

LETTERS TO THE EDITOR

From: Dr. Michael S. Krzemnicki (SSEF Swiss Gemmological Institute, Basel, Switzerland)
Prof. Dr. H.A. Hänni (SSEF Swiss Gemmological Institute, Basel, Switzerland)
Dr. Roy A. Walters, Ocean Optics, Inc (Orlando, Florida, USA)

Basel, 17. March 2005

Dear editor,

In a previous issue of the journal of The Gemmological Association of Australia (Volume 22, Number 4), Mr. Themelis reports on the application of laser induced breakdown spectroscopy in gemmology (LIBS: a spark of inspiration in the gemmological analytical instrumentation). In this article the author has made a number of statements, which are not conclusive and - on a scientific point of view - incorrect. As he is furthermore accusing our LIBS research group of incompetence and being misleading the gemmological community, we would like to clarify the following:

In his article, Mr. Themelis describes the results he obtained on 26 gemstones for which he collected numerous LIBS spectra. Unfortunately, in his article there is only one spectrum shown (fig. 5). Interested readers, who actually want to compare spectra of Be-diffusion treated sapphires with spectra of Be-free (heated or untreated) sapphires, should consult our recent article in *Gems & Gemology* (Krzemnicki *et al.*, 2004).

The displayed spectrum in the article of Mr. Themelis is even more misleading, as the high Be peak at 313 nm does not reflect the beryllium concentration of the green sapphire (A-04). The stone has been measured on the rough (only preformed) surface of the Be-treated sapphire, therefore, the Be-peak is reflecting the high Be concentration in the flux relics typically present on the surface of such a sample.

The general statement of Mr. Themelis, that LIBS is a rather unreliable method (with 20% "tolerance of error") is in total contradiction to our experience at the SSEF Swiss Gemmological Institute (LIBS in operation since April 2004 and offered as a service to our clients). We have compared more than one hundred cut stones from clients and many research samples with well-documented LA-ICP-MS data. No complaints

about damages were made, although LIBS is a slightly destructive method (Krzemnicki *et al.*, 2004). Our experience shows, that with optimized measurement parameters, we are able to detect Be concentrations as low as 2 ppm. Each stone with documented Be concentration higher than 2 ppm (LA-ICP-MS data) was positively detected with LIBS. As some stones are quite inhomogeneous, they may have to be tested on several spots along the girdle (see Krzemnicki *et al.* 2004). Concerning detection limits, Mr. Themelis states that concentrations as low as 1 ppm Be can be detected with LIBS. This statement is not explained by his experiments nor does he give any credits to literature (e.g. Radziemski *et al.* in 1983, describing a detection limit of 0.5 ppm for beryllium using LIBS). This is not astonishing, as in the whole text, Mr. Themelis does not mention research papers other than his own.

A closer look at the "tolerance of error" shows, that Mr. Themelis sums up different samples (chrysoberyl, beryl, corundum), analyzed with different measurement parameters representing different detection failures (Be not detected although it is present, and Be detected although it should not be present). Such a summing up is scientifically not correct. As an illustration: dark pearls may be treated with silver nitrate. Using X-ray fluorescence (XRF), silver is readily detected; but only when analyzing the treated pearl with adequate energy (e.g. 50 kV). When using lower energies (e.g. 10 kV), silver will not show up. In untreated pearls, however, sometimes an X-ray diffraction peak might occasionally be seen on the position of the silver peak. Obviously, nobody would calculate a "tolerance of error" without exactly defining an adequate energy level for silver detection with XRF and without prior subtraction for any diffraction features in that spectrum. For LIBS, it is the same. It is incorrect to calculate a "tolerances of errors" when the measurement parameters have neither been optimized or defined. In our numerous articles published since April 2004 (Hänni *et al.*, 2004; Krzemnicki & Hänni, 2004; Hänni & Krzemnicki, 2004; Hänni & Krzemnicki 2004; Krzemnicki *et al.* 2004) we have described in great detail our measurement parameters, which unfortunately Mr. Themelis, although known to him personally, did not take into consideration nor did he even mention any of our previous articles in his text.

