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Detection of Pb in Tieguanyin tea and ash by laser-induced breakdown spectroscopy*

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In this work, laser-induced breakdown spectroscopy (LIBS) was applied for the detection of Pb in Tieguanyin tea and ash. Firstly, the Tieguanyin tea and ash containing Pb were prepared, and the difference of intensities of Pb I spectral lines before and after the ashing treatment was studied. It was found that the intensities of Pb I lines increased by 30 times and the standard deviation of background signal decreased by 41% after the ashing treatment. Therefore, the enrichment of Pb element by ashing treatment was used to detect Pb in tea with high sensitivity. Then, the calibration curve of Pb was established using spectral lines without self-absorption, and the determination coefficient (R^2) for the linear fitting of calibration curve was 0.979 9. Finally, it was found that the limit of detection of Pb was 233.8 ppb. Compared with the results of other works which detect Pb directly, the enrichment of Pb by ashing treatment improved the detection sensitivity of Pb by about 200 times. In addition, this method can be applied to the high sensitivity detection of other heavy metals, such as Cr, Cd, Hg, etc in plants, Chinese herbal medicine, flour, rice, coal and other solid materials.

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China is the hometown and birthplace of tea. Drinking tea is a popular and healthy lifestyle. Today, tea culture has spread all over the world. Tea contains caffeine, tea polyphenols, carbohydrates, vitamins, minerals and a variety of trace elements[1]. Therefore, drinking tea has many benefits for people, such as moistening the intestine, reducing cholesterol and blood pressure, dilating blood vessels, stimulating fluid and quenching thirst[2]. Heavy metal elements, such as Pb and Cr, are discharged into the environment through industrial pollution, automobile exhaust, chemical fertilizers, pesticides, domestic waste and other ways. If the local air, water or soil pollution is serious, the Pb content in tea may exceed the food safety standard, and even if the concentration of Pb is very low, it will endanger human health[3]. The content of Pb, Cr and other harmful heavy metal elements in tea has always been a common concern of the public. According to China's National Food Safety Standard GB 2762-2017, the maximum allowable limit of Pb in tea is 5 ppm, and that in agricultural products is 0.2 ppm[4]. Similarly, the World Health Organization (WHO) and Food and Agriculture Organization (FAO) of the United Nations have issued relevant standards stipulating the maximum allowable limit of 0.3 ppm of Pb in agricultural products[4]. Hence, it is necessary to find a rapid and highly sensitive method to detect Pb in tea or agricultural products.

Laser-induced breakdown spectroscopy (LIBS) is a spectral analysis technology based on atomic emission, which has the advantages of simple sample preparation, real-time in situ monitoring, fast analysis speed and multi-element analysis[5]. It has been applied in many fields such as agriculture[6], atmospheric environment[7] and food[8]. In recent years, there are also studies on the application of LIBS technology in tea sample detection. GONDAL et al[9] identified the elements in tea, and quantified Fe, Cr, K, Br, Cu, Si, Ca and other elements. The limit of detection (LoD) of these elements was between 1—22 ppm. LU et al[10] studied the differences of element species and contents of green tea in different seasons, and calculated quantitatively that the LoD of Pb element was 48.4 ppm. WANG et al[11] compared the external standard method, internal standard method and multiple linear regression method for quantitative analysis of Pb in Pu'er tea and determined that the LoD of Pb was 47.22 ppm. Due to serious self-absorption and matrix effects, these traditional LIBS detection technologies have low detection sensitivity, and the LoD for heavy metal elements is generally in tens of ppm.

Lots of scholars have done many researches on improving the detection sensitivity of LIBS technology and lowering the detection limit of elements. These researches mainly focused on two aspects. The first aspect

