

Untreated yellowish orange sapphire exhibiting its natural colour

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Abstract: Orange sapphires of natural colour are rather rare. A 3.85 ct sapphire recently submitted for identification was confirmed as natural using conventional gemmological equipment and infrared spectrometry. Colour zoning, inclusions and twinning are described and compared with the features shown by synthetic sapphires.

Keywords: colour zoning, heat treatment, inclusions, infrared spectra, orange sapphire, synthetic



Introduction

Recently, the author received a 3.85 ct pear-shaped yellowish orange gemstone, measuring 11.38 × 9.55 × 4.88 mm, for identification (*Figure 1*).

The refractive index (RI) determinations were carried out using a Rayner Dialdex critical angle refractometer with the use of a polarizing filter and monochromatic sodium light. Using the table facet, the stone was rotated every 45° and the indices recorded until a rotation of 180° was reached. The indices obtained showed two constant and parallel shadow edges, 1.762 and 1.770 (birefringence 0.008), proving the stone uniaxial, with its table facet cut perpendicular to the optic axis. A polarizing filter is needed to obtain the optic sign (Sturman and Parker, 2010), and this was checked by testing one of the pavilion facets, under the same working conditions, this gave $\epsilon = 1.762$, $\omega = 1.770$, optic sign U/-.

To confirm the uniaxial nature of the stone, it was examined table down in a Gem Illuminator Polariscopes, set to its dark position (where the vibration

directions of the polarizer and analyser are perpendicular to one another) and with a conoscopes placed on the stone's pavilion; a uniaxial interference figure could be seen.

The specific gravity (SG) was obtained by hydrostatic weighing of the stone, employing a Mettler PL 300c electronic balance (accuracy ± 0.001 ct) with SG attachments. The SG is 3.99.

The pleochroism observed through the pavilion with a Rayner calcite dichroscope was very weak with a small range from yellow orange to slightly darker yellow orange.

The absorption spectrum seen through a Gem Beck Spectroscope Unit, showed no lines in the blue portion of the visible spectrum, but lines in the red at 660 and 680 nm.

A faint uneven dark apricot fluorescence could be seen with a Multispec combined LW/SW unit.

These physical properties correspond to those of corundum, yellowish orange sapphire, so to determine whether it was natural or synthetic, treated or untreated, further testing was necessary.

Distinguishing natural from synthetic corundum

Synthetic corundum was first obtained by M.A. Gaudin in 1837 by the Verneuil flame-fusion process (Bourgeois, 1884); this was followed by J. Czochralski in 1918 using the pulling method (Elwell, 1979), later by C.C. Chatham and F.T. Brown by flux fusion in the mid 1960s (Nassau, 1980) and more recently by Tairus using hydrothermal synthesis in the 1990s (Koivula *et al.*, 2000).

To test whether this orange yellow sapphire was synthetic, the stone was examined under a Bausch & Lomb Mark V Gemolite binocular microscope using dark field illumination or overhead lighting as appropriate. It revealed immediately under the table facet, broad parallel straight growth zonal striae lying in different planes, crossing each other at angles (*Figure 2*). Numerous clouds of exsolved substances are aligned with these zonal striae and are responsible for

Figure 1 (above): Pear-shaped yellowish orange sapphire of 3.85 ct. Magnification 10x.

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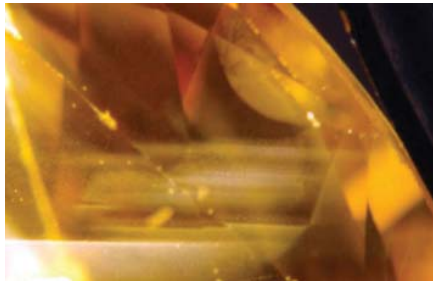


Figure 2: Broad parallel straight growth zonal striae lying in different planes and crossing each other at angles. Dark field illumination, magnification 15 \times .

the 'sleepy' appearance of the stone. Lying in the bottom of the pavilion, parallel to a basal pinacoid is a tiny 'feather' consisting of very fine acicular droplets (Figure 3). Polysynthetic twin lamellae (Figure 4) are visible with the stone immersed in ethyl alcohol between crossed polaroids.

