Green Lead-Glass-Filled Sapphires

Thanong Leelawatanasuk, Namrawee Susawee, Supparat Promwongnan and Nicharee Atsawatanapirom

In April 2014, the Gem and Jewelry Institute of Thailand's Gem Testing Laboratory (GIT-GTL) received several rough and cut samples of green lead-glass-filled sapphire for examination, and in December 2014 the treater invited GIT to tour his facility. These stones show many characteristics similar to those of previously known cobalt-doped lead-glass-filled blue sapphires: orange and blue flash effects and colour concentrations along filled fissures, flattened gas bubbles trapped within the filler, and chalky blue fluorescence of the filler when viewed with the DiamondView instrument. Chemical analysis of the green glass showed mostly Pb with some Si, minor Cu, and traces of Fe and Cr. The latter three elements could possibly be responsible for the green coloration of the glass filler.

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Introduction

Lead-glass-filled corundum was introduced to the gem market in 2004 (see, e.g., Rockwell and Breeding, 2004; Smith et al., 2005). Initially, highly fractured rubies from various sources in East Africa were used as raw material for this treatment, and the finished products were sold under the trade name 'Newly Treated Ruby' in local markets in Bangkok and Chanthaburi, Thailand. Shortly thereafter, the fillers were proven to consist of lead-containing glasses (see references above and McClure et al., 2006; Milisenda et al., 2006). The principle behind this technique of filling fractures was not new, as it had already been applied to diamond (see, e.g., Koivula et al., 1989). However, some modifications were made by using high-temperature furnaces for melting the glass and filling fissures in corundum. Due to the poor durability of the filling material, many problems occurred during jewellery manufacturing/repair and cleaning. The glass filler could be etched by certain acidic or basic solutions, and heat from a jeweller's torch might easily melt the glass.

Although the lead-glass fillers may pose durability problems, there are still certain advantages of these treated products. With proper precautions during jewellery making, repairing and cleaning (e.g. using cold mounting techniques and avoiding contact with acidic or basic solutions), the drawbacks can be avoided. And due to their affordability, mass availability and wide range of quality, these products are still in demand after almost a decade on the market.

In 2012, a new type of blue cobalt-doped lead-glass-filled corundum entered the market (Leelawatanasuk, 2012; Leelawatanasuk et al., 2013). This product showed many identifying features similar to those of the previous lead-glass-filled rubies. Subsequently, Henn et al. (2014) documented additional coloured lead-glass

Figure 1: The five green lead-glass-filled sapphires studied for this report weigh 0.89, 2.79, 5.90, 2.64 and 1.06 ct (from left to right). Photo by N. Atsawatanapirom.

fillings in corundum that were red and pale green. Most recently, in April 2014 GIT-GTL received for examination several rough and cut stones (Figures 1 and 2) that were claimed to be 'the latest lead-glass-treated sapphire'. In December 2014 the owner of the process, Dhiranant Charoenjit (Figure 3), kindly allowed authors NS and SP to visit his facility at Nichima Gems in Chanthaburi Province, eastern Thailand.

According to Charoenjit, the starting material is sorted from low-quality, highly fractured pale-coloured sapphire rough. Some of the corundum shows well-formed hexagonal crystal shapes. The stones are cleaned in an acidic solution to remove impurities from the surface and within the open fissures. After this process, the material appears dull white (Figure 4, left) or is somewhat transparent with many open fissures. The stones are put into an alumina crucible with a sufficient amount of glass powder. The crucible is then heated in an electric furnace to approximately 1,300°C. After treatment, the stones are usually fused together into a glassy mass (e.g. Figure 2). The treatment is reportedly successful on only ~20% of the material, and the remaining 80% is rejected.

Material and Methods

Three pieces of rough and five faceted samples of the treated green sapphire were selected for this study. Standard gemmological equipment was used to obtain refractive indices, hydrostatic specific gravity, pleochroism, and fluorescence to long- and short-wave UV radiation for all of the faceted samples; they also were examined with a gemmological microscope. Chemical analysis by energy-dispersive X-ray fluorescence (EDXRF)

Figure 2: Shown here is an example of the low-quality pale coloured corundum that is used as the starting material for glass filling (bottom right, 3.15 g), together with two fused pieces of corundum and green glass after the treatment process (10.17 and 1.76 g). Photo by N. Atsawatanapirom.

spectroscopy was performed on all samples with an Eagle III instrument using an Rh X-ray tube, an accelerating voltage of 30 kV and a beam current of 200 mA. The diameter of the X-ray beam was 2,000 μm, and diffraction artefacts were avoided by sample rotation. Absorption

Figure 3: Dhiranant Charoenjit, managing director of Nichima Gems in Chanthaburi Province, explains the treatment process and shows the material before and after glass filling. Photo by S. Promwongnan.

