A Barium (Ba) Glass Filled Ruby.

A 3.71 ct oval cabochon cut ruby (Fig. 1, left) was sent to the Liechtenstein branch of GGTL Laboratories for treatment analysis. Microscopic observation revealed rather obvious glassy residues in fissures of the stone, and even some noticeable cavities were filled, showing gas bubbles from the shrinking of the glass upon cooling (Fig. 2, left).
In order to see whether there was a high density glass involved in the treatment of this stone or "only" a silica glass (such as the typical borax flux [sometimes combined with quartz] used in heat treatments), a three dimensional HD radiograph was recorded, of which one position can be seen in figure 1, right. In the radiograph it is apparent that the density of the glass used for the filling is considerably higher than the density of the ruby: all the white and very light grey portions in the radiograph represent the glass fillings.

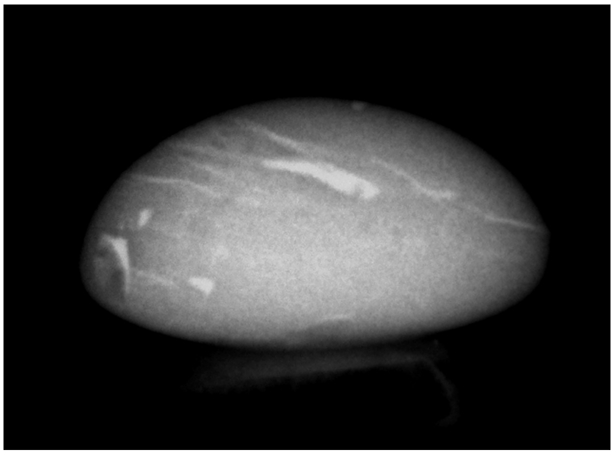

Figure 1. Left: The 3.71 ct barium glass filled ruby. Right: The radiograph showing the filled fissures and cavities of the ruby indicates that the glass contains far heavier elements than the elements usually encountered in corundum (atomic weight from ≈ 48 to 70). Photo on the left by C. Nacht, GGTL Laboratories; radiograph by T. Hainschwang.

Even though the inclusions of the ruby were quite apparent and the glass bore some similarities with regular glassy residues from "flux assisted heating", the appearance of the gas bubbles in the large fillings and the stark contrast in the radiograph made us suspect that the glass used may be lead glass, or that the stone may have been treated by a combination of both, regular flux assisted heat treatment plus lead glass treatment.

The stone was then analysed under the DFI fluorescence imaging and spectroscopy system and all the fissures exhibited blue fluorescence under the shortwave UV excitation (Fig. 2, right). The typical reaction of lead glass is a dull and very chalky appearing blue to olive, a much less bright emission than the one observed for this sample.

Infrared spectroscopy has revealed a small 3309 cm^{-1} absorption which for ruby is generally a good indicator of heat treatment, plus a broad absorption band centred at 2640 cm^{-1}. Such a broad band in the IR spectrum is typically observed in stones that contain significant quantities of glassy residues, it is basically the glass absorption spectrum overlaying the corundum spectrum. While such a band is seen for most lead glass filled rubies, it only very rarely shows up in the spectra of regular flux heat treated stones.

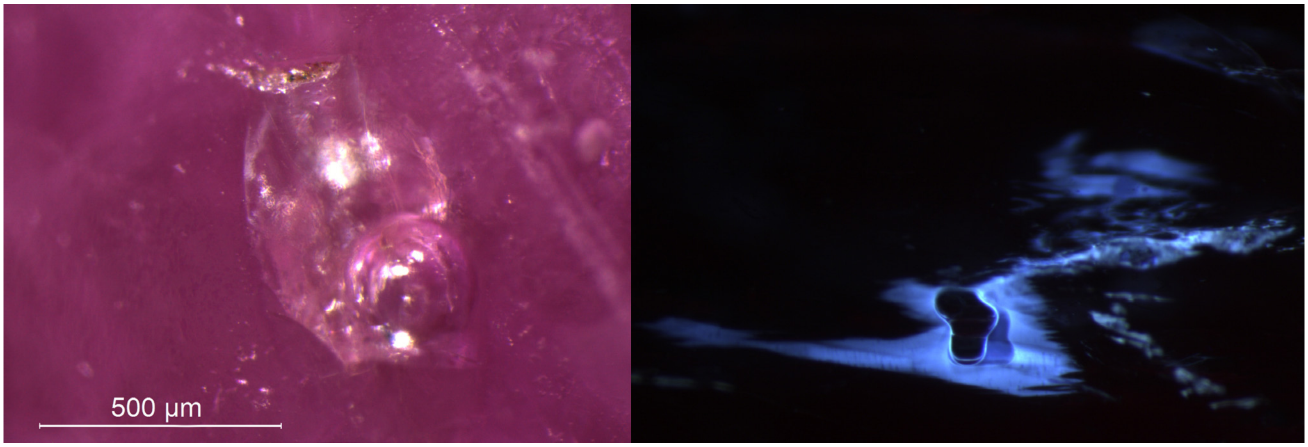

Figure 2. Left: A filled surface-reaching cavity of the ruby, containing a large round gas bubble. Right: under the deep UV excitation of DFI fluorescence microscopy and imaging system the glass fluoresces distinct blue. Micrographs by T. Hainschwang.

