Quantitative elemental analysis by laser-induced breakdown spectroscopy

Taihei Tanaka, Shoji Harada, Tomoaki Ikegami, Fumiaki Mitsugi

Graduate School of Science and Technology, Kumamoto University
2-39-1 Kurokami Chuo-ku, Kumamoto, Japan

Abstract: Laser-induced breakdown spectroscopy (LIBS) has been popular in elemental analysis for various kinds of samples due to its rapid and *in-situ* measurement using simple equipment. However, quantitative analysis by LIBS is still inferior to conventional element analysis methods in sensitivity and accuracy. In this paper improvement in LIBS is attempted applying computational processing to low-resolution spectra.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) [1,2] is based on the generation of laser-induced breakdown plasma on a sample by focusing a high-power pulsed laser beam onto the sample. The emission spectrum from the plasma is used to determine the elemental composition of the sample. The LIBS technique has many advantages: pre-preparation of sample is unnecessary, analysis can be done rapidly with low cost. From these advantages, LIBS is expected to be the analytical tool in the field of environmental monitoring. However, LIBS is inferior to the conventional element analysis methods such as atomic absorption/emission spectroscopy (AAS/AES), and x-ray fluorescence analysis (XRF) in sensitivity and accuracy.

LIBS depends on the following assumptions: the composition of the plasma generated by the laser ablation is the same as the target sample, and the LIBS plasma is uniform and optical thin, and in local thermal equilibrium (LTE) state. In LIBS, identification of spectral lines and accurate measurement of spectral profiles and intensities are important for the quantitative analysis. It is also necessary to characterize the time-evolving LIBS plasma in terms of its temperature and electron number density and find out the time window where the LIBS plasma is optically thin and in LTE.

In practical application of LIBS for quantitative element analysis, standard samples of which composition is known are necessary to calibrate the system. Recently a LIBS method referred as calibration-free LIBS (CF-LIBS) which needs no standard samples was reported [3,4,5]. In CF-LIBS, plasma temperature and element composition are estimated using the Boltzmann plot of specific atomic and ionic spectral line intensities.

In recent years, a new LIBS method to determine plasma temperature, composition ratio, and spectral broadening by fitting the calculated spectrum to the measured one have been attempted[6].

In this work, we have analyzed the composition of solid samples such as metal, metal oxide and soil using LIBS. To improve precision in LIBS with low-resolution spectra, various computational processing are applied to spectra. By fitting the calculated spectrum to the measured one by modifying plasma parameters iteratively, the best fit plasma parameters will be able to estimate element composition ratios of the sample.

2. Theoretical spectral intensity

Spectral line integral intensity is given by Eq. (1) using classical theory

$$I = \alpha \frac{8\pi hc}{\lambda^3} \frac{N_k}{N_i} \frac{g_i}{g_k} \int (1 - e^{-k(v)l}) dv. \tag{1}$$

Here α is constant characteristic of the instrument, λ is the transition wavelength, h is Plank's constant, N_k, N_i are number densities and g_k, g_i are statistical weights, where subscripts k and i refer to values of k (upper)-level and i (lower)-level, respectively. $k(v)$ is the absorption coefficient at frequency v.

Using eq.(1), spectral intensity profile is expressed with Eq.(2) assuming the line profile is given by the normalized Voigt function.

$$I = \alpha \frac{8\pi hc}{\lambda^3} e^{-\frac{(E_k - E_i)}{kT}} \{1 - \exp\left[-\frac{\sqrt{ln2}}{4\pi\sqrt{\pi}} \frac{\lambda^2}{\Delta v_D} \frac{g_k A_{ki} N}{U(T)} e^{-\frac{E_i}{kT}} K(a,x)\right] l\}, \tag{2}$$

where A_{ki} is the atomic transition probability, $U(T)$ is a partition function of an atom or ion at equilibrium temperature T, N is the total number density, E_k and E_i are energy of the levels k and i, and $K(a,x)$ is Voigt function defined as

