

A NEW METHOD FOR DETECTING BE DIFFUSION-TREATED SAPPHIRES: LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS)

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This article describes the first application of laser-induced breakdown spectroscopy (LIBS) to gemology. So far, the detection of Be-diffused sapphire and ruby has been based on LA-ICP-MS or SIMS, neither of which is readily available to most laboratories. In this study, we use LIBS to detect beryllium in corundum at very low concentrations (down to ~2 ppm). This technique is a reliable tool for identifying Be diffusion-treated sapphires, and is affordable for most commercial gemological laboratories. As with other laser-based techniques, LIBS may cause slight damage to a gemstone, but this can be minimized by choosing appropriate instrument parameters.

Sapphires treated by beryllium diffusion entered the gem trade in mid-2001, and the first laboratory alert on this treatment was issued by the American Gem Trade Association in New York on January 8, 2002 (Scarratt, 2002). This treatment modifies various colors of corundum into stones of more attractive hues, usually yellow or orange to orangy red (figure 1). Some of these colors are rather rare in untreated or traditionally heated corundum, so the stones may be very valuable, especially the orangy pink variety (“padparadscha”). Several studies of Be-diffused corundum have revealed that the presence of low concentrations of beryllium (i.e., ~5–10 ppm) in the corundum lattice may result in a distinct yellow-to-orange coloration (Hänni and Pettke, 2002; Peretti and Günther, 2002; Emmett et

al., 2003; Pisutha-Arnoud et al., 2004). In contrast, untreated or traditionally heated sapphires of similar color contain no Be or have only minute traces (i.e., parts-per-billion [ppb] levels) of this light element (Emmett et al., 2003; D. Günther, pers. comm., 2004).

Unfortunately, the detection of Be-diffused sapphires has proved difficult, because testing by traditional nondestructive analytical methods (e.g., energy-dispersive X-ray fluorescence [EDXRF]) cannot detect light elements such as Be. Although some Be-diffused sapphires can be identified by a yellowish orange rim when observed in immersion (see, e.g., Hänni and Pettke, 2002; McClure et al., 2002; Peretti and Günther, 2002; Emmett et al., 2003), often no such diffusion feature is present. Until now, the reliable detection of Be diffusion has usually required highly sophisticated methods, such as laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) or secondary ion mass spectrometry (SIMS). Both techniques are slightly destructive, as they vaporize a minute quantity of the sample for analysis with a mass spectrometer (Guillong and Günther, 2001).

Since the two analytical techniques described above are quite expensive, time consuming, and only rarely at the disposal of gemological laboratories, we investigated a more affordable technology. In July 2003, we began to evaluate the potential of

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Figure 1. The attractive colors of the Umba Valley (Tanzania) sapphires in this composite photo were produced by Be diffusion. The loose stones range from 1.27 to 7.91 ct, and the sapphires in the 18K white gold jewelry are 3.19 ct (ring center stone) and 3.52 ct total weight (leaf pendant). Photo by Myriam Naftule Whitney; courtesy of Nafco Gems, Scottsdale, Arizona.

laser-induced breakdown spectroscopy (LIBS) for gemstone analysis. As in the other methods mentioned above, LIBS analysis also is slightly destructive, as a small portion of the sample is ablated by a laser. Our initial results revealed the potential of LIBS to detect Be-diffused corundum (Hänni and Krzemnicki, 2004). In April 2004, SSEF became the first laboratory to install a LIBS instrument that was specially designed for gemstone analysis. Since July 2004, SSEF has offered Be detection in corundum as a regular service to its clients. In this article, we present the first detailed results obtained by LIBS on beryllium-diffused corundum, as analyzed with the SSEF GemLIBS system (table 1).

LIBS BACKGROUND

LIBS can provide qualitative to semiquantitative chemical data. Initial studies on laser spark spectroscopy (Brech and Cross, 1962; Allemand, 1972; Corney, 1977) were further developed in the early 1980s, mainly by scientists at Los Alamos National Laboratory in New Mexico. Radziemski et al. (1983) showed the ability of LIBS to detect trace concentrations of Be (in air) as low as 0.5 ppm. Recently, major improvements in laser and spectrometer technology have dramatically expanded the possibilities and applications of LIBS for military uses, environmental monitoring, process control, and material analysis (Bogue, 2004); these include remote in-situ testing of fine particulate matter (Carranza and Hahn, 2002) and real-time analysis of steel composition during production (Gruber et al., 2004). The use of LIBS in the gem

industry has so far been rather limited, and has involved analyzing the composition of jewelry metal alloys (e.g., García-Ayuso et al., 2002) as well as Be-diffused corundum (Krzemnicki and Hänni, 2004).

