Metrol. Meas. Syst., Vol. 30 (2023) No. 2, pp. 273–287
DOI: 10.24425/mms.2023.144872

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METROLOGY AND MEASUREMENT SYSTEMS
Index 330930, ISSN 0860-8229
www.metrology.wat.edu.pl

M&MS

COLLINEAR DOUBLE-PULSE LASER-INDUCED BREAKDOWN SPECTROSCOPY USING Nd:YAG LASER GENERATING TWO NANOSECOND PULSES OF REGULATED ENERGY RATIOS

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Abstract

In the paper results of single- and double-pulse LIBS (Laser-Induced Breakdown Spectroscopy) measurements in collinear geometry are described. The experiments were performed using a unique self-made Nd:YAG laser operating in the Q-switching regime, where the laser transmission losses are switched. Such a laser allowed for an easy and quick change of the operating mode (one and two pulses), free shaping of the energy ratio of the two pulses (division of the energy of a single pulse into two parts) and a smooth change of the delay time between pulses in the range from 200 ns to 10 µs. To our knowledge, such a laser was used in LIBS measurements for the first time. LIBS experiments revealed strong self-absorption depending on energy ratios carried out in the first and second laser pulse in the double-pulse mode. This was confirmed also by statistical factorial analysis of LIBS spectra. Plasma temperature and LIBS signal enhancement were measured both for energy proportions between the first and the second laser pulse and for the first-to-second-pulse delay.

Keywords: dual-pulse laser, double-pulse LIBS, signal enhancement, self-absorption, factorial analysis.

1. Introduction

Laser-Induced Breakdown Spectroscopy (LIBS), first described in 1963, [1], is a long-known method for quasi non-destructive studying of materials, determining their chemical composition, the content of admixtures, impurities, *etc.* In the LIBS experiment, the process is characterized by dynamics depending on the laser pulse energy and power, focal size, material properties, *etc.*, however, there must always be a rapid creation of a plasma spot (at times of the order of single ns, comparable to the laser pulse length) and its gradual decay related to plasma relaxation processes, usually lasting tens of microseconds. The emission spectrum of plasma radiation generated as a result of these relaxation processes carries information about the presence of chemical composition in the tested sample. The level of the light signal emitted from the surface is very small and sensitive detection equipment is necessary. At the same time, increasing the pulse energy is rather unjustified because we aim at a minimum loss of sample material. A number

Article history: received November 2, 2022; revised January 23, 2023; accepted February 17, 2023; available online June 18, 2023.

of papers devoted to LIBS have been published and useful reviews describing various aspects and applications of LIBS can be found, for example in [2–10]. The way to increase the sensitivity of the LIBS method is to expose the tested sample twice or more. The first work on *double-pulse* (DP) LIBS appeared in 1969 [11]. There is a number of reports in the literature on experiments with the double-pulse LIBS method carried out under different sample exposure conditions (pulse duration, time interval between pulses, pulse energy ratio, radiation wavelength, geometry, *etc.*) [7,9,12,13]. Measurement results and their interpretation are widely described, also in reviews [8, 14–17]. In general, the four main irradiation geometries in DP LIBS are used. In the orthogonal geometry there exist two variants – the so-called pre-spark mode with the first pulse parallel to the target surface and the second pulse perpendicular to it [8, 18, 19], and the second regime –a re-heating configuration with the first pulse creating a plasma from the target and the second pulse parallel to the target additionally heating the plasma [20–22]. The next beam configuration geometry – a collinear one – with two pulses perpendicular to the target [8, 23–25] is the case analyzed in the paper. And the last one, a geometry with crossed beams usually perpendicular to each other, both striking the target, is rather rarely applied and physical phenomena occurring in this experiment can be best described as a specific case of the collinear configuration [26].

For the double-pulse LIBS to make sense, *i.e.*, to introduce a new quality, the interval between the pulses must not be too long, *i.e.*, no longer than the 1^{st}-plasma lifetime. Otherwise, we deal with two isolated processes and the quantitative differences between the single- and double-pulse methods will arise only as a result of a possible non-linear dependence of energy of emitted radiation in relation to the energy of the incident pulse. If, on the other hand, the second pulse appears at the moment of the presence of the first plasma plume above the surface of the irradiated sample, the situation becomes qualitatively different. Due to the relatively short lifetime of the plasma (usually a few μs), the interval between the pulses should be of this order. However, it must not be too short since the first plasma can effectively shield the energy delivered by the second laser pulse [27]. At present, the lasers used in LIBS are mostly Q-switched lasers, in which almost all the energy accumulated in the active material is released in a very short-term generation process in the form of a nanosecond pulse, although there is a number of papers on DP LIBS with ps and fs lasers, for example [28–30]. This energy is accumulated as a result of pumping which lasts much longer, usually within a time comparable to the lifetime of the active material (in solids it is of the order of several hundred μs). Thus, in a pulsed laser, the next strong pulse cannot appear while the plasma is emitting radiation. The solution is to use two identical or similar lasers synchronized with each other, which allows you to arbitrarily change the exposure conditions, but is twice as expensive and more complicated. This drawback can be overcome if one pulsed laser emitting two pulses of comparable energy is used which is the case of the double-pulsed LIBS experiment described in the paper.

