

CHAPTER 4 HEAT TREATMENT OF GEMSTONES

Heat treatment is a natural type of enhancement as it is a continuation of the process that occurs in the earth when mineral was originally formed. During treatment, the Gemstone is heated to very high temperatures (below melting point of gemstone) causing inclusions or removing inclusion by adding or removing chemical elements from gem , and other impurities to reform themselves and change the color of the stone. This color change may result either in the stone being darker, lighter, more intense, or of a different color. An example of this is the dissolving of rutile silk inclusions in blue sapphires, which improves both clarity and color. This heat treatment is permanent and irreversible.

This is the process that caused alteration in physical and chemical structure of the gemstone by heat. Following are some of the several changes induced today by heat treatment (Table. 4.1):

Table 4.1 Changes induced by heat treatment with examples.

Sr. No	Change by heat treatment	Example
1	Darken Colour	Light blue sapphire to dark blue sapphire
2	Lighten Colour	Dark pink tourmaline to light pink tourmaline
3	Colour Change	Amethyst to Citrine
4	Removal of Secondary Colour	Removal of purplish hue from Ruby, Green colours From Aquamarine.
5	Development of Asterism / silk	In Corundum
6	Removal of Asterism / silk	In Corundum
7	Structural Change	Low zircon to high type zircon
8	Crackling	Iris Quartz

HEAT – TREATMENT CONDITIONS

The important factors in specifying the conditions for the heat treatment of a gemstone material are the following:

- (1) The maximum temperature reached.
- (2) The time for which the maximum temperature is sustained.
- (3) The rate of heating to temperature.
- (4) The rate of cooling down from temperature and any holding stages while cooling.
- (5) The chemical nature of the atmosphere.
- (6) The pressure of the atmosphere.
- (7) The nature of material contact in furnace with gemstone
- (8) The quality of gemstone used and gemstone should not be heated above its melting point.

EFFECTS OF HEAT TREATMENT ON CLARITY AND COLOR

Clarity enhancement:

There is more or less micro crystals (inclusion) are present in gemstone. These secondary micro crystals reduce the clarity of the host gemstone. In many cases, when the gemstone is heated to high temperatures, these micro crystals dissolve back into the sapphire and remain in solid solution as the stone cools rapidly {relative to geologic process}, thus substantially improving the clarity.

Gemstones like Corundum Sapphires crystals contain very large numbers of micro crystals (inclusion) of another mineral that are often so small {0.5-20 um} and so numerous that they appear as a cloud or haziness to the unaided eye, Such microcrystal can be removed by heat treatment and the gemstone becomes more clear.

Colour Enhancement:

To understand the color transformation that can be induced by various heat treatment processes, it is necessary first to understand the origins of color in Gemstone.

The colour of gemstones are produced by transition metal ion impurities, transition metal compound, charge of transfer, Organic compound, Pure semiconductor, Doped semiconductor, Colour Center, Oxidation and Reduction. This can be modified in some cases of gemstones like Corundum, Beryl, Chalcedony, Diamond, Quartz, Topaz and Tourmaline. All these parameters are discussed in chapter 3.

Corundum

Corundum crystal consists of Al_2O_3 . The structure of sapphire is related to that of Corundum (Al_2O_3) and involves the Al^{3+} ions being distributed in an ordered fashion in 2/3 of the distorted (trigonal) octahedral sites within a frame work of hexagonal close-packed O^{2-} ions. Chains of face-sharing octahedra are directed along the c-axis, and the Al^{3+} ions within each chain form pairs separated by an empty interstitial site a process known as intervalence charge transfer. Involved in these are traces of both Titanium and Iron or Chromium which are responsible for colour in Corundum.

Chromium in Corundum gives pink to deep red colour, while Iron give pale green or brown or yellow colour. But, Titanium and Iron together gives Green, Blue Green and blue colour by mechanism of charge transfer.

When free of colour producing transition metals or colour center, such material has a transparency range from approximately 160 nm in the far ultraviolet to 5500 nm in the infrared region of the spectrum. Thus, pure sapphire is colorless. All color in sapphire is the result of impurities {other elements} or other point defects in the crystal

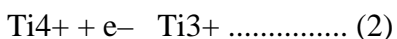
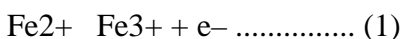
A crystal of Corundum containing a few hundredths of one percent of Titanium is colorless. If, instead, it contains a similar amount of Iron, a very pale yellow color may be seen. If both impurities are present together, however, the result is a magnificent deep-blue color. The process at work is “intervalence charge transfer,” the motion of an electron from one transition-metal ion to the another produced by the absorption of light energy ; this results in a temporary change in the valence state of both ions. Such a

mechanism is the cause of the blue of sapphire and the dark colors of many transition metal oxides such as the black iron oxide magnetite Fe_3O_4 . This mechanism is sometimes also called co-operative charge transfer.

The blue color sapphire, as it is found in nature, is derived from a subtle interaction between two impurities, iron and titanium. This color can be further modified by the presence of other impurities, such as the red-causing chromium or even by the white silk- and asterism- producing titanium itself; these last factors are controlled in part by the heating and cooling conditions to which the material was last exposed in its geological history. The exact shade of blue also depends not only on the relative amounts of Iron and Titanium present, but also on the valence states involved, namely ferrous, Fe^{2+} , and ferric, Fe^{3+} , as well as titanous, Ti^{3+} , and titanic, Ti^{4+} states; this is controlled by the oxidizing-reducing conditions during formation and subsequent heating and cooling in nature. The exact appearance of any specific, as- mined, Fe-Ti-colored blue sapphire, which can range from almost colorless via yellow, green, and blue to almost black with red, purple, brown, or milky over tones, either clear or combined with silk or asterism, is not indicative of an exact composition, but could be derived from a broad range of different compositions and past environmental histories. In attempting to produce a specific color enhancement in such a gemstone by a heat treatment, it is obvious that a wide range conditions might have to be tried to find the correct process,

Development of blue colour in corundum / Blue sapphire

In this method, Corundum (sapphires) are cleaned by diluted sulfuric acid and solvent to remove all stains and other impurities on their surfaces. then, heated gradually with temperature gradient 5°C of treatment by electric furnace at 1300, 1400, 1500 and 1600°C sequentially in nitrogen atmosphere (Table 4.2). Each sample were treated for 12 hours at different temperatures. Then gradually cooled at room temperature with 2 to 5°C to produce deep blue colour This converts some of the Fe^{3+} -ion into Fe^{2+} -ion. With both Fe^{2+} -ion and Ti^{4+} -ion now present, a new interaction becomes possible, this is called charge transfer and one electron transfer from the Fe^{2+} to the Ti^{4+} :



or the combination of reactions (1) and (2):

$\text{Fe}^{2+} + \text{Ti}^{4+} \rightleftharpoons \text{Fe}^{3+} + \text{Ti}^{3+} \dots\dots\dots (3)$ Gives blue colour in sapphire

List of all Possible changes in corundum by heat treatment :

- a) Lightening of dark blue
- b) Darkening of light blue
- c) Reduction of color zoning / yellow patch.
- d) Reduction of blue patch.
- e) Development of pink
- f) Intensity yellow
- g) Development of blue
- h) Removal of silk
- i) Development of silk.

