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## Revelation of Causes of Colour Change in Beryllium-Treated Sapphires \*

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*Blue sapphires are treated with Be in oxidizing atmosphere to change the blue colour into yellow. Untreated and Be-treated samples are examined using laser ablation inductively coupled-plasma-mass spectrometry (LA-ICP-MS), electron spin resonance (ESR) and ultraviolet-visible (UV-vis) spectroscopy. The results show that the yellow colouration in Be-heated blue sapphires is not due to Be diffusion from the surface of sapphire. Be behaves as a sole catalyst in this process. We find that the charge transfer between the ferrous ( $\text{Fe}^{2+}$ ) and ferric ( $\text{Fe}^{3+}$ ) is the reason of the colour change. The above conclusions are confirmed by ESR measurements to determine the connections between the  $\text{Fe}^{3+}$  ions before and after Be-treated heat treatments.*

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Corundum is composed of aluminium oxide or alumina ( $\text{Al}_2\text{O}_3$ ) which, in its pure state, is colourless. In general, a small number of impurity metals such as iron, titanium and chromium may individually or together replace Al atoms in the crystal structure, thus imparting colour. Sapphire includes many varieties of the mineral corundum except the fully saturated red variety, which is known as ruby, and the pinkish-orange variety known as padparadscha. The blue colour is thus far the most popular colour for sapphire. The colour of blue sapphire results from a process known as intervalence charge transfer (IVCT).<sup>[1]</sup> Involved in this are traces of both titanium and iron. Iron and titanium both substitute for aluminium in the corundum crystal structure. A few hundredths of one percent of titanium in corundum produces no colour whatsoever, while the same amount of iron imparts only a pale-yellow colour. However, if both iron and titanium are present together, a deep-blue colour results. The iron may be present either in a ferrous ( $\text{Fe}^{2+}$ ) or ferric ( $\text{Fe}^{3+}$ ) state, while the titanium is found as  $\text{Ti}^{4+}$ . The  $\text{Fe}^{2+}\text{-O-Ti}^{4+}$  and  $\text{Fe}^{2+}\text{-O-Fe}^{3+}$  IVCT mechanisms, and also  $\text{Fe}^{3+}$  pairs produce a blue colour in sapphire.<sup>[2]</sup> Depending upon the Ti/Fe ratios, shades of blue colours are produced (light, medium, dark blue).

In the gem trade, the natural colour and clarity of sapphires are rendered non-fashionable, so there have been various attempts over the years to improve the appearance and stability of inferior .<sup>[3,4]</sup> In early 2002, the gemstone industry of Thailand has surprised the world with a new corundum enhancement technique, beryllium-heating process, which shows a new and un-

expected colour distribution and reaction. With this new heating technique, pink-orange or orange sapphires can be produced from original pink or reddish-brown corundum, also even colourless or white sapphires can be enhanced by the addition of yellow hue to the stones. Furthermore, some yellow sapphires can be obtained by the treatment of original green or blue sapphires.<sup>[5,6]</sup>

Many significant efforts were quickly launched to try to identify the cause of yellow and brown colouration in Be-treated sapphires.<sup>[5,7,8]</sup> They endeavored to point out that this colour alteration would have been caused by the diffusion of beryllium from an external source. However, primary analysis provided by the Gemological Institute of America (GIA) laboratories using x-ray electron probe microscopy analysis (EPMA) and laser ablation inductively coupled-plasma-mass spectrometry (LA-ICP-MS) was unable to detect any physical differences between the core and the rim parts of Be-treated sapphires.<sup>[7]</sup> These treated sapphires were subsequently acquired by Novak *et al.*<sup>[8]</sup> for secondary ion mass spectrometry (SIMS) analysis at Evans East. They presented the mass spectral analysis of the cores and rims of these stones using SIMS and detected a higher Be content in the coloured rims. Although they did not determine the Be content of the sample before treatment, they concluded that there existed diffusion of Be into the sapphires. Therefore, the detected Be in their experiment might be from a trace element in natural stones, not involved in any way with Be diffusion from an external source. Furthermore, some researchers<sup>[5]</sup> reported that yellow or brown colouration could be developed in the Be-

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treated stones depending upon the (Be+Mg)/Ti ratio, the presence or absence of iron, and the heating atmosphere. These previous works could not explain the real reason of colour change in Be-treated sapphire. This present work is therefore undertaken to throw some further light in answering these questions.

