Application of laser ablation and laser-induced breakdown spectroscopy (LIBS) on silicate glass samples

Ph.D. thesis booklet

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Introduction

Laser-Induced Breakdown Spectroscopy (LIBS) is based on the following principle. A high-energy short laser pulse is focused on the sample, a small portion of which evaporates, the size of which is typically in the range of 10-100μm-s in diameter and depth. By excitation and partial ionization of the atoms of the evaporated material plasma is formed, the spectrum of which can be analyzed by optical spectroscopy and the elementary composition of the sample can be determined.

LIBS has many advantages, among others it's fast and flexible: gives almost immediate results after the analysis, easy to automate, the apparatus is relatively easy to operate and the costs are favorable. These advantages make LIBS an excellent choice for industrial applications and in situ field analysis. For the purpose of this work, it is also worth it to point out, that there are many similarities between LIBS instrumentation and that of Raman spectroscopy as well as various other laser ablation techniques, such as laser cleaning and material processing. It makes combined application of these techniques possible.

LIBS is capable of both qualitative and quantitative analysis, however calibration of the latter can be challenging. The correlation of the intensity of the spectral lines and analyte concentration is linear in a wide range, but the slope of the function is subject to matrix effects, and therefore the calibration must be done for all analytes and matrices. It often requires multivariate regression analysis which needs plenty of measurements and calibration samples. One can overcome this difficulty by calibration-free (CFLIBS) and one-sample calibration methods, but these techniques cannot fully substitute calibration-based LIBS due to lower accuracy.

Another important shortcoming of LIBS analysis is, that a certain damage to the sample is inevitable, at least in case of solid samples. In the best case it means generation of craters of couple of microns in depth and diameter, but consecutive laser pulses or suboptimal sampling geometry can lead to more extended sample damage. This phenomenon limits the groups of samples that can be analyzed by LIBS, and in case of valuable or vulnerable samples, special care is needed when choosing measurement parameters to minimize damage.

Objectives

The scope of my work was to analyze feasibility of laser ablation and LIBS technique on silicate glass samples for material analysis and leaser cleaning. Glass manufacturing and processing is of great economic importance, meanwhile LIBS analysis of glasses is technically less studied, compared to analysis of metals. At the same time, it is a reasonable expectation that LIBS can be a very useful tool of glass analysis due to the advantages mentioned above.

I put three questions in the center of my research.

The first was the investigation of laser induced damage during LIBS analysis and laser cleaning in connection with it. My scope was to get measurement settings which allow the analysis of valuable samples: resulting in possibly small sample damage and suitable LIBS spectrum.

Second goal was to analyze Lithium content in glass. It is a relevant industrial problem: Lithium is widely used as an additive in glass manufacturing, while it is not obvious to measure the actual Lithium content of the product during the manufacturing process. This is a shortcoming of cost and quality control, and LIBS is an ideal candidate resolve the issue.

My third task was to carry out realization of the laser-cleaning of a discolored silica optical window. Here, the main difficulty was that the light absorbing layer was inside a closed Rubidium containing silica cell, which could not be opened neither for cleaning nor for analysis purposes.

Furthermore, my scope was to investigate feasibility of common use of LIBS and Raman analysis with laser cleaning on a suitable sample.

Experimental

LIBS apparatus

At the Budapest University of Technology Department of Atomic Physics two LIBS instruments were installed. One is a high-performance tabletop setup, which was assembled from an echelle spectrograph (Andor Mechelle 5000) and an industrial laser (Quantel Brilliant). The laser provides pulses of 1064nm, 532nm and 355nm wavelengths with 350mJ, 180mJ and 60mJ pulse energies respectively and pulse length of 3.8ns. The spectral range of the detection is 200nm-1000nm with the resolution of 1/4000 ($\Delta\lambda/\lambda$). Laser spot size in the experiments was regularly between 0.01mm-0.1mm, dimensions of the laser plasma were typically in the range of mm for diameter and 10mm for length, strongly dependent on the measurement settings.

For most of the experiments this device was used, in some cases it was supported by a StellarNet PortaLIBS-2000 portable LIBS device. Key parameters are: 50mJ pulse energy at 1064nm laser wavelength, 200-800nm spectral range with 0.2nm resolution.

Analysis of crater formation

It is well-known that during LIBS analysis degradation of sample is inevitable, but it can be limited by careful setting of measurement parameters. Glass samples present a special challenge due to their fragility and low tolerance to heat stress. Question is, how they are damaged when using different measurement setups, which setups are suitable for the preservation of the samples and how it influences LIBS spectra.