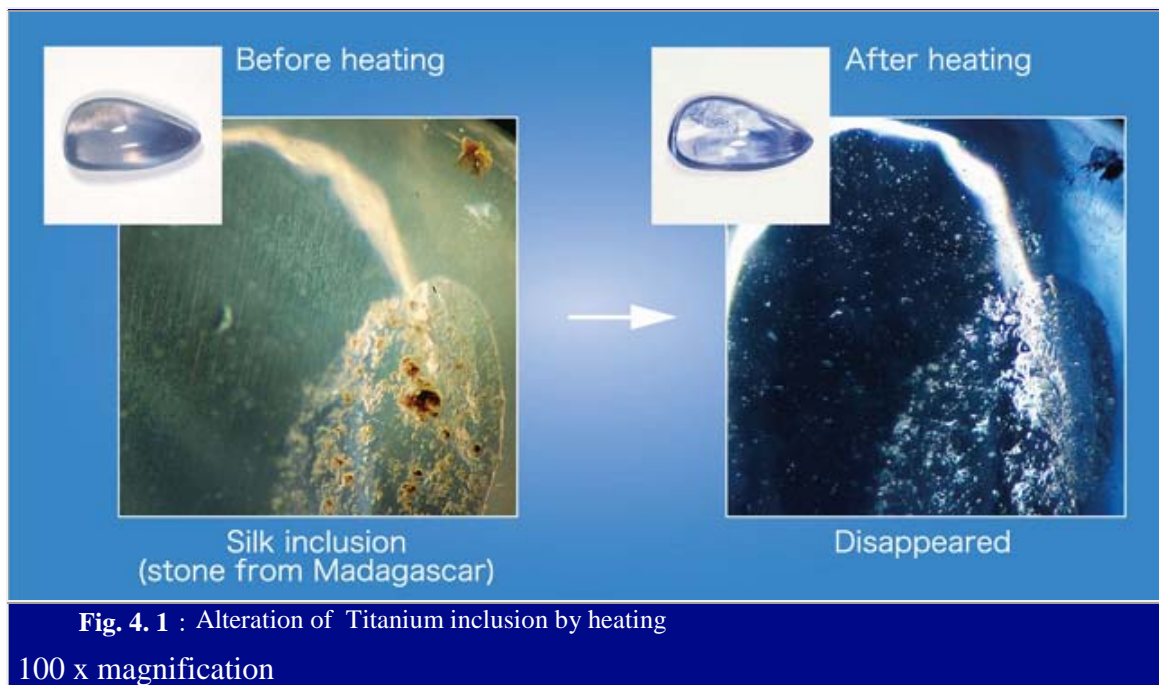
Table 4.2 Basic condition for heat treatment in corundum

TYPE	TEMPERATURE	ATMOSPHERE	TIME
Lightening of dark blue	1700 °C	Oxidizing	Prolonged hrs. (20hrs)
Darkening of light blue	1770 °C	Reducing	6 hrs.
Reduction of color zoning / yellow patch	1800 °C	Oxidizing	3 hrs.
Reduction of blue patch	1800 °C	Oxidizing	4 hrs.
Development of pink	1800 °C	Reducing	3 hrs.
Intensity yellow	1800 °C	Oxidizing	2 hrs.
Development of blue	1600 °C	Reducing	2 hrs.
Removal of silk	1650 °C 1000 °C (At 40 °C /min)	Oxidizing	Cooling at 40°C/min
Development of silk I	1500 °C	Oxidizing	2 hrs.

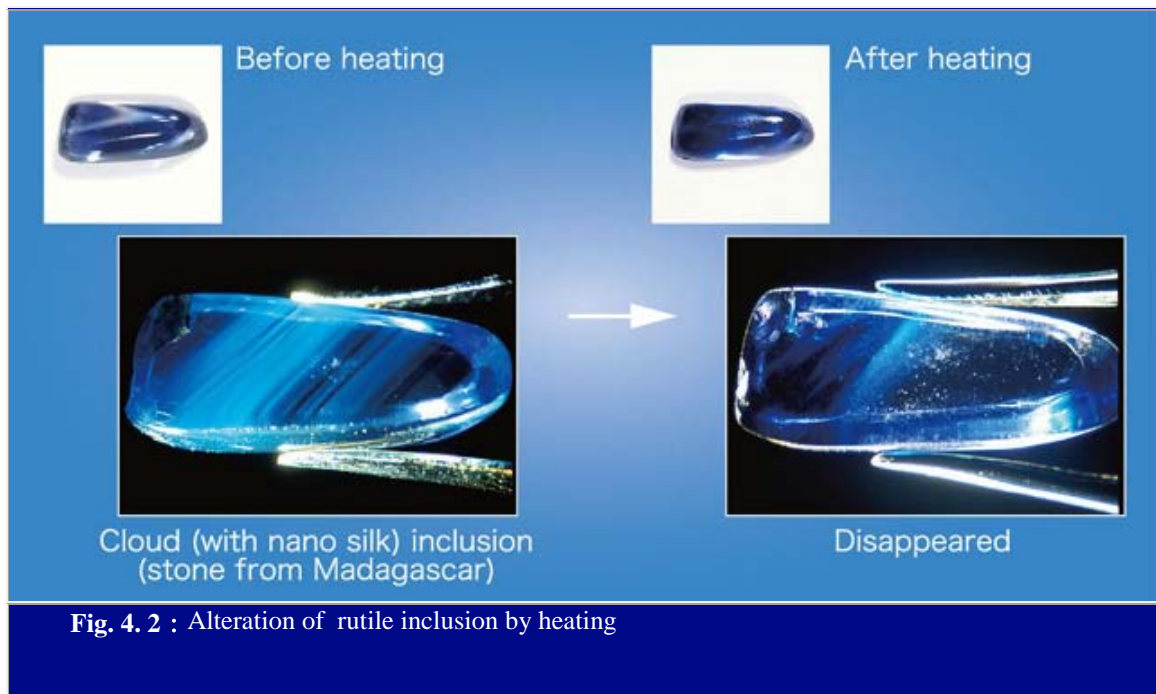
- Stability : All are stable to ordinary temperature but a few fade in months.