The principle behind LIBS is the interaction of a laser with a sample to produce an optical emission spectrum that is specific to that sample. A pulsed laser focused onto a sample (solid, liquid, or gas) vaporizes a small portion for analysis. The superheated, ablated material is transformed into a plasma, a form of matter in which the original chemical bonds of the substance are broken apart and the resulting atoms are converted into a mixture of neutral atoms, ions, and electrons. The atoms and ions within the expanding plasma lose some of their energy by emitting light, which produces a characteristic emission spectrum in the ultraviolet, visible, and near-infrared spectral range. The spectrum is then recorded with a spectrometer. Due to complex plasma dynamics, LIBS does not yield quantitative data. By using reference standards of known composition, it is sometimes possible to calibrate the instrument to generate semiquantitative data, such as for Be in a corundum matrix (Krzemnicki and Hänni, 2004).

MATERIALS AND METHODS

In this study, we present data on 21 well-characterized faceted natural sapphires and rubies, as well as three synthetic corundums (figures 2 and 3; table 2). Six of the natural corundums were Be-diffused (Be-1–Be-6). Fifteen of the natural samples were



Figure 2. These are some of the corundum samples that were analyzed by LIBS for this study. The faceted stones on the left are Be-diffused sapphires (Be-1 to Be-4). On the bottom right are samples that have been heated by traditional methods with no Be-diffusion (NBe-1, NBe-6, and NBe-14). In the background are a split boule of orange flame-fusion synthetic sapphire that was doped with Be (sample BeS-1) and a faceted flame-fusion synthetic ruby without Be (sample NBeS-1). Photo by M. S. Krzemnicki, © SSEF.

not Be-diffused (NBe-1–NBe-15), but nine of them were heated by traditional methods. The natural samples were compared to a flame-fusion synthetic orange sapphire (BeS-1) that was doped with a minute amount of Be (2–3 ppm measured by LA-ICP-MS) to investigate the detection limit of our particular LIBS configuration. In addition, a flame-fusion synthetic ruby (NBeS-1) and a flame-fusion synthetic color-change sapphire (NBeS-2) were

Figure 3. These are the additional non-Be-diffused natural corundum samples that were analyzed for this study. From left to right, top row: NBe-9 (Umba, Tanzania), NBe-15 (Luc Yen, Vietnam), NBe-5 and NBe-3 (Sri Lanka), NBe-10 (Tunduru, Tanzania); and bottom row: NBe-8 and NBe-7 (Tanzania), NBe-13 (Ilakaka, Madagascar), NBe-4 and NBe-2 (Sri Lanka), NBe-11 and NBe-12 (Tunduru, Tanzania). As expected, the LIBS analyses for all of these samples revealed no evidence of beryllium. Photo by H. A. Hänni, © SSEF.



analyzed to study possible peak interference by chromium and vanadium with the Be emission doublet at 313 nm in the LIBS spectra.

All samples were chemically analyzed by EDXRF spectrometry, using a Tracor Spectrace 5000 instrument, to determine semiquantitative concentrations of Ti, V, Cr, Fe, and Ga. Additional elements (such as Na, Mg, Si, Ca, Mn, Ni, Cu, and Zn) were typically below the EDXRF detection limit. As EDXRF spectrometry is not capable of analyzing light elements such as Be, only by using methods such as LIBS, LA-ICP-MS, or SIMS is it possible to detect them in corundum. We used LA-ICP-MS to obtain quantitative data on Be (and other trace elements) in all six Be-treated samples (Be-1–Be-6), in three of the stones treated by traditional heating (NBe-1, NBe-6, and NBe-14), and in the Be-doped synthetic sapphire (BeS-1), for comparison with the LIBS spectra. The LA-ICP-MS analyses were obtained using a pulsed Excimer ArF laser with a characteristic wavelength of 193 nm for sample ablation, combined with special optics to homogenize the energy distribution across the laser beam (Günther et al., 1997; now commercially available as the GeoLas system). The ICP-MS was a quadrupole instrument from PerkinElmer, the ELAN 6100. The size of the ablated laser pits was about 100 μm in diameter and a few tens of micrometers deep. In contrast to many other commercially available LA-ICP mass spectrometers, this instrument is characterized by a perfectly flat laser beam geometry, which enables drilling of very

TABLE 1. Characteristics of the SSEF GemLIBS system.

