Treated ruby

Dr Karl Schmetzer[1], Dr Michael S. Krzemnicki[2] and Alan Hodgkinson FGA DGA[3] investigate a new treatment of ruby.

[1]Petershausen, Germany. [2]SSEF Swiss Gemmological Institute, Basel, Switzerland. [3]Portencross, Scotland, UK

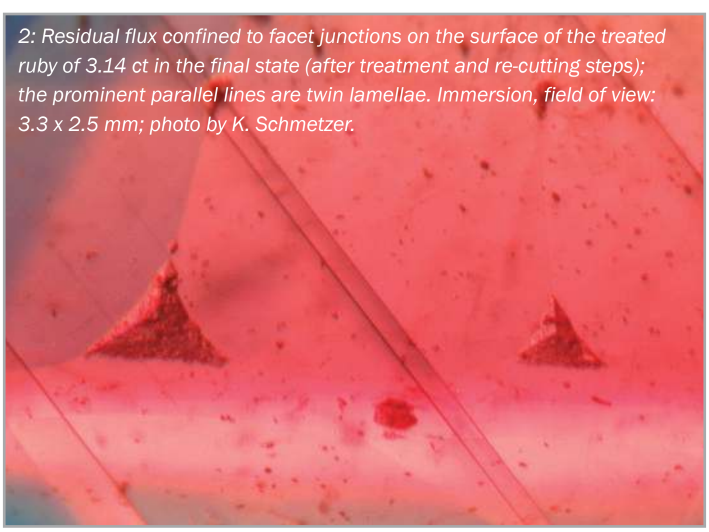
Introduction

At the Tucson gem and mineral show in 2011, Ted Themelis (of Bangkok, Thailand) presented a new treatment process for ruby to a group of staff members of different gemmological laboratories. This is a heating process developed by him especially to lighten darker rubies, and comprises multistep heating in which the samples are annealed in lithium-based fluxes, without the addition of beryllium, at temperatures between 1300 and 1350 °C in an oxygen-bearing atmosphere. The use of lithium-bearing fluxes had already been published by Themelis (2010) prior to this presentation.

Subsequent to the 2011 Tucson show, Mr Themelis presented this new development in several talks in Australia, the United Kingdom, Italy and Korea. He also informed the authors that all samples treated using this technology have been released by him as treated to the trade, but he has been informed by some of his clients that at least some of these rubies, mostly samples above 5 ct in weight, have attracted certificates stating that they were natural ruby without any 'indication of heat' by some gemmological laboratories. We also understand that a heat treatment process using lithium-bearing fluxes is also applied to ruby by other treaters in Thailand.

A faceted dark purplish ruby owned by one of the authors (AH) was submitted to T. Themelis who treated it with his new process in several stages, and the stone was then re-cut. We feel that an examination and description of that particular stone and its gemmological properties may be helpful for the industry to properly describe and distinguish between treated and untreated samples.

1: Original dark purplish violet ruby of 3.80 ct as purchased by one author some years ago (a); the sample in an intermediate state of treatment still covered with residual flux (b); the ruby sample in its final state after re-cutting, viewed in daylight (c) and incandescent light (d). The ruby now weighs 3.14 ct and measures 8.9 x 8.0 mm; photos by A. Hodgkinson (a,b) and K. Schmetzer (c,d).



2: Residual flux confined to facet junctions on the surface of the treated ruby of 3.14 ct in the final state (after treatment and re-cutting steps); the prominent parallel lines are twin lamellae. Immersion, field of view: 3.3 x 2.5 mm; photo by K. Schmetzer.

The ruby

The ruby specimen was purchased by one of the authors (AH) as an untreated cut stone in the 1990s (**1a**). The geographical origin of the sample was not communicated at that time. Originally, the stone weighed 3.80 ct (**1a**) but, after several treatment and re-cutting steps between 2009 and 2011 (**1c**,**d**), it now weighs 3.14 ct. It is clear that the colour after treatment is lighter and less purple. The ruby is shown in an intermediate step, after treatment and before re-cutting (**1b**), where it is still covered with some residual flux. In the final state, the ruby shows typical pleochroism and the normal colour variation of ruby between daylight and incandescent light (**1c**,**d**).