IDENTIFICATION OF HEATED GEMSTONE UNDER MICROSCOPE

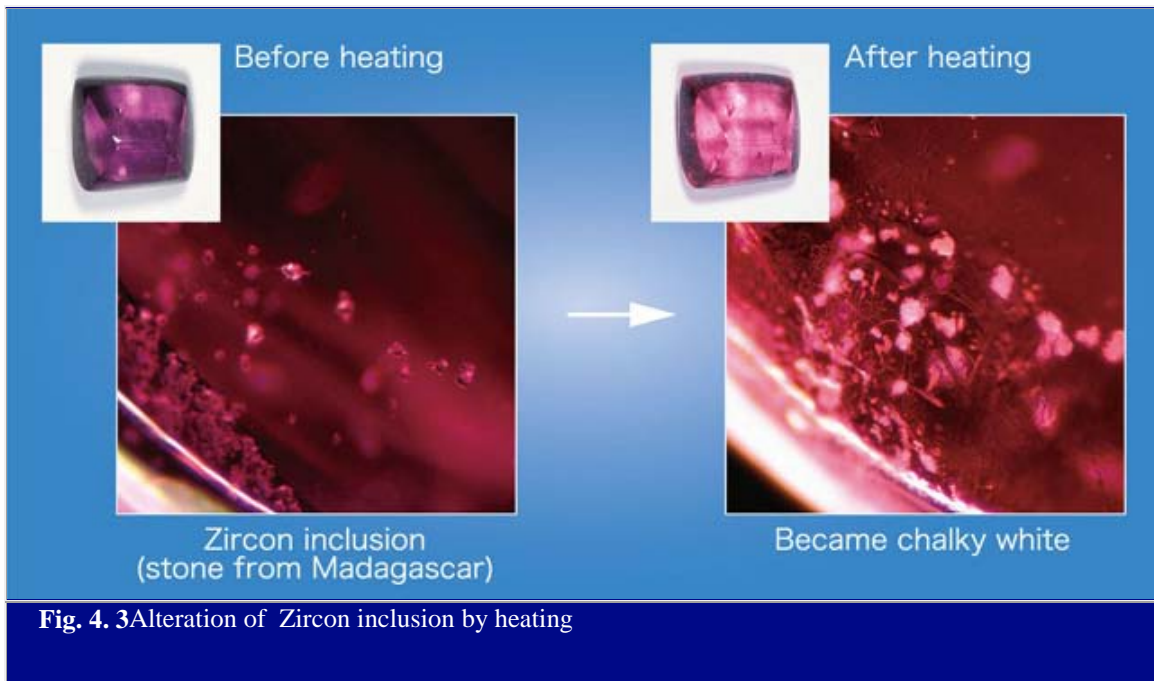
Identification of gemstone inclusion / internal features is very important for identifying heated gemstone including corundum under microscope. There is some crystal inclusion in gemstone having lower melting point than the host Gemstone, This crystal may disappear by melt or altering or healing by heating process. Example :Titanium inclusion say silk inclusion needle-like crystal of rutile, which breaks into dots when heated at high temperature and eventually disappears (Fig. 4.1). The temperature they melt varies according to the atmosphere and other conditions of heating process. The existence of silk inclusion that shows no sign of alteration has been long believed as an evidence of unheated status, however, recently low temperature heating process (under 1000°C) attracted controversy and the identification became more complicated.



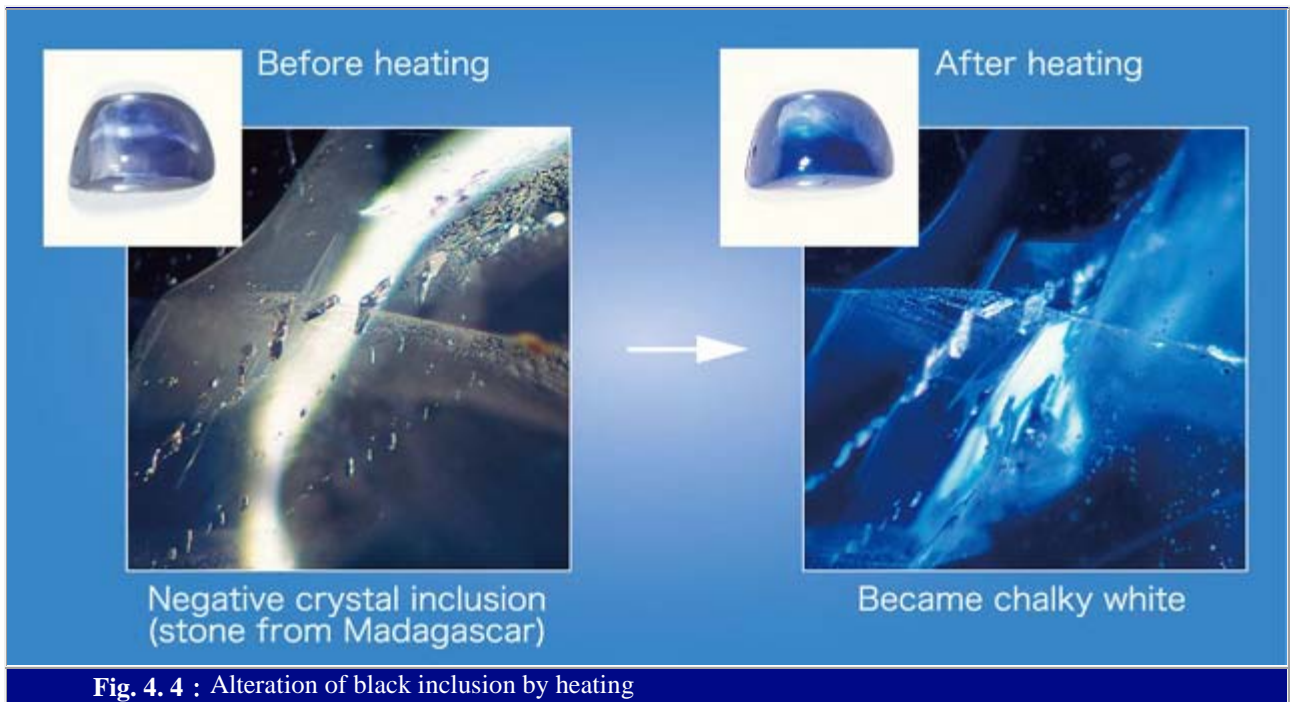
In similar manner, inclusion resembling clouds that is assumed minute rutile crystal is also reduced or disappeared by heating at high temperature (Fig. 4.2).