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was to improve the analytical performance of LIBS technology through different sample pretreatment methods. YANG et al[12] respectively prepared single solution and mixed solution containing Cu, Pb, Cd and Cr, and determined the LoDs of these elements in the range of 13—386 ppb by chemical replacement combined with surface-enhanced LIBS (CR-SENLIBS). This method improved the detection sensitivity of trace heavy metal elements in aqueous solution. WU et al[13] proposed biomimetic array LIBS (BA-LIBS) technology, which enriched low concentration of target elements into the detection area, and simultaneously detected the mixed solution containing nine kinds of metal elements. The LoDs of these elements were in the range of 8.3—13.49 ppb, and the LoD of Pb was 1.48 ppb. ALESSANDRO et al[14] adopted the nanoparticle enhanced LIBS (NELIBS) method to carry out highly sensitive detection of solutions with analyte concentration at sub-ppm level, and the LoDs of Pb and Ag could reach 2 ppb and 0.2 ppb, respectively. Although above three methods had effectively improved the sensitivity, they focused on the analysis of liquid samples and were not suitable for solid samples. YANG et al[4] put forward a sample pretreatment method of solid-liquid-solid transformation (SLST) using LIBS combined with ultrasound-assisted extraction technology and obtained the LoDs of Cd and Pb in rice were 2.8 ppb and 43.7 ppb, respectively. This method was suitable for the analysis of some solid samples, but the pretreatment process was tedious and complex, so it was not suitable for large-scale application.

The second aspect was to upgrade the experimental equipment to enhance the spectral signal, so as to improve the detection sensitivity and accuracy of LIBS technology. ZHU et al[15] proposed the LIBS assisted by laser-induced fluorescence (LIBS-LIF) method, which increased the sensitivity of LIBS technology by more than two orders of magnitude. The content of Pb in rhododendron leaf was determined, and the LoD was 54 ppb. BURAKOV et al[16] used double-pulse LIBS (DP-LIBS) technology to analyze Pb in soil and S in coal, and the LoD of Pb was estimated to be 20 ppm. ZHAO et al[17] used femtosecond-nanosecond double-pulse LIBS (fs-ns DP-LIBS) technology to quantitatively analyze Pb in soil and studied the influence of time-delay of double-pulse on the intensity of Pb element. When the experimental parameters were optimal, the LoD of Pb was 8.13 ppm. In order to improve the sensitivity of LIBS technology detection, AKHTAR et al[18] combined LIBS with an external magnetic field to increase the temperature, electron density and emission intensity of plasma, and reduced the LoD of Pb from 12 ppm to 1.4 ppm. MENG et al[19] designed a hemispherical spatial confined device that could be placed directly on the sample surface to improve the signal intensity and the collection efficiency of plasma. The LoD of Pb in soil by this device was 4.5 ppm. LI et al[20] used laser ablation fast pulse discharge plasma spectroscopy (LA-FPDPS) similar to DP-LIBS, which used an additional pulse source to enhance the light emission of the plasma. They analyzed Pb, Mg and Sn in the soil, and the LoDs were 1.5 ppm, 34 ppm and 0.16 ppm, respectively. However, these methods had high requirements of experimental equipment and parameters, and the detection sensitivities of some methods were not satisfactory.

In this paper, the Pb I spectra lines of tea and the sample after ashing treatment were compared, and the signal enhancement effect of the Pb element was studied by the ashing treatment of tea. Based on this, we prepared tea samples with different Pb contents using $(CH_3COO)_2Pb$ solution, enriched Pb simply and efficiently by firing them into ash, and then quantitatively calculated the LoD of Pb in tea. Compared with the traditional LIBS method, the detection sensitivity was increased by about 200 times.

As shown in Fig.1, computer triggered a home-made Nd: YAG solid laser to produce the laser pulse with the wavelength of 1 064 nm, repetition rate of 1 Hz, and the pulse duration of 20 ns. The laser beam was guided by three high reflection mirrors and focused on the surface of the sample through a lens with a focal length of 60 mm to ablate the sample and generate plasma plumes. In order to avoid the absorption of laser photons by the plasma plumes at the high end of the laser energy without affecting the signal-to-noise ratio (*SNR*)[3], laser pulse energy of 225 mJ was selected. Furthermore, the sample was placed on an *X-Y-Z* translation platform to avoid the influence of the ablation crater to the signals and ensure that the plasma plumes produced by the laser ablation with different thickness of samples were at the same height.

The plasma fluorescence was collected by the collection system and coupled to a four-channel CCD spectrometer (AvaSpec-2048-USB2*). The bands of the four channels were 300—445 nm, 445—570 nm, 570—780 nm and 780—950 nm, respectively, and the resolutions were 0.12 nm, 0.1 nm, 0.15 nm and 0.15 nm, respectively. The collection system, which consisted of four lenses and a fiber probe, had much higher collection efficiency and signal intensity than a single lens. In the process of spectral data acquisition, the spectrometer integration time was 1.05 ms, and the optimal delay time was 1.33 μs. All the spectra were averaged by 200 laser shots at the target to enhance the *SNR*.