2. Materials and Methods

2.1. The laser

In [31] we presented our double-pulse laser, in which the energy accumulated as a result of pumping is released in the form of two pulses of regulated energy ratios (including identical pulses *i.e.*, having the same energy and duration) thanks to the gradual switching of laser transmission losses, while the sum of the energy of these pulses being equal to the energy of a single pulse of the optimized laser with a single loss switching for the same single pump pulse energy. That work, [31], presents the theoretical analysis, the results of calculating the parameters of such a laser and a report on measurements with this double-pulse laser. Same, in terms of measuring conditions, pulses of energy of about 20 mJ and duration of about 30 ns were generated.

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A careful analysis of equations presented in [31] shows that the condition of equal pulse energy, although attractive for practical reasons, is only a special condition and that the division of energy stored in the laser medium into two portions released in two pulses may be in proportions other than 1:1, if we do this by switching transmission losses. The sum of the energies of such pulses is always equal to the energy of a single optimal pulse, but their duration is usually unequal and the stronger pulse is always shorter. For LIBS experiments, this property of ns-pulse generation when switching transmission losses allows the use of one laser generating two pulses with energies and time intervals between them smoothly regulated.

In the experiment, the Nd:YAG laser described in [31] was used. It included an active crystal head transversely pumped with two arrays of laser diodes with a total maximum power of 4 kW. Each matrix had a separate power supply allowing for smooth adjustment of the duration and current of the pump pulse. The resonator consisted of two flat, totally reflecting mirrors, and the role of the output mirror was performed by an electro-optical switch based on the RTP crystal with a quarter-wave voltage of 800 V. The transmission of the Pockels switch acting as the output mirror is expressed by formula (1):

$$T_{oc} = \sin^2 \frac{\pi}{2} \frac{U}{U_4} . \tag{1}$$

With a quarter-wave voltage, the transmission of the output mirror is close to unity (it was kept during pumping the laser), and in the absence of voltage, it is close to zero (fully closed resonator). The intermediate voltages corresponded with a very good accuracy of the transmission expressed in the formula above which was confirmed in [31].

Pulse operation conditions were forced by switching the Pockels cell voltage from the quarter-wave voltage $U_{\lambda/4}$ to the voltage U_0 corresponding to the optimal (for a given pump energy) transmission for the single-pulse operation, while in the case of double-pulse operation, the first voltage switching was from the quarter-wave voltage to the U_1 voltage resulting in the generation of the first pulse of a given energy (depending on the desired energy ratio of the train pulses, for instance 2/3 of the single pulse energy, then the energy ratio of two pulses was 2:1), and the second one from the same voltage U_1 to the voltage U_2, which made the energy of two pulses equal to the energy of a single pulse for the same pump energy. In this way a desired energy ratio was experimentally chosen easily and quickly. In Fig. 1 an example of operational characteristics of the laser in double-pulse mode are presented.

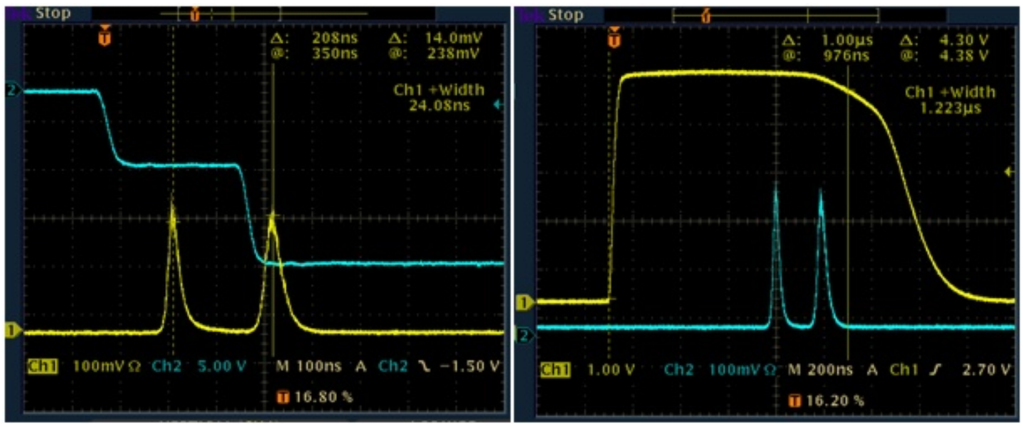

Fig. 1. Voltage switching (left-blue), the synchro pulse (right-yellow), and laser pulses in the DP LIBS mode for different time scales (left and right-bottom traces).

