A New Technique for the Analysis of Corundum Using Laser Ablation ICP-MS

Application

Gemology

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Abstract

A large percentage of rubies and sapphires undergo some degree of heat treatment to enhance their color and, as a result, to increase their value. As the majority of "processors" certify their gems as "heat treated", this practice is accepted by the trade. Established treatment methods involve super-heating the gems to near melting point, around 2000 °C, and diffusing them with hydrogen. Dealers have established analytical methods to differentiate these stones from untreated natural or synthetic ones. With the market value of natural sapphires far outweighing that of both synthetic stones and natural gems that have undergone color-enhancing processing, it is important to be able to make this distinction. However, a new processing technique was developed that involves the addition of beryllium (Be) during the heat treatment stage, making the treated stones very difficult to identify. This technique has been applied to modify some corundum to resemble one of the most valuable colored stones: vivid orange-yellow gems known as padparadscha. Because some processors refuse to disclose the gems as "beryllium-diffused", referring to them only as "heat treated", and because beryllium is difficult to detect by conventional gemological instrumentation, the price and demand for colored stones has weakened [1].

Researchers at the Gemological Association of All Japan found that laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is an extremely effective means of investigating the distribution of Be, and other impurity elements, across the surface of a finished gem. This information allows gemologists to identify the different types of processing applied to individual sapphires. However, more research is required to understand the physical mechanisms that give rise to the color enhancements.

Introduction

Rubies and sapphires belong to the group of gemstones known as "Corundum", which is the gemological name for aluminum oxide (Al_2O_3). Red (and most pink) corundum is known as ruby. Many different colors of corundum occur, the color being derived from the trace metal content (for example, it is the presence of chromium that gives rubies their bright red color). While many people associate sapphires with the color blue, highly saturated orange, pink and yellow gems are widely available on the market and these are named according to their color, for example, yellow sapphire. Among these colored sapphires is one of the most valuable colored stones, a rare orange-pink gem known as "padparadscha", whose color appears even and vivid. Because of the high market value of natural padparadscha, there is concern about a new process which, when applied to certain lower value natural sapphires, could produce stones that are extremely difficult to distinguish from natural padparadschas. The new treatment involves heating stones with beryllium (Be) powder which, when diffused into the corundum, enhances the color of yellow stones. Laboratory studies of enhanced stones have shown the orange-yellow layer forms only on the outer rim of the stone along the faceted surface, while the center is almost pink. Similarly, violet, green, or blue sapphires are available in which a yellow or orange layer forms on the outer rim along the faceted surface. Because of this unusual color distribution, it was suspected that these modified stones had undergone a type of " diffusion" treatment. Initial studies revealed that the heat process used (referred to as a "new heat process") causes Be to diffuse into the corundum.

Several different explanations have been proposed to account for the coloring mechanism, but one difficulty has been the detection of Be by conventional gemological instruments. In this study, LA-ICP-MS was used to analyze impurity elements, including Be, present in unheated, heat-treated, and synthetic corundum samples.

Samples and Methodology

To evaluate the new Be-diffused heat process, "finished" stones were analyzed, using LA-ICP-MS, both before and after treatment by the "new heat process". Samples included:

- Colorless verneuil-processed synthetic sapphire (traditional flame-fusion process)
- Pieces of flux-grown synthetic pink sapphire
- Natural sapphires of each color

The samples were treated using the Be-diffused heat method by processors in Bangkok and Chanthaburi in Thailand. The stones were put into a crucible together with chrysoberyl ($Be–Al_2O_3$) and heated at over 1800 °C in an oxidizing atmosphere for 22 and 10 hours, respectively.

To assess the accuracy of the LA-ICP-MS results, a repeat analysis was done on each sample using secondary ion mass spectrometry (SIMS).

LA-ICP-MS

LA-ICP-MS is widely used to determine elements directly in solid samples with minimal sample preparation. It is a highly sensitive multi-element technique with a wide analytical dynamic range from ppt to ppm-level in the solid. For this study, a Merchantek UP-213 (New Wave Research. Inc, USA) LA system was coupled to an Agilent 7500a ICP-MS. A schematic of the laser ablation system is shown in Figure 1. The sample surface is irradiated with deep-UV (213 nm) output from a frequency-quintupled Nd:YAG (neodymium doped yttrium aluminum garnet crystal) laser. The laser light couples to the surface of the sample, causing very rapid heating which, in turn, causes the matrix to be volatilized or ablated. This ablated material is then carried to the ICP-MS in an argon carrier gas stream for analysis. Calibration is typically against a well-characterized synthetic solid material, such as NIST 612 Trace Elements in Glass.