Zircon is also one of commonly included minerals in rubies and sapphires. Zircon inclusion has been regarded as a characteristic feature of the sapphire from Sri Lanka, but today it is rather that of stones from Madagascar (Ilakaka). Zircon crystal that is included in unheated corundum has high transparency and often shows halo fissure. The crystal reduces its transparency by heating and turns into chalky white colour (Fig. 4.3).



Many crystal minerals (such as feldspars and apatite) are altered so-called snow ball by high temperature heating. Black inclusion will fade or turns to white by heating. Negative crystal is regarded as a type of liquid inclusions. It turns to chalky white by heating (Fig. 4.4).



When a stone to be heated contains a large negative crystal, heating process may cause burst so that such stone should be removed before heating. Brownish colour of contaminated fracture caused by substance such as iron oxide staining will be reduced or disappeared by heating in most cases (Fig. 4.5). Similarly, brown colour zone will generally be improved to blue by heating (Fig. 4.6).

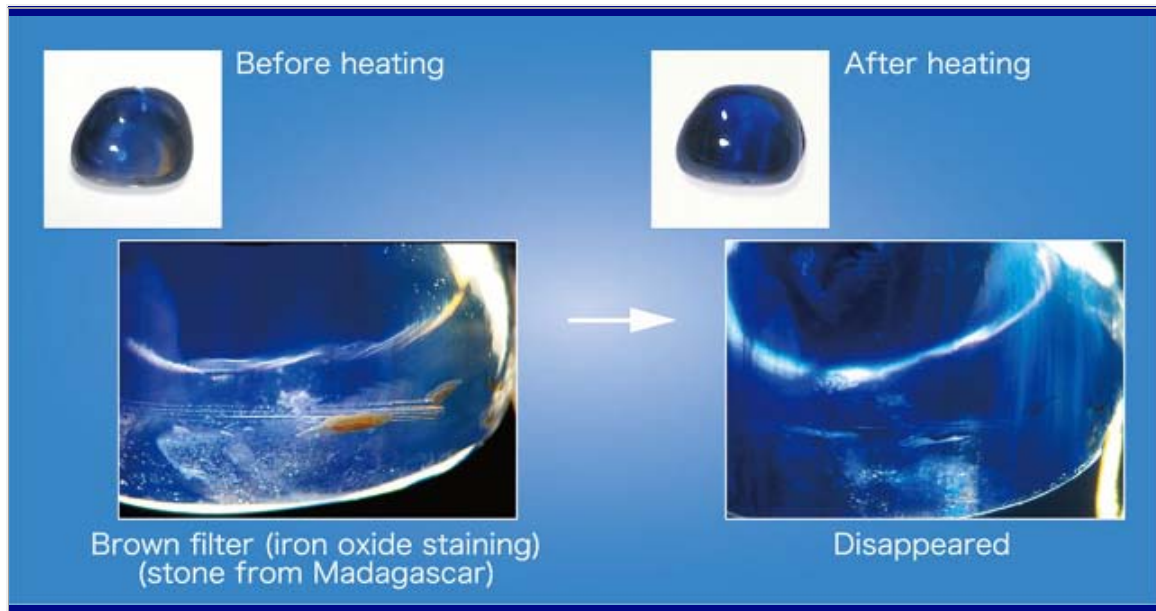


Fig. 4.5 Alteration iron oxide fractures by heat treatment

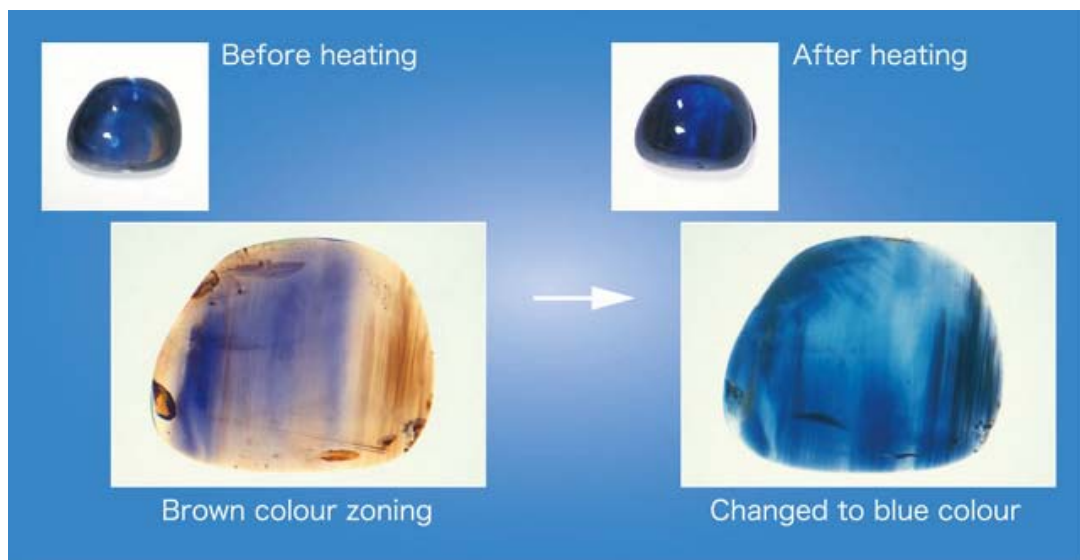


Fig. 4.6 Alteration due to heat treatment in corundum

Liquid inclusion is often healed by heating under high temperature (over 1000° C) and some substances, such as flux including borax, needed for heating process may be observed in fractures as residues (Fig. 4.7).