Figure 4: These images show the corundum starting material after acid cleaning (left), and rough and faceted lead-glass-filled green sapphires after the treatment (centre and right). The rough stones weigh 1–5 g and the faceted samples are 1–3 ct. Photos by S. Promwongnan and N. Susawee.

spectra were recorded on all samples in the mid-infrared range (4000–400 cm^{-1}) with a Thermo Nicolet 6700 Fourier-transform infrared (FTIR) spectrometer equipped with a KBr beam splitter, at a resolution of 4 cm^{-1}. Ultraviolet-visible–near infrared (UV-Vis-NIR) spectra of all samples were recorded in the range 250–800 nm using a PerkinElmer Lambda 950 spectrophotometer with a sampling interval of 3.0 nm and scan speed of 441 nm per minute. X-radiography of all samples was performed using a Softex SFX-100 instrument, and one faceted stone was examined with a DiamondView deep-ultraviolet (<230 nm) luminescence imaging system.

To investigate some of the durability issues associated with lead-glass-filled corundum, preliminary testing was performed on three representative cut stones, which were separately subjected to a soap solution in an ultrasonic cleaning unit, a jewellery torch and a rhodium electroplating agent.

*Table I: Properties of five faceted green lead-glass-filled sapphires.**

Refractive indices	1.760–1.770 (birefringence 0.010)
Polariscope reaction	Doubly refractive
Pleochroism	Slightly dichroic, in greenish yellow to slightly yellowish green
Specific gravity	4.00–4.02
Internal features	Growth tubes, 'fingerprints', lamellar twinning, orange and blue flash effects along filled fissures, green colour concentrations in filled fissures and cavities, flattened gas bubbles trapped in the glass filler
UV fluorescence Long-wave Short-wave	 Inert to weak orange Inert

*Based on the testing of five stones weighing 0.89, 1.06, 2.64, 2.79 and 5.90 ct (see Figure 1).

Gemmological Properties

A distinctive feature of this product is its colour appearance: The faceted stones were yellowish green with low saturation, and the rough samples were a strong green and were coated with deep green glassy material (Figures 1 and 2).

The gemmological properties obtained from the faceted stones (Table I) are consistent with corundum in general. The samples were doubly refractive with RI values of 1.760–1.770. SG was approximately 4.00–4.02. Viewed with a dichroscope, they showed slight dichroism from greenish yellow to slightly yellowish green; the intensity of the green hue remained essentially constant whereas that of the yellow hue varied from pale to almost colourless. Figure 5 shows the differences in dichroism between an untreated green sapphire and this treated material. The dichroism of the treated sapphires suggests that their colour is mainly due to the isotropic green glass filler, and the underlying body colour of the material is likely to be light yellow to almost colourless. The stones were inert to short-wave UV radiation and luminesced weak orange or were inert to long-wave UV.

Microscopic examination proved to be a simple and important method for identifying these treated stones. The five faceted stones all showed features characteristic of natural (i.e. not synthetic) sapphire, such as tube-like features, 'fingerprints' and polysynthetic twinning (Figure 6). In addition, the gems showed many distinct