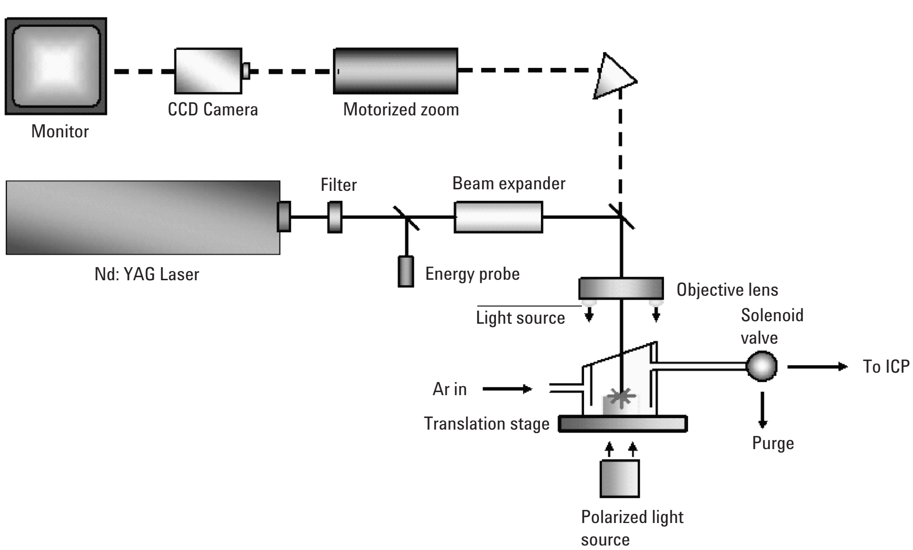

Figure 1. Schematic of Nd: YAG laser ablation system (5th harmonic - 213 nm) for ICP-MS.

Results and Discussion

LA-ICP-MS measurements of Be in unheated and traditionally heat-treated corundum of each color (40 pieces in total) are shown in column 2 of Table 1. Beryllium was present below the background level of the instrument in all of these samples.

Table 1. LA-ICP-MS Analysis of Be in Sapphires of Each Color

	Unheated or "traditional" heat processed, Be, ppm	Number of samples	"New" Be-diffused process, Be, ppm	Number of samples
Natural Stones				
Yellow	<0.035	4	1.79-8.09	8
Padparadscha	<0.002	2	1.54-4.36	10
Orange	<0.048	4	1.95-4.14	7
Pink	<0.033	4	1.92-3.27	4
Purple	<0.008	2	2.63-7.79	10
Blue	<0.012	5	1.43-14.9	20
Color change	<0.016	2	1.71-2.56	2
Colorless	<0.003	5	0.57-1.39	4
Ruby	<0.015	2	0.43-15.7	4
Synthetic Stones				
Colorless	<0.029 (Unheated)	10	0.32-5.03	8
Pink	–	–	0.27-1.73	2
Total number of samples		**40**		**79**

However, Be (in the order of several ppm) was detected in all corundum, natural and synthetic, that were heated in the new process (79 pieces), as shown in column 4 of Table 1. Trace elements that are commonly seen in corundum, such as Ti, V, Cr, Mn, Fe, Ga, and Al, the main constituent element, were also detected by LA-ICP-MS (results not shown).

Further investigation suggested that the concentration of Be was higher in stones heated for a longer period (the “Bangkok” treatment, over 22 hours) than those heated for a shorter period (the Chanthaburi process, 10 hours). Figure 2 summarizes Be data obtained from LA-ICP-MS analysis of colorless synthetic and colorless natural sapphires treated over 10 hours and 22 hours, respectively. The graphs illustrate the change in Be concentration across cut surfaces of the samples and indicate significant differences in the distribution of the element.

There was no color alteration in either the natural or synthetic samples that were treated for 10 hours; however, with the 22-hour heat process, while there was no color change for the colorless synthetic sapphires, the colorless natural sapphires became yellow.

