Spectral Analysis of Rare Earth Elements using Laser-Induced Breakdown Spectroscopy

SPIE DSS

Madhavi Z. Martin, Robert V. Fox, Andrzej W. Miziolek, Frank C. Delucia, Jr., Nicolas Andre

May 2015

The INL is a
U.S. Department of Energy
National Laboratory
operated by
Battelle Energy Alliance

INL

Idaho National Laboratory

Spectral Analysis of Rare Earth Elements using Laser-Induced Breakdown Spectroscopy

Madhavi Z. Martin*, Oak Ridge National Laboratory, Oak Ridge, TN 37831
Robert V. Fox, Idaho National Laboratory, Idaho Falls, ID 83415
Andrzej W. Miziolek and Frank C. DeLucia, Jr., US Army Research Lab, APG, MD 21005
Nicolas André, The University of Tennessee, Center for Renewable Carbon, Knoxville, TN 37831

ABSTRACT

There is growing interest in rapid analysis of rare earth elements (REEs) both due to the need to find new natural sources to satisfy increased demand in their use in various electronic devices, as well as the fact that they are used to estimate actinide masses for nuclear safeguards and nonproliferation. Laser-Induced Breakdown Spectroscopy (LIBS) appears to be a particularly well-suited spectroscopy-based technology to rapidly and accurately analyze the REEs in various matrices at low concentration levels (parts-per-million). Although LIBS spectra of REEs have been reported for a number of years, further work is still necessary in order to be able to quantify the concentrations of various REEs in real-world complex samples. LIBS offers advantages over conventional solution-based radiochemistry in terms of cost, analytical turnaround, waste generation, personnel dose, and contamination risk. Rare earth elements of commercial interest are found in the following three matrix groups: 1) raw ores and unrefined materials, 2) as components in refined products such as magnets, lighting phosphors, consumer electronics (which are mostly magnets and phosphors), catalysts, batteries, etc., and 3) waste/recyclable materials (aka e-waste). LIBS spectra for REEs such as Gd, Nd, and Sm found in rare earth magnets are presented.

Keywords: Laser-induced breakdown spectroscopy, LIBS of rare earth magnets, LIBS for detection rare earth elements.

1. INTRODUCTION

Advanced materials are key for achieving superiority for the US military. For example, performance in imaging, protection, armor, stealth, and lethality is directly dependent on the materials that are used in various weapons systems. Rare earth elements (REEs) play a very important role in various advanced devices including magnets, sensors, lasers, transducers, and motors. These devices, in turn, are key to military systems such as radars, laser rangefinders and target designators, and precision guided munitions. In short, REEs play a critical role in electronics and optics, as well as for electromagnetic properties of a large number of systems. Due to their pivotal role in both military and civilian use, the dependable supply of these materials is crucial for both economic prosperity and national defense.

Rare earths of commercial interest are found in three different matrices: 1) raw ores and unrefined materials, 2) refined products such as magnets, lighting phosphors, consumer electronics (which are mostly magnets and phosphors), catalysts, batteries, etc., and 3) waste/recyclable materials (aka e-waste). The aim of the present work is to examine the applicability of LIBS to the real-time analysis of commercial-grade rare earth magnets commonly found as functioning materials in consumer electronics. The authors will demonstrate that LIBS via this study, has significant potential application as a rapid, accurate, inexpensive analytical technique for the identification of rare earth components commonly found in electronic devices (both consumer-grade and military grade). LIBS can potentially be used for the rapid screening and identification of valuable materials sent to the recycle bin, and for the efficient recovery and diverting of those materials to a rare earth recycle process. Recycle and recovery of rare earth components from electronics will not only serve to relieve market stresses currently assailing lanthanide supplies, but is also a key step towards resource sustainability and minimizing environmental impact. The magnets used in this work are primarily commercial-grade neodymium-iron-boron, or samarium-cobalt-based magnets.