These inclusions exclude Verneuil and Czochralski synthesis which display curved colour and growth banding (Gübelin and Koivula, 1986, 2008), often in the company of rounded gas bubbles with notably bold edges (although there is polysynthetic twinning in some Verneuil synthetics; Duroc-Danner, 1985).

In contrast, the most common inclusions in flux-grown sapphires are twisted veils of flux resembling net curtains or veils blowing in the wind (O'Donoghue, 2005; Gübelin and Koivula, 1986). While hexagonal, herring-bone or sets of straight growth bands forming an angle can occur in flux-grown synthetics, their synthetic origin can be ascertained by crystallographic investigation of structural features such as morphology and growth components. Straight parallel

growth planes of the second-order hexagonal prism as well as growth planes parallel to different second-order hexagonal dipyrramids (with the exception of $n\{2\bar{2}43\}$), do not appear in this type of synthesis (Schmetzer, 1986; Kiefert and Schmetzer, 1988, 1991). Occasionally one encounters inclusions of angular platelets of metallic appearance, often triangular or hexagonal in shape, but also in other forms such as needles. These originate from the platinum crucible in which the corundum is grown and have not been encountered in natural corundum (Gübelin and Koivula, 1986).

Hydrothermally grown synthetic corundums usually show fluid inclusions composed at room temperature of H₂O (liquid), H₂O (vapour) and carbonate solid daughter minerals (such as CaCO₃ and KHCO₃), while the fluid inclusions found in the natural counterparts (including the heat-treated ones) are composed of CO₂-rich compositions with completely different reactions to heating and freezing. By studying these reactions, it is therefore possible to identify this type of synthetic (Peretti *et al.*, 1997). Roiled-to-angular growth structures, sometimes described as chevron-spaced, and scattered flake-like 'breadcrumbs' can also occur (Renfro *et al.*, 2010). Solid inclusions are sometimes also observed, consisting of copper alloys, derived from the steel autoclave (copper inclusions have not yet been observed in natural corundum). Hydrothermally produced yellow, green, blue-green and blue synthetic sapphires owe their colour only to nickel, whereas blue-violet to violet orange and reddish-orange synthetic

hydrothermal sapphires are coloured by traces of both chromium and nickel, while the three main causes of colour in natural corundum are due to colour centres or Fe³⁺ for yellow sapphires; Fe²⁺/Ti⁴⁺ ion pairs with or without additional Fe²⁺/Fe³⁺ pairs, for blue to violet sapphires; and Cr³⁺ for rubies (Schmetzer and Peretti, 1999, 2000).

Magmatic or metamorphic corundum

Corundum can be of two different types:

- Magmatic yellowish orange sapphires owe their colour chiefly to Fe²⁺/Fe³⁺, Fe³⁺ and Fe³⁺/Fe³⁺, and to a lesser degree to IVCT Fe²⁺ → Ti⁴⁺, with high Ga³⁺ and minor Cr³⁺.
- Metamorphic yellowish orange sapphires can owe their colour partially or wholly to trapped-hole centres, or mainly to Fe³⁺, Fe³⁺/Fe³⁺, with sometimes minor IVCT Fe²⁺ → Ti⁴⁺, added to some Mg²⁺ and Cr³⁺ (F.L. Sutherland pers. comm., 2011; Schmetzer and Schwarz, 2005).

Some magmatic sapphires may be transported as xenocrystic passengers by basalt and brought to the surface from depths of up to 100 km (Keller, 1990, p.71) during volcanic eruptions. The infrared spectra of these magmatic sapphires show a peak at ± 3309 cm⁻¹, which is not present in natural metamorphic sapphires, nor in all (non-heat treated) synthetic sapphires except those issued from the Verneuil flame-fusion syntheses; this is due (as for peaks

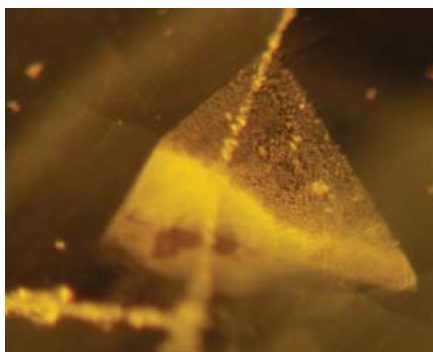


Figure 3: Tiny 'feather' consisting of very fine acicular droplets. Dark field illumination, magnification 30 \times .