2.2. Experimental

The measurement stand is presented in Fig. 2. It is a typical experimental arrangement applied in LIBS research. It consists in two main parts: a laser source for plasma generation and a detection system for data collection and processing. In the work, as mentioned in Subsection 2.1, we used a self-made Nd:YAG laser that could generate both single or double pulses and to easy interpret and analyze the data we set one output laser energy equal to 20 mJ for both operation modes. This energy value was the pulse energy in a single mode operation while in a double-pulse operation it might be divided in the following ratios (first pulse energy-to-second pulse energy): 5–15 mJ, 7–13 mJ, 10–10 mJ, 13–7 mJ, and 15–5 mJ. Pulse energy measurements were performed using a Laser Precision Rj7300 meter with a RjP736 pyroelectric head that allowed to measure the energies of pulses not longer than 1 ms, so the interval between pulses of a few µs was justified. Moreover, it was possible to adjust the pulse spacing in the range from 200 ns to 10 µs.

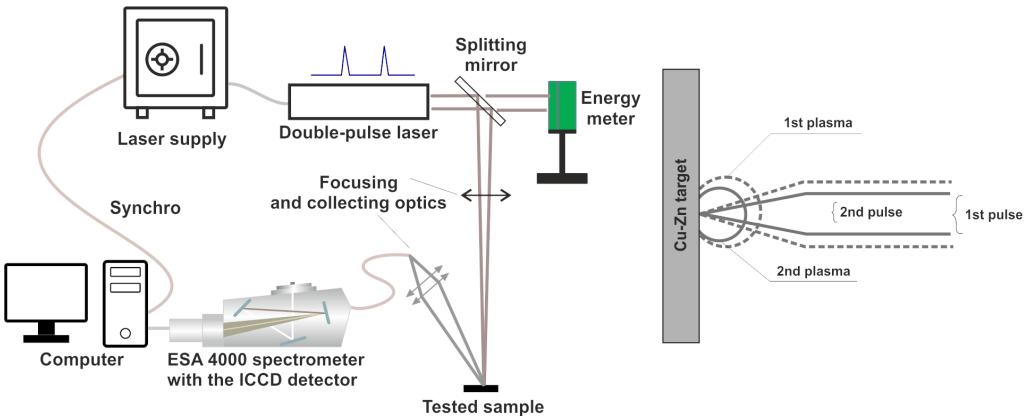

Fig. 2. Scheme of the experimental setup (left) and experiment geometry (right).

The main element of the detection system was an ESA 4000 echelle spectrometer (LLA Instruments GmbH& Co KG, Berlin, Germany). It was equipped with a Kodak KAF 1001 CCD matrix with an ICCD amplifier, thus allowing registration of LIBS spectra with gate widths between 20 ns and 16 ms in the 200–800 nm spectral range. Based on the analysis of the spectra, we found that real spectral resolution of the system was about $\lambda/\Delta\lambda \sim 20000$ (the manufacturer gives the value $\lambda/\Delta\lambda \sim 40000$ with respect to one pixel of the Kodak CCD matrix in the ESA 4000 technical specification – in our measurements, we assumed the use of a safer resolution of two pixels, which gives the value of 20,000). A certified Cu-Zn (Cu 55%, Zn 45%) MB1 binary alloy from the Institute of Non-Ferrous Metals, Gliwice, Poland, was chosen as a LIBS target. The initial stage of the experiment consisted in selection of optimal conditions for LIBS measurements, ensuring the highest signal-to-noise ratio. The best results were observed for a 500 ns interval between laser pulses and for a 500 ns time delay between the second pulse and the beginning of the measurement window. The gate width was set to 500 ns. We started measurements with the analysis of several Cu and Zn atomic spectral lines, namely, Cu I 261.837, Cu I 282.437, Cu I 296.115, Cu I 324.754, Cu I 327.395, Cu I 427.511, Cu I 510.553, Cu I 515.327, Zn I 468.014, Zn I 472.216, and Zn I 481.053 nm. The intensities of Cu II and Zn II lines were weak and too fluctuating to be reasonably measured and processed.

