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December 15–19, 2016, Minsk, Belarus

Edited by A.N. Chumakov, M.M. Kuraica and M.S. Usachonak

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15–19 декабря 2016 г., Минск, Беларусь

Под редакцией А.Н. Чумакова, М.М. Кураицы и М.С. Усачёнка

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The Proceedings have been compiled from materials of reports presented at The XI Belarusian-Serbian Symposium "Physics and Diagnostics of Laboratory and Astrophysical Plasmas" (PDP-11), December 15–19, 2016, Minsk. The scope of papers covers a wide range of topics concerning techniques of plasma generation, methods of plasma diagnostics, and their application in solving real-world challenges of the present day.

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CONTENTS

APPLICABILITY OF TEA CO_2 LASER-BASED LIBS FOR THE ANALYSIS OF GEOLOGICAL SAMPLES IN AIR AT ATMOSPHERIC PRESSURE

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Abstract. In this work, we present a study of the plasma generated by transversely excited atmospheric (TEA) CO_2 laser irradiation of a basalt sample. The plasma was induced in air at atmospheric pressure. For acquisition of emission spectra a time-integrated spatially resolved detection system was used. The excitation temperature was evaluated by the Boltzmann's plot method for selected Fe II spectral lines in the wavelength range 256-263 nm. The electron number density was determined from the Stark broadening of two iron lines, and results from both lines were identical within the experimental error. Signal to noise (SNR), ratio and limits of detection (LOD) for several elements were evaluated and compared to the results obtained using Nd:YAG laser and time-resolved LIBS measurements.

INTRODUCTION

Due to its unique characteristics, laser-induced breakdown spectroscopy (LIBS) has developed as a versatile technique that can be used for elemental analysis of almost any type of material. The vast majority of LIBS applications deal with analysis of solid materials, many of which are geological samples /1/.

''Standard'' LIBS comprises of three basic components, Nd:YAG laser, a monochromator coupled with an Intensified Charge Coupled Device (ICCD) and a pulse generator to synchronize the plasma production and the emission spectra acquisition /2/. In this work LIBS system based on TEA CO_2 laser and non-gated detection was used. This laser system has been previously applied for the analysis of basalt under simulated Martian atmospheric conditions (CO_2 gas, pressure 9 mbar) /3/. It was shown that the proposed LIBS system provides good analytical capabilities for geological studies under low-pressure CO_2 gas. Other studies of this LIBS system, concerning the analysis of metals and metal alloys, were also conducted under reduced pressure conditions /4/. Although LIBS under different atmospheric conditions offers the possibility to improve the resolution, signal intensity, signal-to-noise ratio or enable specific applications /5/, it also introduces a degree of complexity in the experimental set-up. Thus, the present study was undertaken to examine the possibility of using TEA CO_2 laser based LIBS for the analysis of geologic samples in air at atmospheric pressure.

EXPERIMENTAL

The laser employed is a nanosecond pulsed TEA CO_2 laser, developed at the VINCA institute, which operates at 10.6 μm. Typical output pulse energy was 160 mJ, and repetition rate was 1.3 Hz. The laser pulse temporal profile consists of the initial peak (FWHM of the peak is ~100 ns) followed by a long-lasting tail of about 2 μs. About 35 % of the total irradiated laser energy is contained in the initial spike. The plasma was generated by focusing a laser beam on the target using a ZnSe lens. The angle of incidence of the laser beam with respect to the target surface was 90^o. Rotation of the sample ensured that the laser pulse always hits a “fresh” area at the target surface.

The optical emission from the plasma was viewing in the direction parallel to the sample surface. By changing the position of the plasma along the direction of the expanding plasma, while keeping a constant distance between the focusing lens and the target, different parts of the plasma were observed, i.e., a spatial plasma resolution was achieved. The horizontal part of the plasma was projected by an achromatic lens at the entrance slit of the monochromator equipped with a CCD camera. Each LIBS spectrum is an average spectrum, obtained by accumulation of consecutive spectra from 40 different locations on the sample. This procedure was as a rule repeated in triplicate, and the resulting spectra were averaged.