 * Martinm1@ornl.gov; phone 1 865 574-7828; fax 1 865 576-8646

1.1 Introduction to LIBS

Laser ablation of solids can directly fingerprint elemental constituents via their characteristic optical emission spectra. Most elements have easily identifiable emission wavelengths across the uv-vis spectrum. LIBS has the ability to provide rapid multielemental microanalysis of bulk samples (solid, liquid, gas, aerosol) in the parts-per-million (ppm) range with little or no sample preparation [1-11]. Recently there has been a concerted effort in applying LIBS in the detection of and identifying country of origin of explosives and other materials [12-17]. The pulsed laser which is used in the LIBS experimental setup vaporizes a small volume of sample material with sufficient energy for optical excitation of the elemental species in the resultant sample plume and associated plasma. The elements present in the sample volume then undergo de-excitation and optical emission on a microsecond time scale, and time-dependent ultraviolet-visible spectroscopy fingerprints the elements associated with the spectral peaks. LIBS is typically a surface analytical technique, with each laser pulse vaporizing microgram or submicrogram sample masses. However, the rapidity of sampling (typically 10 Hz laser repetition rate) and ability to scan a sample' surface, ablate a hole into a solid sample with repeated laser pulses, or focus the laser spark below the surface of a liquid sample permits more versatile analyses and provides sufficient statistics for bulk sampling.

The greatest advantage of LIBS is its capability for remote chemical analysis of samples with minimal handling and little or no sample preparation, which minimizes generation of waste to the microgram per pulse of ablated material. Further advantages of LIBS are its ability to do real-time identification of metals and non-metals in seconds, capability of multielemental detection with a broad-band spectrum acquisition, and continuous monitoring for depth profiling and surface mapping. Although calibration standards are required for quantitative analysis, the generation of a single calibration curve will suffice for analysis of samples in a similar matrix [18, 19].

1.2 Study Objectives

- Use LIBS technique to differentiate between the surface coating layers and the underlying magnetic surfaces.
- Use LIBS to detect and identify elements from very complex spectra for the Nd and Sm-based magnets.
- Evaluation of LIBS technique to detect Nd, Sm, Fe, Co, and other RE elements.

2. EXPERIMENTAL CONFIGURATION

For this study we utilized three different LIBS systems for spectroscopy studies, while one of these systems was further utilized for depth profiling. The main components of this third experimental system are a pulsed Big Sky laser model CFR-Ultra which is a Q-switched Nd:YAG laser with frequency doubled output wavelength of 532 nm [11]. Laser energy of 45 mJ was used to obtain all the sample spectra. The experimental setup is equipped with an X-Y-Z stage to provide capability of 3 dimensional movements. An autofocusing laser (632 nm) is employed to make sure that the focused laser beam which is exciting the sample surface is always at the same height on the surface of the sample. The light emitted by the plasma at the focal volume was collected by a set of collection optics and focused into a low O-H silica fiber bundle consisting of 7 fibers. The optical fiber is used to deliver the light to an Echelle spectrometer from Catalina Scientific model SE 200 spectrometer that resolves light into different wavelengths by a high order dispersion module (200-800 nm). These were then detected by a 1024x1024 pixel intensified 2D-charge coupled detector (ICCD) made by Andor Technologies. The detector is cooled down to -15 C to reduce the dark current and increase the signal-to-noise ratio. The advantage of using an ICCD is that the detection can be delayed with respect to plasma formation. The data was collected by using a delay of 1 microsecond, a gate width of 10 microseconds, and the repetition rate at which the laser was operated was 5 Hz. The whole process of sample excitation, plasma formation, light collection, and optical-to-digital conversion of the signal takes only a second to a few seconds depending on the number of shots that are averaged.