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2.3. LIBS spectra processing

In each experimental configuration (SP or DP LIBS, energy proportions between the 1st and the 2nd pulse or inter-pulse delay in DP LIBS) we took 10 LIBS spectra. The raw LIBS spectra were processed using three software packages. At the beginning, data processing used the EsaWin software (S/N 5207 version 13.9.0) for qualitative analysis of the spectra and optimization of the laser starting from the LIBS point of view. After selection of the spectral lines of interest, their intensities were transferred to CSV or XLS files which allowed starting a semi-quantitative processing. Finally, to check the trends observed in LIBS results, we used STATISTICA version 10 PL in which we applied *Factorial Analysis* (FA) [32–34]. This is one of techniques used in statistical multivariate analysis, similar to the better-known *Principal Components Analysis* (PCA) method [32, 35, 36]. They both use orthogonal, linear conversion of the input data set (LIBS spectra in our case) into the new variables' set called factors or components. Our input LIBS spectra dataset formed a relatively huge matrix (including 35 LIBS intensities in 54,611 wavelength intervals in the 200–800 nm spectral range). The FA results were presented in a graph showing similarities and differences of LIBS spectra reflecting thermodynamic conditions of plasma generated in SP or DP LIBS experiments.

3. Results and Discussion

3.1. Spectral lines description

Although we selected several spectral lines, not all of them appeared suitable for processing, since two resonance copper lines Cu I 324.754 nm, Cu I 327.395 nm seemed to be undergoing a very strong self-absorption or even self-reversal which is shown in the insert in the measured exemplary LIBS spectrum presented in Fig. 3. The self-absorption was numerously observed in LIBS experiments and described [24, 37, 38]. A useful review concerning self-absorption effects and mechanisms in LIBS plasmas including different approaches to determine the self-absorption

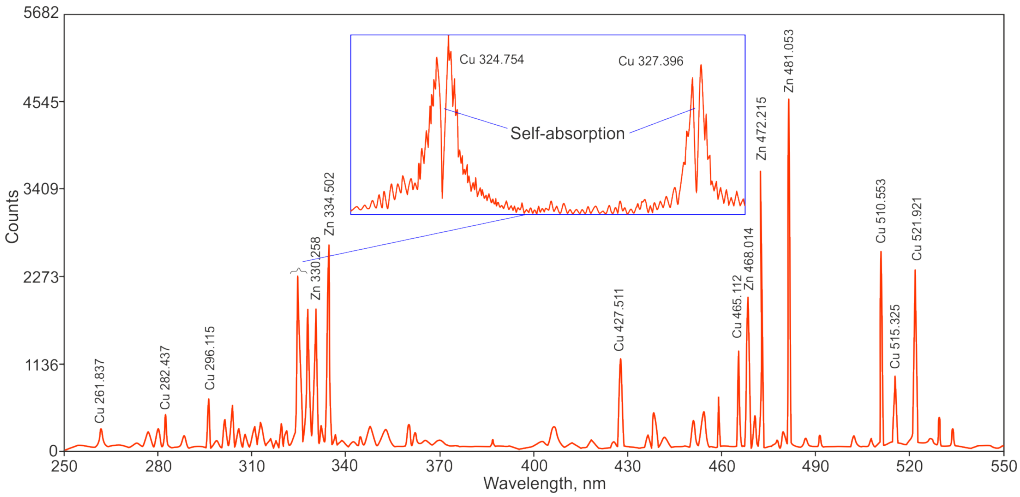

Fig. 3. Exemplary Cu-Zn plasma spectrum in the DP-LIBS experiment (1st pulse 7 mJ, 2nd – 13 mJ, inter-pulse delay 500 ns).

scale and its influence on plasma characteristics is shown in [39]. For further calculations we selected Cu I 261.837, Cu I 282.437, Cu I 510.553, Cu I 515.327, Zn I 472.216, and Zn I 481.053 nm lines.

3.2. Plasma parameters

The first part of the experiment was devoted to selection of optimum parameters for LIBS measurements. Preliminary measurement results showed that the most repeatable and reliable results were registered for a 500 ns inter-pulse delay, a 500 ns gate width and for gate delay also equal to 500 ns. Further, all results were compared to the data for a single laser pulse of 20 mJ energy. The results are shown in Fig. 4 for two Cu I and two Zn I lines and 250 ns and 500 ns inter-pulse delays. The 250 ns inter-pulse delay was too short to observe typical advantages of DP LIBS such as signal enhancement.