RESULTS AND DISCUSSION

Irradiation of a basalt sample, with low energy CO_2 laser pulses (160 mJ) under atmospheric air pressure, induced large-volume, long-lasting plasma with favorable conditions for the excitation of lines of all elements usually found in geological samples. In Fig. 1, LIBS spectrum of basalt in narrow spectral windows is shown. The excitation temperature was evaluated by the Boltzmann's plot method for eight selected Fe II spectral lines in the wavelength range 256-263 nm. The calculated temperature was 14300 ± 700 K. The electron number density was determined from the Stark broadening of two iron lines, 260.709 nm and 261.187 nm. The obtained values were 3.63×10^{17} and 3.75×10^{17} cm^{-3}. The time-integrated measurements represent average values of plasma parameters in spatially selected plasma zone, 2 mm from the target surface.

The obtained spectra were compared to the spectra obtained using a commercial LIBS system based on a Q-switched Nd:YAG laser (wavelength 1064 nm, pulse duration 7 ns, frequency 10 Hz, energy up to 100 mJ) and time-gated detection, Fig. 2. The system possesses 8 spectrometer channels covering 182 – 1057 nm spectral range. Experiments were performed at 50 mJ and 80 mJ energy per laser pulse (corresponding fluences were 3.2 J/cm^2 and 5.2 J/ cm^2).

The signals were averaged on 50 laser pulses. The acquisition is made on an integration time of 1.1 ms and with 1.27 μs delay time from the laser pulse.

The advantage of Nd:YAG laser compared to CO_2 laser is higher mass ablation rate per pulse /6/. However, longer wavelength of TEA CO_2 laser, and specific temporal profile of the pulse may produce a plume with better properties for analytical applications. The leading edge of the CO_2 laser pulse creates plasma, while the remaining part of the pulse (tail) interacts with the plume through the inverse Bremsstrahlung, IB. The rate of IB absorption is strongly dependent on laser wavelength ($\sim\lambda^3$), which means that laser - plasma interaction is much stronger in the case of TEA CO_2 laser than the Nd:YAG laser /6/. Efficient IB absorption "re-heats" the plasma causing an additional plasma excitation and expansion. The plasma takes longer to decay and hence, the emission lasts longer.