Laser: Single-pulsed Nd:YAG laser	
Pulse duration	7 nanoseconds
Wavelength	1064 nm
Energy	100 millijoules
Frequency	3 Hz
Focus lens	35 mm
Spectrometer: Ocean Optics LIBS2000+	
Range	200–980 nm broadband spectrum
Q-switch delay	2 microseconds
Analysis	Simultaneous, real-time
Resolution	0.1 nm FWHM (full width at half maximum)
Sample chamber	
Dimensions	17 × 22 × 14 cm (width × height × depth)
Protection	Laser safety plastic, 180° visibility
Conditions	Measured in air
Sample holder	Manual x-y-z sample stage

precise flat round laser holes. More details about this setup will be provided in an article on the application of LA-ICP-MS in gemology (M. S. Krzemnicki et al., in preparation)

The SSEF GemLIBS system used for the LIBS analyses consists of an Ocean Optics LIBS 2000+ instrument that was modified for gemological purposes with an x-y-z sample holder for precise targeting (see table 1 and figures 4 and 5). The sample was fixed to a glass plate with some Blu-Tack and positioned under the laser. The system uses a single-pulse 1064 nm Nd:YAG laser (pulse duration of 7 nanoseconds with an energy of 100 millijoules [mJ]) from BigSky Quantel. A series of overlapping high-resolution fiber-optic spectrometers enables the simultaneous recording of emission spectra in the range 200–980 nm, in which the emission lines

of all elements are found. The peak resolution (full width at half maximum [FWHM]) is 0.1 nm. Thus, it is possible to detect emission lines that are very close to one another.

Laser safety is an important consideration when performing LIBS analysis or other laser-based experiments (e.g., Raman and LA-ICP-MS). The laser energy used for LIBS analysis is powerful, and reflection from gemstone facets may cause damage to the retina of the eye. The system comes with a transparent laser-protected sample chamber. LIBS analyses should only be carried out while the sample chamber is completely closed.

In our study, numerous emission lines from elements of the corundum matrix (Al, Cr, Fe, V, Ti) and the atmosphere (O, N) were encountered. In accordance with Radziemski et al. (1983), Be

TABLE 2. LIBS samples for this study on Be diffusion-treated corundum.^a

Sample	Mineral	Treatment	Weight (ct)	Form	Origin	LA-ICP-MS Be (ppm)	LIBS Be detection
Be-1	Purple sapphire	Be diffusion	0.63	Faceted	East Africa	34–49	Positive
Be-2	Orange sapphire	Be diffusion	1.26	Polished slab	East Africa	5–21	Positive
Be-3	Orange sapphire	Be diffusion	1.00	Faceted	East Africa	8–11	Positive
Be-4	Orange sapphire	Be diffusion	0.85	Faceted	East Africa	8–10	Positive
Be-5	Orange sapphire	Be diffusion	0.98	Faceted	East Africa	4–10	Positive
Be-6	Yellow sapphire	Be diffusion	0.97	Faceted	Sri Lanka	9–11	Positive
BeS-1	Synthetic orange sapphire ^b	Be diffusion	242.17	Split boule	Flame fusion	2–3	Positive (very low)
NBeS-1	Synthetic ruby	None	5.47	Faceted	Flame fusion	na	Negative
NBeS-2	Synthetic V-corundum	None	2.64	Faceted	Flame fusion	na	Negative
NBe-1	Yellow sapphire	Heated	1.51	Faceted	Sri Lanka	bdl	Negative
NBe-2	Yellow sapphire	Heated	2.57	Faceted	Sri Lanka	na	Negative
NBe-3	Light yellow sapphire	Heated	2.18	Faceted	Sri Lanka	na	Negative
NBe-4	Orangy pink sapphire ^c	None	0.73	Faceted	Sri Lanka	na	Negative
NBe-5	Pink sapphire	None	2.10	Faceted	Sri Lanka	na	Negative
NBe-6	Sapphire	Heated	1.22	Faceted	Sri Lanka	bdl	Negative
NBe-7	Ruby	None	0.60	Faceted	Tanzania	na	Negative
NBe-8	Light purple sapphire	None	0.88	Faceted	Tanzania (Umba)	na	Negative
NBe-9	Slightly brownish pinkish orange sapphire	None	1.53	Faceted	Tanzania (Umba)	na	Negative
NBe-10	Pink sapphire	Heated	1.10	Faceted	Tanzania (Tunduru)	na	Negative
NBe-11	Pink sapphire	Heated	1.27	Faceted	Tanzania (Tunduru)	na	Negative
NBe-12	Light pink sapphire	Heated	1.47	Faceted	Tanzania (Tunduru)	na	Negative
NBe-13	Light pink sapphire	Heated	2.15	Faceted	Madagascar (Ilakaka)	na	Negative
NBe-14	Ruby	Heated	1.05	Faceted	Kenya	bdl	Negative
NBe-15	Ruby	None	2.40	Polished fragment	Vietnam (Luc Yen)	na	Negative