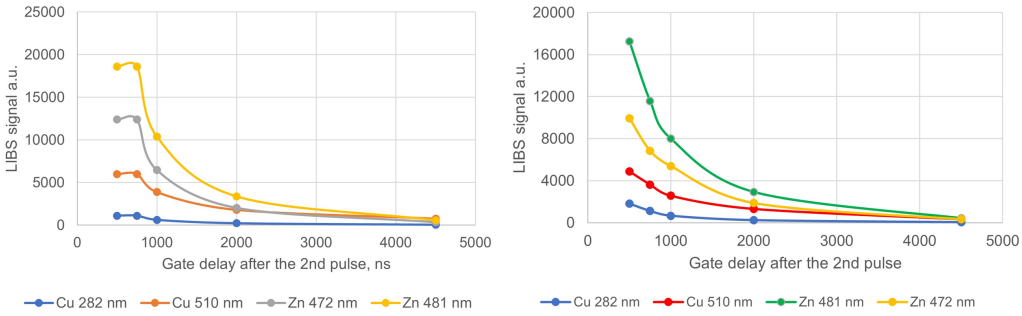

Fig. 4. 500 ns LIBS signals for various gate delays and 250 ns (left) and 500 ns (right) inter-pulse delays.

Measurements for a 750 ns inter-pulse delay were not satisfactory since the LIBS signal was more fluctuating and not stable enough to assure credible results, and, additionally, the counts were weaker.

In both modes, single-pulse or double-pulse LIBS, laser energy amounted to 20 mJ. It is clearly shown in Fig. 5 that in SP LIBS there is almost no self-absorption or self-reversal of Cu I resonance lines observed. The self-absorption was always present in the double-pulse experiment for all investigated energy configurations: 5–15 mJ, 7–13 mJ, 10–10 mJ, 13–7 mJ, and 15–5 mJ, and also for large gate delays – we observed it also for 5 µs delays. In the single-pulse LIBS measurements the stronger self-absorption was stated for 10 mJ pulses, while for a 20 mJ single laser pulse energy it was not observed. An example of this phenomenon is shown for the Cu I 324.754 line profile sequence presented in Fig. 5, where there are shown results for 500 ns gate widths and 500 ns gate delays after the laser pulse, regardless of whether it was a single or double laser pulse. However, a certain tendency was seen in the DP LIBS mode – the stronger first laser pulse, the weaker and shallower self-absorption and self-reversal.

The strong self-absorption can be explained by a larger plasma volume in the case of DP LIBS [23, 37, 40], which additionally supports self-absorption processes enlarging an optical path along which the observation is carried out.

Such behavior of the spectra can be related to plasma temperatures higher for 20 mJ single laser pulses than those for of 5–15 mJ laser energies of the first laser pulse in double-pulse experiment. For higher temperatures occurring mainly in hot central plasma, the population of

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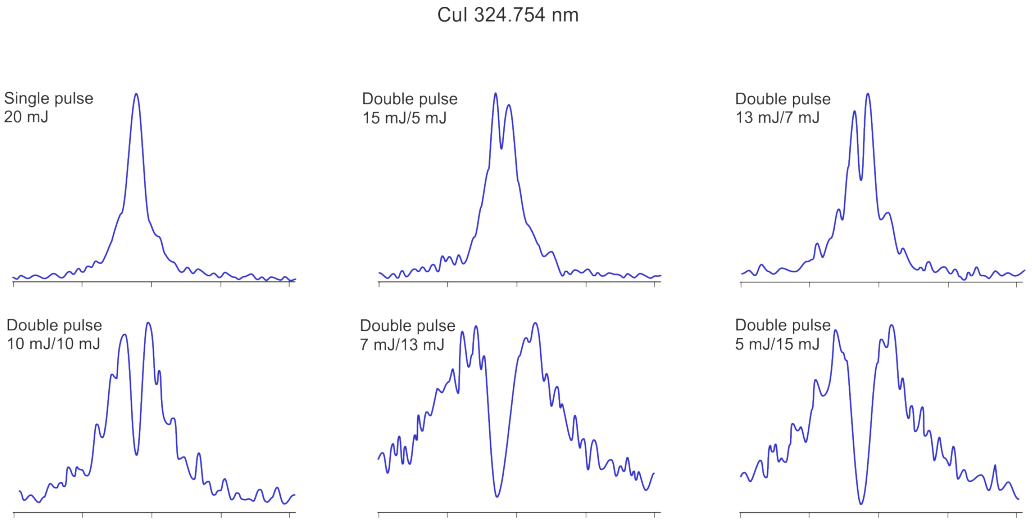

Fig. 5. Cu I 324.754 nm line profile. All spectra were taken for 500 ns gate widths and 500 ns gate delays after the laser pulse (the second one in the DP-LIBS mode). The wavelength scale starts at 324.4 nm and ends at 325.2 nm.

highly excited levels is larger than in low temperature outer regions of the plasma plume. Atoms in cooler outer zones reabsorb mostly radiation from the first excited levels. In hot plasma, lower excited levels are relatively less populated than other highly excited levels and that is why the self-absorption was not observed for the single pulse 20 mJ plasma. For 5–15 mJ and 7–13 mJ cases (the lowest row in Fig. 4) the 1st pulse-plasma temperature is lower, and the self-absorption of radiation emitted from relatively cooler central plasma is more effective than for 20 mJ plasma in which it was not observed. To check plasma temperature in SP and DP LIBS we have calculated excitation temperature for Cu I, Cu II, Zn I, and Zn II lines appearing in the spectra. Average plasma temperatures measured for DP LIBS pulse energy configurations are shown in Fig. 6. The results refer to the time distance between pulses equal to 500 ns. For comparison, temperatures for single-pulse LIBS (10 mJ and 20 mJ) are also shown in Fig. 6.