In order to detect the heavy element(s) present in the apparently specific glass that has been used for the treatment of this ruby, EDXRF spectra were recorded. The first spectrum was recorded with the X-ray tube set at 24 kV, the typical settings for the detection of chromogenic elements in corundum, since the K lines of the lighter elements and the L lines of the heavier elements are found here. In this first analysis nothing obviously unusual was detected, only chromium, vanadium, gallium, iron and titanium appeared to be present, but not a trace of lead or any other heavy element; the only curiosity seemed to be the unusually high titanium content and the somewhat large vanadium peak. In consequence a second EDXRF analysis was performed, with the X-ray tube set to 50 kV, and this one then gave away the composition of this glass: strong barium K lines showed up in the spectrum (Fig. 3, right), and since these are at energies >24 keV, they could not be easily seen with the X-ray tube set at 24 kV. The L lines of barium can be detected at 24 kV, but they coincide almost exactly with the titanium and vanadium lines (Fig. 3, left). One has thus to be very careful when testing rubies by EDXRF analysis in order to identify a potential high refractive index barium glass: while lead glass will be easily detected with the standard setting, it requires high energy setting to properly identify barium.

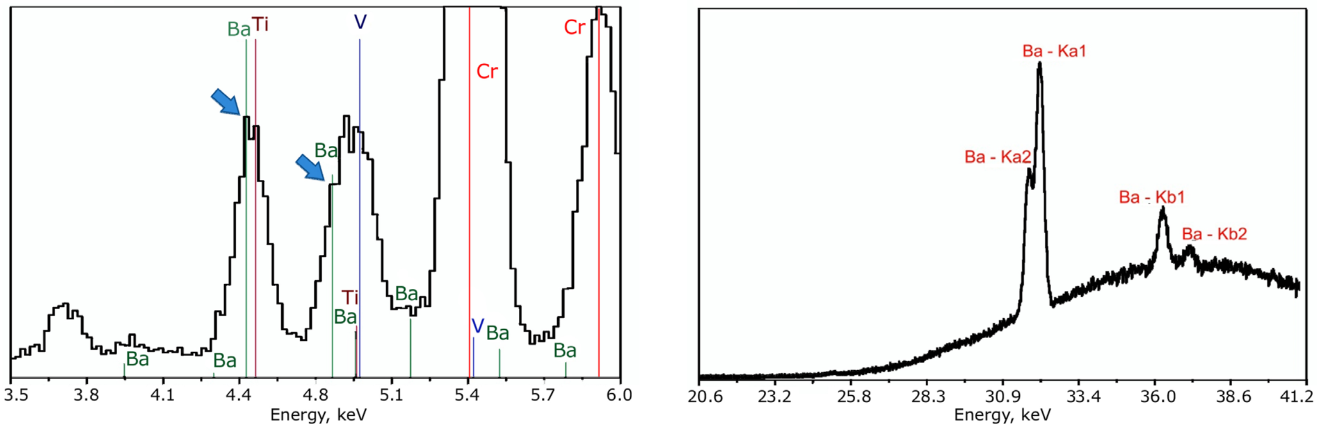

Figure 3. The two EDXRF spectra recorded for the ruby: on the left the 24 kV (with Al filter) setting typically used to see the chromogenic elements in corundum and on the right the 50 kV (with Pd filter) setting that allowed to properly identify the barium. The barium peaks are difficult to distinguish at the low energy setting, only the intensity increasing of the Ti Kα by the Ba Lα line, and the widening of the V Kα by the Ba Lβ line can show us the presence of barium. The Ba Lλ and Lγ lines, as well as the small Ba Lα do not modify substantially the spectrum appearance in this energy area. Note that in rubies lacking vanadium, the Ba Lβ line should immediately be identifiable and cannot be confused with the V Kα.

This is the first ruby we have ever seen at our laboratories that has been filled with a high refractive index barium glass. Barium glass can have a refractive index N above 1.7, but this depends on barium content; the refractive index of this glass could not be determined since the cavities were not large enough to measure it.

According to the client this stone has been in stock for more than 10 years, which seems to indicate that this was possibly one of the experimental treatment products that finally lead to the most efficient fissure filling procedure using lead glass starting in 2004.

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