As an important argument for the unreliability of LIBS, Mr. Themelis used the failure to detect beryllium in one chrysoberyl (sample A-18) with his LIBS setup. He explains this failure with a self-quenching effect, totally reducing the Be emission at 313 nm. Such self-absorption or line reversal may theoretically occur in a single

spectral line in perfect plasma, but such is not the case for LIBS, an imperfect plasma. Also, beryllium at such a high concentration level (about 18 wt% BeO in chrysoberyl) presents numerous emission lines in the spectral range between 200-900 nm. Self-absorption may explain the reduction (or even absence) of one emission line of beryllium, but not a simultaneous self-absorption of all emission lines in the whole spectrum. Prior to postulating self-absorption, it is absolutely necessary to check the intensity of the other Be-emission lines (e.g. at 234,9 nm, 265,1 nm, and 332,1 nm). In his article, Mr. Themelis does not give any hints that he even checked any further Be emission lines. In contradiction to Mr. Themelis, we have analyzed hundreds of beryls and many chrysoberyl samples with LIBS and have never seen any self-absorption for beryllium at 313,1 nm. We thus suppose, that the analyzed stone was in fact a yellowish sapphire (remember the stone was preformed, so no RI readings can be taken!, please consult also table 1, where the gemstone identity is given as yellow sapphire, and treated as chrysoberyl!). For comparison reasons, we include a spectrum of a chrysoberyl analyzed with our specially designed Ocean Optics LIBS2000 system. When our method of analyzing Be traces in sapphire was presented at the 3rd International Conference on LIBS and Applications 2004 in Spain, our paper (Krzemnicki & Hänni, 2004) was well received and positively commented by the professional LIBS researchers.

A final comment concerns the acknowledgement made by Mr. Themelis to Dr. J. Ponahlo from Ocean Optics, Inc. (USA). There has never been a person with the name Dr. J. Ponahlo working at Ocean Optics (Dunedin, USA) or even associated with the company! On his website, Mr. Themelis further explains that his conclusions are based also on tests conducted by the "chief scientist who developed the LIBS 2000 instrument at Ocean Optics". As that person, Dr. Roy A. Walters, Director of Research and Development at Ocean Optics, Inc., would like to point out, that he in no way participated in the testing or agrees with the conclusions of the article by Mr. Themelis. In fact he had never heard of him before this situation arose.

To conclude, we would like to express our astonishment that Mr. Themelis was able to present his very preliminary data in the much respected journal of the Gemmological Association of Australia, but also that with his personal arguments he is demeaning the possibilities of LIBS in gemmology and also our scientific integrity.

References:

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Reply from: Ted Themelis
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Dear Editor,

Well-informed members of the gemological community sensed the gem politics being played behind the scenes and the efforts Dr. Hänni exercised among colleagues, trade associations and organizers of gemological conferences to discredit my work. Nevertheless, I am glad that my opinion has made an impact in the industry. Here, I simply state the facts and stick to my guns:

- 1) My article "LIBS: A Spark of Inspiration in Gemmological Analytical Instrumentation" was the first article on LIBS published in gemmological literature (*Australian Gemmologist*, Oct.2004). Dr. Hänni should have given credit to my work in his article, which was published several months later (*Gems & Gemology*, Winter 2005).
- 2) As stated in my article the LIBS experiments were conducted early-May 2004 at Applied Photonics LTD (Skipton, UK), using a bench-type LIBS set-up. The conclusions were summarized in my article emphasizing the preliminary nature of my pioneer work, pending future developments. [Further details and illustrations were reserved for a different, on-going LIBS research project accepted in September 2004 by the Australian Gemmological Association]. On June 2004, similar samples were submitted to Ocean Optics for LIBS testing using a portable LIBS2000+, the same LIBS configuration Dr. Hänni is advertising and trying to sell. The LIBS test results conducted by Ocean Optics along with the samples were received on Jan.10, 2005 where 3 out of 20 samples were wrongly