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METAL-SUPPORTED LASER-INDUCED BREAKDOWN SPECTROSCOPY FOR THE TRACE ELEMENTAL IDENTIFICATION OF MATERIAL

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ABSTRACT

Trace elemental identification of Cr deposited on a material target was made using metal-supported laser-induced breakdown spectroscopy. Experimentally, an almite material containing a trace element of Cr on its surface was perpendicularly placed on a Cu metal plate. A pulse CO_2 laser beam was irradiated on the Cu plate to produce a plasma. The plasma then interacts with the trace elements deposited on the material surface, and finally, the elements are effectively excited in the gas plasma region. The role of laser irradiation in the analyte intensity was examined. The results certified that the intensity of impurity decreased with the number of laser bombardments on the material target. Furthermore, rapid identification and analysis of Cr as a trace element can be made successfully. The limit detection of Cr as a trace element was 1 mg/kg. This method has a great deal of promise for use in the surface examination of material businesses to systematically check the material's quality.

Keywords: Trace Elemental Analysis, TEA CO_2, LIBS, Laser Laser-Induced Breakdown Spectroscopy

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INTRODUCTION

Trace elemental analysis of material targets is very urgent in many fields such as material science and industry.[1-3] In material science, trace elements deposited on the fabricated material can reduce the quality of the material. In industry, trace metal analysis is necessary for the quality control of material products. The methods commonly used to identify the trace elements on a material include XRF (X-ray fluorescence) and XRD (X-ray diffraction) spectroscopies.[4-8] Using those techniques, trace elements in material targets can be identified and analyzed with a sensitivity of tens to hundreds ppm level. However, the technique requires tedious sample preparation, still lacks sensitivity and is high-cost in an instrumentation system. Laser-induced breakdown spectroscopy (LIBS) is a leading method for conducting the identification and analysis of elements on a variety of materials, including liquids, gases, and solids.[9-14] The most common energy source utilized to excite and ionize atoms ablated from the material target is a high-intensity Nd: YAG laser.[15] Spectrometers are used to get spectra of elements emitted from a plasma generated on the target of material.[16] The LIBS technique is powerful and superior compared to other elemental techniques such as XRD and XRF. Namely, the technique is less sample pretreatment, quite sensitive, and quite a low cost in the analytical instrument. This technique has been employed in many fields including materials,[17] energy,[18-19] environments,[20-21] and space.[22-23] However, for analysis of trace elements deposits on the surface of the material, the material itself will ablate and break when the pulse laser is irradiated on the material's surface, and as a result, the analytical emission lines from the material will perturb the trace elemental lines. As a result, this approach cannot be utilized to perform elemental analysis on material surfaces. In the opposite way, we carried out a soft material investigation using a pulse CO_2 laser.

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This laser is appropriate for soft materials, this is due to its longer wavelength and longer pulse duration than the case of the Nd: YAG laser.[24] As a result, plasma absorption is much more effective in producing high-temperature and large-volume plasma because it is proportional to the inverse square of laser light frequency. Using this laser, we have also applied LIBS to perform surface analysis of materials. However, we noticed that the sensitivity is quite low, especially for the analysis of the Elamite sample. In this study, we present a novel method for analyzing trace elements on a material surface using a metal plate-supported plasma-induced TEA CO_2 laser. In an experiment, a metal plate had a material target mounted perpendicularly to it. The laser produced a large volume and high-intense plasma when it was directed at a metal plate. The trace element that has been deposited on the material surface is then immediately contacted by the plasma. Finally, the trace elements enter the plasma area where they will be excited. The examination of a trace element on a material surface has been effectively completed using the current technique with minimal material ablation.

EXPERIMENTAL

Almite solid sample (Al_2O_3) was the sample target used in this investigation. The sample contains some impurities including Ca and Na. The sample also contains Cr at a concentration of 25 mg/kg. During an experiment, the sample was kept in a chamber with a dimension of 12 cm^3. In the metal chamber used for the experiment, 99.999 % helium gas was flowing while the surrounding gas pressure was maintained at 1 atmosphere. The gas flowed at a rate of 4 liters per minute (Lpm). Figure-1 shows an illustration of the experimental setup used in this work. A material target was set perpendicularly with a Cu metal plate.