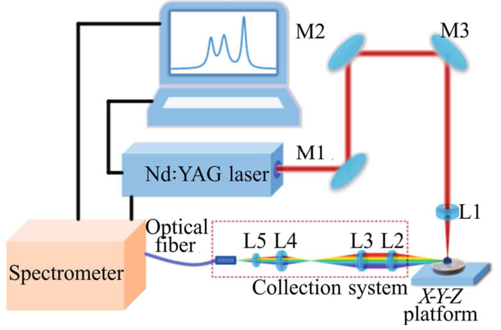

Fig.1 Schematic of LIBS experimental setup (Optical components included three mirrors (M) and five lenses (L) with focal lengths of 60 mm, 60 mm, 150 mm, 60 mm and 10 mm, respectively)

In the experiment, Tieguanyin tea from Anxi County, Quanzhou City, Fujian Province and $(CH_3COO)_2Pb\cdot3H_2O$ reagents were used to prepare tea samples and ash samples, as shown in Tab.1. The detailed preparation process was as follows.

Tab.1 Two samples prepared in the experiment

	Sample type	Content of Pb
1	$(CH_3COO)_2Pb$ - tea	10 ppm, 50 ppm
2	$(CH_3COO)_2Pb$ - tea ash	1 ppm, 10 ppm, 25 ppm, 50 ppm, 100 ppm, 1 000 ppm

First step, $(CH_3COO)_2Pb$ solution with Pb content of 1 $g\cdot L^{-1}$ was prepared using analytically pure grade $(CH_3COO)_2Pb\cdot3H_2O$. By adding 0.183 g of accurately weighed $(CH_3COO)_2Pb\cdot3H_2O$ into 100 mL deionized water and continuously stirring to dissolve it completely, $(CH_3COO)_2Pb$ solution with Pb content of 1 $g\cdot L^{-1}$ was obtained.

Second step, $(CH_3COO)_2Pb$-tea samples with Pb contents of 10 ppm and 50 ppm were prepared, and the process was shown in Fig.2. The 1 $g\cdot L^{-1}$ $(CH_3COO)_2Pb$ solution was diluted 100 times to get 0.01 $g\cdot L^{-1}$ $(CH_3COO)_2Pb$ solution. The dilute solution of 10 mL and 50 mL was measured with a measuring cylinder, and then added them to two parts of 10 g tea powder respectively, stirring constantly to mix well. After that, the solid-liquid mixtures were sonicated in an ultrasonic cleaning machine for 10 min to thoroughly mix the tea powder with the $(CH_3COO)_2Pb$ solution. Then, the mixtures dried in the oven at 120 °C for 120 min. This step was called rapid drying. And the dry powders were pressed into pellets at 15 MPa for 60 s.

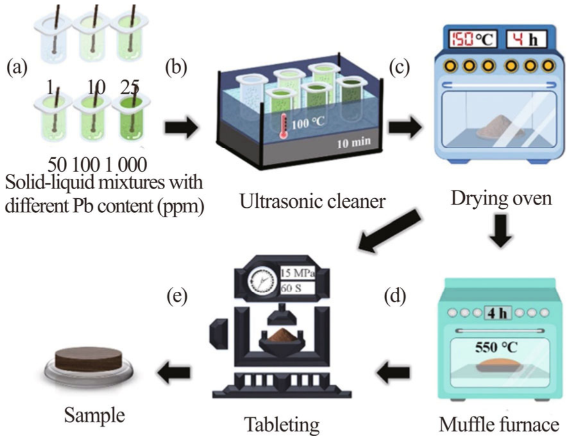

Fig.2 Schematic diagram of pretreatment process of $(CH_3COO)_2Pb$-tea samples ((a), (b), (c) and (e)) and $(CH_3COO)_2Pb$-tea ash samples ((a), (b), (c), (d) and (e))