3. RESULTS AND DISCUSSION

Rare earth magnets are extremely brittle and also vulnerable to corrosion, so they are usually plated or coated to protect them from breaking, chipping, or crumbling. The LIBS technique was used to penetrate the coating with tens of shots on the surface until the laser beam is exciting and sampling the magnetic material below the layer of coating. The sampling sequence that was used to obtain the individual spectra is as follows: The first 50 shots were used to collect the first spectra. This shows the averaged spectra of the coating on the individual magnets. The next 50 shots were used to collect the next spectra and this was repeated again to make sure that the spectra that were collected in this sequence would give us the representation of the real sample surface by the last 50 shots that were averaged. To acquire 50 laser shots with a repetition rate of 5 Hz takes only 10 seconds to obtain the spectra. So in 40 seconds it has been shown that it is possible to penetrate the coating of the magnets to the actual material of the Nd and Sm- based magnets. This is shown very clearly in figure 1 for laser pulse burn- through the coating layer and then reaching the Nd-based magnetic material on the last 50 laser shots.
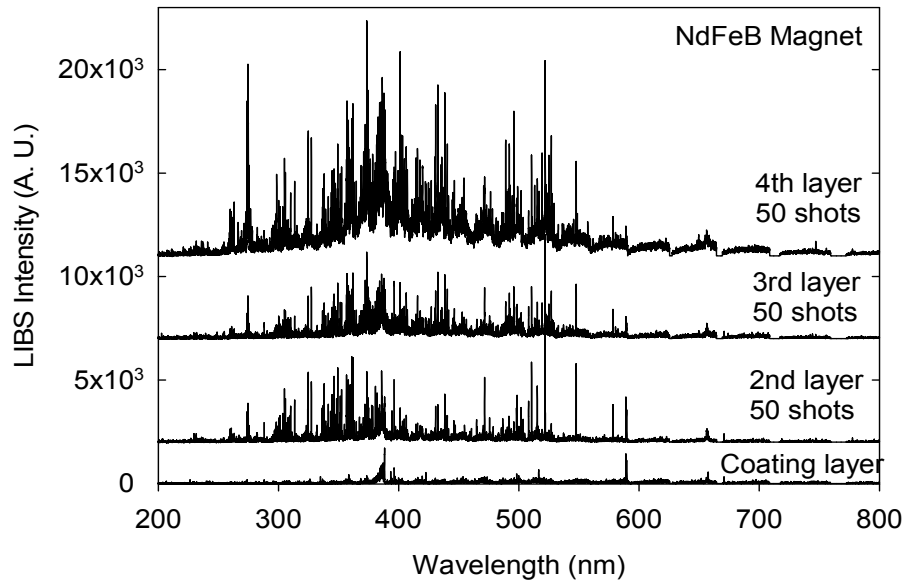

Figure 1. Spectra for NdFeB magnet with 50 shots depth profiling to separate coating layer from the magnet material.

A similar sequence of data acquisition strategy was undertaken for SmCo-based magnets. Figure 2 shows the depth profiling for these magnets where the coating layer is burned through in the first 150-200 shots. It can be observed that the top coating layer for the Nd- versus Sm-based material is different. The information provided by the manufacturers is that the Nd magnets have a coating of either epoxy only or Nickel, Cu-Ni or a combination of both epoxy and Cu-Nickel. Figure 1 shows a coating layer of the Nd magnet that was tested using LIBS has an epoxy only top layer. In case of the Sm-base magnets the coating can be penetrated using between 150-200 laser shots. The coating as shown in figure 2 is a combination of copper and nickel metals.
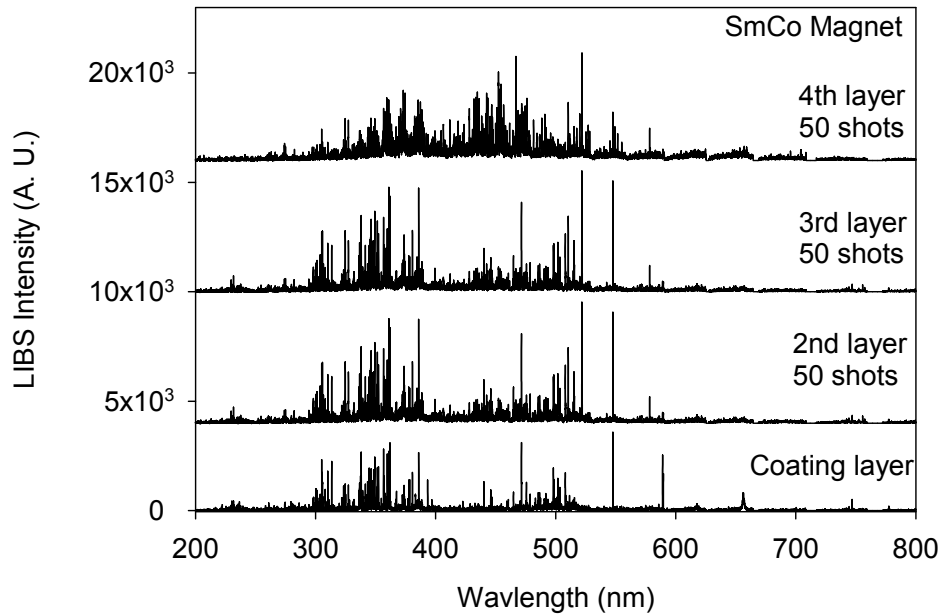
Figure 2. Spectra for SmCo magnet with 50 shots depth profiling to separate coating layer from the magnet material

