



A RAPID METHOD OF IDENTIFICATION OF GARNET IN BEACH SANDS USING LASER-INDUCED BREAKDOWN SPECTROSCOPY

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ABSTRACT

In this work, Laser Induced Breakdown Spectroscopy (LIBS) has been used for investigating the presence of heavy mineral garnet ($X_3Y_2(SiO_4)_3$, where the X represent either of Ca^{2+} , Mg^{2+} , Fe^{2+} , Mn^{2+} and the Y site contain either of Fe^{3+} , Cr^{2+} , Al^{3+}) in beach sand samples collected from Sitakunda, Bangladesh. To achieve the goal, in the first attempt, a comprehensive spectral profiling of the laboratory grade garnet was done and the identified emission lines were employed as the reference lines for discovering the presence of the elements of garnet in the LIBS spectra of different sand samples and an arbitrary soil sample. The average intensity ratio for these reference lines of Mg, Al, Fe, Mn, Ca, estimated in different sand samples and the isolated garnet sample, is found to be about 60 % (against the average intensity ratio of about 20 % estimated for general soil sample and garnet), substantiating the presence of garnet in sand with significant concentration. Therefore, LIBS can be used as a useful alternative experimental tool for predicting the presence of minerals in the sand samples and for the exploration of new geological site in Bangladesh.

Keywords: Laser Induced Breakdown Spectroscopy, Laser Ablation, Ionized Plasma, Heavy Mineral, Garnet.

INTRODUCTION

Laser-induced breakdown spectroscopy is an atomic emission spectroscopy (Harmon *et al.* 2006), where a beam of highly energetic laser pulses is focused onto the surface of the sample under investigation to produce a small cloud of weakly ionized plasma upon ablation of a tiny portion of the specimen. Initially, the temperature and density of the plasma are very high, leading to a broadband continuum emission. As time evolves, the plasma cloud expands and cools. During the process of the expansion and subsequent cooling, a significant fraction of ions within the plasma cloud recombines with electron to form excited atoms/ions, which eventually decay by spontaneous emission to the atomic lower/ground state. The photons emitted during spontaneous emission can be collected and spectrally analyzed with the aid of suitable spectrograph coupled detection system, which provides a “spectral fingerprint” of all the constituent elements of the plasma created from the target material. Since each element has a unique spectral signature, relative and absolute elemental concentrations within the target material can be determined by analyzing the spectral intensity of the constituent atoms. As a matter of fact, LIBS has emerged nowadays as an efficient and useful experimental tool for elemental analysis. LIBS-based technology is a helpful tool in various fields, such as geological analysis and applications (Harmon *et al.* 2006), analysis of biological microparticles (Samuels *et al.* 2003, Boyain-Goitia *et al.* 2003) and

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detection of biological hazards (Morel *et al.* 2003), environmental problems (Rusak *et al.* 1997) and mineral analysis (Haider *et al.* 2011, McMillan *et al.* 2007, McMillan *et al.* 2006).

Heavy minerals have great economic interest due to their extensive use for many purposes, for example, garnet sand is an excellent abrasive which is widely used in sand-blasting, cutting steel in water jets and water filtration. For identification, exploration and separation of heavy minerals from sand, detecting its presence beforehand is of fundamental requirement. Typically, detection of heavy minerals is performed by identifying the mineral under a petrological microscope and then mineral grains are quantified by counting the grains (Reddy *et al.* 2012, Cheepurupalli *et al.* 2012). While the identity of a heavy mineral can be inferred from color (Manson and Stockton 1984), refractive index (Sriramadas 1957) or magnetic susceptibility measurements (Hoover 2018), elemental analysis by LIBS is yet another way for positive identification of heavy minerals. LIBS is a straightforward and noninvasive technique which is capable of yielding desired result almost in real-time. LIBS followed by appropriate statistical analysis has already found useful for identifying different high grade or pure heavy minerals such as hematite, chalcopyrite (Khajehzadeh and Kauppinen 2015) and garnet (Alvey *et al.* 2010).