^a Abbreviations: bdl = below detection limit (0.3–0.8 ppm); na = not analyzed by LA-ICP-MS (only EDXRF), so Be was not quantified.

^b Analyses performed near the rim of the cleaved Be-doped synthetic orange sapphire.

^c Also referred to as the “padparadscha” variety of corundum.



Figure 4. The SFEF GemLIBS system consists of a sample chamber with an attached pulsed Nd:YAG laser, a series of high-resolution fiber-optic spectrometers, the laser power supply, and a computer for controlling the system and analyzing the spectra.
Photo by H. A. Hänni, © SFEF.

detection was based on the presence of the first-order ionic Be II doublet at 313.042 and 313.107 nm (NIST database). Using our LIBS system, this

doublet was not resolved but appeared as a single peak centered at 313.08 nm. A weaker Be emission was found at 234.86 nm. However, this emission was not used, since Fe from the corundum matrix may produce overlapping peaks.

Repeated testing revealed that about 20 laser shots per LIBS analysis resulted in a high signal-to-background ratio for the Be emission at 313 nm. Additional laser pulses only slightly increased this ratio. The method was further improved by focusing the laser slightly above the surface of the sample. We found that the delay after the laser pulse, which is when the characteristic optical emission of an element is analyzed, is also an important factor. Immediately after the laser pulse, the plasma emission is dominated by continuous light emission. Only after a certain delay can the characteristic optical emission of the elements be detected. However, different elements may reveal maximum characteristic optical emissions at different delays after the laser