$$K(a,x) = \frac{a}{\pi} \int_{-\infty}^{\infty} \frac{e^{-t^2}}{a^2 + (x-t)^2} dt, \tag{3}$$

where a and x are defined as follows

$$a = \frac{\Delta v_N + \Delta v_L}{\Delta v_D} \sqrt{ln2} \tag{4}$$

$$x = \frac{2(v - v_0)}{\Delta v_D} \sqrt{ln2} . \tag{5}$$

Here $\Delta v_N, \Delta v_L$ and Δv_D are the natural, Doppler and Lorentzian line widths, respectively, and v_0 is the center frequency of the emission line.

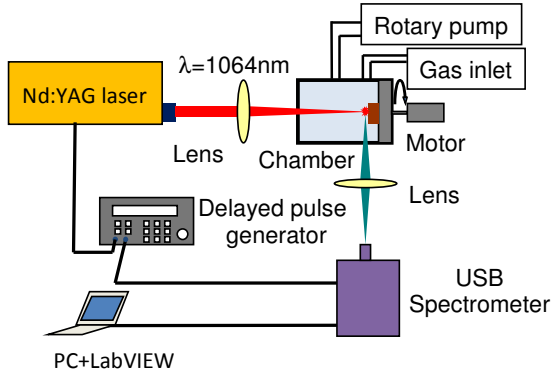The Voigt function $K(a,x)$ was calculated using the following equation [7]

Fig. 1 LIBS experimental setup.

$$K(a, x) = \exp(a^2)\, \mathrm{erfc}(a)\, \exp(-x^2)\cos(2ax)$$
$$+ \frac{2}{\sqrt{\pi}} \int_0^x \exp[-(x^2 - u^2)]\sin[2a(x - u)]\mathrm{d}u. \qquad (6)$$

The partition function $U(T)$ is defined as

$$U(T) = \sum_j g_j \mathrm{e}^{-E_j/kT}\ , \qquad (7)$$

and the values for atomic and ionic species were calculated in the temperature range 1,000 K $\leqq T \leqq$ 16,000 K using the polynomial approximations[8].

3．Experimental setup

Figure 1 shows the experiment setup for the LIBS. A Q-switched Nd:YAG laser (Spectra-Physics GCR-130, wavelength 1064 nm, pulse duration 8 ns, repetition rate 10 Hz, and laser energy 50-200mJ) produced LIBS plasma on the sample (metal alloy, ceramics, soil etc.) in a sample chamber filled with ambient gas (air, He, Ar). The target sample was rotated during laser ablation to avoid pitting. Emission light from the target surface was collected by a quartz lens (f=150mm) and transferred by a quartz optical fiber into the USB spectrometer（Ocean Optics, USB4000), of which wavelength and sensitivity were calibrated using a deuterium and a mercury lamp. To obtain clear atomic spectral lines, trigger delay time and gate width of the spectrometer were adjusted and controlled by the delay pulse generator (SR GD535). In addition, we improved the SN ratio of the spectral data by outlier rejection and averaging. The spectral resolution was also improved by Fourier Self-Deconvolution method.

A program using LabVIEW was developed to acquire LIBS spectra and analyze them. The program detects peaks in the LIBS spectrum and identifies atomic and ionic lines referring to the spectral database[9][10]. Theoretical spectral profiles are calculated using Eqs.(2)-(6) with corresponding atomic data under assumption of plasma temperature T, electron number density n_e, and number density of j-th species N_j in the LIBS plasma.

4. Result and discussion

As a solid metal oxide sample, PZT(lead zirconate titanate) was used. The LIBS spectra of PZT was measured in air of reduced pressure about 70 kPa to suppress the emission from N_2 molecules. In Fig. 2 LIBS spectrum of PZT is shown and marked at the identified emission lines with the symbols. The emission intensity is plotted in the logarithmical scale. The atomic emission lines Ti I, Zr I, Pb I and ionic lines Ti II, Zr II are observed.