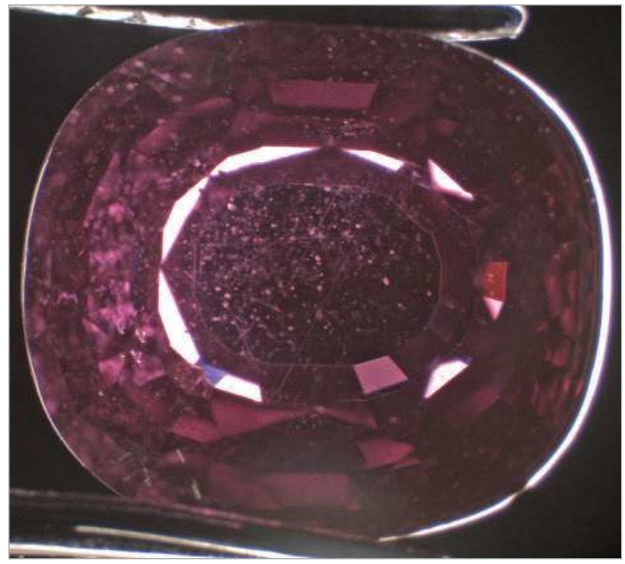
Examination of residual flux

After recutting, parts of the surface of the ruby still retained some triangular spots at facet junctions which have lower reflectivity than the ruby (**2**); these obviously did not represent ruby material. Chemical examination by Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) showed the material to be composed of boron (B), lithium (Li), sodium (Na), aluminium (Al) and silicon (Si) as major components. This result confirms the details given by Mr Themelis about the fluxes used in his treatment process. The flux remained only on original facets which had not been completely re-cut and we did not see any evidence of flux penetrating into or actively healing open fissures in the stone.

