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一种小型化的低能量、高重频激光诱导击穿光谱系统用于铅元素分析

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摘　要:研制了一款小型化的激光诱导击穿光谱系统.光源采用低能量、高重频的二极管泵浦固体 Nd:YAG 激光器,分析了激光重频和激光能量对光谱信号的影响.激光器工作在重频 4 kHz、单脉冲能量为 745 μJ、脉宽为 17ns 时,得到了 7 条铅元素的特征谱线.与单脉冲激光诱导击穿光谱系统相比,不仅特征谱线数量增加,光谱的信噪比也提高了 73%。简化的系统设置和低的激光能量使得激光诱导击穿光谱技术能够应用于更多领域.

关键词:光谱学;激光诱导击穿光谱;等离子体;重金属;光谱强度

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Compact Low-energy High-repetition Rate Laser-induced Breakdown Spectroscopy for Lead Element Detection

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Abstract: A compact laser-induced breakdown spectroscopy using a low-energy, high-repetition rate Nd:YAG DPSS laser as excitation source has been developed. The influences of laser repetition rate and laser power on LIBS signal were analyzed. When the laser operated at 4 kHz, pulse energy of 745 μJ and pulse width of 17 ns, the seven emission lines of Lead (Pb) was obtained. Compared with the traditional single pulse LIBS, the number of emission lines is increase, also the signal-to-noise ratio is improved by almost 73%. Based on simplified setup and low energy, high-repetition rate laser-induced breakdown spectroscopy will be applied in more emerging fields.

Key words: Spectroscopy; Laser-induced breakdown spectroscopy; Plasma; Heavy metal; Spectral intensity

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0 Introduction

In recent years, Laser-Induced Breakdown Spectroscopy (LIBS), with the developments of laser

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technology and spectral instruments, has been established as a popular method in applications like environmental monitoring, bio-chemical or explosive agent detection[1-2] or medical diagnosis[3]. LIBS has many advantages as real-time, on-line, non-contact and multiple element detection. Especially its samples basically need no pretreatment[4-7]. It is worth noting that in the detection of low-Z elements LIBS performance is far better than other handheld devices like X-Ray Fluorescence (XRF)[8]. For the future development, improving performance and achieving miniaturization of LIBS devices have been the first targets for spectral workers.

Currently, the most setups of LIBS for research and application are based on high energy Q-switched Nd:YAG lasers, which deliver pulses with low repetition rate and single pulse energy of hundreds millijoules. This kind of LIBS system uses one single laser pulse to excite the plasma, called Single Pulse LIBS (SP LIBS). Chen, et al.[9] used the SP LIBS system based on nanosecond laser to detect soil. By using the plane mirror device to constrain the plasma, they obtained emission spectral intensity of element Mg, Al, Fe and Ba increased by 93%～160% and spectral Signal-to-Noise Ratio (SNR) rose 17%～40%. But there are some problems in the quantitative analysis of SP LIBS. The measurement deviation of the SP LIBS is usually in the 5%～10%. The deviation is due to the poor stability of the laser pulse, the noise signal of detector and the interference of matrix effect from sample.

For improving the performance of LIBS system, the Double Pulse LIBS (DP LIBS) was invented. Spectral workers use two single laser pulses to excite and strengthen plasma. The plasma absorbs the second laser pulse and will excite stronger emission spectrum. Gustavo et al.[10] used DP LIBS system as a potential tool for the analysis of contaminants and macro/micronutrients in organic mineral fertilizers. The Limit Of Detection (LOD) values obtained by DP LIBS increased up to seven times as compared to SP LIBS. The enhancement of elemental emission line intensity and LOD values was attributed mainly to the larger emitting volume and increased mass ablated. However, high power laser pulses will cause damage of the sample. The obvious thermal effect will lead molecules to be decomposed into atoms and ions instantly. It is impossible to obtain emission line of molecules. Besides, the complexity and large size of the DP LIBS laser system will hinder the miniaturization progress of the LIBS instrument.

In order to promote the miniaturization progress of LIBS system and reduce the energy of excitation, some research of LIBS with low-energy, high-repetition rate laser have been demonstrated. Gabriele Cristoforetti et al.[11] analyzed the aluminum alloys by a high-repetition rate LIBS. A diode-pumped mini-laser at 8 kHz has been tested as laser source in the LIBS setup. The LOD of the high-repetition rate LIBS were in the range of tens of ppm, comparable with typical values obtained with traditional LIBS setups. In addition, Christian Wagner et al.[12] used a low-energy, high-repetition rate Nd:YAG laser at 3 kHz as excitation source. Elemental analyses were performed on various samples including non-metallic compounds and metal alloys. The entire setup fitted well in a box with dimensions of 30×30×20 cm. It can be supplied by a standard 12 V car battery. The presented work shows that a compact low pulse energy and high-repetition rate laser can be used as excitation source of LIBS system. But the effect of repetition rate on experimental results has not been explored. The high-repetition rate LIBS still need a large number of experiments to research the relationship between LIBS performance and laser parameter settings.