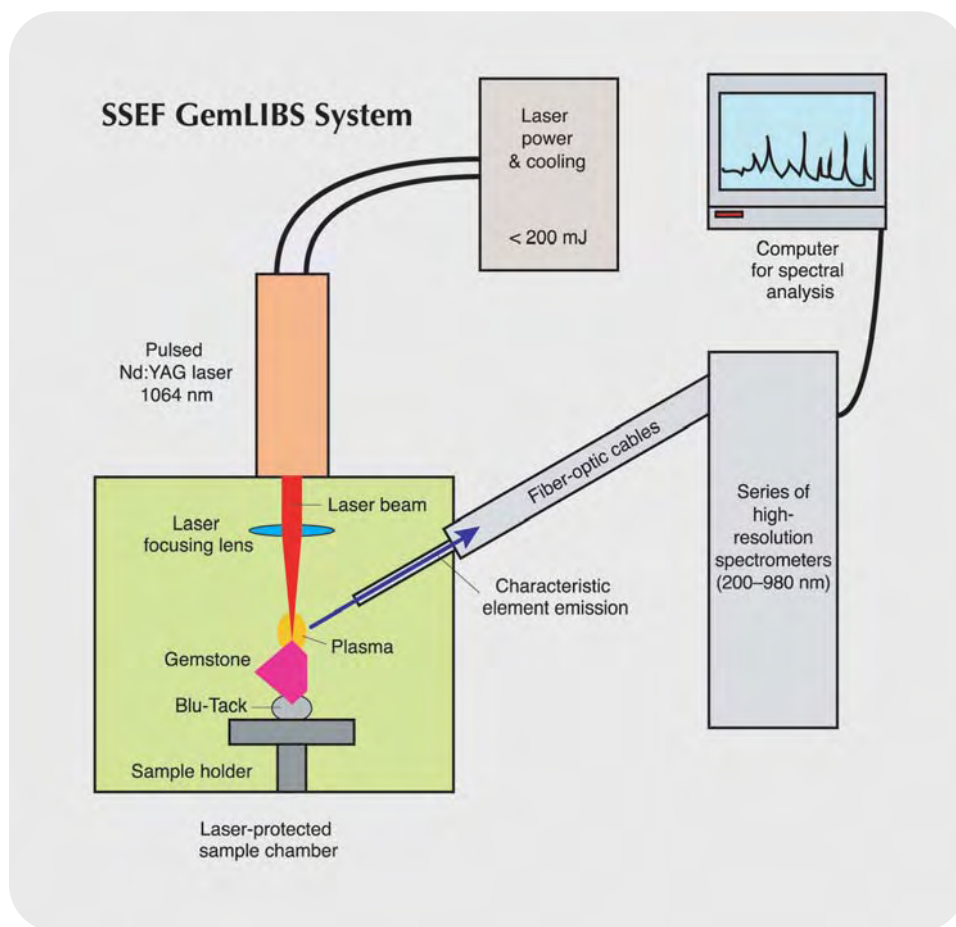


Figure 5. This schematic diagram shows the individual constituents of the SFEF GemLIBS system.

pulse. We found that a delay of 2 microseconds was ideal for beryllium detection in corundum.

We performed extensive testing to minimize the possibility of laser-induced internal damage to the gem sample. We established that a laser energy of 100 mJ is ideal for Be detection in a corundum matrix. At this energy, the laser ablation spot on the surface of the gemstone is minimized and internal damage is avoided. Higher energies (e.g., 150 or 200 mJ) may lead to damage, as part of the laser energy is transmitted through the sample, resulting in small disc-like tension cracks along the laser path. Note, too, that the analyzed spot should not be located close to a near-surface fracture or inclusion, as in rare cases this may cause a tiny tension crack. It is therefore recommended that a gemologist examine the sample with a microscope before choosing the spot for LIBS analysis.

With our optimized setup, the tiny laser spots on a sample's surface have a diameter of less than 0.1 mm (100 μm) and a maximum depth of 30–50 μm (figure 6). This is similar to the size of the laser holes generated by LA-ICP-MS. The LIBS laser spots may be detected by a close inspection of the sample with a 10 \times loupe, but they do not affect the overall appearance of the gemstone. As the vaporized portion of the sample is redeposited around the hole after the breakdown of the plasma, a small iridescent zone may be visible around the LIBS spot (about 2 mm in diameter). It can be easily removed with a slight repolishing. By analyzing faceted samples on or near their girdle, the tiny laser spots are inconsequential. The girdle also is of interest because it is usually rather poorly repolished after treatment, thus offering a better possibility of finding minute areas that are filled with residual Be-enriched flux material (Hänni and Pettke, 2002; Emmett et al., 2003). For the detection of Be-diffusion treatment by LIBS, a maximum of two or three spots is chosen for analysis.

RESULTS

The LIBS spectra were averaged from 20 individual laser pulses to obtain the best counting statistics over the whole broad-band range from 200 to 980 nm (see, e.g., figure 7). The highest peaks in the ultraviolet to mid-visible spectral range are due to Al. The peaks in the upper spectral range (>600 nm)