The broad-band spectral comparison between the Nd-based and Sm-based magnets is shown in figure 3. It is very time-consuming to identify each elemental peak that is characteristic to Sm-Co or Nd-Fe-B magnet material when observing the broad-band spectra but the overall spectra show differences. A cursory look at the two LIBS spectra for Nd-Fe-B magnet and the Sm-Co magnet shows very distinctive peaks that can differentiate between the two compound materials. It is best to look into narrower regions of these spectra and identify the fingerprint for each element in detail.
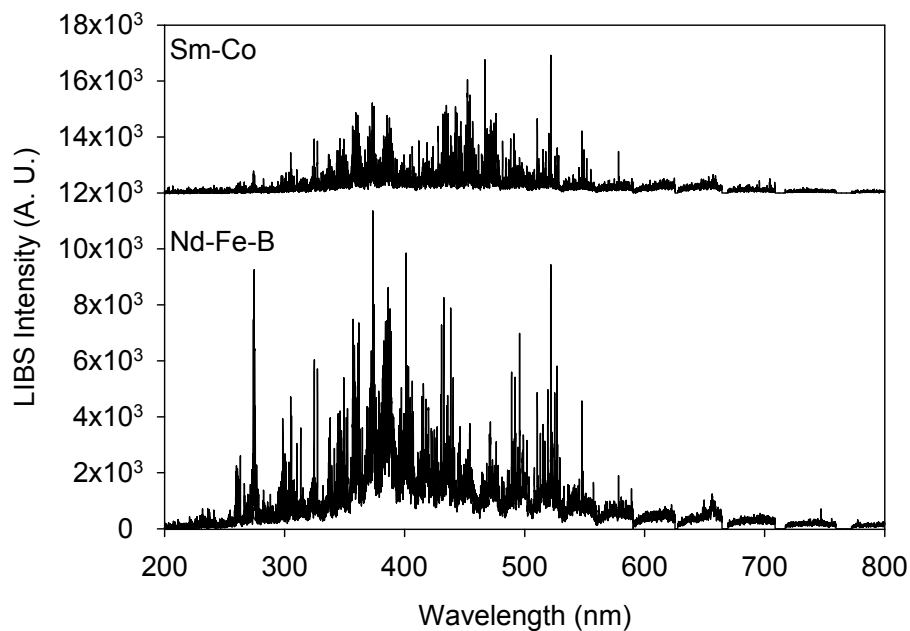

Figure 3. The broad-band spectral comparison between the Nd-based and Sm-based magnets

The iron lines are in both the magnets but it can be easily shown as in figure 4a and 4b and 4(c) that the neodymium and the samarium and iron lines can be seen separately in the two different spectra. The iron lines dominate the broad-band