In this study, the excitation source of LIBS system is a compact low-energy, high-repetition rate laser. The LIBS performance with different laser power and repetition rate was explored. The element analysis was carried out on samples of heavy metal Lead (Pb). When the laser operated at 4 kHz, pulse energy of 745 μJ and a pulse width of 17 ns, seven emission lines of Lead (Pb) was obtained. A single pulse LIBS system with high energy, low-repetition rate laser was built as reference to further illustrate the performance of high-repetition rate LIBS. By comparing the spectra of the two system we found the using high-repetition laser cause more emission lines and signal-to-noise ratio improved by almost 73%. Finally, we summarized the significance of using the high repetition rate laser for LIBS development.

1 Experimental setup

The experimental arrangement is shown in Fig.1 The setup of LIBS includes a high-repetition rate laser source , sample test system (reflecting mirror, focusing mirror and rotating disk) and a compact spectrometer. The laser source is a diode pumped Nd:YAG Q-switched laser emitting at the fundamental wavelength of 1 064 nm. The maximum average power is 8 W. The repetition rate can be adjusted from 1 kHz to 25 kHz with pulse width at range of tens nanoseconds. A compact UV spectrometer (Ocean Optics HR4000) was used for receiving spectra. It is working at wavelength range from 200 nm to 428 nm.

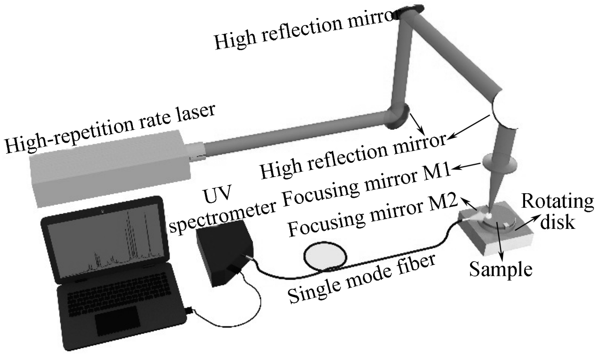

Fig. 1 The arrangement diagram of high repetition rate LIBS system

The sample was placed on a rotating disk, which driven by a computer controlled micrometric translation stage. The rotating disk rotated at an angular velocity of about 5 Hz, for which the single craters are clearly separated. The move of the sample was necessary to sustain the plasma formation. In fact, there will be thousands of laser pulses falling within one second. A large number of laser pulses focusing on the same spot leads to a deep crater, which will cause the disappearance of the plasma. The cause of plasma disappearance is in the progressive de-focusing of the laser pulse at the crater bottom during the consecutive ablations and in the optical masking of the beam by the sides of the crater.

The craters drilled by laser ablation on the Lead (Pb) were observed by opticalmicroscope. In Fig.2 the image of a crater obtained by focusing the 6 kHz laser beam in the same point for 1 s is shown. In Fig. 3 the craters obtained by rotating the target at an angular velocity of about 5 Hz (for which the single holes are clearly separated) are shown.

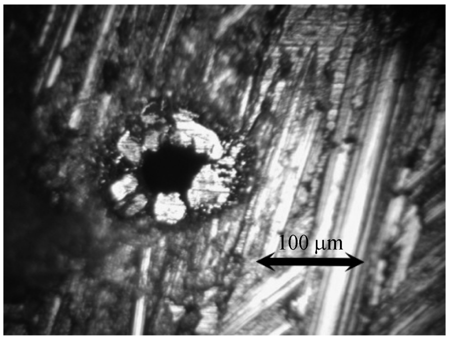

Fig.2 Crater obtained by irradiating about 6000 laser shots on the same spot

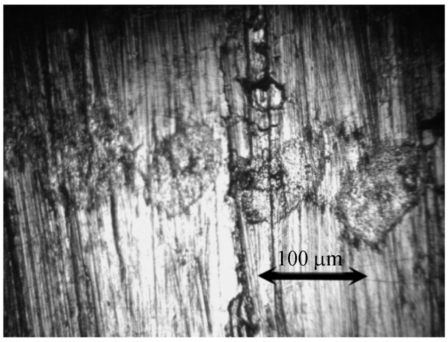

Fig.3 Series of single shot craters obtained by rotating the target at 5 Hz during irradiation

The laser beam was focused on thesample surface by a focusing mirror M1 ($f=100$ mm), Another focusing mirror M2 ($f=25$ mm), in consideration of the optical masking by the sides of the crater and danger of being laser burned, placed at 45° with respect to the beam axis, collected the emission light of plasma into an optical fiber. The export of the optical fiber was connected with the entrance of the compact UV spectrometer. The computer is used to display and analyze spectra. Considering that the plasma produced by the nanosecond laser lasting several milliseconds, the integration time of the spectrometer was set at 10 milliseconds.