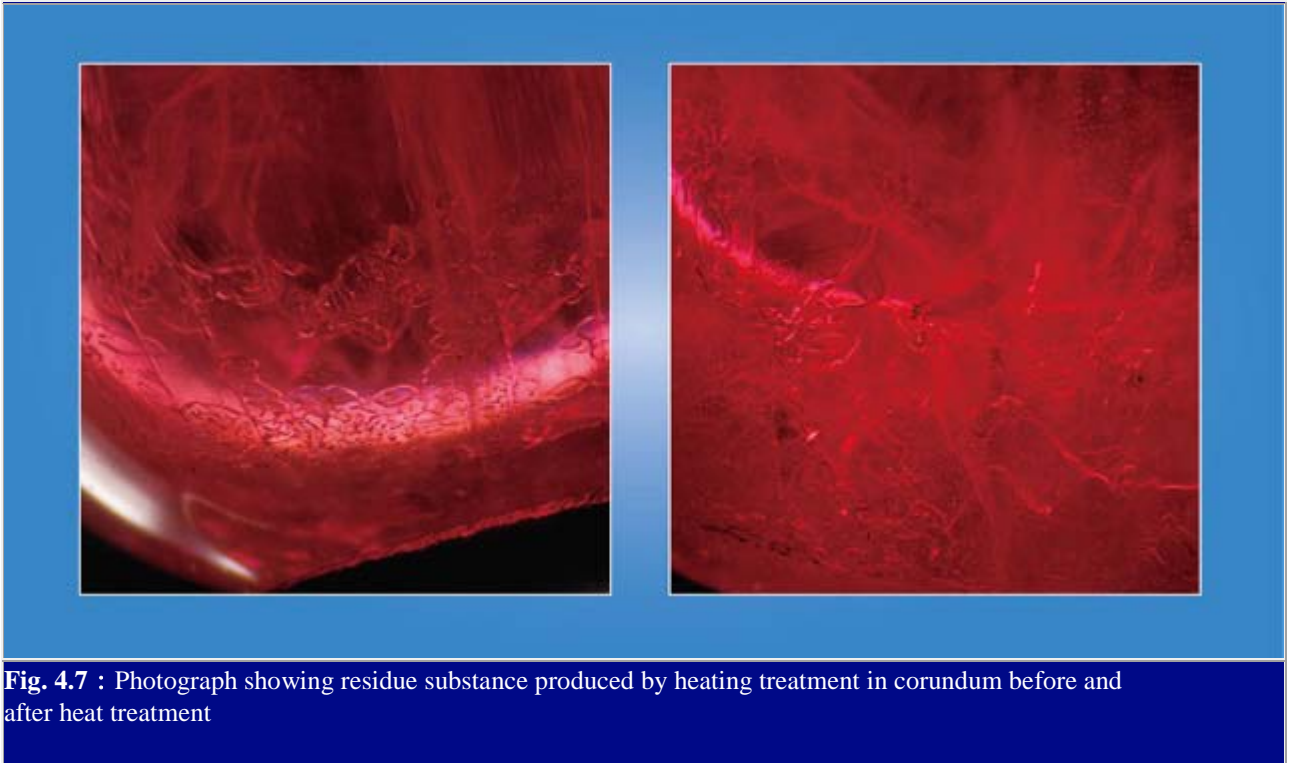


Fig. 4.7 : Photograph showing residue substance produced by heating treatment in corundum before and after heat treatment

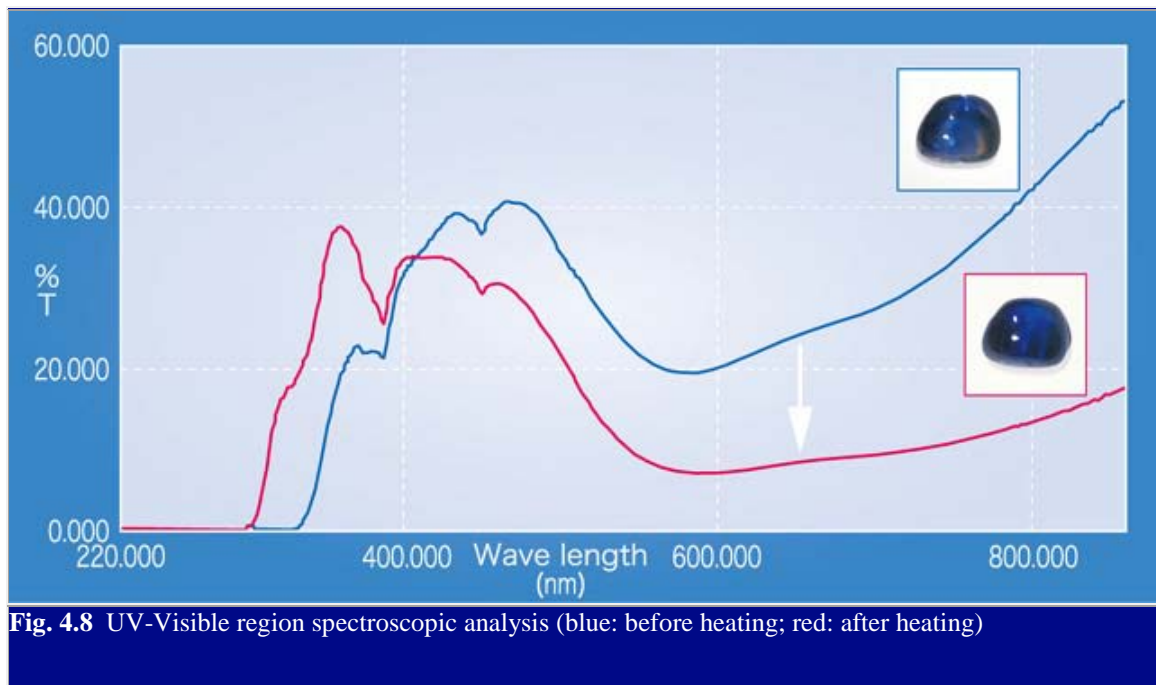
UV FLUORESCENCE FEATURES

Ruby generally shows red fluorescence under UV light. The intensity of the fluorescence is strong in stones of contact metamorphic rock origin in general such as from Myanmar, and rather weak in stones of igneous rock origin such as from Thailand or Cambodia. When a stone is heated, the intensity tends to be increased both under longwave and shortwave. Some rubies may show orange fluorescence under LWUV and more chalky appearance under SWUV after heating.