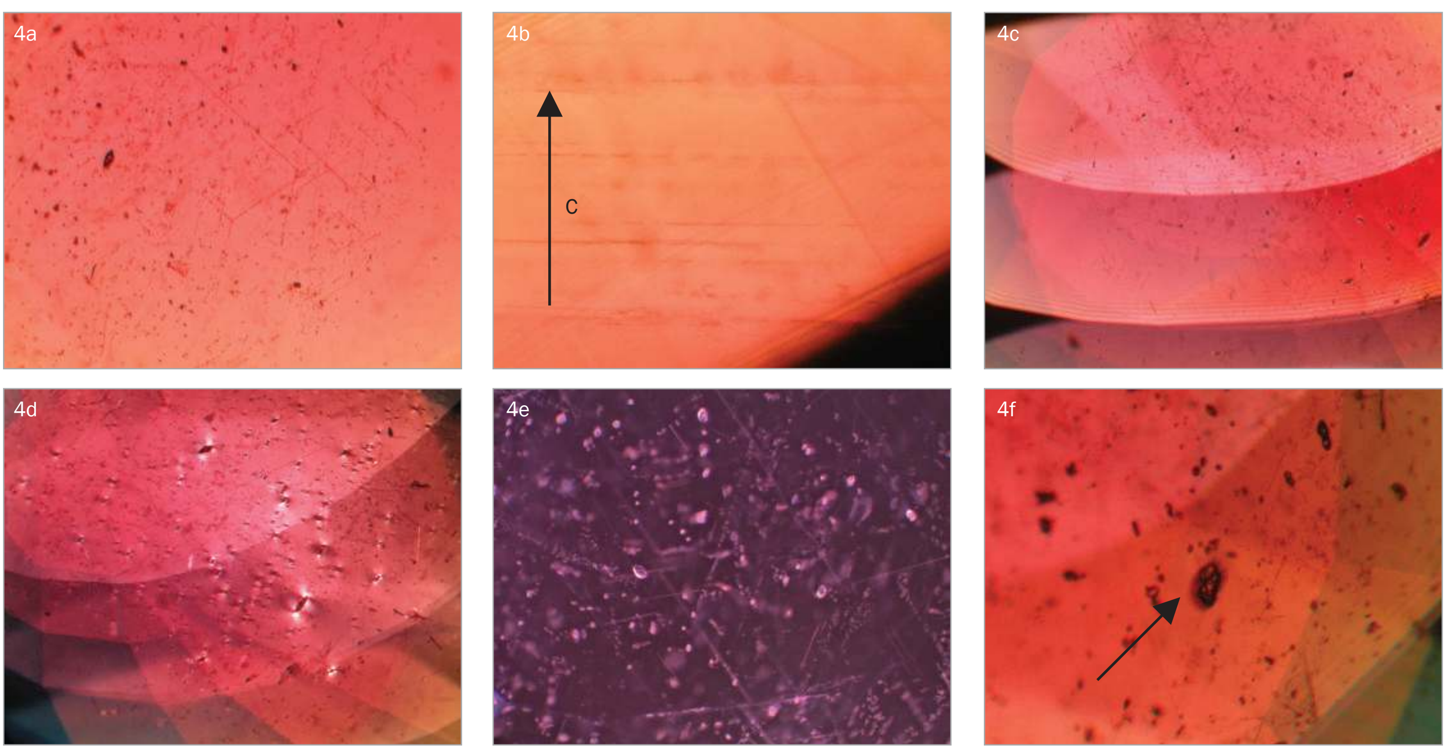
Microscopic features

The ruby shows some microscopic inclusion features which seem to be unaltered by the heat treatment (**3**). In particular, a network of oriented rutile needles, particles or dust is present (**4a**), and the needles are concentrated on planes or layers perpendicular to the optic axis of the ruby (**4b**). Furthermore, the sample showed several twin lamellae (**4c**) as well as numerous tiny birefringent mineral inclusions, mostly zircon crystals (**4d**,**e**), which in places form clusters of inclusions. No internal colour banding or growth pattern was detected. This absence of a specific growth structure is related only to very few natural sources.

Other inclusion features, however, might indicate heat treatment (**4f**): some of the larger zircon crystals were surrounded by disc-shaped tension cracks. This feature, however, is not definitive,



3: General overview of the inclusion pattern in the heat-treated ruby of 3.14 ct, size 8.9 x 8.0 mm. Darkfield; photo by M.S. Krzemnicki.



4: Microscopic properties of the treated ruby of 3.14 ct; network of oriented rutile needles and particles in a direction of view parallel (a) and perpendicular (b) to the c-axis (indicated by an arrow); oriented rutile needles and twin lamellae (c); twin lamellae, rutile needles and birefringent mineral inclusions, most probably all tiny zircon crystals (d,e); zircon crystal with tension cracks (f). Immersion, plane polarized light (a,b) and crossed polarizers (c,d,f); darkfield (e); field of view: 4.6 x 3.5 mm (a); 2.1 x 1.6 mm (b); 5.9 x 4.4 mm (c); 6.0 x 4.5 mm (d), 4.2 x 3.1 mm (e); 3.6 x 2.7 mm (f); photos (a-d, f) by K. Schmetzer, photo (e) by M. S. Krzemnicki.

Gems and Minerals

Treated ruby (cont.)

5: Our heat-treated ruby of 3.14 ct (8.9 x 8.0 mm) is probably from Vatomandry, Madagascar, which is the source of the untreated sample of 0.62 ct (5.8 x 4.6 mm) on the right; photo by M. S. Krzemnicki.

as similar tension cracks can be present in unheated rubies from several localities, but more detailed microscopic and spectroscopic data on the zircon inclusions do lead to a clear result (see below).

Comparing these microscopic features and the chemical composition (determined using Energy Dispersive X-Ray Fluorescence (EDXRF)) with samples of known origin, the closest match is found with rubies from the Vatomandry deposit in Madagascar (see Schwarz and Schmetzer, 2001).