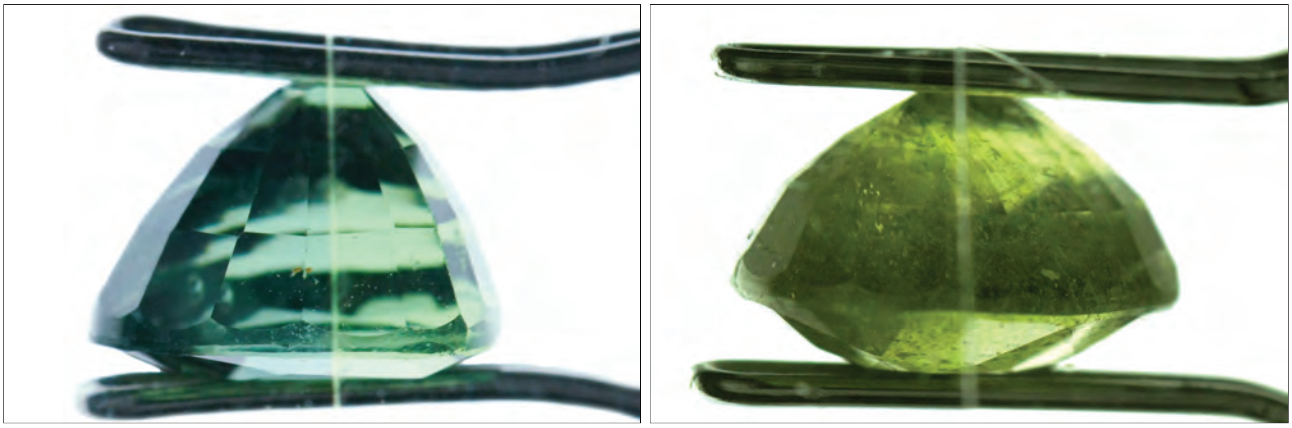


Figure 5: The 2.40 ct untreated green sapphire on the left shows typical bluish green to yellowish green dichroism, in contrast to the 2.79 ct green lead-glass-filled corundum on the right that displays greenish yellow and slightly yellowish green pleochroism. Photos by S. Promwongnan.

microscopic features associated with lead-glass-filled corundum, such as orange and blue flash effects, green colour concentrations along fissures and in cavities, and flattened gas bubbles trapped within filled fissures (Figures 7–9). Reflected light was useful for detecting cavities and fissures that were glass filled, as the surface lustre of the filler was noticeably lower than that of the host sapphire (Figures 9 and 10).

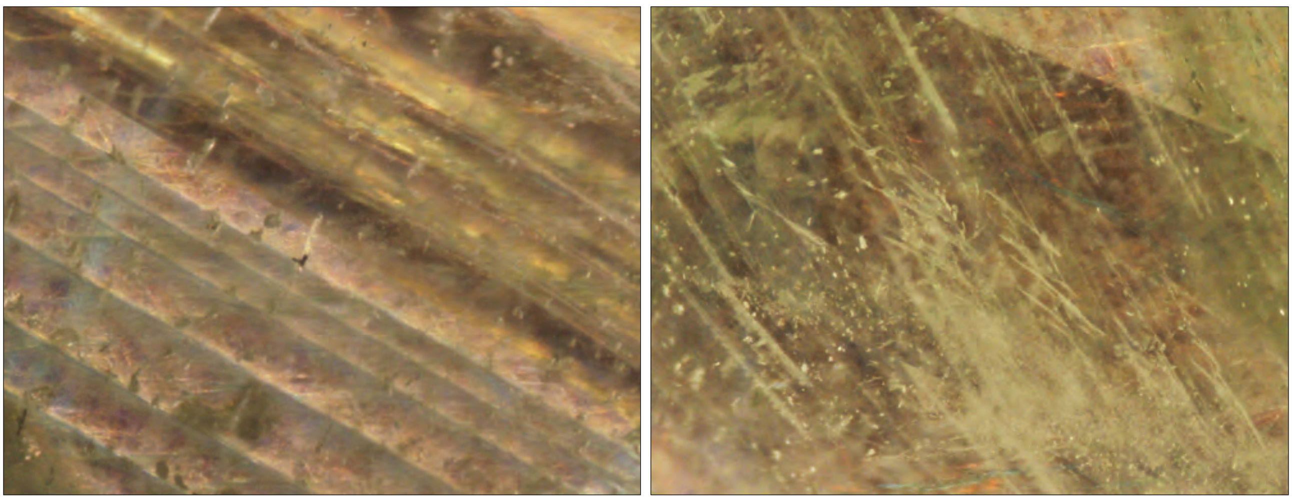
Chemical Composition

Semi-quantitative chemical analysis was performed by EDXRF spectroscopy on the green glassy residue at the surface of a 1.76 g rough sample (see Figure 2) to avoid sampling the host corundum. The analysis showed mostly Pb with some Al (from the corundum) and Si, minor Cu, and traces of Fe and Cr. By contrast, chemical analysis of the cut stones mainly showed the composition of the host sapphire with small amounts of the glassy constituents.

