A quantitative analysis for a Lanthanum series element using Laser induced breakdown spectroscopy

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1. Introduction

LIBS (Laser induced breakdown spectroscopy) is a technology to analyze both qualitatively and quantitatively. An experiment was carried out by way of a spectroscopic analysis on plasma directly produced from a high powered Laser ablation on a sample. In view of Safeguards implementation, LIBS method has an advantage of a timely analysis of multi element in a sample taken from a nuclear fuel cycle facility when compared to a time consuming chemical analysis method. And yet the accuracy of the performance is expected to be not favorable due to a high degree of freedom in a plasma sphere derived from a Laser. This experiment is focused on stabilizing a plasma sphere in order to enhance the accuracy on LIBS.

2. Methods and Results

This study was to derive an optimized measurement condition with a high reproducibility and to grow a plasma sphere to 20 mm high under 500±12 mtorr vacuum.

The signal intensity was measurement at the point of 5.4 mm distance in the direction of a plasma sphere from a sample. A preliminary experiment was implemented quantitatively on non-radiation elements such as Nd (U replaced element) and Gd of the Lanthanide family in a clean lab area, and then the concerned elements, U and Pu.

2.1 Instrumentation of Experiment

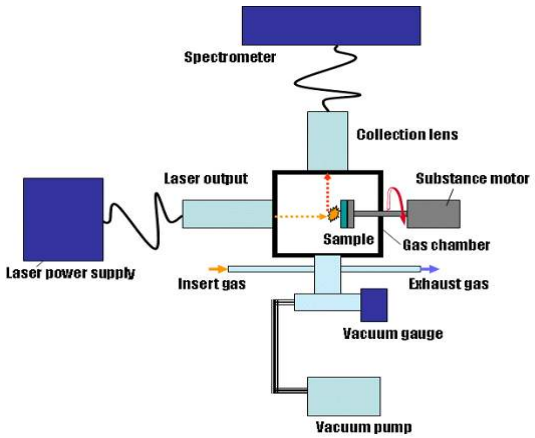

Fig. 1 The composition of actuality LIBS

Fig.1 shows the LIBS system that way actually arranged to do the experiment in the Lab. The wavelength of the laser source was 1064 nm, having a power output of 37.5 mJ, 6 ~ 8 ns of a pulse duration, and 2% of a energy stability. Spectrometer used a CCD type detector with 14,336 pixels with a 0.1 mm(FWHM) resolution and a 2.1 ms integration time. Gas chamber was manufactured with SUS material having build-in 3 directional quartz windows. The opposite side of the laser input window was located by a sample supporter. The substance motor was installed to minimize sample surface damage by a high powered laser beam.

2.2 Sample Preparation

A preliminary measurement was carried out on the elements belong to the Lanthanide family prior to a measurement of the actinium elements. Two of each ingot type sample were prepared in on Arc Melting Furnace at 3000℃ starting with a homogeneously mixed powder form of Nd and Gd. In order to secure its standard signal an ingot type of a reference sample of Nd and Gd with a known composition equivalent to unknown samples was also prepared. All of the samples prepared have a thickness of 5.40 mm for the same measurement condition.

2.3 Derivation of optimized measurement condition

To obtain a signal with a high reproducibility a substance motor was introduced to make a sample revalue for less damage to a sample surface by a high procured laser beam. The optimized measurement condition was found to be at output power of 18.75 mJ as a gradual increase of a laser power at which the reproducibility was the highest. The plasma sphere size was sustained at 500±12 mtorr of a vacuum condition for a plasma sphere stabilization. The measurement results will be discussed in 2.5.

2.4 Determination of Standard Signals

The measurement was made in the range of 400 ~ 600 nm signals Nd and Gd reference sample. The signals were taken selectively based on a non-overlapping and the highest reproducibility. The measurements of the standard signals were determined as 430.2 nm for Nd and 425.2 nm for Gd respectively.