Figure 4: Polysynthetic twin lamellae, stone immersed in ethyl alcohol, between crossed polaroids, magnification 20 \times .



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$\pm 3295 \text{ cm}^{-1}$, $\pm 3232 \text{ cm}^{-1}$, and $\pm 3185 \text{ cm}^{-1}$) to a OH-dipole linked to atoms of iron and titanium in the corundum structure. The peak $\pm 3366 \text{ cm}^{-1}$ is due to OH clusters linked to a titanium atom (Duroc-Danner, 2002).

The FTIR spectrum in the mid-infrared region between 4000 and 2100 cm^{-1} of the yellowish orange sapphire is shown in *Figure 5*. There is a strong absorption in the range 2300 – 1700 cm^{-1} , a 3161 cm^{-1} peak, accompanied by peaks at 3240 cm^{-1} and 3354 cm^{-1} .

The 3161 -series occurs most commonly in natural-colour yellow-to-orange and padparadscha sapphires from low-iron metamorphic environments, which owe their colour partially or wholly to trapped-hole centres. LA-ICP-MS chemical data and heating experiments suggest that the 3161 -series is actually due to structurally bonded OH associated with Mg^{2+} (Smith and Van der Bogert, 2006).

The absence of a 3309 cm^{-1} peak (location indicated on *Figure 5*), also confirms that this yellowish orange sapphire is of non-magmatic origin (probably metamorphic) and has not suffered heat-treatment.

Natural colour versus beryllium treated corundum

Heat-treatment of corundum, with more or less colour improvement occurred in Sri Lanka around the second century AD, and is still performed today. Corundums were embedded in an open charcoal fire and air was blown through a bamboo pipe to raise the temperature up to 1000°C (Gunaratne, 1981; Hughes,

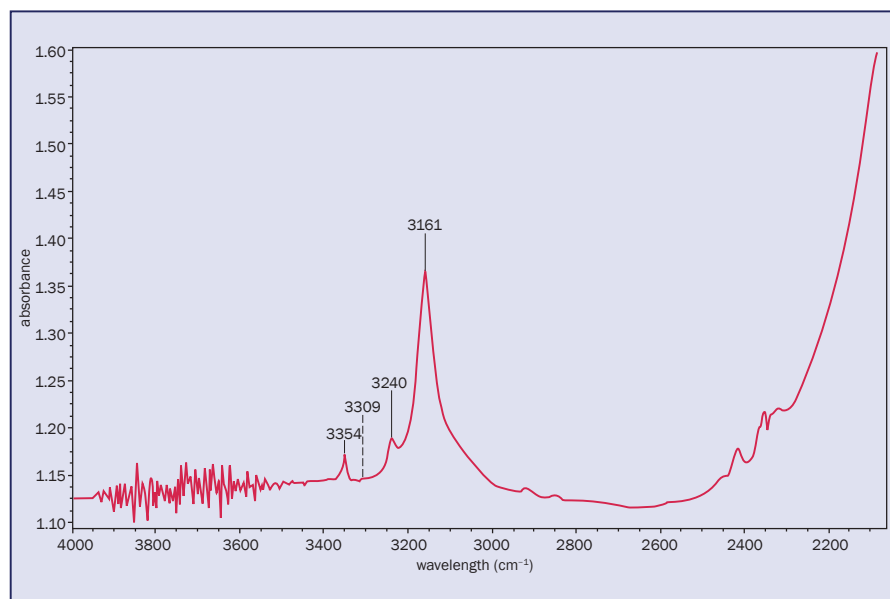


Figure 5: FTIR spectrum showing the 3161 cm^{-1} series of peaks due to structurally bonded OH associated with Mg^{2+} , and the absence of a 3309 cm^{-1} peak (indicated on the spectrum to show its location).