The sample preparation process was shown in Fig.2. Six parts of 10 g of tea powder were weighed, and 1 mL, 10 mL, 25 mL, 50 mL, 100 mL and 1 000 mL of 0.01 $g\cdot L^{-1}$ $(CH_3COO)_2Pb$ solution were measured and mixed with tea powder, respectively, to prepare solid-liquid mixture with Pb contents of 1 ppm, 10 ppm, 25 ppm, 50 ppm, 100 ppm, and 1 000 ppm. After ultrasonic shock and rapid drying, the tea ash samples containing Pb were obtained by reaction in Muffle furnace for 4 h. The most important step here was to determine the reaction time of tea in the Muffle furnace. The tea samples were put into the Muffle furnace and burned for 4 h after the temperature rose to 550 °C. After the temperature dropped to 60 °C, the tea samples were removed, cooled and weighed. Then it was transferred to the Muffle furnace again at 550 °C and burned for 1 h. Then it was cooled and weighed. Since the results of ash weight for 4 h and (4+1) h were within the error range (less than 0.001 g), tea was completely converted into ash after 4 h burning in Muffle furnace. Finally, the ash samples were pressed into pellets separately for LIBS analysis.

In the experiment, we studied the Pb element in tea and ash samples containing Pb. The Pb signal in the ash was significantly enhanced. In order to study the signal enhancement effect of ashing treatment on Pb signal, the Pb I 368.346 nm and 405.781 nm in tea and ash were compared and analyzed, with the Pb content of 50 ppm as an example, as shown in Fig.3(a). It can be clearly seen that the spectral line intensity of Pb element in ash is much higher than that in tea, and the absolute intensities of Pb I 368.375 nm and 405.873 nm in ash were 26 times and 31 times stronger than these in tea, respectively. Fig.3(b) shows the background spectral signal of tea and ash within 932.5—935.0 nm. It can be seen that the background signal fluctuation of ash was smaller, and its standard deviation was 11.069, which was less than 18.397 of the standard deviation of the tea background signal. The spectral line signal in the ash was stronger and the standard deviation of the background signal was smaller, so the *SNR* of the ash LIBS spectra was much better than that of the tea.

There are three possible reasons for the obvious signal enhancement effect and better *SNR* after ashing treatment of tea. Firstly, in the ashing process, most of the organic matter decomposed and volatilized in the form of gas. The mass of the organic matter after ashing was about 4% of that before ashing, and the residual matter almost was metal elements and metal element oxides. Therefore, the contents of metal elements, including Pb, were greatly increased, and the spectral lines intensities of metal elements, such as Pb, were greatly enhanced. Secondly, the molecular free radicals produced by organic matter disappeared with the evaporation of organic matter, avoiding the interference of free radical spectral lines on spectral lines of other elements. Finally, the tea powder had a large particle size, while the ash powder was silty-fine and the Pb element was evenly distributed, so the surface flatness of the ash pellets was better than that of the tea pellets. The spectrum fluctuation was reduced effectively, so the ash spectrum had a better *SNR*.

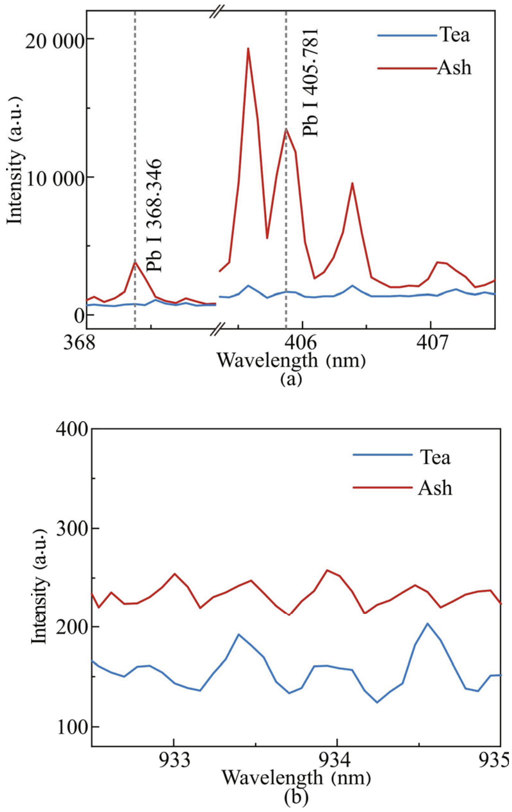

Fig.3 Comparison of spectral lines between tea and ash with Pb content of 50 ppm: (a) Pb I 368.346 nm and Pb I 405.781 nm; (b) Background signal

In conclusion, the signal of Pb element can be significantly enhanced by the ashing treatment of tea, which can realize the high sensitivity detection of Pb element in tea. Ashing treatment can increase the absolute signal intensity of Pb in tea by about 30 times, and the standard deviation of background signal can be reduced by 41%, thus improving the *SNR* of the spectra. Therefore, this method has a good application prospect in the high sensitivity detection of Pb in tea.