In this work, the natural Vietnamese blue sapphire samples, noted from a Phu mine, Luc Yen district, Yenbai province, were separated into two groups; the first group (G1) was analysed using LA-ICP-MS and UV-vis spectroscopy; the second group (G2) was examined using ESR spectroscopy. The LA-ICP-MS and UV-vis methods were performed in parallel. Samples were treated according to the standard Thai heat process, which is the method to produce yellow hue in the sapphire market. They were mixed with ground chrysoberyl ( $\text{BeAl}_2\text{O}_4$ ), which is 7.1% Be or 19.7% by weight  $\text{BeO}$ , to provide Be. The coated blue sapphires were placed in shallow alumina crucibles made from Coors 99.8%  $\text{Al}_2\text{O}_3$  ceramic and heated at  $1700^\circ\text{C}$  in oxidizing condition for 40 h.

LA-ICP-MS was used to determine the Be amounts at the inside and the outside of solid samples without any requirement of special preparation which might cause significant damages to the samples. In this work, a Nd:YAG (neodymium doped yttrium aluminium garnet crystal) laser (266 nm; LSX-500, CETAC, Nebraska, USA) coupled to a quadrupole mass spectrometer (Perkin-Elmer Elan 6000, Massachusetts, USA) was used. The operating parameters for the ICP-MS are given in Table 1. The Be concentrations in the samples were calculated using SRM NIST 612 glass as an external standard, with Al being used as an internal standard. Using the Al normalized sensitivity, changes in the ablated volume (mass) of samples were corrected. The detection limit for Be is approximately 3 ppm.

Table 1. Parameters of the systems used for the standardized working conditions.

Parameters	Value
Output energy	9 mJ at 266 nm
Repetition rate	20 Hz
Pit size	100 $\mu\text{m}$
Argon as carrier gas flow	0.4 L/min
Intermediate gas flow	1 L/min
Plasma gas flow	14 L/min
External standard	SRM NIST 612
Internal standard	Aluminium
RF power	1350 W
Repetitions	10
Sample	Sapphire

UV-vis and ESR spectroscopy was used to investigate the trace of  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and the charge transfer in the samples before and after heat treatment with Be. UV-vis spectroscopy was carried out with a Lambda 800 spectrophotometer (Perkin-Elmer) over the wavelength ranging from 200 to 900 nm. The sample spectra were recorded before and after Be-heat treatment.

For ESR measurement, samples from G2 were divided into three groups: (1) unheated (G2U), (2) heated at  $1700^\circ\text{C}$  in oxidizing conditions for 40 h (G2H), and (3) mixed with ground chrysoberyl and heated at  $1700^\circ\text{C}$  in oxidizing conditions for 40 h (G2HB). ESR measurements of G2U and G2H were performed at room temperature on a Bruker E 500 CW ESR spectrometer operated in an X-band. The spectrometer operating conditions adopted during the experiment were as follows: 498.5 mT central magnetic field; 2.5 to 999.5 mT scan ranges; 9.864 GHz microwave frequency; 20.18 mW microwave power; 5 kHz field modulation frequency; 2 mT field modulation amplitude and 0.045 s time constant. Samples were crushed manually and yielded into very fine powder using an agate mortar. Approximately 0.2 g of each ground sample was inserted in a fused quartz tube of 3 mm internal diameter. Then the sample tube was positioned in such a way that the sample was situated symmetrically with respect to the cavity centre. Each sample was scanned ten times.