To estimate composition ratio in the plasma, each emission spectral profile was calculated by the above-mentioned method for identified emission lines using various parameters. The spectrum calculated with
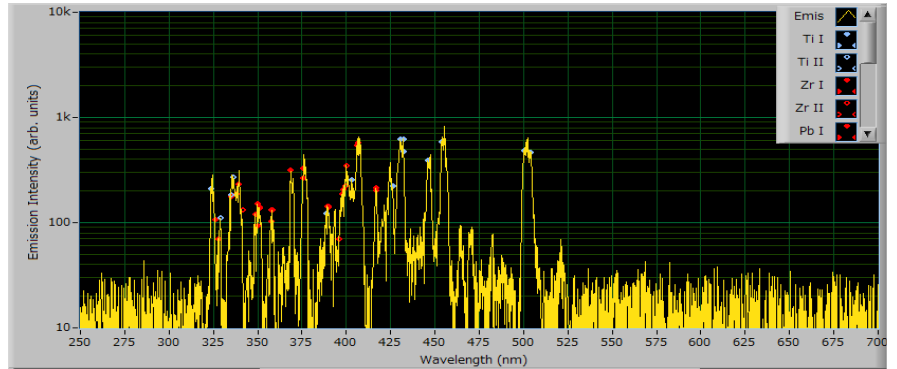

Fig. 2 LIBS spectrum from a PZT sample.
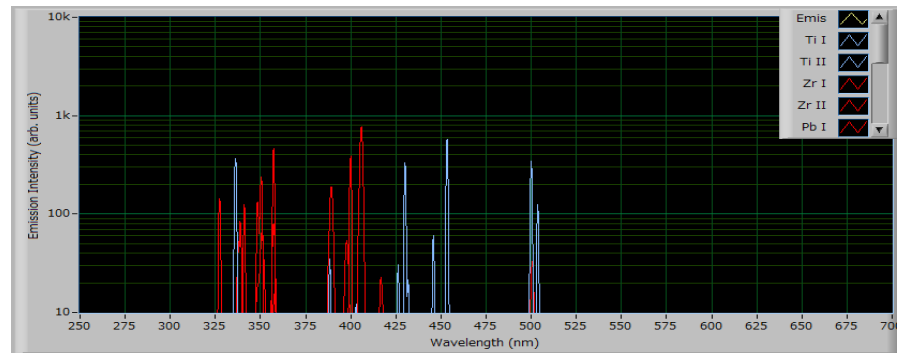composition ratio Pb : Zr : Ti = 41 : 39 : 20 at T=7,000

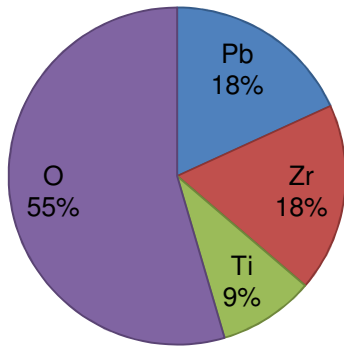Fig. 3 Calculated spectrum using identified spectral lines in Fig. 2.

Fig. 4　Composition of PZT measured by XRF.

Fig. 5　Composition of soil measured by XRF.

K is shown in Fig.3. Since oxygen atoms are contained in both the PZT sample and the ambient air, it is not able to discriminate their origins, so oxygen atoms are excluded in the calculation. A good similarity can be seen between the observed spectrum and calculated one. The composition ratio of the PZT sample was measured by XRF (Rigaku ZSX PrimusII) and shown in Fig.4. The composition ratio of the PZT is Pb : Zr : Ti : O = 18 : 18: 9 : 55 and it seems definitely accurate. Excluding oxygen component, the metal atoms composition ratio is Pb : Zr : Ti = 40 : 40: 20, which is very close to that estimated by LIBS.

To apply LIBS to more complex composition samples, soil in a field was used. Soil was ground using a mortar to make uniform in grain size and composition, then it was molded by a hydraulic press into a disk of 5 mm in thickness and 30 mm in diameter, and then dried.