In this work, by utilizing LIBS technique, the sand samples collected from different geologically important sites, specially in the context of Bangladesh have been studied, for investigating the potential presence of garnet. It is found that comparison of the intensity of appropriate elements such as Mg, Al, Fe, Mn, Ca is an easy alternative way for predicting the presence of minerals in the sand samples.

EXPERIMENTAL SETUP

The schematic diagram of the experimental LIBS set up is shown in Fig. 1. The excitation laser used in this setup is a Q-switched Nd:YAG laser system (Spectra-Physics LAB-170-10) which gives the output at 1064 nm (the fundamental wavelength) with pulse duration 8 ns, repetition rate 10 Hz and pulse energy of 850 mJ. The laser is also equipped with harmonic generators (typically made of KD*P crystal) capable of generating up to fourth harmonics of the fundamental at 532 nm,

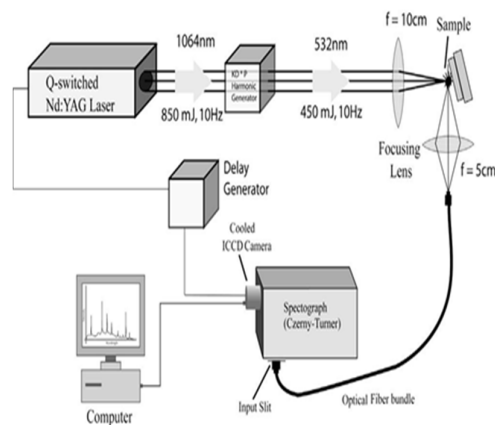


Fig. 1. Schematic diagram of the LIBS experimental setup.

354 nm and 266 nm. In this experiment, the second harmonic (532 nm) of this laser was used as an excitation beam for producing LIBS.

A high-power industrial chiller, one most important accessories of the Nd:YAG laser system, provides precise control of the temperature for the laser system. To maintain a certain desired temperature within the laser system, two pipelines were used to ensure the in and out flow of the water from the chiller to the laser setup. Intense, transient plasma is produced by focusing the laser beam (the second harmonic emitted at 532 nm) using a convex lens of 100 mm focal length.

The plasma is generated at the frequency of the laser, i.e. at 10 times per second. The radiation emitted following plasma cooling is focused via a convex lens to the outlet window of a 3 m long multimode optical fiber. The radiation is then transmitted through the fiber whose other end is connected to the entrance slit of a 750 nm focal length computerized Czerny-Turner spectrograph (Acton Model SP-2758). The spectrograph is equipped by three ruled gratings system, such as, 300 grooves/mm blazed at 300 nm, 600 grooves/mm blazed at 500 nm and 2400 grooves/mm blazed at 240nm. These gratings are interchangeable under computer control. The selection of the gratings determines the resolution of the instruments as well as the width of the spectral window per single step. Grating 600 grooves/mm blazed at 500 nm was used for carrying all the LIBS experiments in this study.

The output end of the spectrograph is coupled with an intensified and gated CCD camera (Princeton PI-MAX with Unigen II coating and programmable delay generator). The ICCD camera has 1024 x 1024 pixels and is cooled to -20°C by a Peltier cooler to reduce noise. The ICCD camera is electrically triggered by the Nd:YAG laser pulses after a software-controlled, adjustable time delay. In this way, the intense background initially created by the high-temperature plasma can be largely diminished, and the atomic/ionic emission lines of the elements can be observed more clearly. In the present experiments, a delay time of 1.5 microsecond and a gate width of 500 nanosecond were selected for the optimum signal. Usually, spectra from a number of laser shots (about 40-80) are acquired and averaged to increase the signal-to-noise ratio. The spectrum captured by the ICCD camera is transferred to

the personal computer by USB cable. All the functions of the ICCD camera and the Acton spectrograph can be fully controlled by WinSpec/32 software provided by the manufacturer.