spectra for the Nd-Fe-B magnets. The spectral regions have been expanded to be able to distinguish the spectral lines that belong to Nd, Sm and other elements which can be smeared when observed in the broad spectral range (200-800 nm). After expanding the broadband spectra between 405-420 nm, the samarium and neodymium characteristic peaks can be seen very clearly. This is shown in figure 4(a) below,
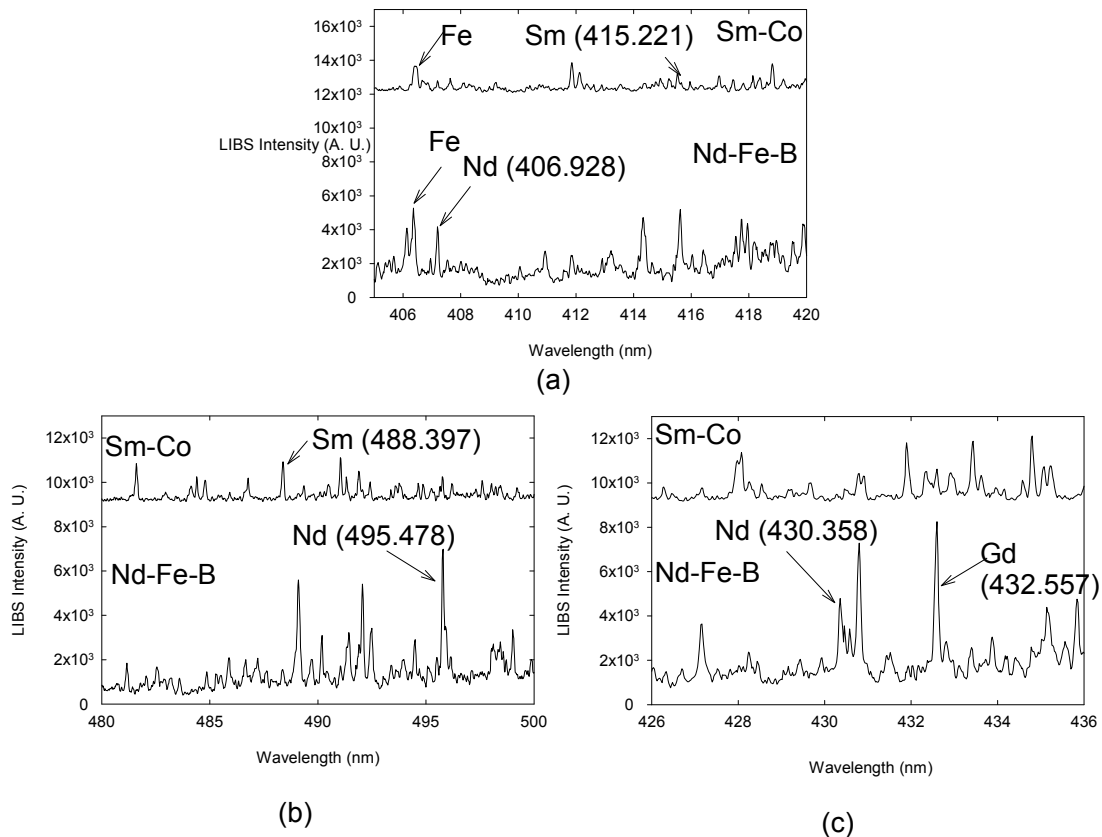

(a)

(b)

(c)

Figure 4. (a) Spectral region between 405-420 nm shows the Nd peak at 406.928 nm and Sm peak at 415.221 nm) (b) Spectral region between 480-500 nm shows the Nd peak at 495.478 nm and a Sm peak at 488.397 nm, and (c) Spectral region between 426-436 nm shows the Nd peak at 430.358 nm and a Gd peak at 432.557 nm.

The distinguishing peaks for Neodymium is 430.358 nm and for Samarium is 488.397 [20-22]. When we expand into those windows those peaks are easily identifiable. This is shown in the figures 4(a), 4(b), and 4(c).

It is well known that samarium peaks are not very easy to detect within a complex matrix and comparison of these peaks for three different systems is shown in figure 5. These three spectra were obtained by an Applied Photonics Ltd (Skipton North Yorkshire, UK) LIBSCAN 100 housed at the US Army Research Laboratory (Aberdeen Proving Ground, MD), an Applied Photonics Ltd LIBSCAN 150 located at Idaho National Laboratory (Idaho Falls, ID), and a custom-built LIBS system housed at Oak Ridge National Laboratory (Oak Ridge, TN).

Figure 5 shows the LIBS spectra for Sm-Co magnet taken using three different LIBS systems. As stated previously, the experimental parameters used for the ORNL spectrum were: a laser wavelength of 532 nm, energy/pulse of 50 mJ, pulse width of 4 nanoseconds, and a repetition rate of 5 Hz. An Andor (Andor Technology Ltd., Belfast, UK) ICCD detector was operated with a gate width of 10 microseconds and a delay of 1 microsecond for data acquisition. The ORNL LIBS system uses a Catalina Scientific (Tucson, AZ) echelle spectrometer with a wavelength range from 200-800 nm. The LIBSCAN 100 system located at ARL employs a 1064 nm laser having an average pulse energy of 100 mJ/pulse, a