According to signal enhancement effect of Pb, we mixed 1 g·L^{-1} $(CH_3COO)_2Pb$ solution and tea powder to prepare tea samples with Pb contents of 1 ppm, 10 ppm, 25 ppm, 50 ppm, 100 ppm and 1 000 ppm, respectively, and then burned them into ash samples. After obtaining the LIBS spectra of each sample, the relationship between Pb content and Pb spectral line intensity was explored, and the linear regression equation was used to evaluate the Pb content and LoD of unknown samples. Fig.4(a) shows the LIBS spectra of Pb I at 405.781 nm with different Pb contents. Comparing the spectra, it can be obviously seen that the intensity of Pb I spectral line decreased with the reduction of Pb content. The signal of Pb I could be also detected in sample with Pb content of 1 ppm, indicating that the LoD of Pb was below 1 ppm.

The LoD is defined as[21]

$$\alpha_{\text{LoD}} = \frac{3\sigma}{S}, \tag{1}$$

where σ is the standard deviation of the background signal intensity in the spectra, and S is the slope of the calibration curve of the target element. The spectra of background signals in the band range of 932.5—935.0 nm were shown in Fig.4(b), and the average standard deviation of the intensity of background signal of the six spectra was 9.664. The data sets of Pb contents of 1 ppm, 10 ppm, 25 ppm, 50 ppm, 100 ppm and 1 000 ppm were selected, and a linear calibration curve was constructed with Pb content as the independent variable and Pb I spectral line intensity as the dependent variable, as shown in Fig.5(a). The fitting determination coefficient R^2 was only 0.888 4, indicating that the linear fitting result of these points was not good, and there was obvious nonlinearity. The possible reason was that high Pb content (100 ppm and 1 000 ppm) showed a saturation because of self-absorption effect, and the overall trend was consistent with the curve-of-growth model[22,23] (blue curve in Fig.5(a), R^2=0.979 9). In this case, there will be a large error in calculating the LoD by linear fitting[23]. Therefore, we abandoned the data in the high-content region and only selected the data sets of Pb content of 1 ppm, 10 ppm, 25 ppm and 50 ppm to establish the linear calibration curve, and the results were shown in Fig.5(b). The R^2 between the spectral line intensity and Pb content was 0.979 9, indicating that the intensity of Pb I in LIBS spectra after ashing treatment was almost proportional to Pb content in tea when Pb content in tea was less than 50 ppm. Through calculation, the LoD for Pb was

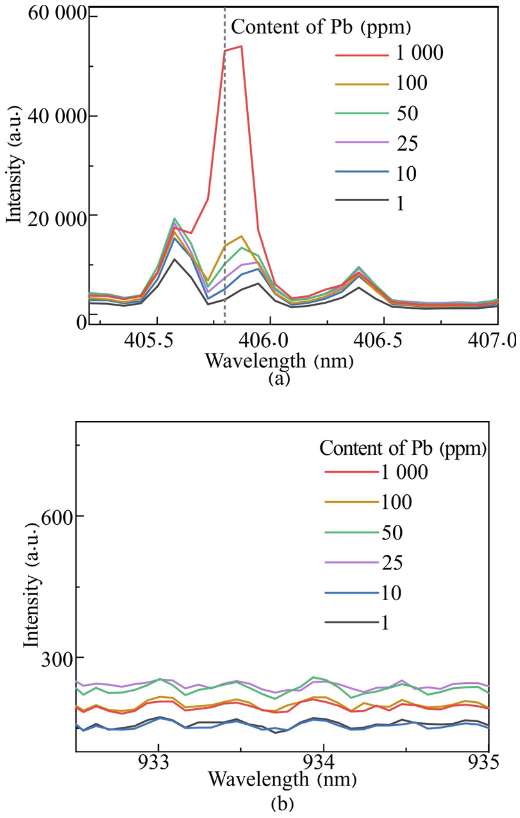

Fig.4 (a) LIBS spectra of Pb I 405.781 nm in $(CH_3COO)_2Pb$-ash; (b) Background signal

233.8 ppb, reaching sub-ppm level. Compared with traditional LIBS (LoD for Pb was 48.4 ppm[10]), the detection sensitivity of Pb was increased by about 200 times. Compared with other methods as shown in Tab.2, ashing treatment has the advantages of simple experimental setup, simple sample preparation and high sensitivity for Pb detection.