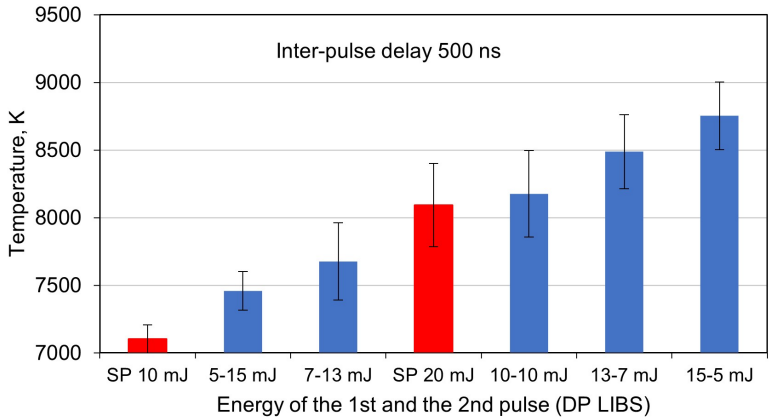

Fig. 6. Plasma temperature versus pulse energy (red bars – SP, blue bars – DP).

For experimental parameters presented in Fig. 6, the stronger second laser pulses in our collinear geometry (left side in Fig. 6) did not increase plasma/excitation temperature. Plasma temperature was higher for stronger first DP LIBS pulses (the right part of Fig. 6).

In many papers [8, 19] there were also observed higher plasma temperatures in DP LIBS as compared to SP LIBS, but in [23] DP LIBS temperatures were similar to SP LIBS ones. As it is seen in Fig. 6, in our case we measured temperatures of 7000–8700 K for DP LIBS while in SP LIBS around 7000 K for a single 10 mJ pulse and a little bit more than 8000 K for 20 mJ plasma. Temperature values in our work are similar to those reported in papers [8, 19].

Moreover, due to observation geometry, we registered signals averaged along the direction of observation. This, of course, could result in lower measured temperature values. In our measurements, the maximum excitation temperature was observed for DP LIBS with 13–7 mJ and 15–5 mJ pulse configurations.

It was suggested in [41] that in collinear geometry, due to lowered density of the first pulse plasma near the sample surface, the stronger second laser pulse interacts mainly with the sample surface and the plasma can expand easier and faster which leads to enlargement in the plasma volume which, in turns, can lead to stronger self-absorption. On the other hand, the larger volume can create a larger signal which, consequently, can give larger enhancement observed in non-resonant lines.

Temporal plasma temperature and plasma electron density variations related to the time delay of the registration window are shown in Fig. 7 in which results for 10–10 mJ DP LIBS are presented. To evaluate electron density, we used the Cu I 510.554 line. Like other lines, it was broadened mainly as a result of the Stark effect in which the main contribution to the line broadening was due to the electron collision component. To calculate the electron density, we measured the widths of this Cu I line and used data shown in [42].

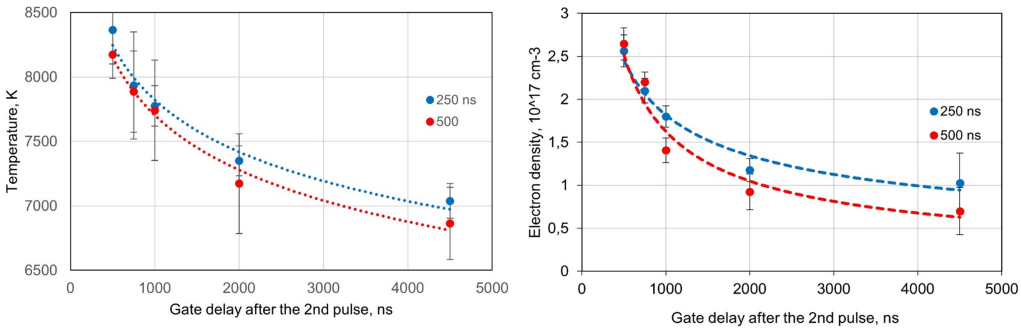

Fig. 7. DP LIBS plasma temperature and electron density versus time of registration for 250 ns and 500 ns inter-pulse delays.