The case of laser cleaning is very similar, effect of laser irradiation to glass samples is a fundamental issue. By laser cleaning the aim is the minimization of the damage to the sample. In case of LIBS analysis, being the ablation of the sample material inevitable, the question is the extension of the minimal damage that is still necessary to perform the analysis. Since the literature gives little support, the investigation had to be done from the very fundamentals.

In both cases key question is the position of the plasma to the sample. In case of cleaning, no damage visible by optical microscopy can be accepted, in case of analysis, it is necessary to investigate the damage that corresponds the settings of a conclusive analysis.

In the experiments plasma was generated by focusing the laser beam in front of the sample surface, on the surface and behind the surface, into the bulk of the sample. Also the effect of laser wavelength was investigated. During the tests, LIBS spectra generated by various irradiation settings were analyzed together with optical and electron microscope images of the damage and occasional profile measurements. Finally, the spectral information was correlated to the damage.

Systematic analysis of commercial window glass samples showed conchoidal fractures, microcracks and diffuse internal damages inside the bulk of the sample. None of these can be accepted at an object that is either intended for later use or representing a significant value. When focusing a 532nm beam in front of the sample, the aforementioned damage patterns do not appear and many

consecutive shots – as much as 100 – can be applied to the same location. In this case, the plasma is predominantly formed in the air and the glass material is ablated into the air plasma. By setting the focal position, the amount of ablated material can be optimized and damage to the sample minimized. The emission spectrum of sample can be well analyzed since there is no overlapping between spectral lines of Nitrogen and metallic constituents of glass.

All the settings in my experiments proved to be suitable for LIBS analysis, but there were strong differences in spectral quality. To achieve good analytical capabilities, low standard deviation and high signal-to-noise ratio of the spectral line intensities are required. From this point of view, the best results were obtained by 1064nm laser beam focused to the bulk. But it leads to extensive damage to the sample, so these settings are not suitable to analysis of precious objects.

Lithium analysis in silicate glass

Lithium is added to the glass batch in form of oxide or carbonate, in small concentration to set melting temperature, in high concentration to set thermal expansion coefficient or electric conductivity. The use of Lithium is therefore a common practice, but the measurement of its concentration is challenging, since X-ray fluorescence (XRF) is not sensitive to it. At the same time Lithium exhibits strong optical spectral lines, which are well detectable even at low concentration. They are at 610.4nm and 670.8nm, the latter being the stronger one, and it does not overlap with any spectral line of other constituents of silicate glass. Considering the literature of LIBS analysis of Lithium bearing minerals, LIBS is an optimal candidate for Lithium analysis in silicate glasses. The figures merit is the key point, such as limits of detectable concentration and accuracy of measurement. To get them, I decided to use a univariate regression analysis using the spectral line at 670.8nm.

First and technically challenging task was getting the calibration sample series. Since it was not possible to purchase any, the sample series was prepared at the BUTE Department of Atomic Physics. Results with mixture of Lithium-niobate and silica powder were encouraging, but the accuracy of the measurements were below the expectations – mostly due to unsatisfactory glassification of the samples.

Considering these experiences an 8-piece calibration series was prepared by adding 0-3% w% Lithium-carbonate to Lithium-free soft glass and melting them together in a graphite jar. (Advantage of Lithium-carbonate over other Lithium bearing additives is the low melting temperature.) The intensity-concentration calibration curve was created by analyzing 10 measurement points on each sample, and was found linear. The measurement results were much better with the 670.8nm line than with the 610.4nm line, that corresponds the expectations of the literature. Limit of detection was 7ppm Lithium carbonate (1.3ppm pure Lithium), relative error of concentration measurement was 5%.

Cleaning of Rubidium vapor cell

The third goal of my research was to remove a layer of unknown origin from the internal surface of the optical window of a Rubidium vapor cell used in homogenous plasma experiments.

I was provided a worn-off Rubidium vapor cell in the frame of a cooperation between Wigner Research Center and BUTE Department of Atomic Physics targeting common use of LIBS and Raman spectroscopy. The cell had been used by the Laser Particle Accelerator Research Group in experiments for real-time diagnosis of Rubidium plasmas, where it was replaced due to discoloration

of an optical window. The unwanted layer had been formed apparently on the internal surface of the window.

Cleaning the window was challenging due to multiple reasons: the cell could not be opened and the window was not get damaged during the procedure. The standard solution with these damaged cells was replacing the cell with a new one.

