Treatment of corundum
characteristics, detection and declaration

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Every gemstone deposit produces stones of high and low quality. Usually the quality distribution has the shape of a pyramid. Top stones are rare, stones of lower quality are very abundant. The exploitation of gems is expensive, regardless of their quality. It is economically and important to be able to enhance stones of the lower part of the quality pyramid (also for the miners!) Once a treatment is developed and successful, it often is also applied on stones of better quality to make them even better looking.

**Treatment options for corundum...**

To modify transparency:
- filling of fissures with colourless substance (oil, artificial resin, glass)
- heating to dissolve inclusions

To modify colour
- filling of fissures with coloured substance (oil, artificial resin, glass)
- heating in oxidising or reducing conditions (± with additives)
- diffusion of „colouring“ elements into the corundum lattice
- irradiation

To enhance stability
- filling of fissures/cavities with solidifying substances

To create optical effects
- heating with additives

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Treatment options for corundum...

Fissure filling and dyeing
Foil, painting

Time scale

0 1000 1900 2000

Future

Heating with blow-pipe
Heating with electrical furnace
Irradiation
Heating combined with surface diffusion
Heating with borax to induce fissure "healing"
Beryllium diffusion
Lead-glass fissure filling
Cobalt-glass fissure filling

Acceptance in the trade and stability

Stability

low high

Acceptance

low high

Heating with borax to induce fissure "healing"
Beryllium diffusion
Cobalt-glass fillings
Lead-glass fillings
Irradiation
Surface diffusion
dyeing
Fissure filling with oil (± colourless)
Talking about treatments...

Fissure filling with colourless oil:

Oiled fissures often found in rubies or sapphires polished as beads.

SSEF discloses oil in corundum only if the amount in fissures is moderate to significant.

A fissure filled with oil, showing a characteristic dendritic pattern.
Dyeing/staining with coloured oil:

red dye in a colourless sapphire and in pinkish grey star corundum.

On SSEF reports, such a dyeing treatment is fully disclosed!

Irradiation of corundum:

Irradiation with high energy electromagnetic radiation (intense SWUV, X-rays, gamma-rays). Colourless or pale yellow stones become intensely brownish yellow (amber colour) due to an induced colour centre. The colour centre is however not stable and the colour will thus fade in daylight after some time.

Some natural untreated yellow sapphires also show unstable colour!

Detection is difficult. Usually these stones are exposed to a „fading test“ under a strong light source (beware of heating!).
Colour in corundum is due to the presence of iron (Fe²⁺, Fe³⁺), titanium, magnesium and chromium. Very important in this respect are the so-called "intervalence charge transfer processes" with titanium Ti⁴⁺/Fe²⁺ and with iron itself Fe²⁺/Fe³⁺.

- Fe²⁺/Ti⁴⁺ results in blue
- Fe²⁺/Fe³⁺ results in yellow

Heating of corundum mostly affects the valency of iron Fe²⁺ and Fe³⁺ found as chemical impurities within the corundum lattice. Secondly it may also result in the release of titanium Ti⁴⁺ into the lattice by dissolving rutile (internal diffusion)

- Fe²⁺ oxidising heating
- Fe³⁺ reducing heating

By this, many (but not all) colour changes due to heating can be explained.
Heating of corundum

- Low temperature heating (<1000 °C), e.g. Mong Hsu rubies and pink sapphires
  - effect: colour shift, blue colour component is reduced

- Heating > 1000 °C, e.g. for geuda corundum, rubies from Thailand
  - effect: colour modification, reducing visibility of inclusions

- Heating with high refractive glass flux, e.g. lead glass
  - effect: significant enhancement of transparency and colour (and stability)

- Heating with borax flux, e.g. rubies from Mong Hsu (Burma)
  - effect: significant enhancement of transparency and colour

- Heating with chromium diffusion (shallow)
  - effect: creation of shallow colour zone

- Heating with beryllium diffusion (lattice, bulk), e.g. corundum from Songea
  - effect: significant colour modification

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Low Temperature heating (below 1000° C)

By the heating at low temperature at oxidising conditions, the blue colour component is reduced, thus a better red to pink colour is achieved!

Detection of low-Temperature heated corundum with the microscope is very difficult
Raman spectra or FTIR spectra can be very important for detection of low-T heating of corundum!

Heating of corundum above 1000° C

At higher temperatures, it is possible to significantly enhance or modify the colour of corundum. Furthermore, it is possible to reduce visibility of inclusions.
Surface features indicating a heat treatment

High temperature heating may produce “burnmarks” on the surface (but usually stones heated at high temperature are re-polished).

Atoll structures

Melting and explosion of inclusions results in characteristic discoid features, the so-called “atoll-structures.”
The dissolution of rutile needles

Rutile needles may partly dissolve and leave dust tracks in their former place.

Partly dissolved rutile results in blue dots due to the release of titanium into the corundum lattice (internal diffusion).
Heating with high refractive glass flux

In the last few years large quantities of rubies heated at low temperatures with a high refractive glass flux (e.g. containing lead, bismuth...) have entered the market.