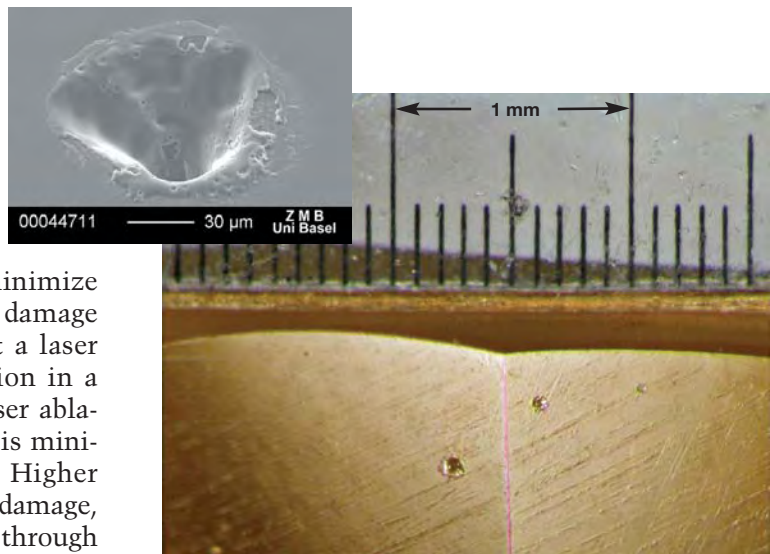
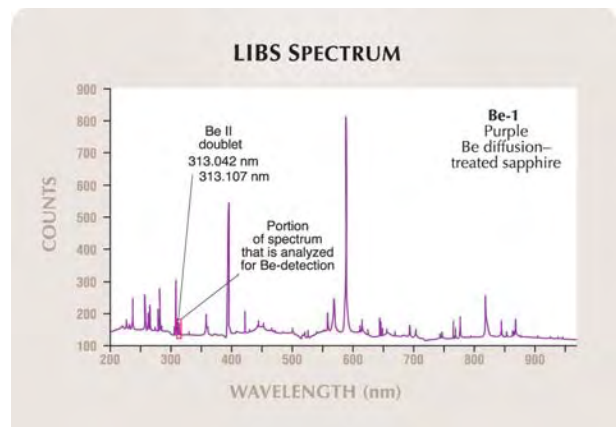


Figure 6. Two LIBS laser spots are visible near the girdle of this yellow sapphire. A micrometer scale is shown for comparison. The diameter of these tiny laser spots is less than 0.1 mm, similar to that of the holes produced by LA-ICP-MS. They are hardly visible with 10 \times magnification, and are particularly inconspicuous when located on or near the girdle (photo by H. A. Hänni, © SSEF). The SEM image in the inset shows a closer view of a LIBS laser hole, which in this case is about 0.03 mm deep (micrograph by M. Düggelein, © SEM Laboratory, University of Basel, Switzerland).

are mainly due to oxygen and some nitrogen from the atmosphere (air).

Figure 8 compares the LIBS spectra of the Be diffusion-treated sapphires (Be-1–Be-6 and BeS-1) to those of two Be-free flame-fusion synthetic

Figure 7. This LIBS spectrum of a purple Be-diffused sapphire (sample Be-1) shows the full spectral range between 200 and 980 nm. Numerous atomic and ionic emission lines are present, which may partially interfere with one another. The main peaks are due to aluminum. Emission due to beryllium produces a peak at approximately 313.08 nm.