Detailed examination of zircon inclusions

Zircon crystals are common inclusions in rubies from several localities worldwide and may be used as indicators for high temperature treatment. As inclusions in corundum, pure zircons are stable up to about 1685°C and decompose to ZrO_2 and SiO_2 above this temperature. Any presence of melt indicates that the stone has been heated above 1750°C (Schmetzer and Schwarz, 2005).

At lower temperatures, the crystalline structure of zircon crystals (present as inclusions in rubies and sapphires) also undergoes some alteration. Many natural zircons are in a metamict or partial metamict state due to damage to their structure by radioactive decay (caused by traces of uranium or thorium). Upon low temperature heat treatment, these zircons undergo some healing process and regain their crystal structure. These changes are reflected or indicated in the Raman spectra of the zircon inclusions. Two effects can be observed: compared to untreated zircon inclusions in rubies the spectra of heat-treated zircons show a shift of the peak position and a reduced peak diameter, described as full width at half maximum (FWHM) (Zhang *et al.*, 2000; Nasdala *et al.*, 2001; Krzemnicki, 2010 a,b).

This new method was applied to our stone. For comparison, we selected (from about 10 samples available) an untreated ruby from Vatomandry which has been kept in a private collection since the discovery of the deposit (**5**). The sample showed the typical inclusion pattern of rubies from Vatomandry, especially numerous clusters of tiny zircon crystals (**6a**). At higher magnification, several slightly elongated euhedral zircon individuals are visible (**6b**,**c**). The zircon crystals in the treated ruby, in contrast, show a somewhat inhomogeneous, patchy white appearance (**7**).

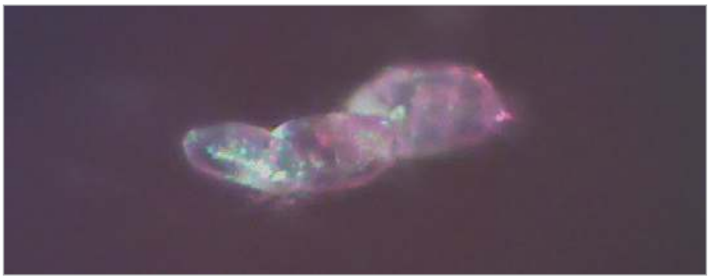
The Raman spectra obtained from several zircon inclusions in both samples are quite similar (**8a**), but clear shifts of peak positions near 980 and 1015 cm^{-1} and differences in their peak shape (FWHM) are clearly visible (**8b**). These results indicate that the zircon inclusions in the untreated sample were in a partly, but not in a full, metamict state.

Discussion

The authors want to underline that it is beyond the scope of this contribution to discuss the reaction mechanism of the colour alteration in detail. From the examination of one single sample with analytical data from the surface only and without chemical data from a traverse from the rim to the centre of the treated stone, we are unable to decide at this point if there is any boron or lithium diffusion into the corundum structure at the annealing temperatures applied to the sample. Furthermore it is unknown to us if this would have any effect on the colour of the ruby.

6: Inclusion pattern in the untreated ruby from Vatomandry, Madagascar (see 5), showing rutile needles and clusters of tiny zircon crystals (a); at higher magnification, euhedral zircon crystals with elongated prismatic habit are visible (b,c). Transmitted light, field of view: 3.5 x 2.6 mm (a), 0.30 x 0.23 mm (b), 0.30 x 0.23 mm (c); photos by M. S. Krzemnicki.

Treated ruby (cont.)



7: Cluster of zircon crystals in the heat-treated ruby (see 1 and 5); the tiny zircons show a diffuse white encrusting surface, which is a characteristic result of heating zircon inclusions, even at relatively low temperatures. Transmitted light, field of view: 0.30 x 0.23 mm; photo by M. S. Krzemnicki.

However, it has been known for decades that the intensity of the Fe^{2+}-Ti^{4+} charge-transfer absorption band of blue sapphire or purplish ruby is effectively reduced by low temperature heat treatment under oxidising conditions (see, e.g., Schmetzer and Bank, 1980; Nassau, 1984; Krzemnicki, 2010 a,b). The colour of dark blue sapphires can be somewhat lightened, and the colour of purplish rubies can be shifted towards a more pure ruby red. Based on present data, we suppose that this mechanism is mainly involved in the colour alteration of our ruby, but we cannot exclude that other additional mechanisms might also be involved.