I realized that the layer could be ablated by focusing the laser beam through the intact (not discolored) window and gradually increasing its energy. Using my experiences with crater formation on glass samples I focused the laser beam in front of the target surface. As a result, the cleaning was achieved by the divergent beam decreasing heat stress of the material of the window. By this method, the layer was ablated without opening the cell or damaging the window. The removal of the layer was verified by optical microscope and subsequent Raman spectroscopy analysis.

Thorough investigation of the layer by Raman spectroscopy revealed that its material was Rubidium-silicate.

Novel scientific achievements

Thesis 1: I showed that LIBS is a suitable technique for quasi non-destructive analysis of glass objects. I specified measurement settings that ensure quasi non-destructive analysis and provide LIBS spectra of good quality. From the point of sample preservation, the best settings were the application of 532nm laser beam focused 1mm in front of the sample. I also concluded that focusing an 1064nm beam in the bulk of the sample results in better signal-to-noise ratio, but leads to stronger degradation of the sample.

Thesis 2: I showed, that LIBS technique is suitable for quantitative analysis of Lithium in silicate glasses. With a self-made sample set I calibrated the measurement using univariate regression analysis, I determined the limit of detection and the accuracy of the quantification. Based on the linear fit to the intensity-concentration function of the Lithium spectral line at 670.8nm, the limit of detection is 1.3ppm.

Thesis 3: I recognized that laser cleaning was suitable for the removal of an absorbing layer, that hinders normal operation, from the internal surface of a Rubidium vapor cell without opening the cell itself. During the procedure a high-power laser beam was focused through the intact window of the cell by a long focal length lens in front of the surface to be cleaned, which removes the layer using selective ablation by single pulses of appropriate energy. In the same time no ablation crater or microcrack occur on the window. With this method, I realized a laser cleaning technique capable of removing Rubidium-silicate layers from silica substrates.

Publications related to the thesis points

[T1.] **Gádoros, P.**, Péczeli, I., Kocsányi, L., & Richter, P. (2023). Crater Formation and Damage Optimisation on Soda-Lime Glass for LIBS Analysis. *JOURNAL OF LASER MICRO NANOENGINEERING*, *18*(1), 51–57. http://doi.org/10.2961/jlmn.2023.01.2009

[T2.] **Gádoros, P.**, Váczi, T., Himics, L., Holomb, R., Bolla, R., Veres, M., & Kocsányi, L. (2021). Comparative analysis of lithiated silica glasses by laser-induced breakdown spectroscopy and Raman spectroscopy. *JOURNAL OF NON-CRYSTALLINE SOLIDS*, *553*. http://doi.org/10.1016/j.jnoncrysol.2020.120472

[T3.] **Gádoros, P.**, Czitrovszky, A., Nagy, A., Holomb, R., Kocsányi, L., & Veres, M. (2022). Laser cleaning and Raman analysis of the contamination on the optical window of a rubidium vapor cell. *SCIENTIFIC REPORTS*, *12*(1). http://doi.org/10.1038/s41598-022-19645-z

Other publications

[4] Majer-Baranyi, K., Barócsi, A., **Gádoros, P.**, Kocsányi, L., Székács, A., Adányi, N. (2022). Development of an Immunofluorescent Capillary Sensor for the Detection of Zearalenone Mycotoxin. *TOXINS*, *14*(12), 866. http://doi.org/10.3390/toxins14120866

[5] Gémes, B., Takács, E., **Gádoros, P.**, Barócsi, A., Kocsányi, L., Lenk, S., Székács, A. (2021). Development of an Immunofluorescence Assay Module for Determination of the Mycotoxin Zearalenone in Water. *TOXINS*, *13*(3). http://doi.org/10.3390/toxins13030182

[6] Lenk, S., **Gádoros, P.**, Kocsányi, L., Barócsi, A. (2016). Teaching laser induced fluorescence of plant leaves. *EUROPEAN JOURNAL OF PHYSICS*, *37*(6). http://doi.org/10.1088/0143-0807/37/6/064003

[7] Lenk, S., **Gádoros P.**, Kocsányi, L., Barócsi A. (2015). Demonstration of plant fluorescence by imaging technique and Intelligent FluoroSensor. *PROCEEDINGS OF SPIE - THE INTERNATIONAL SOCIETY FOR OPTICAL ENGINEERING*, *9793*. http://doi.org/10.1117/12.2223179

[8] **Gádoros P.**, Péczeli I., Kocsányi L., Richter P. (2012). Damage optimization of LIBS analysis of glass samples. Poster section, 7th International Conference on Laser Induced Breakdown Spectroscopy (LIBS 2012), Luxor, Egypt, 29 September-4 October 2012