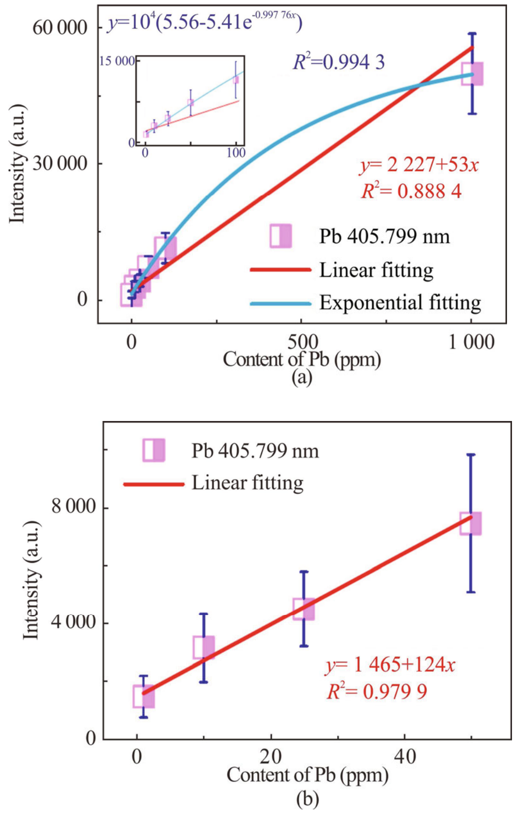

Fig.5 Calibration curves with different data sets of Pb contents: (a) Calibration curve (red) and curve-of-growth (blue) of Pb I 405.799 nm with Pb contents of 1 ppm, 10 ppm, 25 ppm, 50 ppm, 100 ppm and 1 000 ppm; (b) Calibration curve (red) of Pb I 405.799 nm with Pb contents of 1 ppm, 10 ppm, 25 ppm and 50 ppm

In this work, the tea samples containing Pb were studied, and the ashing treatment of tea can effectively enrich the Pb element in tea, so as to detect the Pb with high sensitivity. Firstly, compared with the LIBS spectra of tea, the spectral lines intensities of Pb in ash significantly enhanced, indicating that the relative content of Pb increased during the burning tea into ash. It was found that ashing treatment of tea could efficiently enrich Pb element in tea, and the spectral intensity of Pb in ash was about 30 times higher than that in tea. By burning tea samples with different Pb contents into ash samples and establishing the calibration curve, the LoD for Pb was calculated to be 233.8 ppb, which was below the maximum content required by tea and agricultural products in the National Food Safety Standards of China. Although the ashing treatment of tea was time-consuming, the operation was simple and the detection sensitivity of Pb element can be increased by about 200 times than that using traditional LIBS. It showed that the ashing treatment of tea has high detection sensitivity and obvious advantages and application prospects in detecting the content of metal elements in tea. In addition, this method can be applied to the high sensitivity detection of heavy metals, such as Pb, Cr, Cd and Hg, in plants, Chinese herbal medicine, flour, rice, coal and other solid materials. Combined with DP-LIBS, LIBS-LIF and MA-LIBS can further improve the detection sensitivity of Pb and other heavy metals.

Tab.2 Comparison of LoDs of Pb in this work and other LIBS methods

Method	State of sample	LoD (ppb)	References
Ashing treatment	Solid	233.8	This work
Traditional LIBS	Solid	48 400	[24]
		47 200	[11]
SLST	Solid	47.3	[4]
CR-SENLIBS	Liquid	16—386	[12]
BA-LIBS	Liquid	1.48	[13]
NELIBS	Liquid	2	[14]
LIBS-LIF	Solid	54	[15]
DP-LIBS	Solid	20 000	[16]
fs-ns DP-LIBS	Solid	8 130	[17]
LIBS with an external magnetic field	Solid	4 100	[18]
LIBS using hemispherical spatial confinement	Solid	4 450	[19]

Ethics declarations

Conflicts of interest

The authors declare no conflict of interest.

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