repetition rate up to 20 Hz, and a laser pulse width of 5 – 7 nsec. Spectra acquired using the LIBSCAN 100 were taken single shot. The LIBSCAN 100 system utilizes six Avantes (Avantes BV, Apeldoorn, the Netherlands) spectrometers that cover the wavelength range of 182-905 nm and the CCD arrays operated with a gate width of 1.1 milliseconds and with a delay of 1.27 microseconds. The LIBSCAN 150 located at INL is equipped with a 1064 nm laser delivering ~150 mJ/pulse at up to 6 Hz, and has a pulse width of ~5 – 8 ns. Spectra were acquired in single-shot mode. The LIBSCAN 150 is equipped with a Catalina Scientific EMU-65 echelle spectrograph and an Andor iXon 885 EMCCD camera with a wavelength range of 190 – 1000 nm. The spectrograph/camera were operated using a delay time of 1.0 microseconds and an exposure time (gate width) of 60 microseconds.
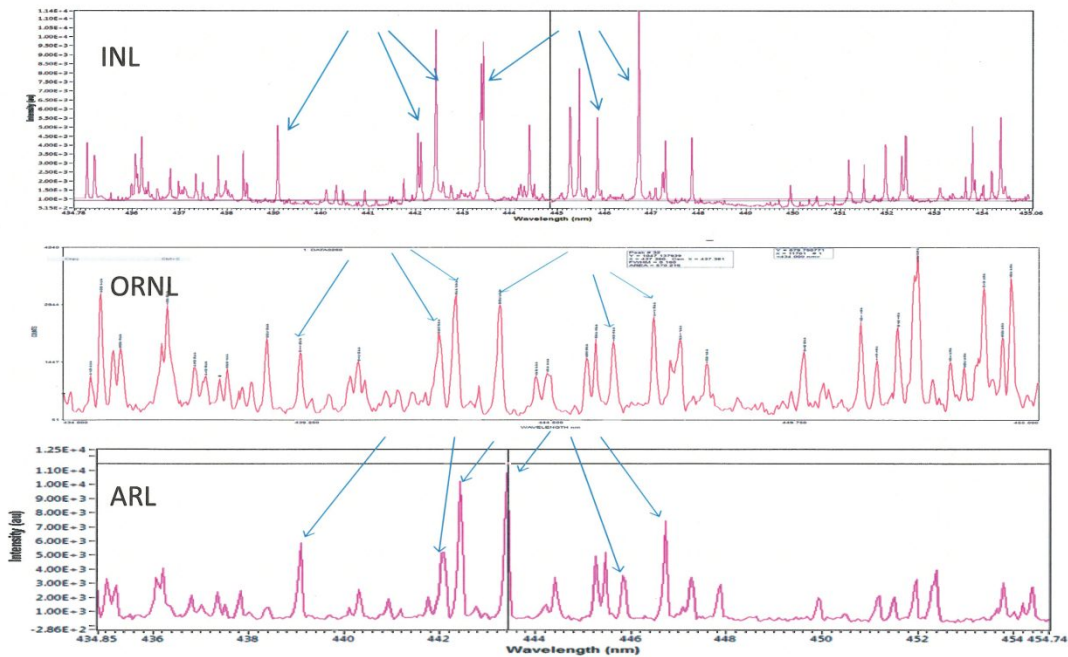

Figure 5. Samarium lines from the Sm-Co magnet comparing three different LIBS systems.

Note that the wavelengths listed in Table 1 are the ones listed on the NIST on-line spectral data base. The actual wavelengths of the peaks observed by our 3 LIBS instruments differ slightly from the NIST ones due to variations in calibrations. We chose to report only the NIST wavelengths to avoid confusion that would result if we had reported the actual wavelengths from our three different instruments. A key finding illustrated in Figure 5 is that all 3 LIBS systems, whose properties vary significantly in terms of wavelength and laser pulse intensity, can be used to detect all key elements. This emphasizes that LIBS can be used in mining applications to detect major REE from a complex matrix. However, for quantification purposes the use of a LIBS system such as the INL one with superior spectral resolution and higher signal-to-noise will likely lead to improved performance in terms of limits of detection.