Blue sapphire will be inert or show orange to red fluorescence under UV light. The stone showing orange fluorescence under LWUV tends to gain red tint after heating. Some stones may show chalky appearance under SWUV after heating.

Features in UV-Visible range spectral analysis

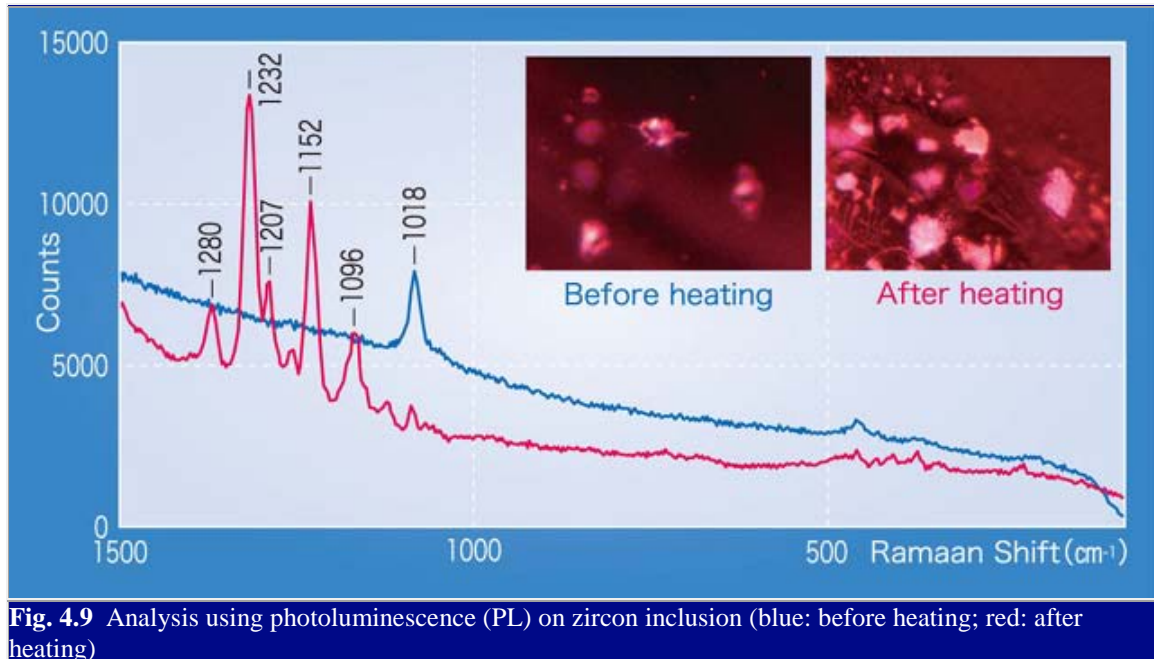
When colour of a stone is improved by heating process, spectra in UV-visible and infrared region will change. In particular, when stones from Sri Lanka or Madagascar are heated their spectra tend to show deeper absorption in yellow and better transparency in UV region (Fig. 4.8).



Features in Raman spectroscopic analysis

Microscopic Raman spectroscopy has advanced special resolution and it is effective to identify inclusions in gemstones non-destructively. Hence it can help identification of locality in ruby or sapphire and also it becomes useful indirectly in identifying heated / unheated status. It can be used for determination of heat treatment directly (Fig. 4.9) because the Raman spectrum from a zircon crystal in corundum is known to be changed by heating process. The spectrum observed after heating is actually assumed to be derived from resolving of zircon crystal into SiO_2 and ZrO_2 caused by

photoluminescence. Raman spectroscopic analysis is useful to identify heated / unheated status both directly and indirectly.



Removal of Silk / Clarity enhancement in corundum

In some case, iron-stained fractures in sapphires may become somewhat less visible if heat treated at high temperatures (1800°C), because at such temperatures iron oxides decompose and vaporize out of the fracture and gemstone become more clear. The inclusion is solid or liquid. Rutile, for example, has a melting point of about 1830.C, yet rutile needles 1-5 um in diameter will dissolve rapidly into sapphire at 1600.C. In this case, a combination of the finite solubility of TiO₂ in sapphire at 1600.C and the unusually high diffusion rate of Ti⁴⁺ determines the apparent rate of dissolution. Heat treatment that dissolves the rutile produces extraordinarily high clarity in the sapphire.

n case of ruby color caused by chromium and where a heat treatment can not change the valence state or the color of the Al₂O₃-Cr³⁺ combination. Yet here, too, the color may contain a brown, purple, or milky component derived from iron and titanium

impurities which could be enhanced by a heat treatment possible by Diffusion method.

Diffusion method

In this Surface Diffusion Treated Corundums (STDCs) process impurities like Chromium, Iron, Titanium & Beryllium are diffused in the corundum to produce Red and blue colour as well as for development silk or asterism in corundum. In diffusion method gemstone is heated at 1600 °C to 1850 °C temperature. The time for heating ranges from 2 to 200 hours, depending on nature of the crystal

This process is too slow. In this diffusion process Al move outward and impurities like Cr, Fe, Ti and Be atoms move inward.

Recently this method is widely used to remove circular line & for development of silk in synthetic corundum. This makes it very difficult to identify synthetic corundum.

Conditions :

- Temperature : The elevated temperature range from 1600 °C to about 1850 °C (almost near melting point of corundum).
- At temperature below 1600 °C, the process becomes uneconomical, slow and at high temperatures the surface may be damaged.
- Time: heating time can vary from two hours to 200 hours.
- Atmosphere : Oxidizing.

Procedure :

Currently, this treatment is done to obtain blue sapphire and ruby. The color of corundum is due to transition elements Iron, Chromium, Titanium, Beryllium or Nickel. Diffusion treatment first brings the necessary coloring agents (chemicals) into contact with the stone's surface. The stone is heated to high temperature, causing the lattice structure to expand and allow the energized transition ions to migrate within the surface and hence a thin layer of color develops around the stone. The higher the temperature and longer the time used, the greater the depth of color penetration.

