Orange Treated Sapphire - Towards Finding a Name for a New Product

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Introduction

The following text, pictures, analytical strategies, and figures have been produced independently by the author, instrumental assistance was given by Daniel Mathys (ZMB, Basel University), Dr. Thomas Pettke (SFIT, Zürich), Dr. Lore Kiefert and Peter Giese (SSEF). The subject has been discussed openly among a small group of colleagues, whose intellectual input is appreciated: Kenneth Scarratt (AGTA), Prof. Visut Pisutha-Arnond, Dr. Pornsawat and Wilawan Atichat (GIT), Richard Hughes, Dr. John Emmett, Prof. George Rossman, Dr. Wuyi Wang, Shane McClure and Dr. James Shigley (GIA). Samples provided kindly by Multicolour and Werner Spaltenstein, Chantaburi. The following text is a preliminary contribution based on a small number of selected stones with typical characteristics.

A new kind of orange sapphire has become available in the trade. Its colours range from a vibrant orange to orangey red (Fig. 1). Lemon yellow stones are also available but we shall concentrate here on the orange stones among the new material. Naming these sapphires has resulted in an international controversy, which has not yet led to a generally accepted name for the new variety of artificially induced colour. The main problem being, that the stones are heat treated in the presence of foreign substances. Some dealers and laboratories have used the name "padparadscha" for the orange stones. But this name is very sensitive because it has been used for rare unheated gems from Sri Lanka, which fetch high prices in the marketplace.

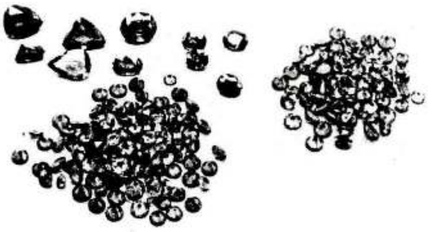

Fig. 1: Orange treated sapphires from 0.4 to 2.2 ct

Individual stones of this kind started to appear in 1999 and were identified as heated sapphires from southern Tanzania, probably Songea area. While extremely rare before the year 2000, they became increasingly frequent. Japan soaked up an important number of stones, and thousands of test reports were released stating that the sapphires were natural padparadschas. In June 2001, when the new orange stones reached the American market, it appeared that they were heat treated, and often the colouration was not the same throughout a sample (Scarratt, 2001; Hughes, 2002; GIA Insider, 2002). Scarratt found that many stones showed surface related zones of an orangey colour, while in the centre they were pink. Gemmologists of the GIT (Gemmological Institute of Thailand) made the same observation. This is reminiscent of the diffusion treated blue (or red) sapphires, first produced and described in the early 80's (Nassau, 1981). An obvious difference between traditional diffusion treated sapphires and the new orange ones lies in the thickness of the relatively shallow layer of blue compared to the orange layer in the latter. While diffusion treatment is relatively easy to see in the blue stones, more care and attention is needed to identify the orange layer in the new stones. In fact a considerable portion of the new stones show a thick diffusion layer and are called '*bulk diffusion treated*' in the US. Where the layers are so deep that they reach the centre of the stone it is not possible to see a layer at all. We are thus facing a difficult problem of identification and nomenclature.

The problem was discussed at international meetings of laboratory gemmologists (Tucson, January 2002, and Carlsbad, May 2002). Representatives of the GIA (Gemological Institute of America) and the GIT (Gemmological Institute of Thailand) presented research results. Scientists discussed the cause of yellow colour in sapphire, paying special attention to the chromophore element of iron, as well as magnesium, beryllium, hydrogen and other impurities. While the diffusion of medium light elements like titanium is relatively easy to prove, a light element like beryllium is extremely difficult to identify, even with sophisticated methods. One possible analytical method of analysing the composition down to trace element levels is Laser Ablation Mass Spectrometry. Identification involves a slightly destructive test, which consumes a small amount of the stone e.g. by burning a tiny hole into the surface with a laser pulse, damage which can sometimes be accepted in research situations.

Are the new orange sapphires diffusion treated?

Diffusion takes place when atoms or molecules travel into or within a material, usually from a place where they are frequent to a place where they are less abundant. It can be a slow process and the migration rate depends on the size of the atom and other conditions. Introduced foreign elements such as Ti in the case of blue treated sapphire do not usually travel fully through a stone because the process is stopped earlier. The treatment is thus applied to faceted stones in order to achieve at least a shallow coloration. The colour layer produced by diffusion from outside is easily visible in blue and red treated sapphires. It can be more difficult to recognise with lighter colours.