In addition, for G2U and G2HB their paramagnetic ions were studied using high frequency electron paramagnetic resonance (HF-EPR) spectrometry which gives the highly distinct signal. HF-EPR measurements were performed at the National High Magnetic Field Laboratory in Tallahassee, Florida, U.S.A. The experimental setup was based on a sweepable superconducting magnet (Oxford Instruments) and was similar to that described in detail in the research of Hassan *et al.*<sup>[9]</sup> with the exception of the millimetre wave source (Virginia Diodes Inc., VA, U.S.A), which used a  $13 \pm 1$  GHz frequency synthesizer followed by a double, an amplifier and a cascade of frequency multipliers. A very low temperature (5 K) was obtained using a helium-flow cryostat (Oxford Instruments). Each fine ground samples of about 200 mg were used.

To prove that Be diffusion is not the cause of yellow colouration in Be-treated blue sapphire, examinations of Be concentrations in the core and outer surface of sapphire crystals is necessary. For this purpose, G1 samples (4 pieces: G101, G102, G103, and G104) were investigated using an LA-ICP-MS system. At the surface of samples, an average of Be quantities before and after Be-heating process, which became yellow after the treatment, is listed in Table 2. To determine the Be amounts in the core of the sapphire crystals after treatment, a set of representative samples after treatment were cut in half, lightly polished on the cut surfaces and then analysed by LA-ICP-MS all over again. The 10-point profile analysis, as shown in Fig. 1, was performed across the cut surface by this technique. Their Be concentrations are also listed in Table 2. These obtained results indicate that trace of Be is not established in natural blue sapphire samples but it is found in sample surfaces after treatment due to being mixed with pulverized chrysoberyl in the

Be-heating process. Furthermore, the results clearly demonstrate that Be from the outside of the sapphire sample do not diffuse into the bulk of stone because no trace of Be emerges across the cut surface. Therefore, these results prove convincingly that Be diffusion is not the genuine cause of creating the observed colour. The actual cause will be demonstrated presently.

Table 2. The summary of Be concentrations for the sapphires examined. Here <DL means below detection limit (< 3 ppm).

Sapphire	Be concentration (ppm)		
	Untreated (Surface)	Heat-treated with Be	
		Surface	Across the profile
G101	< DL	124.56	< DL
G102	< DL	82.01	< DL
G103	< DL	179.74	< DL
G104	< DL	74.87	< DL
Average	< DL	115.29	< DL



Fig. 1. Drawing of sapphire G1 showing the location of the LA-ICP-MS analysis.

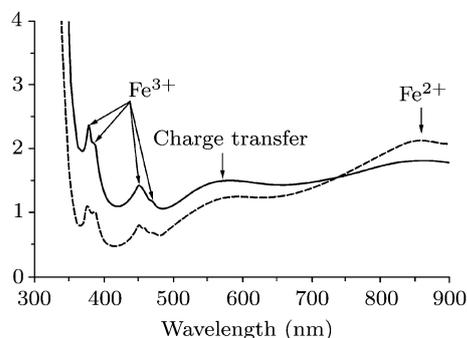


Fig. 2. Absorption spectra from 300 to 800 nm of G1 untreated blue sapphire samples (two pieces).

We have recorded the UV-visible absorption spectra of G1 sapphires in parallel to the LA-ICP-MS measurement. The absorbance spectra of samples before and after the Be-heat treatment are depicted in Figs. 2 and 3, respectively. In Fig. 2, the evolution shows the appearance of many absorption bands, the absorbance bands near 470, 450, 388 and 377 nm are attributed

to  $\text{Fe}^{3+}$ ,  $\text{Fe}^{3+}/\text{Fe}^{3+}$  pairs,  $\text{Fe}^{3+}$  and  $\text{Fe}^{3+}/\text{Fe}^{3+}$  pairs, respectively. A small poorly resolved peak at about 860 nm was assigned to  $\text{Fe}^{2+}$  and a broader peak around 560 nm is associated with  $\text{Fe}^{2+}-\text{Fe}^{3+}$  charge transfer. On the contrary, the absorption band corresponded to iron in ferrous state ( $\text{Fe}^{2+}$ ) was not present in the absorbance spectra of Be-treated samples, as shown in Fig. 3.