To investigate a possible content of lithium and/or boron in the corundum structure which might indicate diffusion processes needs a more detailed study of chemical zoning in samples in the treated and untreated states. Hopefully, some other well documented samples will be available in the near future to be then chemically examined to prove a possible chemical zoning with traverses from the rim to the core of the sample and to shed more light on the treatment process and the mechanism of colour alteration. Only after this can we be sure of whether we are dealing with a new treatment involving diffusion of lithium or just with a classical flux-assisted heating, with a variation of the flux composition applied for the treatment process.

It is clear that the rutile needles have not been affected by this treatment process at relatively low temperatures. If the sample had been cut with complete removal of the residual flux, it would have lost some more weight, but this indication of treatment in a lithium-bearing flux could have been completely removed. The microscopic examination of zircon inclusions at high magnification, however, gave a first indication for possible heat treatment of the ruby, and this was then confirmed by the Raman spectra obtained from the slightly altered zircon crystals.

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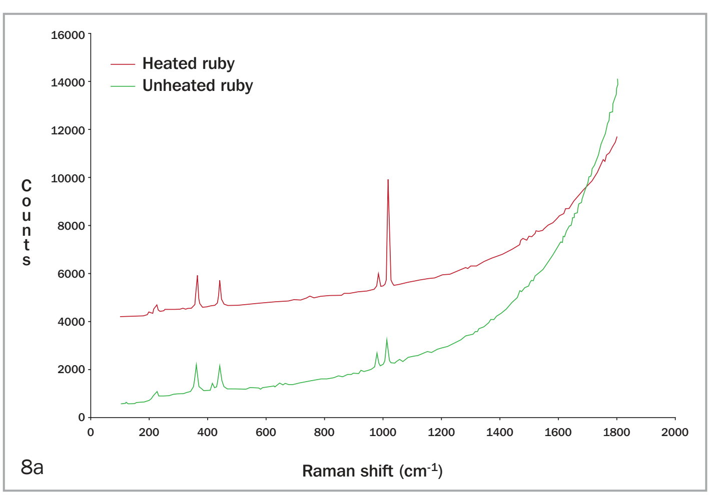

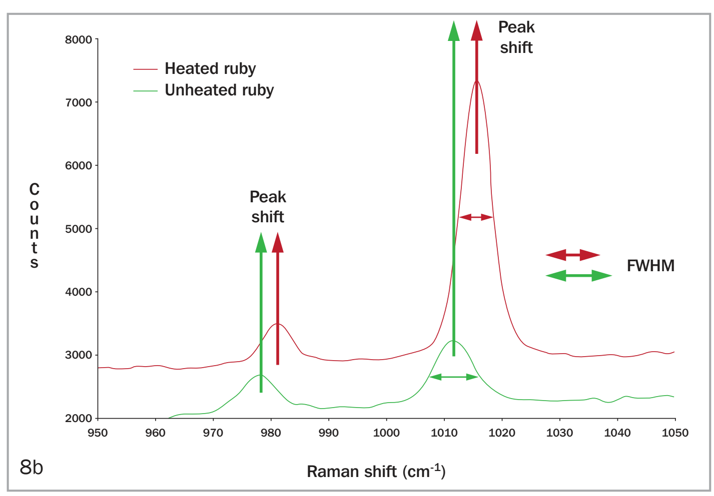

8: Raman spectra of zircon inclusions in heat-treated and untreated ruby; overview of the spectra (a) and details in the 950 to 1050 cm^{-1} range (b); the spectrum of the heat-treated ruby shows more intense and somewhat sharper Raman lines (i.e. lines with smaller FWHM); a shift of the peak positions between the treated and untreated sample is clearly visible; similar shifts were also observed for Raman lines in the 350 to 450 cm^{-1} range.