Table 1 below gives the major samarium lines between 300 and 500 nm as obtained from the NIST data base.

Table 1. Major Samarium lines between 300 and 500 nm observed using the LIBSCAN 100 system.

Ion	Observed Wavelength (nm)	Ion	Observed Wavelength (nm)	Ion	Observed Wavelength (nm)
Sm II	329.028	Sm II	375.753	Sm II	397.140
Sm II	329.810*	Sm II	376.069	Sm II	397.643*
Sm II	330.639	Sm II	378.812	Sm II	399.000
Sm II	332.118	Sm II	379.773	Sm II	428.079*
Sm II	336.586	Sm II	382.620*	Sm I	429.674
Sm II	356.827*	Sm II	383.150	Sm II	432.902
Sm II	359.260*	Sm II	384.350*	Sm II	434.780
Sm II	360.949*	Sm II	385.421*	Sm II	439.086*
Sm II	363.429*	Sm II	388.529*	Sm II	442.434*
Sm II	366.136	Sm II	389.698	Sm II	443.388*
Sm II	367.084*	Sm II	390.342	Sm II	443.432*
Sm II	373.126*	Sm II	392.240*	Sm II	446.734
Sm II	373.912*	Sm II	394.187	Sm I	484.170
Sm II	374.387	Sm II	396.300		
*= Strong Lines					

Note that the wavelengths listed in Table 1 are the ones listed on the NIST on-line spectral data base. The actual wavelengths of the peaks observed by our 3 LIBS instruments differ slightly from the NIST ones due to variations in calibrations. We chose to report only the NIST wavelengths to avoid confusion that would result if we had reported the actual wavelengths from our three different instruments.

4. CONCLUSIONS

Our preliminary results show that LIBS can be used to differentiate between the surface coating layers and the underlying magnetic surfaces. For both the Nd-Fe-B and Sm-Co –based magnets the LIBS spectra are very complex. It was shown that LIBS can be used to detect and identify elements from very complex spectra for the Nd and Sm-based magnets. With these present results it has been established that LIBS can be used to detect Nd, Sm, Fe, Co, and other RE elements that may be present in the samples. The study objectives that were discussed in the article initially have been successfully achieved. The LIBS systems at INL, ORNL, and ARL have been shown to differentiate and detect Samarium peaks very easily. Further work needs to be done to be able to quantify the different elements using a standard statistical multivariate analytical methodology. This will be presented in a subsequent article.

5. ACKNOWLEDGMENTS

6. REFERENCES

[1] Pakhomov, A.V., Nichols, and W., Borysow, J. "Laser-induced breakdown spectroscopy for detection of lead in concrete," Appl. Spectrosc. 50, 880 (1996).

[2] Eppler, A.S., Cremers, D.A., Hickmott, D.D., Ferris, M.J., and Koskelo, A.C. "Matrix effects in the detection of Pb and Ba in soils using laser-induced breakdown spectroscopy," Appl. Spectrosc. 50 1181 (1996).

[3] Vadillo, J.M., Palanco, S., Romero, M.D., and Laserna, J.J. Fresenius. J. Anal. Chem. 355, 909 (1996).

[4] Davis, C.M., Telle, H.H., and Williams, A.W. Fresnius. J. Anal. Chem. 355, 895 (1996).

[5] Cremers, D.A., Barefield II, J.E., and Koskelo, A.C. "Remote elemental analysis by laser-induced breakdown spectroscopy using fiber-optic cable", Appl. Spectrosc. 49, 857 (1995).

[6] Yamamoto, K.Y., Cremers, D.A. Ferris, M.J., and Foster, L.E. "Detection of metals in the environment using a portable laser-induced breakdown spectroscopy instrument," Appl. Spectrosc. 50, 222 (1996).

[7] Geertsen, C., Lacour, J.L., Mauchien, P., and Pierrard, L. "Comparative study of laser induced plasma spectroscopy and spark-optical emission spectroscopy for quantitative analysis of aluminium alloys," Spectrochim. Acta Part B 51, 1403 (1996).

[8] Grant, K.J., Paul, G.L., and O'Neill, J.A. "Time resolved laser induced breakdown spectroscopy of iron ore," Appl. Spectrosc. 45, 701 (1991).