Sample Processing

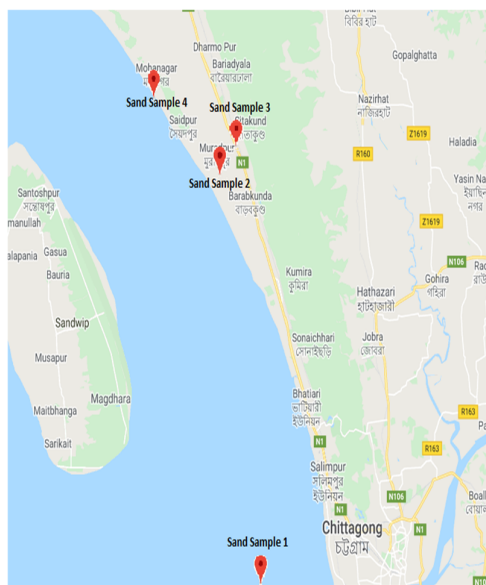


Fig. 2. Geological locations from where all the four sand samples were collected.

For locating a new geological important sites for future mineral exploration, sand samples were collected from four locations around Sitakunda area of Chattagram district having GPS locations mentioned in Table 1. Laboratory grade garnet (90% pure) was collected from the Beach Sand Mineral Exploitation Centre (BSMEC) of Bangladesh Atomic Energy Commission (BAEC), Cox's Bazar, Bangladesh. The soil sample was collected from an arbitrary place within the campus of University of Dhaka. Finally, small pellets of high grade garnet, sand and soil samples were prepared using a hand

press with sufficient pressure (~ 80 bars). For measuring LIBS, the pallet of each sample was irradiated with a laser beam (the second harmonics of Nd:YAG laser emitting at 532 nm) of same average power (220±4 mW).

RESULTS AND DISCUSSION

Garnets are silicates having general chemical formula $X_3Y_2(SiO_4)_3$, where the X site hosting large divalent cations (e.g., Ca^{2+} , Mg^{2+} , Fe^{2+} , Mn^{2+}) and the Y site occupied by smaller trivalent cations (e.g., Fe^{3+} , Cr^{2+} , Al^{3+}). On the basis of dominant molecular type, six major garnets names are assigned as andradite [$Ca_3Fe_2(SiO_4)_3$], grossular [$Ca_3Al_2(SiO_4)_3$], uvarovite [$Ca_3Cr_2(SiO_4)_3$], almandine [$Fe_3Al_2(SiO_4)_3$], pyrope [$Mg_3Al_2(SiO_4)_3$], and spessartite [$Mn_3Al_2(SiO_4)_3$]. In sand samples, garnet species originated from different kind of rocks are found as mixtures of more than one type. In Bangladesh, almandine, spessartite, grossular, and andradite types of garnet are found in sand sample by BAEC.

Table 1: GPS Locations of Collected Sand Samples

Sand Sample	Latitude	Longitude
1	N 22° 10' 19"	E 91° 38' 54"
2	N 22° 36' 15.1"	E 91° 41' 9"
3	N 22° 36' 58.1"	E 91° 41' 25.1"
4	N 22° 40' 19"	E 91° 31' 54"

Table 2: Selected elemental and ionic emission lines from the garnet LIBS spectra.

