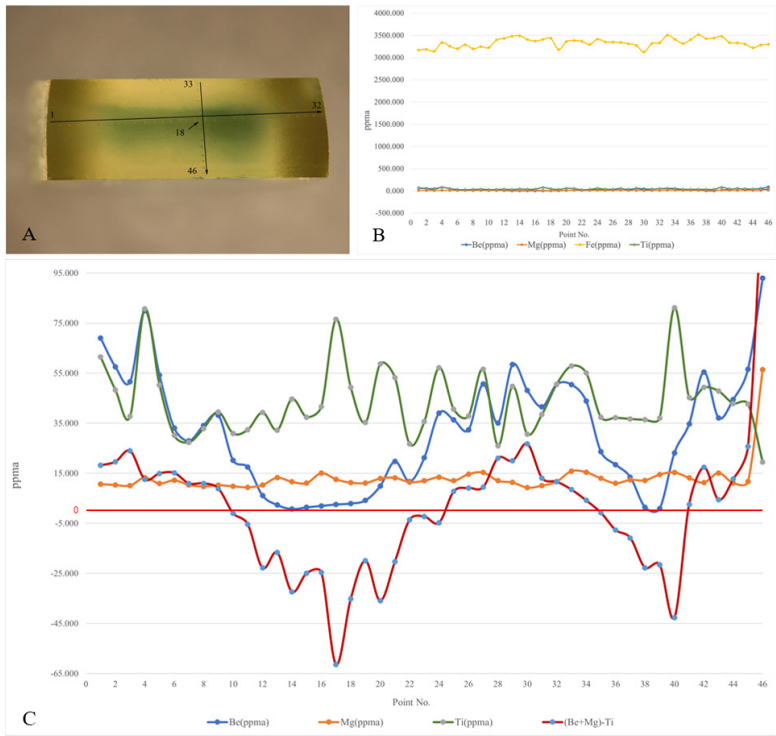


Figure 5 : a 46-points traverse analyses by LA-ICP-MS across yellow-blue zones of the Be-heated sample (A). The concentrations of Be, Mg, Fe and Ti are shown on the top diagram (B) and the enlarged plots of these elements, except Fe, accompanied by subtraction of $(\text{Be}+\text{Mg})-\text{Ti}$ concentration on the below diagram (C).

Conclusion

The low-quality semitransparent-opaque, as well as black star sapphire from the basalt-related sources, which had low market demand, became the significant raw material for Be-heated yellow sapphire. Although the final products have yielded relatively a good yellow color, it is sometimes dependent on a quantity of Ti-contained silk inclusions affecting clarity in a starting material. Otherwise, it had a surplus Ti concentration and thus also for the so far inevitable remaining blue area. The causes of color modification can be supported by UV-Vis-NIR spectra and trace elements analyses, as well as the improvement of clarity through careful microscopic observations.



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