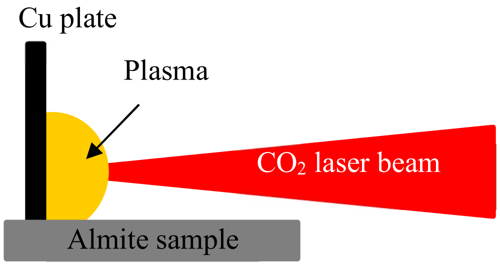

Fig.-1: Experimental Setup Used in This Work

During an experiment, a 20 cm focal length ZnSe lens was used to focus a pulsed TEA CO_2 laser (10.64 m, 200 ns) beam on a Cu metal plate in order to create a large-volume plasma. The laser energy of 750 mJ was chosen; It must be noted that no Cu metal was ablated during the laser bombardment. Only high-intensity gas plasma could be created using the metal plate. The plasma then came into direct contact with trace elements that had been applied to a material target. The plasma emission was then transmitted via optical fiber into an optical multichannel analyzer (OMA) system. The OMA systems were configured in time-gated mode with 10 µs and 100 µs gate delays and gate widths, respectively.

RESULTS AND DISCUSSION

First, the examination of the trace elements deposited on the material surface of the almite sample was carried out using a standard method of pulse CO_2 laser-induced breakdown spectroscopy without assisting a metal Cu plate; namely, the pulse laser was directly focused on the material surface. In particular, the almite sample served as the material target. The surface of the almite material has deposits of the trace elements of Ca and Na.

Figure-2 displays the emission spectra obtained from an almite sample at wavelengths between 360 and 410 nm using 20, 40, and 60 laser pulses, respectively. Ionic Ca lines' emission spectra at 393.3 nm and 396.8 nm clearly shows high intensity and little background emission. The neutral He line at 388.8 nm manifests with strong intensity. The He surrounding gas employed in this study led to the formation of this emission line. Additionally, emission lines that definitely belong to neutral Al lines can be seen at 394.1 nm and 396.1 nm. These lines originate from the actual almite sample. Additionally, it should be noted that when the number of laser shots increases, the intensity of all analyte emission lines, with the exception of

He I at 388.8 nm, drops. This proved that the trace elements deposited on the almite surface are finished as the number of laser shots increases since they have already entered the gas plasma area to be excited.

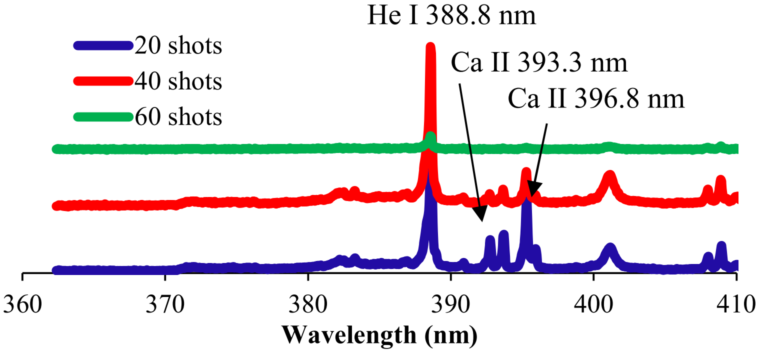

Fig.-2: Emission Spectrum of Ionic Ca Obtained from the Almite Sample Using Standard CO_2 LIBS

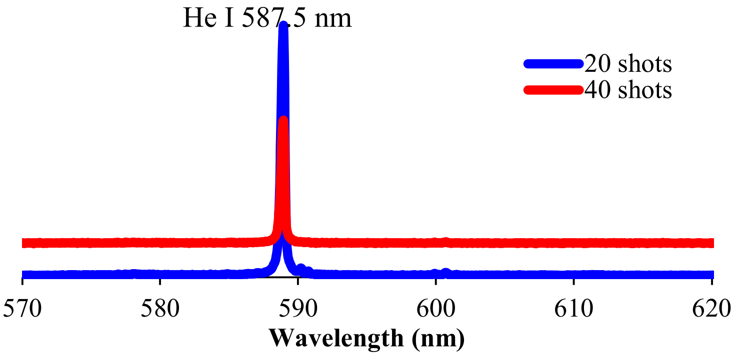

Fig.-3: Emission Spectrum of Na Obtained from the Almite Sample Using Standard CO_2 LIBS