Rutile needles may be still present (sometimes rubies show even star effect!)

Blue and orange „flashes“ (interferences) along lead-glass filled fissures. Also with distinct flattened air bubbles along fissures. At these low temperatures, no „healing“ of fissures occurs!

Detection easy with the microscope!
SEM BSE micrograph: Fissures filled with Pb-glass are bright.

Pb-glass filled ruby is easy to detect with chemical analysis, radiography and X-ray microtomography.

X-ray microtomography of Pb-glass filled ruby.

New: Heating with Co-bearing flux

Coloured corundum with distinct Co-blue fissure fillings (and distinct Co spectra !)

Easy to detect with microscope!
Heating with a Flux (Borax: Na-B-Hydroxide):
Microscopic Evidences

Flux residues in tentacle-like irregular pattern in a ruby from Thailand (Siam) heated with a borax flux.

Attention: polycrystalline flux in flux-melt synthetic ruby!
Quantification of flux residues

<table>
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<tr>
<th>Condition</th>
<th>Report numeric</th>
<th>Report Text</th>
<th>No indications of heating</th>
<th>Indications of heating with residues in fissures</th>
<th>No indications of heating</th>
<th>Indications of heating with residues in cavities</th>
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<tbody>
<tr>
<td>NTE</td>
<td>NTE</td>
<td>Minor</td>
<td>Minor residue in fissures</td>
<td>Minor residue in fissures</td>
<td>Minor residue in fissures</td>
<td>Minor residue in fissures</td>
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<tr>
<td>TE1</td>
<td>TE1</td>
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<td>Moderate residue in fissures</td>
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<td>Significant residue in fissures</td>
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<tr>
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<td>TE3</td>
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<td>Minor residue in cavities</td>
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<tr>
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</tbody>
</table>

Note 1: As an option, e.g., for "simplified reporting" situations, the quantification of residues in healed fissures may be replaced by the statement 'residues in healed fissures'.

Note 2: Wording in parenthesis is optional.

Note 3: This clause may include the presence of small filled cavities.

Heating with surface diffusion (shallow)

A colouring element (titanium or chromium) from an external source is entering the corundum lattice during a prolonged heat treatment at high temperature. The result is a very shallow intensely coloured zone at the surface. The colour is easily lost after repolishing.

Detection with the microscope and chemically
Comparison of a diffusion treated sapphire (left) with a natural sapphire (right) in immersion. The facet edges and the girdle of the diffusion treated stone show characteristic colour concentrations.

Heating with beryllium diffusion (lattice, bulk)

Beryllium from an external source is deeply penetrating the corundum lattice during a prolonged heat treatment at high temperature. The result is usually a significant colour modification. This treatment is microscopically very difficult to detect, as an eventual orange rim is often very difficult to see. The colour is usually stable even after a repolish!
Detection of heating with beryllium diffusion

Difficult with the microscope!

Safe detection only with LIBS, LA-ICP-MS and SIMS

LIBS spectra of beryllium diffusion treated orange sapphire. The high beryllium peak is measured in the glassy residue at the surface! The corundum shows smaller peaks, indicating approx. 30 ppm Be (low traces!), but which is already enough for a colour modification.
Multi-step Treatments: Creating a star effect

Beryllium diffusion treatment followed by titanium diffusion treatment and subsequent annealing results in a precipitation of tiny oriented rutile needles creating a surface-related star effect (asterism).

Disclosure

Internationally harmonized wording for the confidence of the customers!

The Swiss Gemmological Institute SSEF uses a full disclosure policy following CIBJO and LMHC (Laboratory Manual Harmonization Committee with the members CISGEM, GAAJ, GIA, Gübelin GGL, GIT, SSEF) recommendations:

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Indications of heating</th>
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</thead>
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<tr>
<td>Unheated ruby</td>
<td>- No indications of heating</td>
</tr>
<tr>
<td>Heated ruby</td>
<td>- Indications of heating</td>
</tr>
<tr>
<td>Heated with flux</td>
<td>- Lead glass filled fissures and cavities</td>
</tr>
<tr>
<td></td>
<td>Extent: significant (minor, moderate)</td>
</tr>
<tr>
<td></td>
<td>The introduction of lead glass into fissures involves heating</td>
</tr>
<tr>
<td></td>
<td>This treatment usually applies on low quality stones.</td>
</tr>
<tr>
<td></td>
<td>- Indications of heating with minor/moderate/significant</td>
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<tr>
<td></td>
<td>residues in healed fissures</td>
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<tr>
<td>Heating with diffusion</td>
<td>- Indications of heating</td>
</tr>
<tr>
<td></td>
<td>Colour modified by shallow/lattice diffusion of titanium/</td>
</tr>
<tr>
<td></td>
<td>chromium/beryllium from an external source</td>
</tr>
</tbody>
</table>
Thank you for your attention