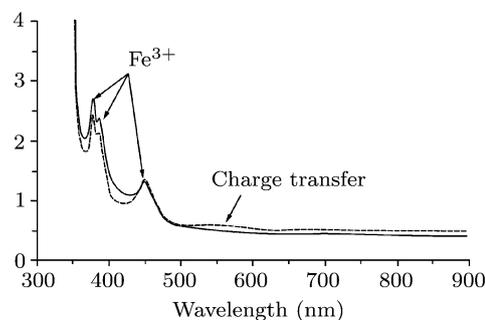


Fig. 3. Absorption spectra from 300 to 800 nm of G1 Be-treated samples which became yellow sapphires (two pieces).

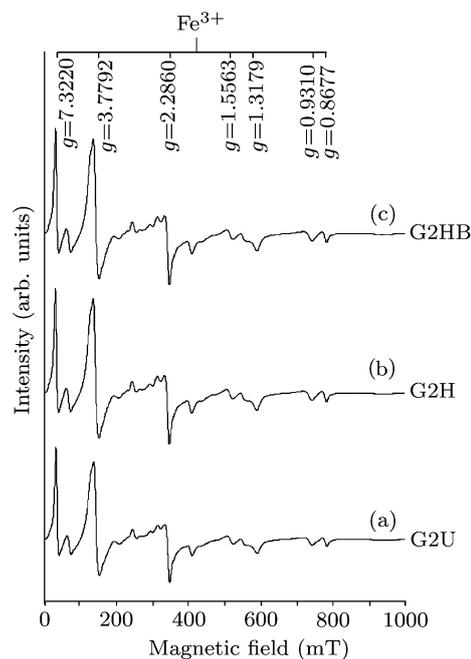
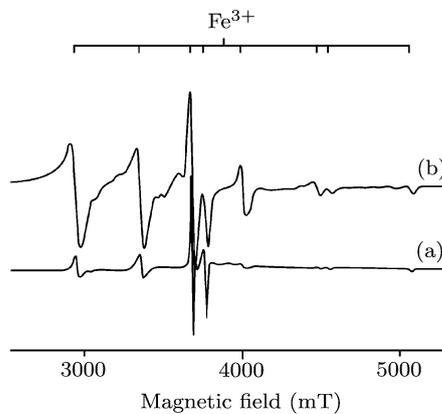


Fig. 4. X-band ESR spectra at room temperature of (a) untreated blue sapphire, (b) heated blue sapphires at  $1700^{\circ}\text{C}$  in oxidizing condition for 40 h and (c) heated blue sapphires with Be at  $1700^{\circ}\text{C}$  in oxidizing condition for 40 h.

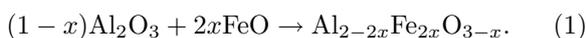
$\text{Fe}^{3+}$  ion is a paramagnetic ion because of the existence of unpaired electrons in its orbital.  $\text{Fe}^{2+}$  ion is also in this position most of the time. When  $\text{Fe}^{2+}$  is bonded to certain ligands, however, the resulting compound may be diamagnetic because of the creation of a low-spin situation in the  $d$  orbital. All of the electrons are paired and, as a result, the complex is diamagnetic. For that reason, the quantity of  $\text{Fe}^{3+}$  can

be determined by ESR technique. In the ESR experimental section, the G2 samples were heated with two conditions: with and without Be. Within the same heating period, the Be-treated sapphires were rapidly altered to yellow, but the heated sapphires without Be were gradually changed. The ESR spectrum of G2U (untreated), G2H (conventional heat treated) and G2HB (Be-heat treated) sapphires are shown in Fig. 4 and Fig. 5. The figures show that only  $\text{Fe}^{3+}$  ion is found in G2U, G2H and G2HB. The area under the ESR spectrum, which is proportional to  $\text{Fe}^{3+}$  ion concentrations, is obtained by integration. Hence, we can determine the ratio of  $\text{Fe}^{3+}$  concentrations in each sample to  $\text{Fe}^{3+}$  concentrations before treatment ( $\text{Fe}_{\text{BT}}^{3+}$ ). It was found that the  $\text{Fe}^{3+}/\text{Fe}_{\text{BT}}^{3+}$  ratios of conventional heat treated sample and Be-heat treated sample were 1.02 and 1.10, respectively. These figures indicate that the amounts of  $\text{Fe}^{3+}$  ion in samples increase after Be-heating process or conventional heat treatment. However, within the same treatment period, the  $\text{Fe}^{3+}$  ion concentrations after treatment with Be are higher than those treated without Be.