When small ions (as e.g. Be) diffuse into corundum, they move more quickly. The diffusion layer may be much thicker, and in the end most (bulk diffusion, volume diffusion, see Hughes, 1998, page 112) or the entire volume of the stone is affected. This fact is part of the problem we have with the orange treated sapphires. The originally pink sapphires receive a treatment, which produces a yellow colour that overlies the pink from the surface towards the centre. The second colour is thus surface related and follows the faceted outline as a consequence of the diffusion treatment.

Sample material

The investigated samples consisted of a lot of 3-4 mm round faceted stones, 12 faceted stones between 1 and 2 carats, a lot of mixed colours just from the furnace, and some yellow sapphires. The yellow sapphires were used as references; one was heated in 1982, and one in 2002. A further pink sapphire from Tunduru was treated in 1998. These samples were also compared with a large collection of corundum, forming the SSEF reference material for sapphire origin determination.

Colour zoned material from Songea (Tanzania) is an interesting material to use to produce "padparadscha like" sapphires since the chromium red rim results in an "inversely zoned" stone, where the pink zone is often in the core.

The author also investigated rough, usually crystal chips, being prepared for heating. It became evident that the lots included chrysoberyl, topaz and zircon, which had not been separated out due to their similar appearance.

Analytical steps

In order to understand the nature of the new material, besides classical gemmological tests, a number of analytical procedures were carried out, among them Scanning electron microscopy SEM-EDS, UV-VIS spectrometry, energy-dispersive X-ray fluorescence EDXRF, laser ablation inductively-coupled plasma mass spectrometry LA ICPMS, and Raman spectrometry.

Microscopic observations

Normal microscopic inspection of the new orange treated sapphires may reveal inclusions that prove the stone has been heat treated. Relatively large blue clouds around dark rutile crystals appear in material from Songes (Tanzania). Since most of these sapphires from Ilakaka (Madagascar) are clean, internal features are rare. Immersed in liquid some stones may show an orange rim along the surface, and a pink central area (Fig. 2). However, not all show this clearly, and many stones, especially the smaller ones, are homogeneous in colour. It was the surface related character of the orange colour that first alarmed the gemmological laboratories and the trade. On the surface of some stones strange patterns and polycrystalline formations were found, which could be related to precipitations in residues (Hänni, 1993).

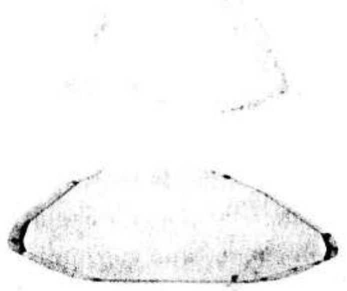

Fig. 2: Two cross sections of orange treated sapphires, displaying an orange rim and a pink core, as observed in methylene iodide, with blue filter for contrast

Fig. 3: Treated yellow & orange sapphires, after treatment, still bearing glassy flux layer

Scanning electron microscopic investigations

A scanning electron microscope with energy dispersive system was used in order to investigate the surface of some treated stones still showing glassy residues from the flux melt that covered them during the treatment. The idea was to analyse the surface covering in order to find out what chemical constituents had been added for the thermal treatment and boron, sodium, magnesium, aluminium, silicium, zirconium, calcium, and traces of iron and chromium were found.

Spectrophotometric investigations

With a conventional photospectrometer (Varian Cary 500), spectra were taken in absorption mode, and normalised to the sample thickness. The differences in spectral curve are always due to the number of chromophore elements (Cr, Fe) and colour centre, and a typical spectrum of an orange sample is shown in Fig. 6. The treated orange sapphires characteristically show absorption maxima at 694 and 554 nm (Cr), 450, 388 nm, and 460 nm (THC). The resulting spectra are always a combination of the causes of colour mentioned above, and a de-convolution of the spectra is expected to show the significance of the contribution caused by trapped hole centre (THC) mechanism. Further investigations will hopefully reveal more on this subject.

Mass spectroscopic investigations

Laser ablation inductively coupled plasma mass spectrometry (LA ICPMS) analyses of a selection of samples was performed at the Swiss Federal Institute of Technology (ETH) in Zürich. With a prototype excimer ArF laser (193 nm) sample material is ablated (craters of 5 - 80 m in diameter) and then flushed into an Elan 6000 quadrupole ICP mass spectrometer for "simultaneous" multi-element analysis. LA ICPMS allows us to investigate the beryllium content in a sapphire and its distribution in the stone

In treated orange sapphires, and most prominently in the glassy flux where present on heated stones before re-polishing, Be was found in concentrations between 10 (sapphire) and 50 ppm (flux). Comparison measurements in older heated material and in unheated stones showed 10 times lower concentrations. Other elements, such as Mg, Fe, Ti, V, Cr and Ga were also analysed. These results are in line with findings of other gemmological laboratories working on this topic with LA ICPMS (e.g. GIA, GRS, GIT).