To get blue /red color, commonly a colorless or light colored faceted corundum embedded in a powder (Cr, Fe, Ti and Be) or slurry of powder is painted on the surface of

the gemstone .For development of blue color this powder consists of a major amount of Aluminium oxide, a minor amount of titanium oxide, and lesser amount of iron oxide.

But for development of red/ pink colour slurry consisting of 3-6% of chromium oxide and 22-24% titanium oxide is taken in powder form. Then samples embedded in powder or painted slurry on surface of gem are kept in an alumina crucible .Then this crucible is put in furnace for heating .

Results :

The thickness of the color layer varies from 0.07m, (weak color) to 0.42m,(deep color) in corundum depending on temperature, time of heating and nature of gemstone / crystal After this process, the stones become pockmarked. Have a burnt and crazed surface and show some melting. This can removed by very light repolishing.

Identification :

- a) The most effective means of detecting a Surface Diffusion Treated Corundums (STDCs) stone is its appearance in Methylene Iodide liquid or in glycerine
 - i) Greater relief, as indicated by a concentration of color along facet junctions and around the girdle uneven or patchy facet-to –facet colouration.
 - ii) Healed finger prints, burst halos, melted crystals, partially absorbed and dot like (diffused) silk inclusions are typical.
 - iii) Localization, blotchiness of color (caused by uneven diffusion and repolishing) seen just below the surface or as color bleeding in surface reaching fractures or cavities.
 - iv) Pock marked and burnt surfaces on facets or over the girdle.
 - v) Dense concentration of very small, white inclusions with color spotting just below the gemstone.
- b) U.V. L amp : It does not provide diagnostic information for the identification, but sometimes – weak to moderate, chalky bluish, white to yellowish white under Short Wave is seen.

- c) Refractometer : In case of diffusion treated ruby, multiple readings on individual facets and reading over the range are seen.

Identification of surface diffusion-treated corundums is a fairly straightforward process in many cases, but there are just enough potholes in the road for the unwary to fall into. In most cases, a stereoscopic microscope (with provisions for immersion in methylene iodide) is necessary.

The identification centers around the fact that, in natural corundums, crystals grow in the ground and such crystals bear only a cursory relationship to the gemstone after cutting. Color in natural single crystals forms in bands or zones parallel to crystal faces, not along polished facets, because the stone was not faceted when it was growing in the ground.

Proper setup and use of the microscope is vital to the identification. The stone should be immersed in pure methylene iodide (RI = 1.735 approx.) and viewed under magnification with a diffused white (frosted) plastic or glass plate covering the light source. This is often referred to as diffused light-field illumination. Under these conditions, reflections from the corundum's external surfaces are largely eliminated (Fig.4.10). This allows the stone's interior to be seen with virtually no distortion from the reflection and refraction of light off internal and external surfaces. Thus, the true distribution of color is revealed.

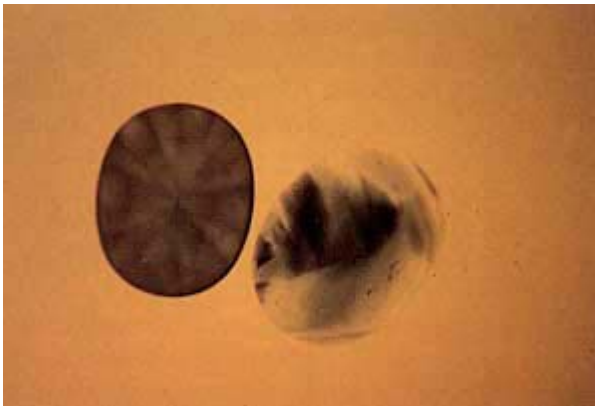


Fig. 4.10 Methylene iodide immersion coupled with magnification clearly reveals the difference between an SDTC and a sapphire heated in the normal way. The SDTC has a dark girdle, dark facet junctions and sharp changes in color which follow the facet pattern exactly. At right, a non-SDTC sapphire shows a near-invisible girdle and facet junctions, with the color pattern.

Identification diffusion-treated corundums (SDTCs) centers around the following characteristics, observed most easily while immersed as described above:

1. a. The color of SDTCs will be seen to be concentrated just inside the girdle of the stone, unless cutters have attempted to avoid detection by heavily repolishing the girdle itself and the facets close to the girdle. This is because the coloring agents are concentrated close to the surface; when the stone is placed table down in the immersion cell, one's line of vision crosses the greatest amount of diffused color in the vicinity of the girdle. In a non-SDTC, the color is inside the stone and is distributed throughout the entire volume; therefore, one looks through the greatest amount of color at the culet.

b. The color of SDTCs will also be seen to be concentrated on the facet junctions. This results from a greater penetration of the coloring agents at edges as opposed to the center of facets (Koivula, 1988), as well as the fact that edges are polished less during the mandatory repolishing that stones must undergo after treatment. According to Koivula, convection currents develop during the treatment that create a "dumping" of colorants at the edges. This is, I suppose, somewhat similar to the dumping of alluvium at a bend in a river. The result is a deeper penetration of coloring agents at edges and facet junctions, as compared with the center of facets.

2. If an SDTC has any fractures, feathers, cracks, pits, cavities, etc. which break the surface, then immersion reveals a "bleeding" of color into these breaks. Even well-healed liquid fingerprints can show this effect, but it is seen best, of course, in completely open cracks. The reason for the bleeding of color is that the cracks offer a ready means for the entry of the coloring agent, but are not touched during the repolishing process.

3. One further means of identifying SDTCs exists, and of late has become the most important. As mentioned earlier, color in natural corundums forms along specific directions representing crystal faces (or potential faces) of that mineral. In the SDTCs, the penetration of the process is so shallow (0.05 to 0.50 mm) that the stones must be preformed before the treatment is effected. To treat a rough gem would be to lose a large

percentage of the color in the cutting process; thus, the treatment is done on preforms rather than rough stones.