The other trace element of Na deposited on the almite sample was also identified using the ordinary pulse CO_2 LIBS. Figure-3 shows the emission spectrum of Na at the wavelength of 588.9 nm and 589.5 nm. The spectrum was identified clearly with quite high intensity and low background emission together with the triplet He emission at 587.5 nm. With increasing the number of laser shots, the emission intensity of Na lines diminished after 40 laser shots. It should be noticed that even the ordinary LIBS using pulse TEA CO_2 laser can be used to identify impurities on the material surface, the sensitivity detection is still quite low and the material itself is so much ablated by direct laser bombardment. We developed a novel metal-supported laser plasma approach to address the issue, as shown in Fig.-1. In comparison to the instance of plasma generated using a regular Nd: YAG laser, the generation of gas plasma utilizing a TEA CO_2 laser with the assistance of a metal plate is very advanced. In this instance, when the laser beam was focused on a metal surface, multiphoton absorption via the photoelectric effect prevented any metal from being ablated and only caused electrons to escape from the metal surface. The electrons then speed in the laser's electric field and crash with gaseous particles to create a gas plasma. As an excitation source for the target material's atoms, the plasma is employed. First, we applied the developed technique for the identification of the trace elements as the same sample used in the previous Fig.-2 and Fig.-3. Figure-4 displays the emission spectrum of Ca using the developed technique of metal-supported laser plasma.

Along with the emission lines of Al, high ionic Ca emission intensity is clearly visible between 393.3 and 396.8 nm. As seen in Fig.-4, the intensity of ionic Ca is noticeably higher than it would be for a standard LIBS (Fig.-2). In addition, the Al lines are substantially less intense than the Al lines produced utilizing the mesh-assisted gas plasma approach described in our earlier work.[25] This outcome demonstrated that the current method contributes significantly less ablation of the material sample than the prior method did, as well as effective dissociation and excitation of trace elements.

It should be emphasized that the new technology has a lot lower laser intensity than standard LIBS or the earlier mesh-aided gas plasma technique because the laser is not directly focused on the material itself. The metal was positioned perpendicular to the material target, and the laser was directed at it.

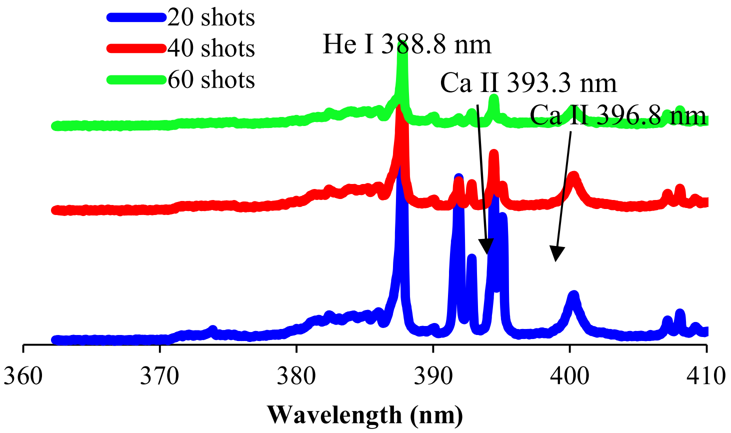

Fig.-4: Emission Spectrum of Ca Taken from the Almite Sample Using Developed Technique of Metal-Supported Laser-Induced Breakdown Spectroscopy

A significant volume of gas plasma was created just above the material surface when the laser impinged on the metal surface. It is proposed that the trace element put on the material surface directly interacts with the gas plasma. After that, the trace elements enter the gas plasma area to be excited. Comparing the developed method to the case of standard LIBS and mesh-assisted gas plasma, the intensity of the trace element is substantially higher. This may be due to the fact that the plasma in the developed technique directly interacts with the trace elements in a wider area, resulting in a much higher concentration of trace elements that enter and dissociate in the gas plasma region than in the case of standard LIBS and mesh-assisted gas plasma technique.