Discussion

The findings and results of this preliminary investigation confirm the outlines displayed by other authors working on the topic of orange treated sapphires (Häger, 2002; Hughes, 2002; Scarratt, 2002; Swarovski, 2002; McClure, 2002). During heat treatment, pre-facetted corundum of different origins (e.g. Tanzania and Madagascar) is heated with borax and a combination of other substances creating a melt or flux that spreads over the surface of the stones and enables an exchange of chemical constituents during the thermal treatment. This diffusion process enables the creation of a new colour (or colour component). The responsible chemical element has been found to be beryllium, as proved by LA ICPMS in comparison with untreated samples. The created colour is yellow that may overlay a pre-existing pink in the sapphire. The depth of diffusion of Be is clearly greater than we experienced with Ti in the case of blue diffusion treated sapphires. This is not unexpected since the ionic radius of beryllium Be^{2+} is considerably smaller than that of Ti^{4+}.

In both cases the introduced foreign elements have to find a fitting partner. In the case of blue sapphire this partner is iron Fe^{2+}. We know that magnesium Mg^{2+}, another bivalent ion, is responsible for yellow coloration in corundum, and conclude that Be could do the same job, or just move Mg to a favourable location. The colour created in colourless sapphires by Be-diffusion is, however, brown and not yellow. It is still not clear whether the colour centres in the treated orangey sapphires are produced by the original Mg alone or by introduced Be.

It has also been reported that chrysoberyl, first accidentally present among the treated sapphires and later purposely crushed in the crucibles of the treated sapphires, released the necessary Be for the creation of the yellow colour component. Experiments with crushed chrysoberyl $BeAl_2O_4$ performed by Swarovski researchers (Swarovski, 2002) have proved this capacity of Be. Not all sapphires offer conditions suitable to form yellow colour centres. Some may contain Be and still not turn yellow. It probably depends on the content of Mg and if the latter is in an independent location to form the trapped hole colour centres and is not trapped by Ti^{4+}.

Nomenclature

When the term "natural sapphire" is used to describe a gemstone, one might expect a stone which is more or less as found in nature. The natural formation temperature for corundum rarely exceeds 1200°C, as explained by George Rossman (Rossman, 2002). Submitting a corundum crystal to elevated temperatures such as 1800°C and above re-arranges its crystal structure totally since this is close to melting point. Introducing foreign elements with chromophore character by diffusion produces a new colour. A stone treated in such ways is far from its natural state. The fact that natural chrysoberyl may be used for the Be-diffusion is not important, since it decomposes in the furnace and acts like any chemical substance. The substantial changes to the orange treated sapphires should be reflected in the name. At the very least the term "treated" or "diffusion treated" should appear with the gemstone name, as e.g. "orange treated sapphire". Future meetings such as CIBJO or GILC will hopefully result in a uniform naming of this new product. In the meantime SSEF stays with the disclosure policy, which was agreed by four major laboratories AGTA, GIA, Gübelin & SSEF in January 2001:

They are **not called Padparadscha.**

Identification:	Treated Orange Sapphire (Variety of Corundum)
Comment:	With indications of heating, the orange coloration of this stone is confined to a surface related layer.

GIA and AGTA quit this agreement after the May 2002 meeting in Carlsbad, when they introduced the term *"bulk diffusion"* for their laboratories.

Future comments on a test report for orange treated sapphires should take into consideration the fact that Be diffusion cannot be tested in every case, and depth of penetration may vary from visible rims to full volume. Joint trade and laboratory meetings will hopefully work out a proper disclosure for this situation, which is internationally recognised.

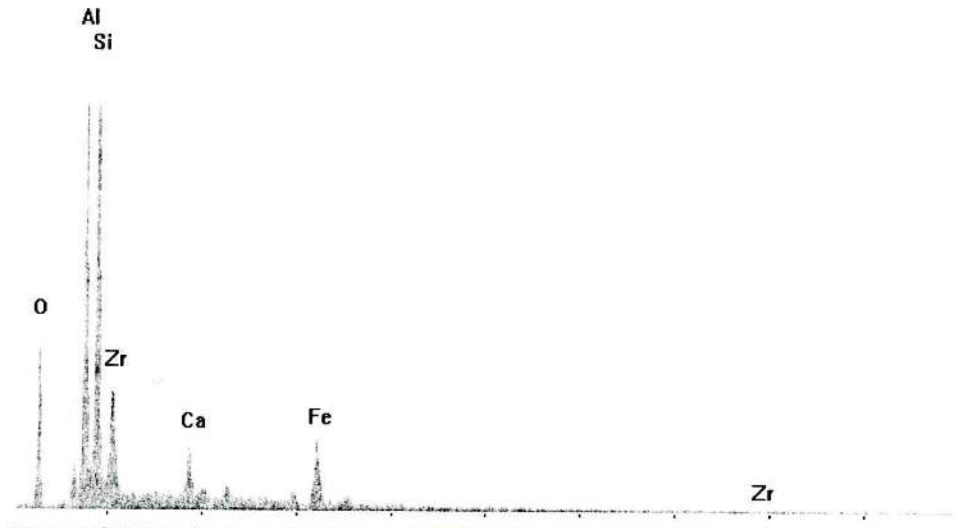

Fig. 5: SEM-EDS spectrum showing qualitative composition of flux layer encountered on a sample of orange treated sapphire. The composition in other locations is found to be different in respect of elements present, and relative amounts.