Elements with charge state	Observed wavelength (nm)
Al I	304.87, 305.56, 308.06, 309.08, 394.29, 396.05, 783.47, 877.36, 877.58
Ca I	422.57, 428.22, 430.13, 430.70, 445.42, 616.14, 643.80, 644.91, 646.19, 649.34, 671.72, 714.75, 732.44, 741.73
Ca II	315.24, 317.81, 330.14, 330.54, 370.54, 373.43, 393.22, 396.73, 854.14, 866.03
Fe I	301.92, 305.61, 335.37, 340.66, 342.64, 344.01, 347.53, 349, 356.49, 358.53, 363.06, 374.51, 381.53, 381.98, 385.86, 387.67, 425.96, 427.09, 432.45
Fe II	234.25, 238.02, 243.43, 248.97, 256.68, 258.49, 259.81, 263, 275.44, 271.74, 274.13, 275.44, 277.84, 786.64
Cr I	358.26, 359.04, 360.53, 424.94, 427.09, 428.84
Mg I	285.07, 382.83, 383.17, 383.73, 779.97, 780.99
Mg II	279.38, 279.72, 280.12, 438.31, 634.53, 654.55, 882.24, 924.61
Mn I	353.57, 354.28, 356.94, 358.08, 402.95, 403.29, 476.24, 476.78, 478.07, 482.19
Mn II	257.42, 259.59, 260.50, 261.02, 293.31, 294.22, 749.03
Si I	212.47, 220.43, 221.33, 221.83, 230.64, 243.50, 244.04, 245.67, 250.62, 251.48, 252.33, 252.73, 252.28, 288.03, 728.80, 740.96, 742.28, 779.90
Si II	236.42, 237.81, 334.06, 385.54, 503.90, 505.69, 634.58, 637.21
O I	715.23, 777.13, 777.40, 788.72, 794.73, 795.68, 844.59, 926.37
H I	485.99, 656.09
K I	404.47, 691.13, 693.89, 766.40, 769.79
Li I	610.19, 670.73, 812.30
N I	742.28, 744.15, 746.78, 821.35, 822.53, 824.09, 859.51, 862.74, 868.39, 870.82, 871.27, 871.83
Na I	568.21, 568.83, 589.02, 589.64, 615.14, 616.36, 818.06, 819.56
Ti I	399.78, 400.40, 429.96, 430.70, 468.23, 498.17, 499.07, 506.48, 793.63
Ti II	299.87, 323.33, 328.60, 332.19, 334.86, 336.05, 338.33, 375.81
Mo I	390.44, 406.23, 407.07, 443.45, 553.56, 792.27
C I	247.69, 404.02, 747.33, 909.58, 940.47, 965.98

Therefore, Mg, Al, Fe, Mn, Ca, Si emission lines should be identified properly in the LIBS spectra of laboratory grade garnet sample with the help of ‘National Institute of Standards and Technology (NIST)’ database and the identified lines should be considered as reference lines for detecting presence of garnet in unknown samples. Selection of proper peaks is an important task for correct identification of minerals such as garnet. With an aim to identify the mineral contents in sand, LIBS spectra of laboratory grade garnet (90% pure) collected from the BSMEC, Bangladesh were analyzed at first. The separation of the laboratory grade garnet is usually performed in a pilot plant by utilizing different properties of heavy minerals such as specific gravity, electrical

conductivity and magnetic susceptibility (Alam *et al.* 1999).The wavelength of the relevant spectral lines for garnet is listed in Table 2. Most of these lines are also found in the garnet LIBS spectra obtained by Alvey *et al.* (Alvey *et al.* 2010).

Under the local thermodynamic equilibrium (LTE) condition, the total intensity of a spectral line ‘I’ from an excited atom or ion in homogeneous and optically thin plasma for a transition from $j \rightarrow i$ is given by (Abdellatif and Imam 2002).