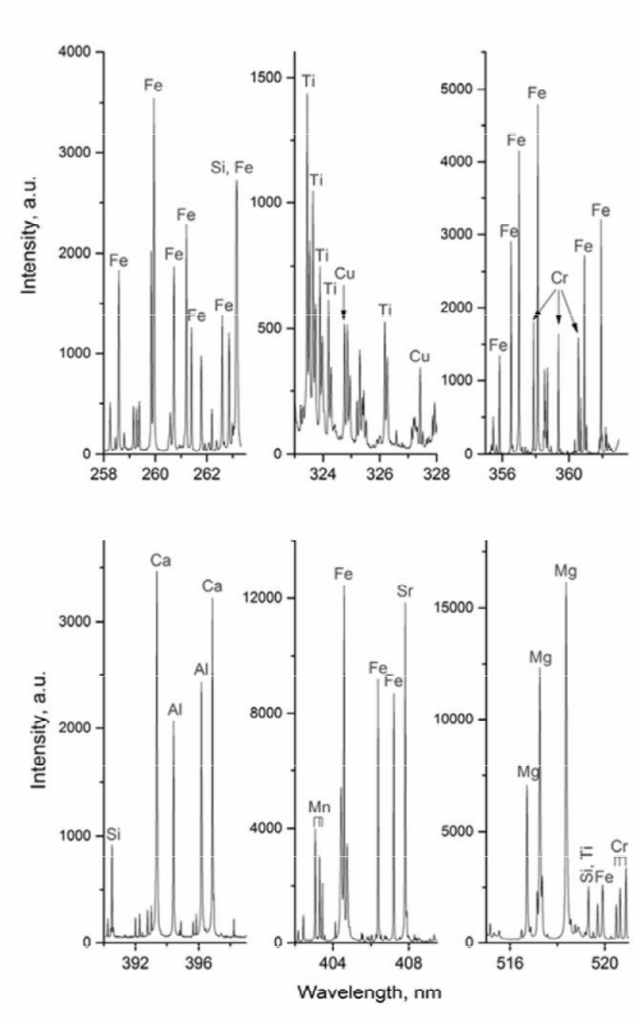

Fig. 1 LIBS spectra of basalt sample recorded in air at atmospheric pressure. TEA CO_2 laser fluence 8.5 J/ cm^2.

For both laser systems, spectral data were processed by calculating the integrated peak area of the emission line, the baseline continuum emission intensity, and the root mean square (*rms*) noise of the continuum radiation intensity in regions adjacent to the emission line. The signal-to-noise ratio (SNR) was calculated as the integrated peak area *A*, divided by the width of the peak area *w*, times the absolute value of the *rms* noise, SNR $= A / (w \times rms)$. The limit of detection (LOD) was then calculated using the formula LOD = $(3 \times c)$ / SNR, where *c* is a known analyte concentration obtained by ICP measurements. Comparison of estimated limits of detection obtained for the two laser systems is shown in Fig. 3. As it can be seen comparable LOD values were obtained.

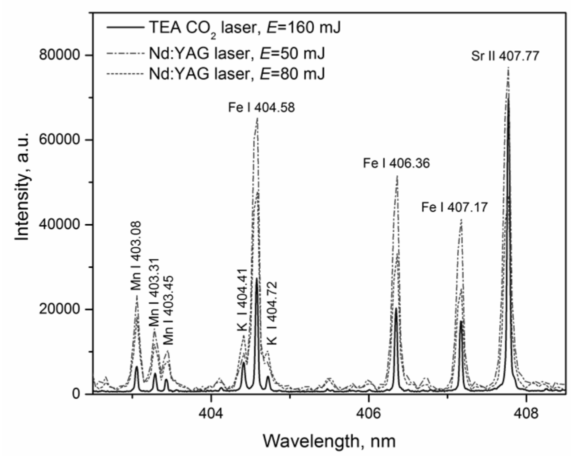

Fig. 2 Comparison of spectra obtained on the basalt sample with a TEA CO_2 laser pulse using a non-gated detection, and with Nd:YAG laser and time gated detection.

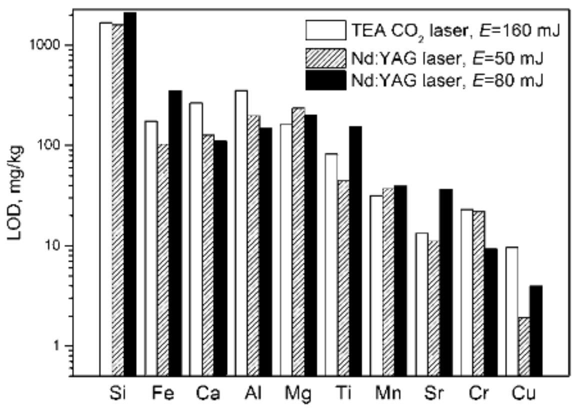

Fig. 3 Comparison of estimated limits of detection obtained for TEA CO_2 and Nd:YAG laser induced plasma over basalt sample in air at atmospheric pressure

CONCLUSION

Laser induced breakdown spectroscopy based on TEA CO_2 laser has been applied to elemental analysis of geological sample in air at atmospheric pressure. Results of qualitative analysis were compared to those obtained using a commercial LIBS system based on pulsed Nd:YAG. Taking all into consideration: low-cost detection system; well-resolved, sharp spectral lines; LODs in the ppm range, typical for LIBS, it can be concluded that the proposed system may be a suitable alternative to conventional LIBS that comprises Nd:YAG laser and time-gated detection.

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