2 Results and discussion

Fig.4 shows the high-repetition rate LIBS spectra of Lead (Pb) obtained at different average power from 1.538 W to 5.15 W.

It can be concluded that, with growing laser power, the intensity of the LIBS signal is also increased. The higher laser power will excite bigger plasma with higher temperature. Those two factors will cause plasma inspiring higher intensity emission lines in the cooling state[13]. But excessive laser power will rapidly cause deep crater on sample surface, which will limit plasma expansion and interrupt emission lines. The lowest power that can excite plasma in the experiments was 1.393 W. For optimizing high signal intensity and low excitation energy simultaneously, 2.98 W was chosen as laser power for the high-repetition experiments.

With a fixed pump power, laser pulse width and pulse energy are entirely dependent on the repetition rate of laser. We tested performance of the high-repetition rate LIBS at different repetition rate as shown in Fig. 5. The laser average power was set at 2.98 W. In Fig. 6, peak values at 368.3 nm (the highest peak in every spectrum) were selected as characterization of intensity of each spectrum. From Fig. 5 and Fig. 6 we can find that the most powerful LIBS signal will be obtained at the repetition rate of 4 kHz. This phenomenon has great agreement with the theoretical analysis of Gabriele Cristoforetti *et al*[11]. The pulse energy and FWHM depend on the repetition rate are not linear. The trend of FWHM is down first, then rise, and the lowest in the 4 KHz. Contrary to the FWHM, energy reached the highest point at 4 kHz. The wide FWHM will lead to the plasma barrier effect, which will reduce the spectral intensity. So, the strongest spectrum was obtained at 4 kHz. Based on this finding, the repetition rate of 4 kHz was chosen as the optimal operating point of the high-repetition rate laser. When the high-repetition rate laser is working at 2.98 W and 4 kHz, the pulse width is 17 ns and single pulse energy is 745 μJ.

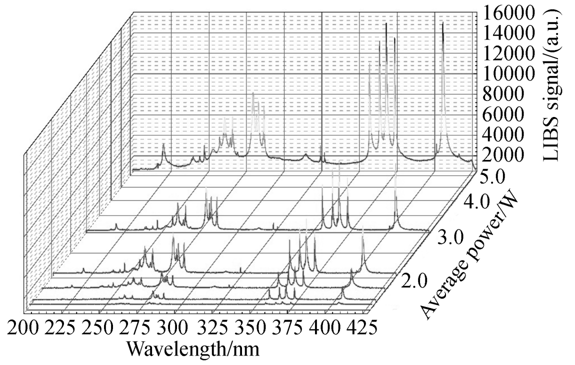

Fig.4 High-repetition rate LIBS spectra of Lead (Pb) obtained at different average power