The next step was to state whether the solutions applied in our laser give effects observed in other DP LIBS experiments. There exists a common agreement [17] that in DP LIBS an improved signal-to-noise ratio as well as the enhancement of the DP LIBS signal compared to SP LIBS are observed. In Fig. 8 we show an example of 3 overlaid LIBS spectra fragments in the 509–524 nm range registered for SP LIBS 20 mJ, 5–15 mJ, and 7–13 DP LIBS plasmas. The LIBS signal enhancement measured as the net area under the spectral line profile is evident. A similar approach was used in [43].

The results of enhancement measurements for various configurations tested in the experiment are shown in Fig. 9. The left-side diagram was built for 500ns/500ns/500ns inter-pulse delay/gate

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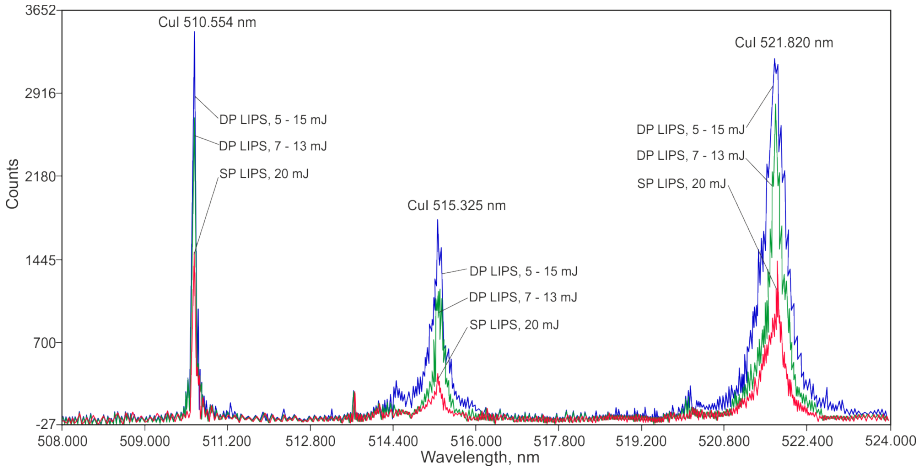

Fig. 8. Overlaid SP and DP LIBS spectra fragments in the 508–524 nm spectral range.

width/gate delay while in the right one the energy ratio was set to 5–15 mJ and the inter-pulse delay was 500 ns. In our experiment, the highest enhancement of the DP LIBS signal compared to 20 mJ SP LIBS one has been observed for the 5–15 mJ and 7–13 mJ configuration for a 500 ns inter-pulse delay and a 500 ns gate delay (Fig. 8 left), unlike the temperatures shown in Fig. 6. The LIBS enhancement was measured for the 500 ns and 1000 ns gate delays (a 500 ns inter-pulse delay) and it is at the level of 9–14 for the Cu I 262 nm line and at about 10–12 for the Cu I 515 line which is shown in the right part of Fig. 9.

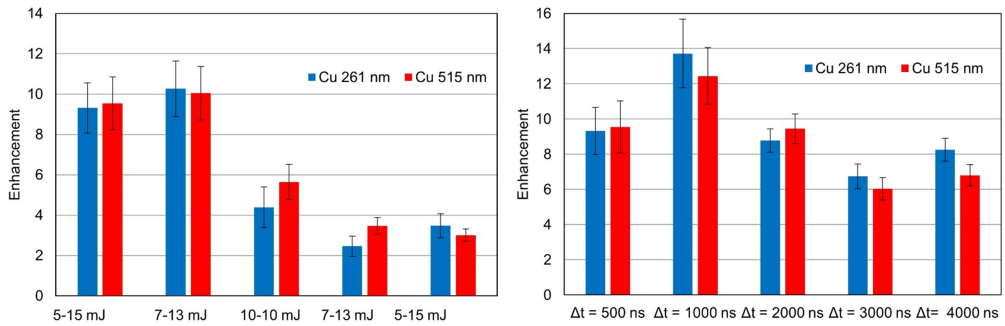

Fig. 9. Maximum enhancement of the LIBS signal for different energies of DP pulses (left) and for different gate delays (right).