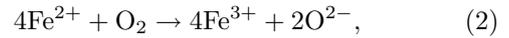
**Fig. 5.** Representative HF EPR spectra at 5 K of (a) untreated blue sapphire, and (b) Be-treated blue sapphires at 1700°C in oxidizing conditions for 40 h.

From the above results, we can conclude and confirm that the process of yellow colouration in G2H and G2HB are the same as that of iron acting as the most important agency. The presence of varying amounts of oxygen can affect the valence state of an iron presence in  $\text{Al}_2\text{O}_3$ . Iron usually exists either in the ferrous state, i.e. as  $\text{FeO}$ , or in the ferric state, i.e. as  $\text{Fe}_2\text{O}_3$ . At the high temperature of crystal growth the iron is normally in the divalent state as  $\text{Fe}^{2+}$  or  $\text{FeO}$ . When such a  $\text{Fe}^{2+}$  replaces one of the  $\text{Al}^{3+}$  in corundum, there is one oxygen vacancy for every two  $\text{Fe}^{2+}$ , to maintain an electrically neutral crystal. The composition can be written as



By heating under oxidizing conditions is considered now as the oxidation process of  $\text{Fe}^{2+}$  by gaseous oxy-

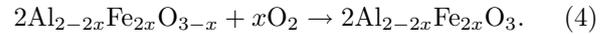
gen, which is



or as the oxide

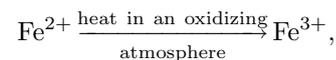


or in corundum



All the three equation are equivalent and result in an electrically neutral state containing only  $\text{Fe}^{3+}$ ; in corundum the result now corresponds to  $\text{Fe}_2\text{O}_3$  being present in  $\text{Al}_2\text{O}_3$ , having a pale-to-medium yellow colour, depending on the concentration. Heat treatment can reduce or eliminate the blue colour. However, it was found that Be was a catalyst in this new heating process because the G2HB samples were changed from blue colour to yellow colour within a shorter heating duration than G2H.

In conclusion, the cause of yellow colouration in Be-heated blue sapphires is not due to Be diffusion from the outside of sapphire into the bulk of the stone as the previous reports.<sup>[5–8]</sup> However, Be behaves as a catalyst in this process; the actual reason is the charge transfer between the ferrous and ferric states. The entails heating the stone in an oxidizing atmosphere produces the reaction



with the conversion of the ferrous state to the ferric state, resulting in a yellow colour replaces the blue.  $\text{Fe}^{3+}$  may be present as isolated ions scattered around the substance. Generally, as the concentration of these iron ions increases, the intensity of the yellow colour increases proportionally.<sup>[1]</sup> Furthermore, the produced colour is stable under the fading test.<sup>[5]</sup> Therefore, this new treatment technique, Be-heating process, can be used as a method for qualitative gemstone enhancement without diffusion of any impurities into the stone.

## References

- [1] Hughes R W 1990 *Corundum* (London: Butterworth-Heinemann)
- [2] Themelis T 1992 *The Heat Treatment of Ruby and Sapphire* (USA: Gemlab Inc)
- [3] Nassau K 1994 *Gemstone Enhancement: History, Science, and State of the Art* (Oxford: Butterworth-Heinemann)
- [4] Udomkan N et al 2005 *Int. J. Mod. Phys. B* **19** 3273
- [5] Arnon V P, Häer T, Wathanakul P and Atichat W 2004 *J. Gemm.* **29** 77
- [6] Coldham T 2002 *Australian Gemologist* **22** 288
- [7] Emmett J L et al 2003 *Gems Gemology* **39** 84
- [8] Novak S W et al 2004 *Appl. Sur. Sci.* **231–232** 917
- [9] Hassan A K et al 2000 *J. Magn. Reson.* **142** 300