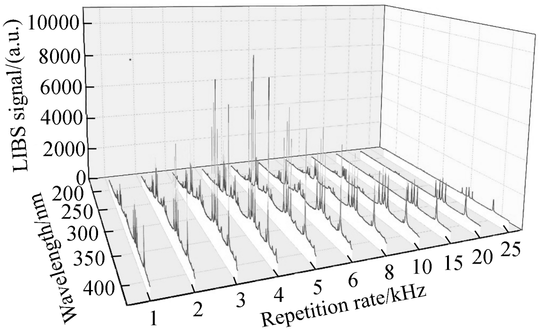

Fig.5 LIBS spectra at different repetition rate

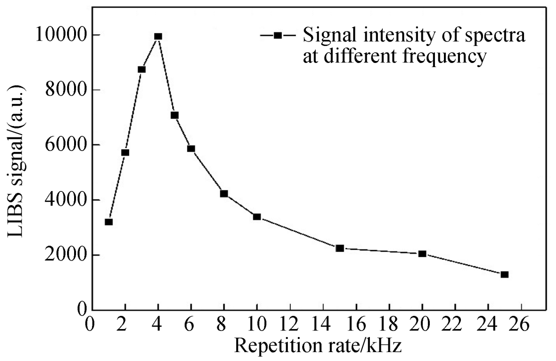

Fig. 6 Relationship between LIBS signal intensity and repetition rate

It is worth noting that when the laser repetition rate reached more than 10 kHz, the waveform of LIBS spectral will change, as shown in Fig. 7. The spectra at 15 kHz, 20 kHz and 25 kHz are different from the other several spectra at repetition rate lower than 10 kHz. The excessive repetition rate caused losing of emission lines between 200 nm and 350 nm. The LIBS spectra include atomic spectra and molecular spectra. Generally, the laser pulse with narrow pulse width and low energy will reduce the thermal effect on the sample surface. The non-thermal processes dominating ionization keeps the molecular structure of the sample. But the excessive repetition rate brings too much laser pulses acting on plasma. Laser pulse width also will be widened since the excessive repetition rate. These two factors cause thermal effect more remarkable in the process of plasma excitation. Under powerful thermal effect, the chemical bonds of sample components will be broken. Therefore, the LIBS spectra will miss the

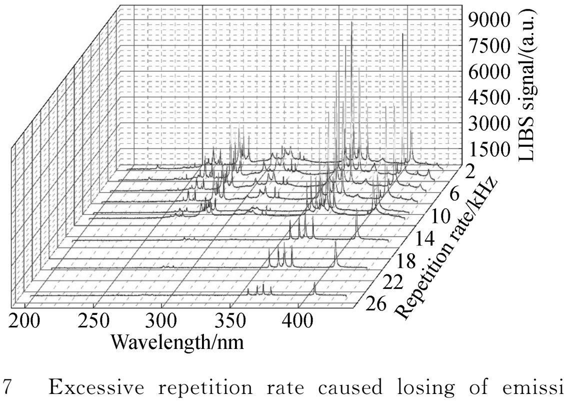

Fig. 7 Excessive repetition rate caused losing of emission lines between 200 nm and 350 nm

emission lines of molecular.

All of the emission lines of neutral Lead (Pb) element and correspondingrelative intensity are showed in Table1[14]. In general, the wavelength of 405.8 nm is the most frequently used emission line to detect the Lead (Pb) element. It is also one of the most easily obtained emission lines of Lead (Pb)[15]. Fig.8 is a complete emission spectrum of Lead (Pb) with the high-repetition rate laser operating at 4 kHz, single pulse energy of 745 μJ and pulse width of 17 ns. In the Fig.8, we can see seven clear emission lines of Lead (Pb) element. Their wavelength was marked out. By referring to Table1 we find that except for five high relative intensity lines, there are two weaker relative intensity lines at374 nm and 364 nm. The distribution of emission lines is relatively dispersed. These results will ensure the reliability of detection through the method of multi spectral lines synthetic analysis. Besides, the intensity of emission lines is much higher than noise, which condition shows high-repetition rate LIBS will have a good SNR. In short, the high-repetition rate LIBS system has enough ability to identify Lead (Pb) elements.

Table 1 The emission lines of neutral Lead (Pb) atoms and corresponding relative intensity

Relative intensity	Wavelength	Relative intensity	Wavelength	Relative intensity	Wavelength
200	202.2 nm	200	261.4 nm	400	368.3 nm
200	205.3 nm	300	280.2 nm	80	374 nm
150	217 nm	300	283.3 nm	1 000	405.8 nm
50	239.4 nm	150	364 nm	15	406.2 nm

A single pulse LIBS system based on a high-power, low-repetition rate laser was built. The laser was working at 1 Hz with single pulse energy of 182.2 mJ and pulse width of 10 ns. Experiments were carried out on the Lead (Pb) in the same environment. In Fig.9, the high-repetition rate LIBS spectrum and the SP LIBS spectrum were put together to make a comparison. Details are shown in Fig.10.