Spectroscopy

The mid-FTIR spectra of the green glass clearly showed strong absorption bands at approximately 3400, 2597 and 2256 cm^{-1} that are related to the glass filler (Figure 11). A UV-Vis-NIR spectrum of the green glass residue protruding from the surface of a rough sample showed strong absorption through almost the entire visible spectrum, except for a transmission window in the green region at ~500–570 nm (Figure 12). This spectral pattern and the presence of Fe, Cu and Cr (measured by EDXRF spectroscopy) suggest that the green coloration

Figure 6: Polysynthetic twinning (left) and tube-like features (right) are characteristics of the natural corundum starting material used for these green lead-glass-filled sapphires. Photomicrographs by N. Atsawatanapirom; magnified 10×.



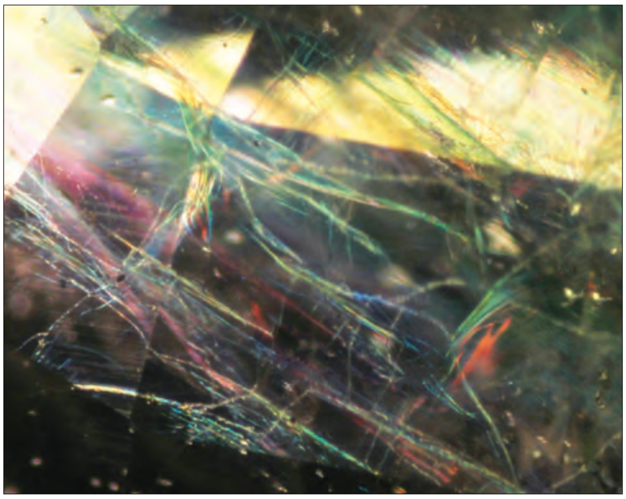


Figure 7: The lead-glass-filled fissures in the corundum show green colour concentrations as well as orange and blue flash effects depending on their orientation to the viewer. Photomicrograph by N. Atsawatanapirom; magnified 16×.

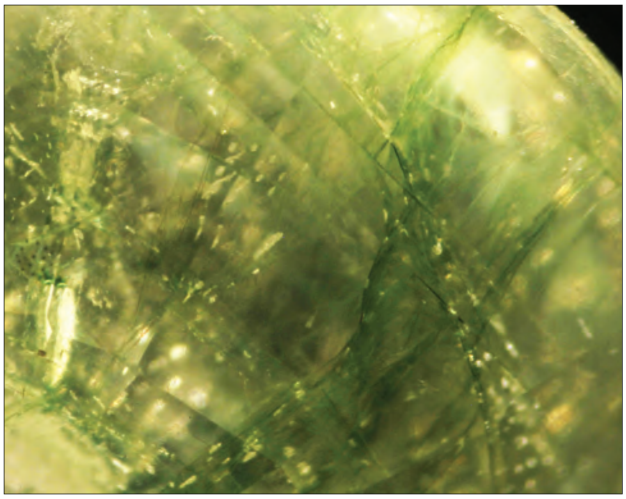


Figure 8: This 2.64 ct lead-glass-filled sapphire exhibits green colour concentrations along fissures that also contain flattened gas bubbles. Photomicrograph by N. Atsawatanapirom; magnified 10×.