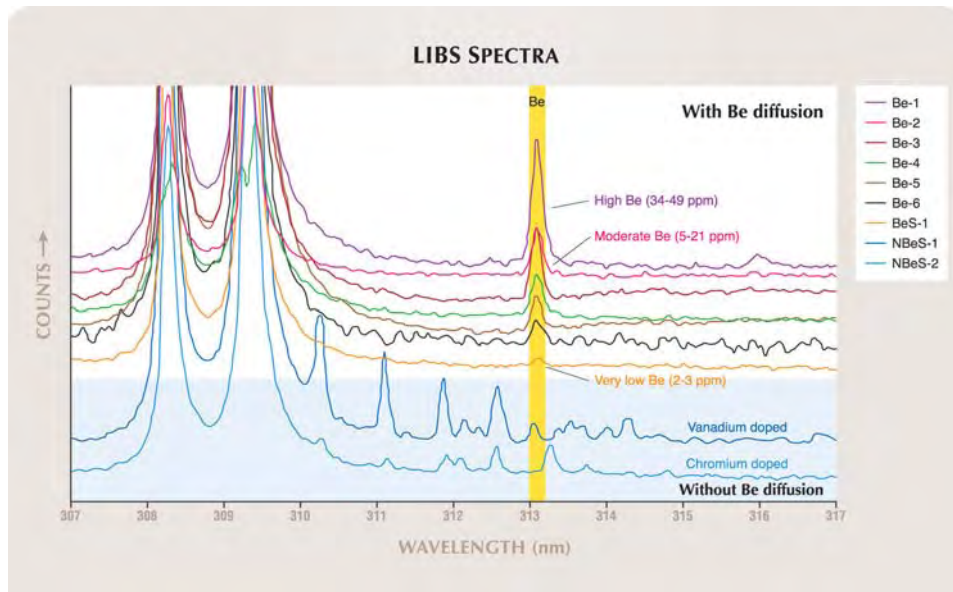


Figure 8. These LIBS spectra in the range of 307–317 nm are of Be-treated sapphires (Be-1 to Be-6) and an orange Be-doped flame-fusion synthetic sapphire (BeS-1) shown in comparison to the spectra of two Be-free flame-fusion synthetic samples (NBeS-1 and NBeS-2). The 313.08 nm Be peak is the basis for the detection of Be-treated sapphires. Fortunately, this peak does not exactly overlap any of the numerous Cr and V peaks in that region.

corundum samples (NBeS-1 and NBeS-2). The dominant (and truncated) peaks at about 308 and 309 nm are due to the Al in corundum. The spectra are shown without normalization of the Al II emission at 309.27 nm. Nevertheless, there is a distinct positive correlation between the height of the 313.08 nm Be peak and the beryllium concentration as measured by LA-ICP-MS. At a low concentration of 2–3 ppm (BeS-1), the Be peak is very small. The LIBS analyses on this cleaved Be-doped synthetic sample were taken close to the

LA-ICP-MS spots, near the rim. Based on the analysis of this sample, we estimate that the detection limit for Be in corundum is ~2 ppm with our LIBS system.

At a much higher Be concentration (Be-1, 34–49 ppm), the Be peak measured with LIBS was much stronger. The range of Be indicated for each sample in table 2 is based on several LA-ICP-MS analyses and reflects the inhomogeneity of these samples (especially sample Be-2, with concentrations ranging from 5 to 21 ppm Be). As each spec-

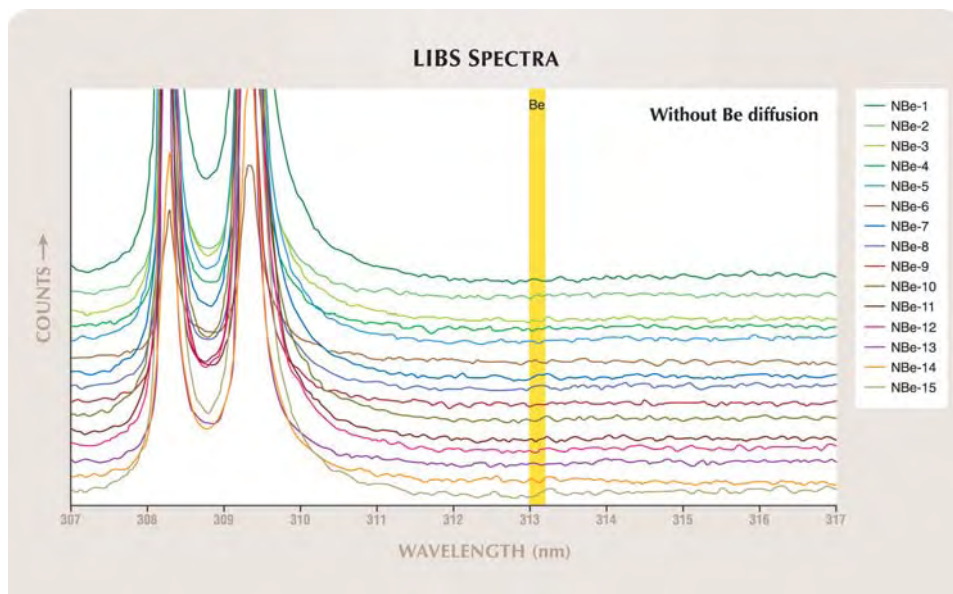


Figure 9. The LIBS spectra of the samples that were either untreated or heated by traditional methods (NBe-1 to NBe-15) do not show Be emission at 313.08 nm. The dominant peaks at about 308 and 309 nm are due to Al.

trum in figure 8 represents a single LIBS spot, it reflects only the Be concentration at that particular location. Consequently, to better characterize a sample with LIBS, it is often useful to analyze the stone in several places.