The best results were observed for Cu lines, the enhancement for Zn 472 nm and 481 lines was a bit lower and the Zn lines are not shown in Fig. 9. It is worth noting that the highest enhancement was observed for 5–15 mJ and 7–13 mJ DP LIBS configurations i.e., for spectra where the strongest self-absorption in Cu I resonance lines was measured. Although highest temperatures were measured for 13–7 mJ and 15–5 mJ configurations, it seems to us that the larger plasma volume causing stronger self-absorption can lead to bigger enhancement. Besides, due to a high difference between energy levels of the transitions used for enhancement calculations and measured plasma temperatures (temperatures are 8–10 times lower than the upper-level

energies for Cu I 262 and Cu I 515 nm lines), the influence of higher plasma temperature for DP LIBS seems not to be dominant in the experiment. The obtained LIBS signal enhancement, maximum for 7–13 and 5–15 mJ proportions between the first and the second laser pulse is in good accordance with the statements in [41] where maximum enhancement was observed for the second laser pulses 2–3 times stronger than the first ones. Measured enhancements at the level of 10–15 were observed in many papers, for example in [18, 20, 25, 43].

3.3. Statistical classification

Finally, we tried to use Factorial Analysis to show in a simple way how different experimental conditions affect plasma parameters, which is reflected in LIBS spectra. In Fig. 10, the points on the plot represent the LIBS spectra. The closer the spectra are, the greater the similarity of thermodynamic conditions in the plasma. In the right part of Fig. 10, the DP spectra with stronger first laser pulse lie closer to SP LIBS spectra – thermodynamic parameters of plasmas must be more similar. This confirms the self-absorption sequence shown in Fig. 4.

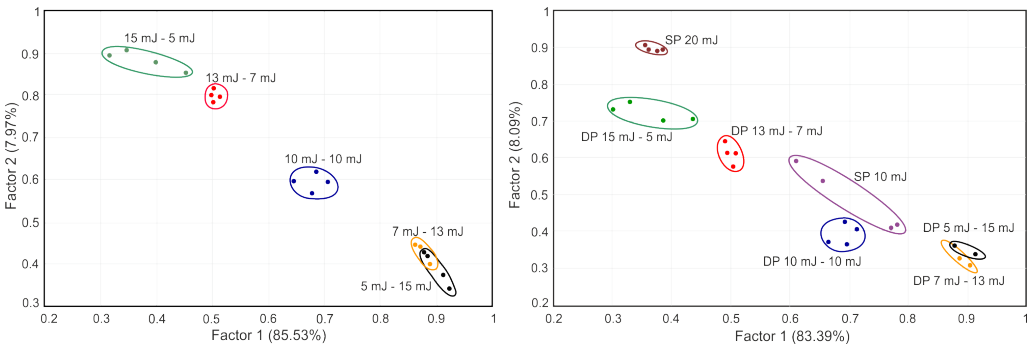

Fig. 10. Factorial Analysis for DP (left) and SP-DP (right) LIBS spectra in the 200–800 nm wavelength range.

The obvious advantage of using Factorial Analysis is the simplicity of showing the differences and similarities in the input LIBS spectra. It is done, however, at the cost of reducing the input variance. In the FA or PCA approaches the results are assumed to be correct if about 60% of the input variance is kept [32, 35, 36]. In our case, the FA representation of LIBS spectra includes over 90% of input variability. There are few papers devoted to applications of PCA analysis in DP LIBS experiments, mainly dealing with hazardous materials [44–46]. A useful review of multivariate statistical analysis applied to both SP and DP LIBS measurements can be found in [47]. In conclusion, it should be noted that in the literature on LIBS, both with a single pulse and with two pulses, there is an ever-growing number of publications, from which one can mention, for example, recent papers [48–55].

4. Conclusions

A double-pulse Nd: YAG laser generating two pulses of desired energy was applied in the double-pulse LIBS experiment. DP LIBS results obtained in the collinear geometry revealed strong self-absorption and self-reversal of resonance Cu I 324.754 and 327.395 nm lines, not observed in SP LIBS. The reason of this phenomenon is, in our opinion, a much larger plasma volume generated by two laser pulses despite the same energy carried by a single pulse in

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the SP mode (20 mJ). This reason can be also responsible for bigger enhancements measured for 7–13 mJ and 5–15 mJ DP LIBS configurations. Due to high difference between energy levels of the transitions used for enhancement calculations and measured plasma temperatures (temperatures are 8–10 times lower than the upper-level energies for Cu I 262 and Cu I 515 nm lines), the influence of higher plasma temperature for DP LIBS seems not to be dominant. Excitation temperatures and measured signal enhancement are typical for nanosecond DP LIBS experiments. It is worth emphasizing that all the experiments were performed using one unique double pulse laser characterized by easily adjusted parameters and thus being a flexible device for such applications. Thus, the validity of the use of a laser with gradual switching of transmission losses in practice was demonstrated.

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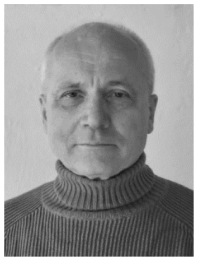

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