[9] Martin, M.Z., Cheng, M.D., and Martin, R.C. "Aerosol Measurement by Laser-Induced Plasma Technique: A Review," Aerosol Sci. Technol. 31(6), 409 (1999).

[10] Cremers, D. A., and Radziemski, L. J. "Laser Plasmas for Chemical Analysis", in Laser Spectroscopy and Its Applications, L. J. Radziemski, R. W. Solarz, and J. A. Paisner, Eds. (Marcel Dekker, NY, 1987), Chap. 5, p. 351.

[11] Martin, Madhavi Z., Allman, Steve, Brice Deanne, J., Martin, Rodger C., and Andre, Nicolas O., "Exploring laser-induced breakdown spectroscopy for nuclear materials analysis and in-situ applications", Spectrochimica Acta Part B. vol 74-75 177-183 (2012).

[12] Bauer, A.J.R., Farrington, M.P., Sorauf, K., and Miziolek, A.W. "Laser-induced Breakdown Spectroscopy and Spectral Analysis of Improvised Explosive Materials" Next-Generation Spectroscopic Technologies VII, edited by Mark A. Druy, Richard A. Crocombe, Proc. of SPIE Vol. 9101, 91010M1-8 (2014).

[13] Miziolek A.W., and DeLucia, Jr. F.C., "A Spectroscopic Tool for Identifying Sources of Origin for Materials of Military Interest", Next-Generation Spectroscopic Technologies VII, edited by Mark A. Druy, Richard A. Crocombe, Proc. of SPIE Vol. 9101, 91010J1-10 (2014).

[14] Miziolek, A.W. "Spark of the Laser", Chemical, Biological, and Nuclear Warfare, vol. 1, p. 56-58, React Media Publishing, London, UK, January (2014).

[15] Hondrogiannis, E., Ehrlinger, E., and Miziolek, A.W. "Spectroscopy methods for identifying the country of origin" Next-Generation Spectroscopic Technologies VI, edited by Mark A. Druy, Richard A. Crocombe, Proc. of SPIE Vol. 8726, 87260Q1-7 (2013).

[16] Hondrogiannis, E., Andersen, D., and Miziolek, A.W. "The evaluation of a new technology for gunshot residue (GSR) analysis in the field", Next-Generation Spectroscopic Technologies VI, edited by Mark A. Druy, Richard A. Crocombe, Proc. of SPIE Vol. 8726, 87260P1-8 (2013).

[17] Fox, R.V., Roberts, L., DeLucia, Jr., F.C., Miziolek, A.W., and Whitehouse, A.I. "A novel laser-based approach for cleaning contaminated metallic surfaces coupled with rapid residue analysis", Next-Generation Spectroscopic Technologies VI, edited by Mark A. Druy, Richard A. Crocombe, Proc. of SPIE Vol. 8726, 87260N1-16 (2013).

[18] Radziemski, L. J., and Cremers, D. A. "Spectrochemical Analysis Using Laser Plasma Excitation," in Laser-Induced Plasmas and Applications, L. J. Radziemski and D. A. Cremers, eds., Marcel Dekker, New York, Chapter 7 (1989).

[19] Martin, M. Z., and Cheng M. D. "Detection of Chromium Aerosol Using Time-Resolved Laser-Induced Plasma Spectroscopy," Appl. Spectrosc., 54, 1279 (2000).

[20] Kim, S. H., Hong, J. S., Ju, J. S., and Sin, H. S. " A quantitative analysis for Lanthanum series element using Laser induced breakdown spectroscopy", Trans. Korean Nucl. Soc., Spring meeting, Gyeongju, Korea May 29-30 (2008).

[21] Kim, S. H., Ju, J. S., Jeong, J. -H., Sin, H. -S., and Kim, H. –D. " Semi- quantitative analysis for Samarium alloys sample using Laser induced breakdown spectroscopy", Trans. Korean Nucl. Soc., Spring meeting, Jeju, Korea May 22 (2009).

[22] Abedin, K. M., Haider, A. F. M. Y., Rony, M. A., and Khan, Z. H. "Identification of multiple rare earths and associated elements in raw monazite sands by laser-induced breakdown spectroscopy", Optics & Laser Technol., 43(1), 45-49 (2011).