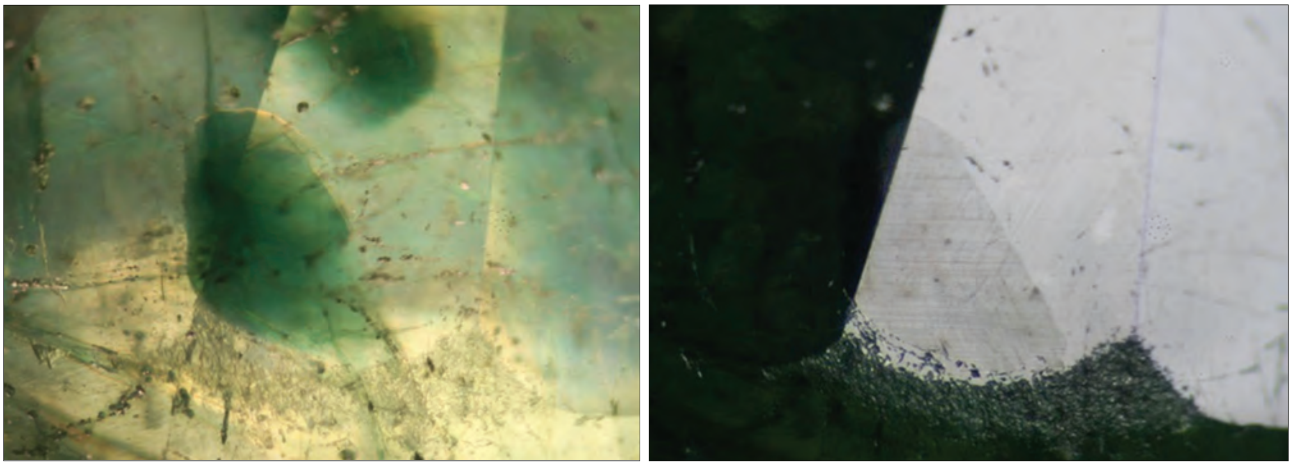


Figure 9: These views show a glass-filled cavity within a treated sapphire in darkfield (left) and reflected light (right). Photomicrographs by N. Susawee; magnified 20×.

Figure 10: Reflected light reveals the lower lustre of the lead-glass filler in fissures (left, magnified 32×) and in a cavity (right, magnified 16×) as compared to the host sapphire. Photomicrographs by N. Atsawatanapirom.

of the glass filler is related to those elements. By comparison, the UV-Vis-NIR absorption spectra of the faceted samples showed strong absorption from around 500 nm toward shorter wavelengths, with a small Fe^{3+}-related peak at ~450 nm and a weak, broad absorption band from ~600 to 800 nm (again, see Figure 12). This pattern is typical of Sri Lankan yellow sapphire (for which the colour is due to the stable colour centres; Pisutha-Arnond et al., 2004) in combination with some absorption contributed by the green glass filler in fissures and/or cavities. This result is consistent with the dichroism observed in the treated material (see Figure 5, right).

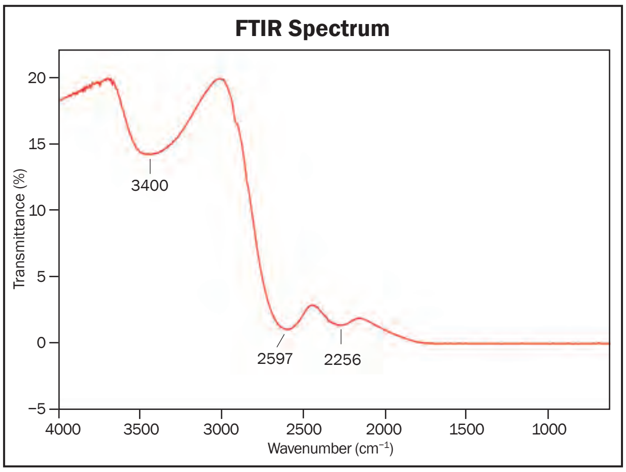


Figure 11: The mid-FTIR spectrum of green glassy residue on the surface of a treated rough sapphire shows strong absorption bands at approximately 3400, 2597 and 2256 cm^{-1}.

X-radiography

As expected, X-radiography of all the samples clearly revealed areas of glass filler within fissures and cavities in the faceted stones (Figure 13) and along the outer surfaces or rims of the rough samples. The filler appears darker than the host sapphire in these positive images; the light and dark patterns correspond to differences in the penetration capability of the X-rays through corundum versus lead glass. Such an appearance is also common for the previous types of lead-glass-filled corundum (e.g. SSEF, 2009).