1988; Themelis, 1992, pp 113–14; Notari and Grobon, 2002).

More modern heat-treatment techniques were discovered apparently in the 1960s (translucent milky white Geuda sapphires from Sri Lanka transformed by atmosphere-controlled high temperatures around 1500°C into transparent richly coloured sapphires). Diffusion-treated corundum which first appeared on the world market in the late 1970s (heating in the range 1800°C with addition of colour-causing elements such as titanium results in a thin outer layer of saturated blue in otherwise colourless or pale coloured sapphire) produced dramatic results when compared with the subtle changes of the past (Kane *et al.*, 1990; Emmett *et al.*, 2003).

More recently, in late 2001, beryllium-diffused treated rubies and sapphires were produced (heating the corundum to around 1800°C with the beryllium obtained, for example, by crushed chrysoberyl, BeAl_2O_4). The reaction penetrates the entire sapphire to impart relatively homogeneous yellow-to-orange hues, although early examples of this treatment could be recognized when the stone was immersed in methylene iodide or ethyl alcohol by the presence of a colour zone that conforms to the external

faceted shape of the stone (Emmett *et al.*, 2003). As can be seen in *Figure 6*, when immersed in ethyl alcohol the present yellowish orange sapphire has a colour distribution of angular yellow zoning alternating with colourless areas, which is characteristic of natural growth origin (Hurwit, 1987).

Discussion

Standard gemmological properties, such as RI, optic character and sign, and SG, confirm that the stone is corundum, variety yellowish orange sapphire, but do not help in determining whether it is natural or synthetic.

Nowadays at least four kinds of process are used worldwide on a commercial basis to produce synthetic corundum, and the products are becoming more sophisticated, thus posing a real challenge to the unwary jeweller:

- Verneuil inverted blow-pipe process (Hrand Djévahirdjian S.A., Switzerland; Union Carbide, U.S.A.; Nakazumi Earth Crystals, Japan; Wiedes Carbidwerke Freyung, Germany; etc).
- Czochralski (pulling) growth technique (Union Carbide, U.S.A.; Deltronics, New Jersey, U.S.A.; Crystal Optics Research, California, U.S.A.;

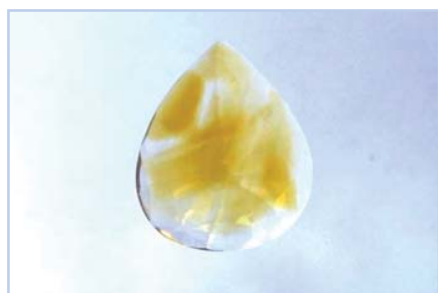


Figure 6: Straight angular yellow zoning alternating with colourless areas. Immersed in ethyl alcohol, magnification $10\times$.

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- Kyocera International Inc., Japan; etc).
- Flux fusion growth technique (C.C. Chatham, California; Douros, Greece; J. Osmer Crystals Co., California, U.S.A.; Kashan Inc., Texas, U.S.A.; P.O. Knischka, Austria; J. Lechleitner, Austria; etc).
- Hydrothermal growth process (Tairus Co., Thailand and Russia; etc).

Also most natural corundums in the gem market are heat-treated between 1000° and 1500°C. Additionally, some are diffusion-treated with colour-causing elements such as titanium (Ti) or more recently beryllium (Be), which can be detected using Secondary Ion Mass Spectrometry (SIMS) or Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS).

The present yellowish orange sapphire was identified with conventional gemmological equipment and infrared spectroscopy, so recourse to the expensive SIMS or LA-ICP-MS facilities was not necessary.

The inclusions and internal characteristics point towards a natural stone devoid of heat-treatment (Panjekar and Panjekar, 2011).

The FTIR spectrum not only confirmed that the stone was not heat-treated, but also established its non-magmatic origin (probably metamorphic).

The faint uneven dark apricot luminescence to ultraviolet radiation provided helpful indications for non-Be-diffusion treatment since Be-diffused areas usually fluoresce a distinctive homogeneous orange (Notari *et al.*, 2003). This indication is also consistent with the angular yellow zoning alternating with colourless areas, which is characteristic of natural origin.

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