LASER INDUCED BREAKDOWN SPECTROSCOPY (LIBS) AND ITS APPLICATION IN GEMSTONE TESTING

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Laser Induced Breakdown Spectroscopy, or LIBS is an analytical technique that uses a laser-induced spark to incorporate a sample of a surface into the very high temperature, 15,000 K, plasma. A spectrometer is used to measure the spectral line emission of ions and atoms as the plasma cools. The emitted spectral lines are indicative of both the presence of elements and their amount. They can be thought of as a 2-dimensional bar code or signature of the material. The sensitivity of the LIBS technique is directly proportional to the resolution of the spectrometer and the expanse of the spectral region it encompasses. A resolution of 0.1 nm FWHM or better is optimal for gem analysis and a range of 200 nm to 980 nm where all elements emit spectral lines is ideal. Since all elements have multiple emission lines in this region, their spectral signatures can easily verify the presence of these elements. Another very important specification for gem analysis is the one event signal-to-noise ratio of the system. A S/N of 250 allows for identification of even small peaks. These are the spectral and S/N specifications of the Ocean Optics LIBS-2000+ spectrometer. Since good LIBS technique involves sampling a surface into a high temperature plasma and not large ablation of the surface to get a sample as in ICP or MS analysis, the design of the laser and subsequent focus technique is paramount to success. Only Q-switched Nd-YAG lasers with a gradient radius mirror design are appropriate. The most common design, the highly efficient "stable resonator" as used in laser ablation technologies produces inadequate plasma for LIBS and great damage to a gemstone. Since the 1,064 nm emission of the class-IV, Nd-YAG laser is not eye safe, a third component of LIBS, the sample chamber is required. Its viewing plastic with an optical density (OD) of 6 at 1064 nm and its safety interlock provide for safe operation in a laboratory.

Its safety features should never be bypassed. The Ocean Optics system provides the tools for LIBS in gemstone analysis, but sampling technique is extremely important.

Only recently, laser induced breakdown spectroscopy LIBS has been applied on gemstones. Especially for the detection of beryllium-diffusion treated sapphires, this method has proven to be very effective (Hänni & Krzemnicki, 2004, Krzemnicki et al., 2004). In such a way it has become a reliable, fast and low-cost analytical tool to detect beryllium at ppm level (Radziemski et al., 1983).

Since the first studies on Be-diffuson treated sapphires, we have analysed a large number of corun-

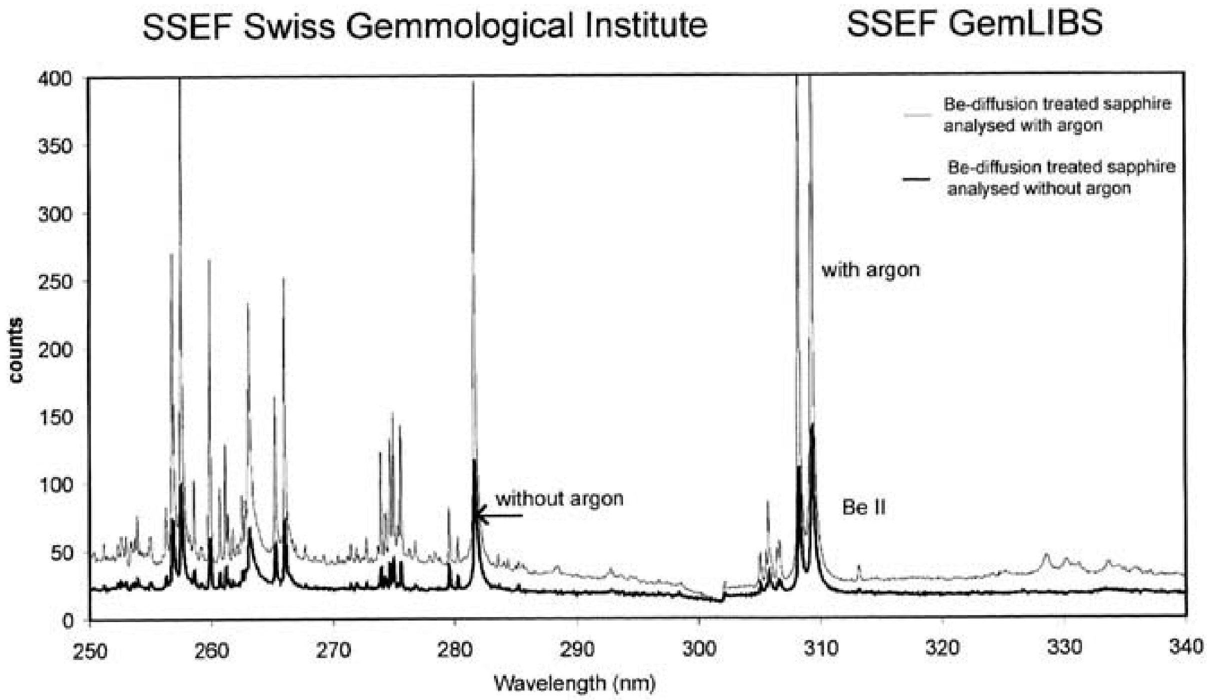

Figure1: LIBS spectra of a Be-diffusion treated sapphire analysed in air (dark line) and in an argon flow (bright line) showing the strong increase of the emission intensities when using argon.

dum, beryl, and chrysoberyl samples with our specially designed SSEF GemLIBS system, which is equipped with a single-pulsed Nd-YAG laser (1,064 nm). The laser vaporizes a tiny portion of the sample. The superheated ions and neutral atoms within the plasma produce a characteristic emission spectrum in the ultraviolet, visible, and near-infrared spectral range. The SSEF GemLIBS is equipped with a series of spectrometers which enable the simultaneous recording of the characteristic emission lines of chemical elements in real-time. Due to complex plasma dynamics, LIBS does not yield quantitative data. By using reference materials 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).

As with other laser-based techniques, LIBS is slightly destructive. Extensive testing has shown, that the laser spot on the surface can be minimized by choosing appropriate instrument parameters (e.g. reduced laser energy). Unfortunately, such a reduction of laser energy lowers the emission intensity. By using a constant argon flow in the sample chamber, we could increase the signal by a factor >4 (Figure 1). Furthermore, the peak-shape becomes sharper and some additional emission lines can be detected, which were hidden in the background when analysing in air.

For the detection of Be-diffusion treated sapphires,

a fast and reliable analysis. Prior to analysis, the sample has to be cleaned with ultrasonic. Be-diffusion is detected based on the main beryllium emission doublet at 313,042 nm and 313,107 nm. By using a constant argon flow even very low concentrations of 2 ppm beryllium are distinctly detectable with LIBS.

References:

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