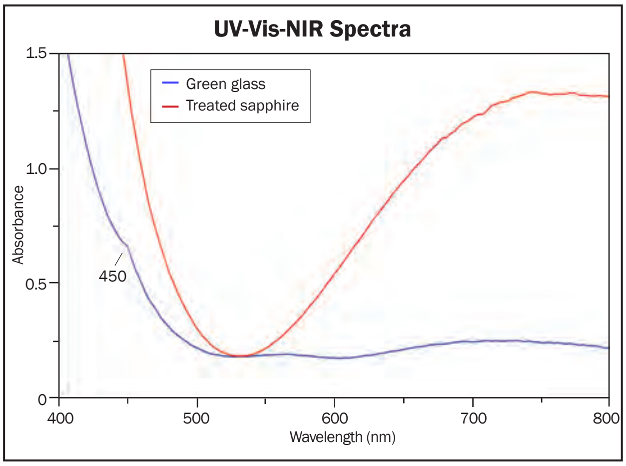
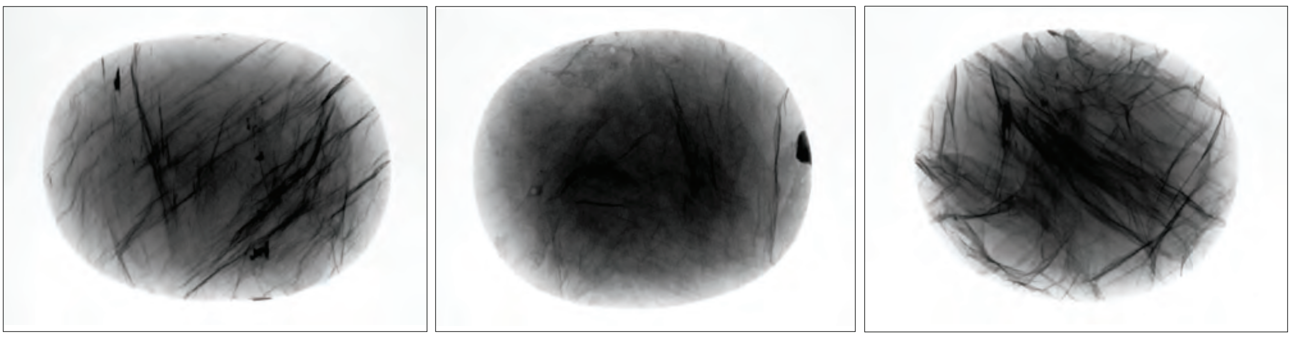


Figure 12: The UV-Vis-NIR spectrum of green glass protruding from a treated rough sapphire shows strong absorption through much of the visible range except for a transmission window in the green region at ~500–570 nm. By contrast, the spectrum of a faceted green lead-glass-filled sapphire shows an absorption edge at ~500 nm extending toward shorter wavelengths, with a small Fe^{3+}-related absorption peak at ~450 nm and a weak, broad absorption band at ~600–800 nm.

DiamondView Imaging

The DiamondView instrument showed intersecting patterns of distinctly chalky blue fluorescence along the glass-filled fissures (Figure 14). Such images can provide valuable information not only for the identification of this type of treatment, but also for giving a rough estimate of the amount of

Figure 13: These X-radiographs of three faceted green glass-filled sapphires (2.64, 5.90 and 2.79 ct, from left to right) show distinct opaque areas along the fractures and cavities. Images by S. Promwongnan.



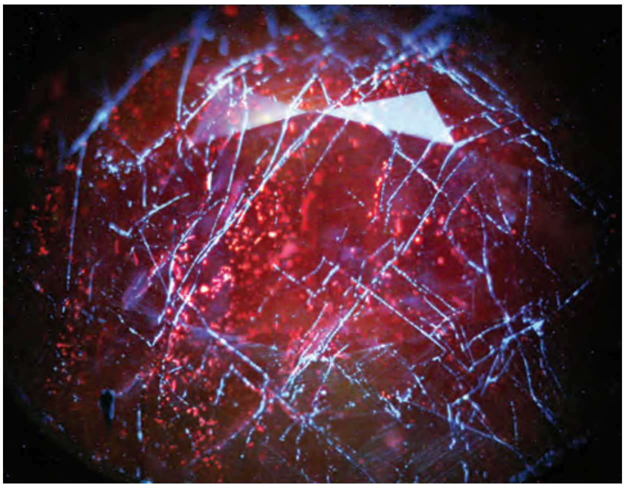


Figure 14: This DiamondView image reveals strong chalky blue fluorescence along the fissures of a 2.64 ct green glass-filled sapphire. Photo by S. Promwongnan.

glass filler that is present in a sample, similar to the X-radiographs.