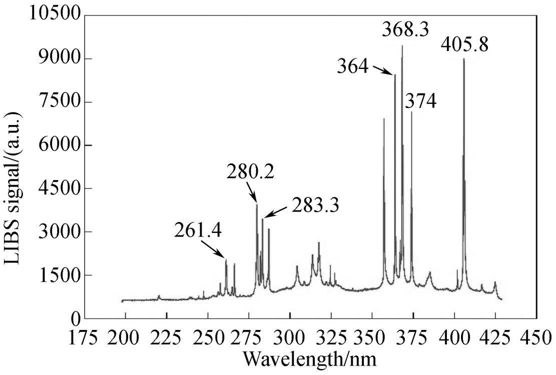

Fig.8 Complete emission spectrum of Lead (Pb) with the high-repetition rate LIBS

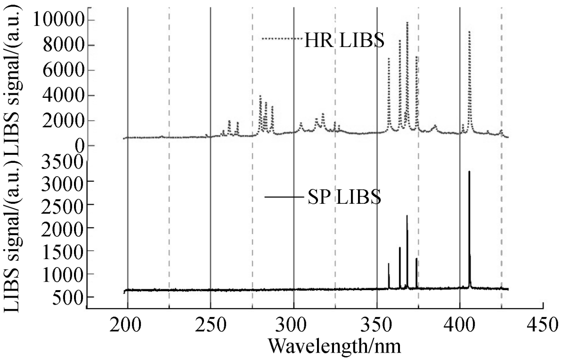

Fig.9 Comparison between high-repetition rate LIBS and SP LIBS

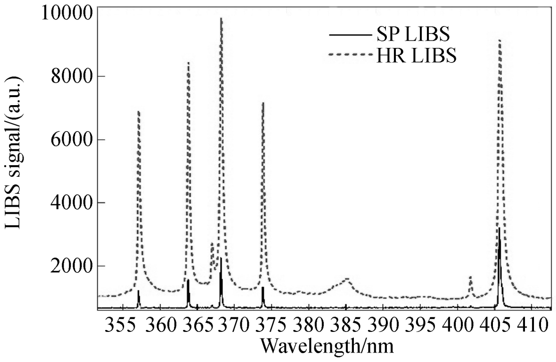

Fig.10 details from 350 nm to 410 nm

As we all know, higher laser energy will inspire higher temperature and more powerful plasma, in which condition the stronger LIBS signal will be obtained. The single pulse energy of high-repetition rate laser was only 745 μJ, which is far below energy of the SP LIBS of 182.2 mJ. However, the signal intensity of the high-repetition rate LIBS is almost 4 times higher than the SP LIBS. Their signal-to-noise ratio (SNR) are 9.08 dB for SP LIBS and 15.64 dB for high-repetition rate LIBS[SNR = 20 · Log(Vs/Vn)]. The SNR of high - repetition rate LIBS is improved by almost 73%. The very strong performance of the high-repetition rate LIBS is due to its very good beam quality and higher temperature short-lived continuum plasma. The high-quality beam will cause higher irradiance and energy density values. The high-repetition rate laser pulses will create higher temperature short-lived continuum plasma, which improves the SNR at the detector level[11,16]. Besides, even if the pulse width was only 10 ns, the high laser energy will greatly enhance the thermal effect in the process of plasma excitation. Therefore, the SP LIBS spectrum lost a number of emission lines at wavelength range of 250 nm to 35 nm. By comparing, the high-repetition rate LIBS has higher SNR and more emission lines.

But a large number of continuum background spectra are also included in the spectra of high-repetition rate LIBS. At the beginning of the formation of the plasma, high intensity continuum background spectra are produced near the surface of the sample. This radiation of plasma is similar to black-body radiation. However, as the plasma expands and leaves the sample surface, the plasma enters the cooling state. At this point, the line spectra play a major role[17]. Because of the short-lived continuum plasma, two periods of cooling and formation will coexist. Therefore, the line spectra are always accompanied by continuum background spectra. There is no way to collect line spectra only by time-resolved method. However, the degrees of polarization of line spectra and continuum background spectra are different. Thus, maybe this situation can be solved to a certain extent with polarization-resolved method[18]. For the same reason, non-gated detectors were allowed use in this work, which greatly simplify the detector requirements and reduce system cost.

3 Conclusion

Adiode pumped Nd:YAG Q-switched laser emitting at low-energy, high-repetition rate has been treated as laser source in a LIBS system. The seven emission lines were obtained with the sample of Lead (Pb). The good detection capability of the high-repetition rate LIBS system was proven. In addition, the influences of laser energy and repetition rate on the LIBS signal intensity were discussed in detail. We also analyzed the reason for losing emission lines at high repetition rate. By comparing with the traditional single pulse LIBS (SP LIBS), the signal intensity increased by 4 times and more emission lines were obtained. The lower energy (745 μJ) and narrow pulse width (17 ns) will improve the shortcoming of missing emission lines. It is noteworthy that the using of the high-repetition rate laser causes the LIBS device smaller and simpler. The diode-pumping and the air-cooling are contributed to the reduction of the volume of the LIBS system. The using of non-gated detectors greatly simplify the detector requirements and reduce system cost. The high-repetition rate LIBS system is closer to the goal of miniaturization. Therefore, it is sure that the high-repetition rate LIBS will be widely used in the future.

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