2.5 Measurement & Analysis

Each measurement was performed after 50 times it laser ablations under the same condition, and repeated 5

times in order to evaluate signal reproducibility. The measurement results are shown on Table.1. In addition, the measurement data from the LIBS were compared with the average values obtained from the EDS of SEM after analyzing it against a sample surface.

Table.1 The reproducibility of signal

		Nd ; 430.2 nm	Gd ; 425.2 nm
Mixed sample 1	means	23.20	28.20
	R.S.D (%)	4.18	6.81
Mixed sample 2	means	26.31	23.72
	R.S.D (%)	7.53	6.11

- R.S.D ; Relative Standard Deviation

The measured signal in intensity by the LIBS of mixed sample1 was corrected to be that of a mixed-sample2 based on an obtained atomic weight percent derived from a average measurement value obtained from a specific element, Gd of mixed-sample2 was normalized to the EDS corrected value of mixed-sample2. After the same correction process to the other remaining elements in mixed-sample1 the corrected measurement values were compared with the EDS values to derive a revision factor through the differences as shown in Table.2. Introduction of a revision factor here is to compensate for an uncertainty in a signal intensity caused by the stability of a laser power output, a degree of reflection on a sample surface, and a sample's homogeneity.

Table.2 The quantitative analysis for Nd

	Gd ; 425.2 nm	Nd ; 430.2 nm
Mixed sample1(real)	28.20	23.20
Mixed sample2(estimate)	38.30	44.26
Mixed sample2(real)	23.72	26.31
Revision Factor	1.61	
Mixed sample2(revision)	38.19	42.36
Different	Basis	4.29 %

- The measurement value for EDS (Atomic percent)
; Mixed sample 1 (Nd-18.42%, Gd-40.29%)
Mixed sample 2 (Nd-35.14%, Gd-54.72%)

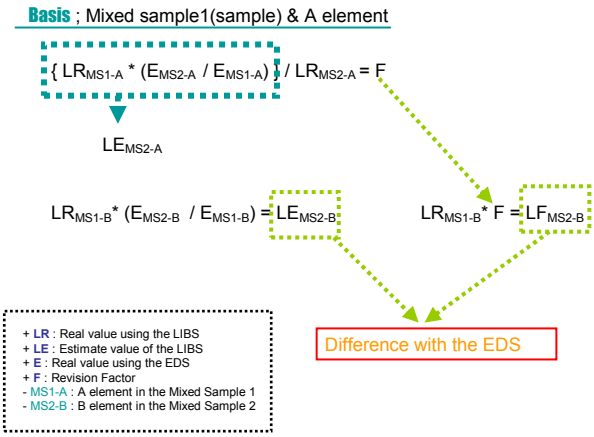

Fig.2 The Quantitative analysis using a signal intensity

Fig.3 shows LIBS' raw data and a real plasma flame incurred in the experiment, Fig.3 describes the SEM image for the EDS analysis.

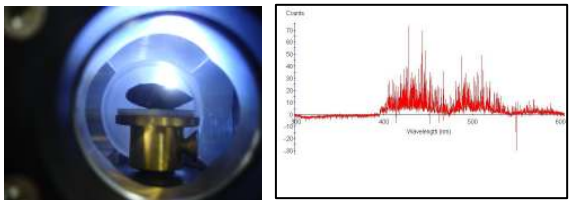

Fig.3. LIBS spectrum & actually plasma sphere of mixed sample 1

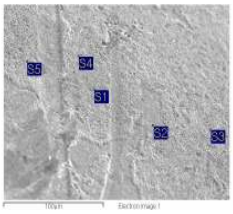

Fig.4 SEM image of mixed-sample 1, S1~S5 is measurement point for EDS analysis

3. Conclusions

LIBS, is making it possible for a real time measurement on sample, displayed about 4~7% of a reproducibility by a proper adjustment of the laser output, plasma environment, and sample geometry. LIBS measurement values gave a 4.29% difference from that of the EDS through a measurement location adjustment of the derived plasma. Further effort is needed for an enhancement of the measurement reproducibility by means of a quantitative analysis of varied mixture of Lanthanide family elements.

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