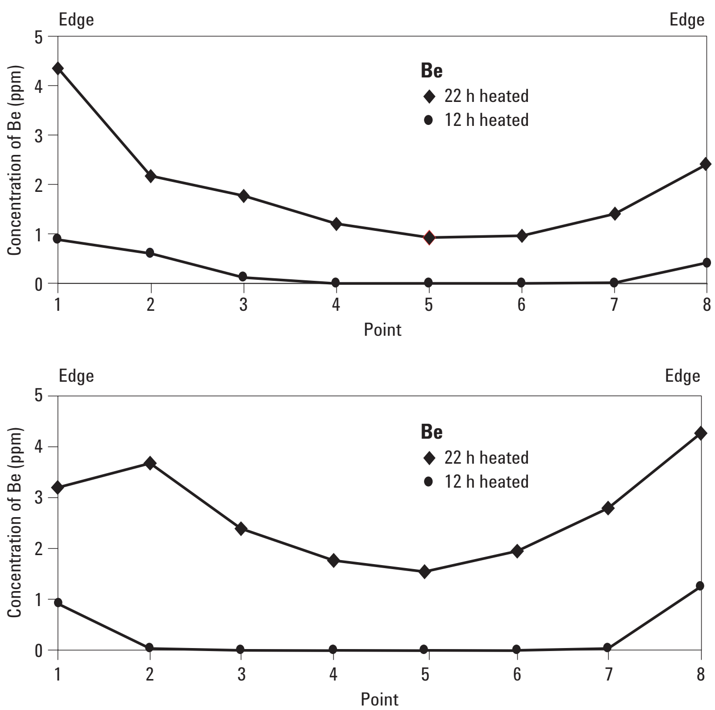

Figure 2. Distribution of Be across the cut surface of synthetic (top) and natural (bottom) sapphires with different heating periods. The length of the cut face analyzed was 500 µm for the synthetic and 300 µm for the natural stone.

SIMS

SIMS is a sensitive elemental surface analysis technique suitable for local analysis. It is used to analyze light elements with sensitivity similar to LA-ICP-MS, but its operation is more complicated and it requires a highly skilled operator. The SIMS analysis was performed by the Foundation of Promotion for Material Science and Technology of Japan using a Cameca IMS-6f magnetic sector instrument (Paris, France).

Figure 3 shows the distribution profile of Be across the cut surface of a padparadscha-colored sample (average 400 µm) that had undergone Be-diffused processing. Both the LA-ICP-MS and SIMS results show a similar trend: a low concentration of Be in the center of the cut stone and a higher concentration towards the outer rim. Different standard samples were used to calibrate the two analysis methods which account for the differences in the concentration values obtained; NIST 612 Trace Elements in Glass was used to calibrate LA-ICP-MS and a “synthetic sapphire with added beryllium” standard was used to calibrate the SIMS.

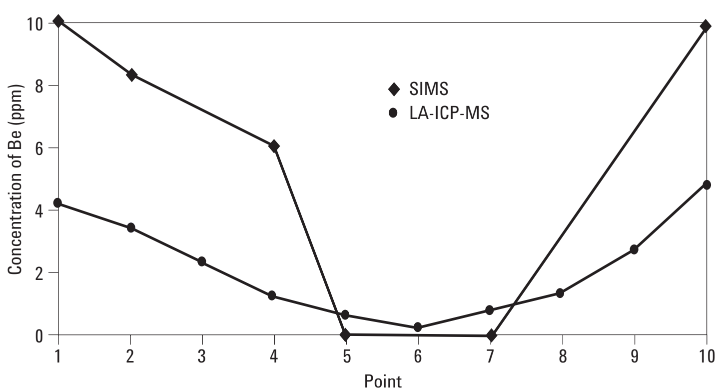

Figure 3. Be-distribution (400 µm) across a Be-diffused processed padparadscha sapphire, measured using both SIMS and LA-ICP-MS. Note the SIMS result for points 5 and 7 is: 0.0086 ppm.

Conclusions

Beryllium was not detected in either unheated or traditionally heat-treated crystals, but it was present in all sapphires of each color that were heated in the new process. The results of the study suggest that some samples underwent a color change as a result of the new heat-treatment processing while some did not. Although Be itself does not directly cause the color change, it is thought that the interaction between the Be metal and other trace transition elements (such as Fe), or between the Be and defects (holes) in the crystal may produce the color change [2, 3]. As the color of some crystals does not change, even when Be is dispersed during the new heat process, more clarification is needed to better understand the mechanism at work.

Investigation of the distribution of Be by LA-ICP-MS is an extremely effective means to determine whether a stone has undergone the new heat process or not. This is important to gemologists who have no alternative method to determine whether a batch of stones is natural or has been treated using the new Be-diffusion method - vital information to restore confidence in the market. Furthermore, the LA-ICP-MS results were in good agreement with the SIMS results.

This new method of heat treatment is expected to diversify in the future as other light element oxides are used. In this case, LA-ICP-MS would be ideally suited to detect Be and other light elements at trace levels in solid gemstones.

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