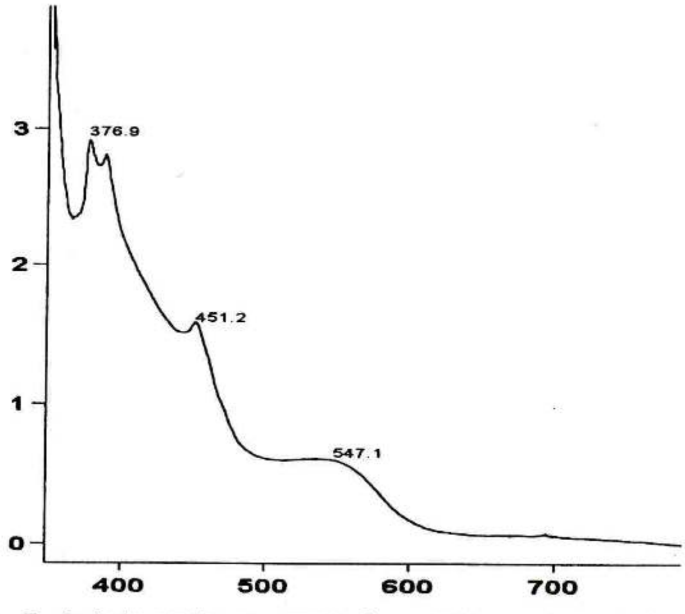

Fig. 6: Typical absorption spectrum of a reddish orange treated sapphire.

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References

Emmett, J.L. & Douthit Troy,R. (1993) Heat treating the sapphires of Rock Creek, Montana. Gems & Gemology, Winter, 250-272.

Emmett, J.L. (2002) personal communication during GILC Meeting, Tucson, USA

GIA Insider (2002) A new corundum treatment from Thailand. Vol. 4, 3, 28th. January

Günther, D., Frischknecht, R. & Heinrich, C.A. (1997) Capabilities of a 193 nm ArF excimer laser for LA ICPMS micro analysis of geological materials. J.Anal.At.Spectrom., 12, 939-944.

Günther, D., Bleiner, D., Guillong, M., Hattendorf, B. & Horn, I. (2001) Access to isotopic and elemental composition and their distribution in solid materials by laser ablation inductively coupoled mass spectrometry. Chimia, 55, 778-782.

Häger, T. (2001) High Temperature Treatment of Natural Corundum. Proc. Intl. Workshop on Material Characterization by Solid State Spectroscopy: The Minerals of Vietnam, Hanoi, April 4 - 10.

Hänni, H.A. (1993) Identification of fissure treated gemstones. J.Gemmol.Assoc.Hong Kong, XV, 29-33

Hughes, R.W. (1998) Ruby and Sapphire. RWH Publishing, Boulder, Colorado, USA

Hughes, R.W. (2002) The skin game. http: www.palagems.com/treated_orange_sapphire.htm

Jomard, C. (1996) Le Saphir Padparadscha. Diplôme d'Université de Gemmologie. Department of Geology, University of Nantes, France. 55 pages

McClure, S. (2002) personal communication during GILC Meeting, Tucson, USA

Moses, T. (2002) personal communication, follow-up meeting, Carlsbad.

Nassau, K. (1982) Heat treating ruby and sapphire: technical aspects. Gems & Gemology, Fall, 121-131

Notari, F. (1996) Le saphir padparadscha. Diplôme d'Université de Gemmologie. Department of Geology, University of Nantes, France. 95 pages

Peretti, A. & Günther, D. (2002) The color enhancement of fancy sapphires with a new heat treatment technique (part A): Inducing colour zoning by internal migration of color centres. Contributions to Gemology, 1, May 2002

Rossman, G. (2002) personal communication, follow-up meeting, Carlsbad.

Scarratt, K. (2001) Further characterization of sapphires recently treated in Bangkok. AGTA e-mail message and pictures to Laboratory Harmonisation Committee members.

Schmetzer, K., Bosshart, G. & Hänni, H.A. (1983) Naturally colored and treated yellow and orange-brown sapphires. J. Gemmol. GB, XVIII, 7, 607-621.