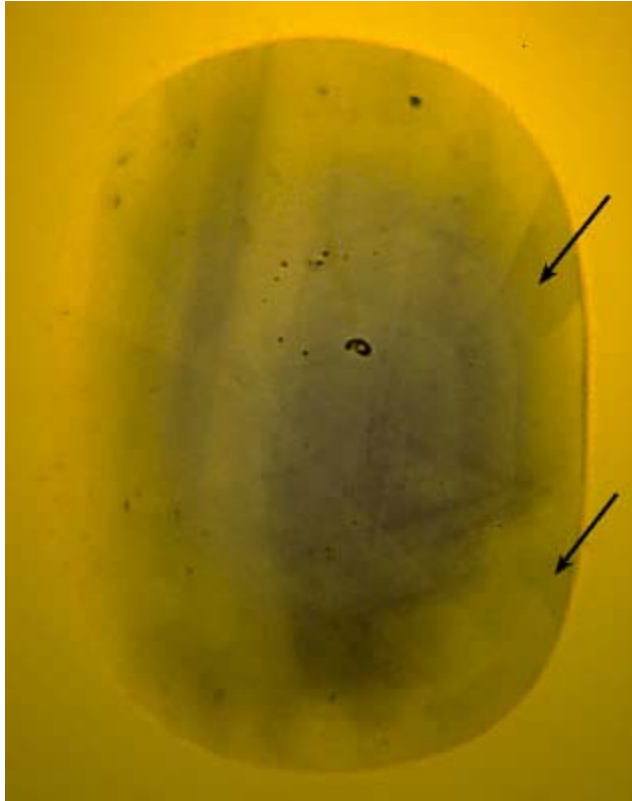


Fig. 4.11 Photo shows a magnified view of a surface diffusion-treated sapphire.

Because of this restriction, and because of the high temperatures reached, the gems must be repolished after treatment. Inevitably some facets will be polished more than others, resulting in the color pattern of the finished stone following the facet patterns exactly. Some of the facets will show more color, some will show less, but the color pattern will follow the facet patterns exactly (Fig.4.11).

Heat treatment in Beryl, chalcedony, Quartz, Topaz, diamond & Tourmaline

Beryl :

- **Possible changes :**

- a) Change yellow green to blue (aqua); yellow to colorless; orange to pink.
- b) Change pink to colorless.
- c) Remove maxixe blue; blue to pink, green to yellow.

- **Conditions :**

Temperature: $450^{\circ}\text{C} \pm 50^{\circ}\text{C}$; Environment: oxidizing atmosphere

- **Causes :**

Iron is present within beryl in two types of locations.

1. One type is located on an aluminum site and gives a yellow color if present as Fe^{3+} . Heating produces the change from Fe^{3+} to Fe^{2+} and hence changes from yellow to deeper yellow.
2. The other type of iron is situated in a channel site and gives a blue color that is unaffected by heating. If both types are present, heating changes green aquamarine to blue aquamarine.
3. Heat also bleaches the color due to a color center in maxixe beryl.

- **Stability :** All treatment is stable.

Chalcedony:

- Possible changes :

- a) Pale colors to brown and red.
- b) Pale colors to milky white.

Conditions :

- Ordinary temperature pressure conditions.
- Causes : Basically hydration alteration, usually from limonite to hematite.
- Stability : stable.

Diamond

- Possible changes ;

- a) Alter the surface by burning.
- b) Change color in chameleon diamond.
- c) Modify natural yellow color.
- d) Modify irradiation colors to produce green, brown, orange, yellow, pink, red, purple etc.

- **Conditions :**

Warmed slightly with an alcohol flame or on exposure to light in case of chameleon diamond.

High temperature (2000 °C) and high pressure to convert type I a to I b vice-versa (yellow colors).

- Causes : Change in platelet structure converts to bright yellow (Type I a)
- Stability : 1. Chameleon diamonds very unstable even at room temperature.
2. Yellow color is stable.

Quartz

- **Possible changes through heat treatment :**

- Amethyst (violet) to Citrine (yellow) or bicolour amethyst- citrine.
- Amethyst to colorless to green.
- Smoky to paler to greenish yellow to green to colorless.
- Rose to lighter to colorless.
- Blue to modified or colorless.
- Yellow or brown to red-brown or red.
- ‘ Crackled’ for Iris quartz.

There are various conditions for heat treatment in Quartz (Table 4.3).

Table 4.3 Conditions for heat treatment in Quartz

Change	Temperature
Smoky to pale brown	280 °C
Smoky to blue green	280 °C
Smoky to colorless	400 °C
Amethyst to Citrine	450 °C + 50 °C
Amethyst to colorless	600 °C
Pink to light pink	450 °C
Pink to colorless	550 °C
Deep blue to light blue	300 °C
Colorless to iris quartz	300 °C (followed by sudden cooling)
Environment: In air (Oxidation)	

- **Causes :**

The cause of color in smoky quartz is color center, equivalent to Al^{3+} . On heating, the electron are displaced and destroy the hole color centers as all the electrons get paired with each other. In case of amethyst, the cause of color is somewhat similar. A transition metal ion is involved in the coloration of amethyst. This metal ion (iron) is the defect and can be removed on heating partially or completely.

In deep blue the color is again due to a color center.

In pink quartz the cause of color is due to Mn as an impurity. On heating, a change of state of Mn gives a light pink colour.

Topaz :

- **Possible changes:**

Brown or orange to pink.

Yellow or green to colorless.

Brown (Irradiated) to blue.

Blue to brown.

There are various conditions for heat treatment in Topaz (Table 4.4).

Table 4.4 Conditions for heat treatment :

Change	Temperature
Brown or orange to pink	500 °C -becomes
Yellow or green to colorless	400 °C
Brown (Irradiated) to blue	200 °C \pm 50 °C
Blue to brown.	450 °C

B. Environment : Ordinary atmospheric condition.

C. Time : Heating time varies from a few minutes to a few hours.

- **Causes :** All colors, except pink, the color is due to color centers. There are two types of color centers. BFCC (Brown fading color center) and BSCC (Brown stable color center). In case of pink / orange topaz, the color is due to chromium as an impurity.
- **Stability :** When BFCC topaz are exposed to sunlight for a few days, the color of the treated topaz fades, while others are stable to light.

Tourmaline :

- **Possible changes :**

Red /pink to lighter shades to colorless.

Purple to blue or dark green.

Dark blue to light blue

Dark green to light green / yellow green

- **Conditions:** Due to the complex structure of tourmaline, the temperature for some colors varies from 260 °C to 1000 °C.
- **Causes :** It is complex, but most of the blue or green is due to Iron as an impurity, red or brown is due to iron and manganese together as an impurity. Heating alters the change of state.
- **Stability :** Stable to ordinary temperature/ pressure conditions.