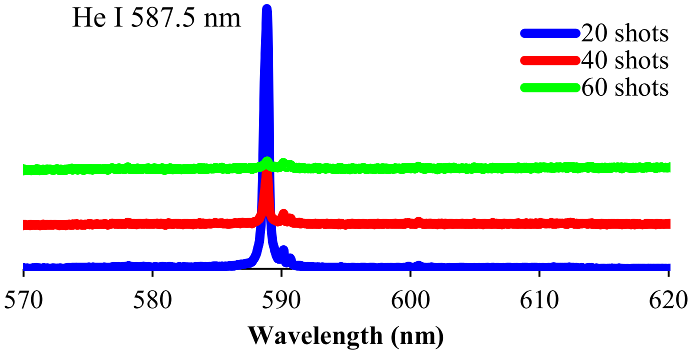

Fig.-5: Emission Spectrum of Nataken from the Almite Sample Using Developed Technique of Metal-Supported Laser-Induced Breakdown Spectroscopy

Further analysis is made for Na impurity deposited on an almite surface. Figure-5 displays the emission spectrum of Na obtained from the almite surface. Together with the He emission line at 587.5 nm, which was contributed by the He surrounding gas, very clear Na emission lines also appears at 588.9 nm and 589.6 nm. In the case of the developed technique in comparison to the standard LIBS (Fig.-3), the intensity of the Na lines is significantly higher.

The developed was then used to analyze the Cr element that had been deposited on the surface of the material. Figure-6 displays the Cr emission spectrum as measured from the material's surface of almite containing 25 mg/kg Cr. With strong emission intensity and little background emission, specific triple emission lines of Cr at the wavelengths of 325.4 nm, 327.4 nm, and 328.9 nm are clearly visible. High-intensity Ca emission lines can also be seen at 422.6 nm, which corresponds to the neutral Ca line. The limit of detection for Cr as a trace element deposited on the surface of the material using this method was 1 mg/kg; it was calculated by dividing the three times noise by the analyte's emission intensity. It is possible to perform surface analysis using this method with good sensitivity and minimal material ablation.

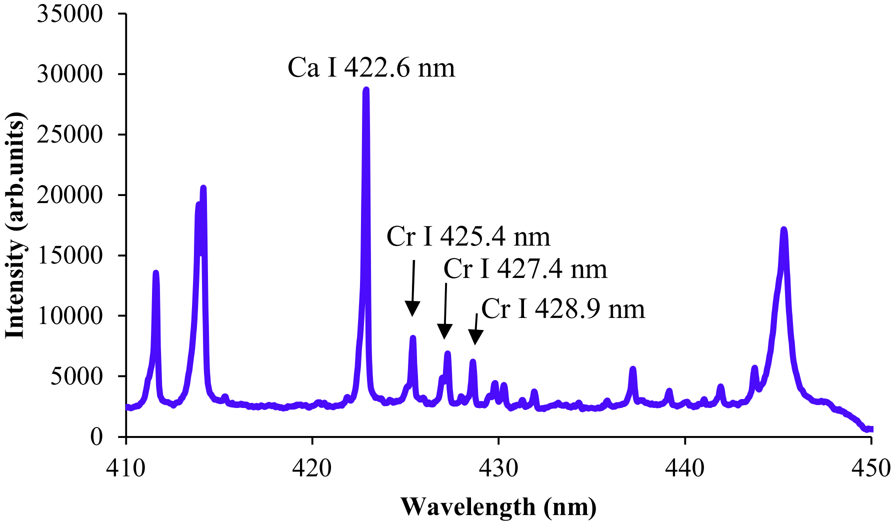

Fig.-6: Emission Spectrum of Cr Taken from the Almite Sample Using Developed Technique of Metal-Supported Laser-Induced Breakdown Spectroscopy

CONCLUSION

Metal-supported laser-induced gas plasma spectroscopy with a pulsed TEA CO_2 laser was used to identify and analyze a trace element on the material surface of an analyte sample target. This method involved placing a substance on a metal plate perpendicularly that had a trace element on its surface. The trace elements that have been deposited on the surface of the material interact with the gas plasma created by helping the metal plate, and eventually the elements are excited and separated there. This method successfully enables the quick detection and analysis of trace elements. On a material surface, the limit of detection for Cr was calculated to be 1 mg/kg. This method has a great deal of promise for use in the surface examination of material businesses to systematically check the material's quality.

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