The composition of soil by XRF is shown in Fig.5, where all constituents are analyzed as oxides and lighter elements than N are undetectable by our XRF. Major constituent elements of the soil are Si, Al, Ca, and Fe.

Figure 6(upper) shows the LIBS spectrum of soil measured in 1 atmospheric He gas. Many spectral peaks are well identified as emission from elements of Na, Mg, Al, Ca, Ti, Fe, V. However there are some unknown peaks because the spectral resolution of the spectrometer is low (instrumental width about 0.6 nm in FWHM) and some spectral lines overlap within the instrumental width. And further, emission lines from major elements such as Si, C cannot be seen. This may result from the poor sensitivity of the spectrometer at short wavelength (<250nm) in which prominent emission lines of Si and C exist.　　The emission line intensity profiles corresponding to the identified lines were calculated at T=11,000 K in the same way as in
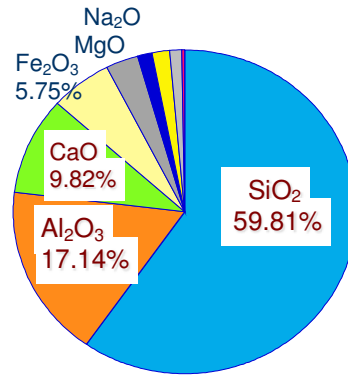
Fig.3. All spectral profiles are summed up and shown in Fig.6 (lower). The similarity among these two spectra (upper and lower) can be seen.

5. Conclusions

Composition ratios of metal alloy, metal oxide and soil were measured by LIBS and XRF. In the case of uniform and simple composition sample such as brass and PZT, by fitting the LIBS spectrum to that of calculated with spectral atomic data under assumed parameters, the composition ratios by LIBS showed a good agreement with those by XRF. In the case of a complex sample like soil, most of elements in soil can be detected from its LIBS spectrum, however, poor agreement with XRF result was obtained. In calculation and fitting spectrum,
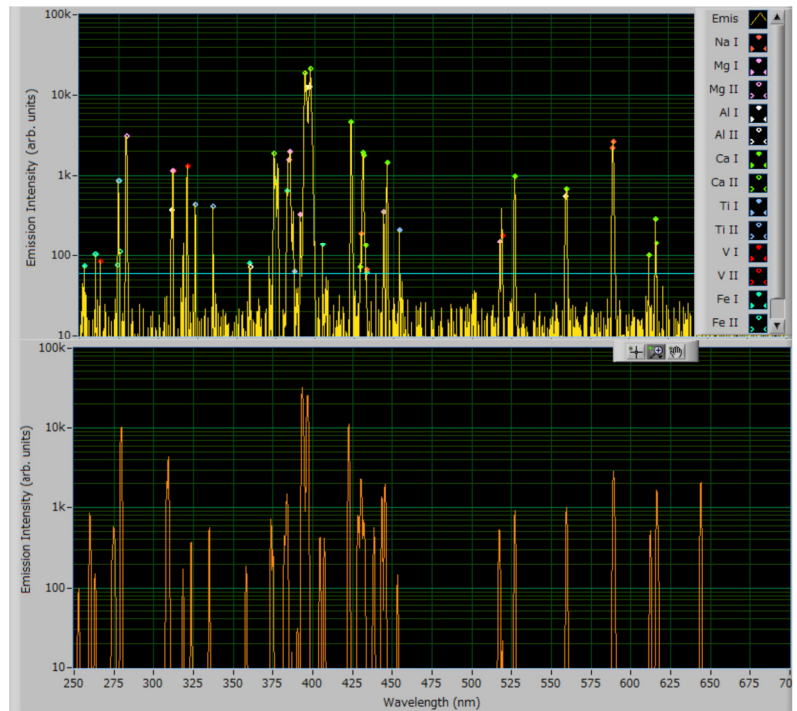

Fig. 6　LIBS spectrum (upper) of soil and
calculated spectrum (lower).

more practical plasma model seems necessary.

6. References

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