The spectra of two beryllium-free synthetic samples showed no Be peak at 313.08 nm, but they did show several peaks in the 310–314 nm region (figure 8) that are due to chromium (NBeS-1) and vanadium (NBeS-2).

Figure 9 presents the LIBS spectra of all the corundum samples that were not subjected to Be-diffusion treatment. The spectra are quite uniform, and none shows a Be peak at 313.08 nm. Although the composition of these samples varied (especially Cr and V), there do not appear to be any distinct chromium or vanadium emissions in the spectral range of 307–317 nm.

DISCUSSION

Our investigations show that Be-diffused sapphires can be reliably detected by LIBS. In one sample (BeS-1), our system was able to detect a Be concentration as low as ~2–3 ppm. As discussed by Pisutha-Arnoud et al. (2004), very low Be concentrations (on the order of 3 ppm) may result in the formation of a stable yellow (or brown, in Fe-free stones) color center in corundum, and this appears to be the case for the orange synthetic sapphire (BeS-1).

The Be diffusion-treated natural sapphires (Be-1 to Be-6) showed distinctly higher Be concentrations than the Be-doped synthetic sample. The levels of Be measured by LA-ICP-MS in these samples (4–49 ppm Be) are consistent with those reported for Be-diffused sapphires in the literature (see, e.g., Hänni and Pettke, 2002; Emmett et al., 2003). All the LIBS spectra from these samples showed a moderate to distinct Be emission peak centered at 313.08 nm.

A comparison of the Be-containing samples with the two untreated flame-fusion synthetics revealed no peak overlap at 313.08 nm from the corundum matrix. Chromium and vanadium peaks may be in the same range near 313 nm, as shown by the highly Cr- and V-doped synthetic samples (NBeS-1 and NBeS-2; figure 8), but they do not exactly overlap with Be emission. Potentially overlapping emissions from other elements were not observed; their emission intensity in the corundum matrix is too low to produce any interference with the Be emission at 313 nm.

In the natural untreated or traditionally heated corundum samples (NBe-1 to NBe-15), no Be emission at 313 nm could be detected. This was expected since LA-ICP-MS data on three of the samples (NBe-1, NBe-6, NBe-14) showed that beryllium was below the detection limit (generally <0.3–0.8 ppm).

CONCLUSIONS

Our investigations using the modified Ocean Optics LIBS 2000+ system (SSEF GemLIBS) were successful in detecting Be-diffusion of corundum. Based on extensive research, we have developed an analytical technique for routine testing of faceted corundum for the presence of beryllium.

Compared to other methods of Be detection, LIBS has several advantages. The sample preparation is very simple (i.e., attaching the stone to a glass plate with Blu-Tack), and no vacuum is needed for analysis. The LIBS instrument is much less expensive than SIMS or LA-ICP-MS, and it also is easier to maintain. (As a general rule, a LIBS system costs US\$20,000–\$90,000, whereas LA-ICP-MS ranges from \$200,000 to \$500,000 and SIMS may run from \$750,000 to over \$2,000,000.) When equipped with broad-band spectrometers, LIBS is capable of simultaneous multi-element detection (from low to high atomic weights). The detection limit for Be in corundum is quite low, at about 2 ppm (depending on the experimental parameters). After calibration and validation of a specific LIBS system, Be detection in corundum can be done by knowledgeable lab personnel without extensive training.

A disadvantage of LIBS is that it is slightly destructive. Even when it is properly used, the laser leaves small spots on the surface of the gemstone, similar to other Be detection methods such as LA-ICP-MS and SIMS. Also, the LIBS technique only yields qualitative to semiquantitative data, unlike the other two Be-detection techniques.

This article describes the first systematic use of LIBS in gemology, that is, for the detection of Be-diffused sapphires. LIBS may also have some potential for determining the geographic origin of gemstones and identifying color modification in pearls and other gem materials, since this technique can detect a full range of elements, even at trace levels. Moreover, its relatively low cost makes it a viable technique for many gemological laboratories.

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