Preliminary Durability Testing

No damage to the lead-glass filler was observed after ultrasonic cleaning in an ordinary liquid soap solution for 15 minutes.

After exposure to a jewellery torch flame for one minute, some damage was observed on the surface of the lead-glass filler. Subsequent exposure to a strong direct torch flame for 30 seconds caused further damage to the filler.

Immersion in the rhodium electroplating agent for two minutes caused significant damage to the glass filler (Figure 15).

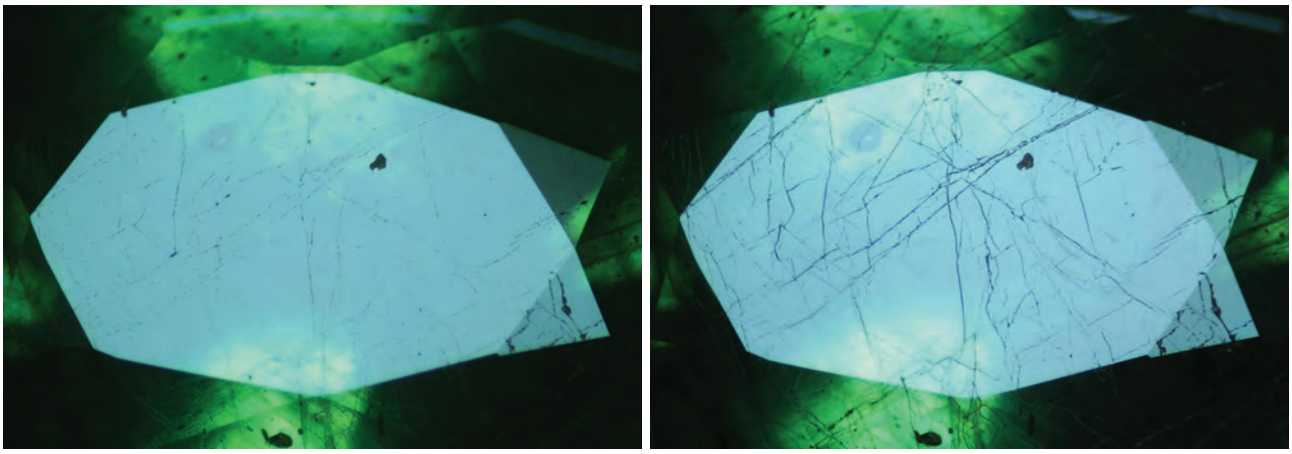
Conclusions

The identification of green lead-glass-filled sapphire is straightforward based on the same criteria used to distinguish previous lead-glass-type treatments. Microscopic observation is probably the simplest method to positively identify such treatments. The most prominent characteristics are orange and blue flash effects and green colour concentrations along fissures, and also flattened gas bubbles trapped within the glass-filled fissures.

EDXRF chemical analyses can reveal the presence of Pb and Si, along with Fe, Cu and Cr that probably act as colouring agents for the green glass filler. Furthermore, FTIR spectroscopy is also useful for proving the existence of a glass filling in such stones. X-radiography can help confirm the presence of lead glass, as well as give a rough estimation of the amount of filling material present in a sample. DiamondView images show chalky blue fluorescence along fissures and cavities, and also can help quantify the degree of filling.

Preliminary durability testing revealed some damage to the glass filler from a jewellery torch and rhodium electroplating solution, similar to results obtained previously for lead-glass-filled corundum (McClure et al., 2006; Leelawatanasuk, 2012; LMHC, 2012; Leelawatanasuk et al., 2013). Thus, we recommend that jewellers and consumers handle these treated stones with the special care that is typically recommended for lead-glass-filled materials.

Figure 15: Lead-glass-filled fractures within the table of a sapphire are shown in reflected light before (left) and after (right) immersion in a rhodium electroplating agent for two minutes. The filler significantly dissolved, leaving many open fractures. Photomicrographs by S. Promwongnan; magnified 15×.



Glass-filled corundum has been circulating in the gem market for many years. With recent developments in this type of treatment, green glass-filled sapphires are now available. There also is the potential for additional colours of glass fillers to be developed in the future.

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