$$I = h\nu_{ji} A_{ji} N_j \tag{1}$$

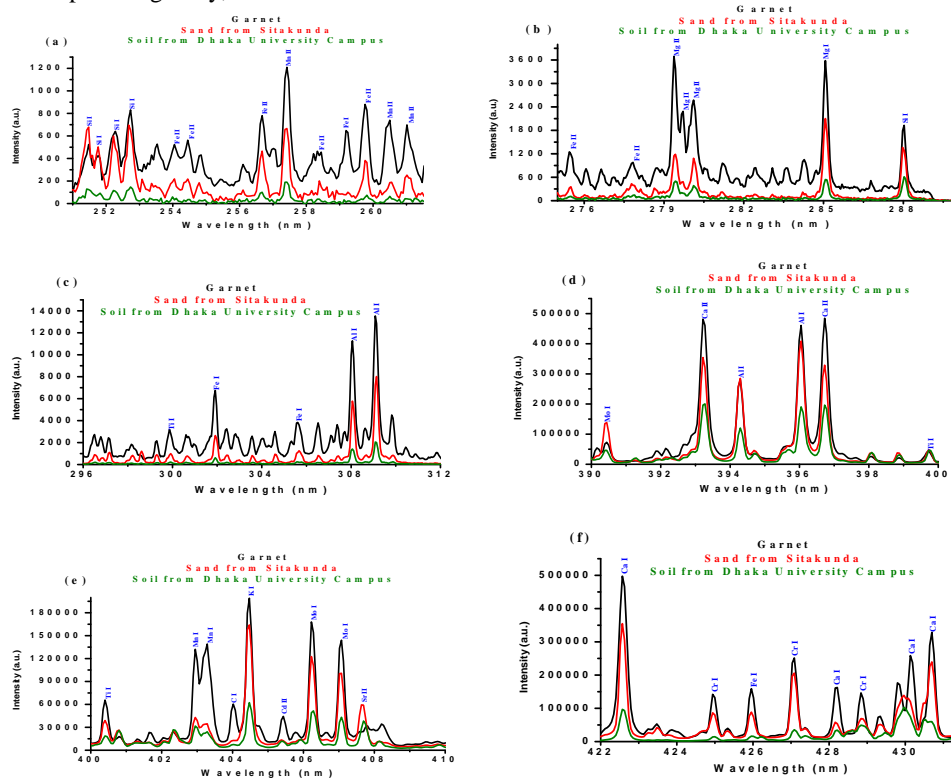


Fig. 3(a)-3(f). LIBS spectra of the sand (red curves), soil (green curves) and laboratory grade garnet (black curves) samples recorded at same laser power.

where ν_{ji} is the frequency of transition from state $j \rightarrow i$, A_{ji} is the Einstein transition co-efficient, N_j is the population of the upper level j and h is the Planck's constant. Now, if the energy level concerned is in LTE, then the population density of upper level N_j is related to ground level number density (N) by Boltzmann's equation:

$$N_j = N g_j Q^{-1} e^{-\frac{E_j}{kT}} \quad (2)$$

Here, g_j and E_j are statistical weight and energy of upper level j , respectively and Q is the partition function of relevant species, k is the Boltzmann constant and T is the electron temperature of the plasma. Therefore, from equations (1) and (2), we get:

$$I = h \nu_{ji} A_{ji} N g_j Q^{-1} e^{-\frac{E_j}{kT}} \quad (3)$$

Now, from the measurement of the absolute intensity of the transition, knowledge of atomic constants and excitation temperature, one can determine the ground level population density (N) of an atom or ion. However, establishing a theoretical relationship of N with concentration (C) is impossible. Therefore, an empirical relationship is found between the observed intensity (I_j) and associated concentration (C) (Gondal and Hussain 2007):

$$I_j = F(C) \quad (4)$$

Here, $F(C)$ is a function of concentration and is called the analyte calibration function (Gondal and Hussain 2007). Typically, the intensity of an emission line of a particular element in the LIBS spectrum is proportional to the abundance of that element in the sample. In order to make a quantitative inference about the abundance of garnet content in the sand samples, comparison of average spectral line intensities of reference lines was performed.

To infer the future commercial exploration of heavy minerals from the coastal belt, we have collected sand samples from four different locations around Sitakunda, Chattagram (Fig. 2) which is located about 165 km away from BSMEC mineral

Table 3: Summary of the presence of garnet constituents in the beach sand samples.

Elements	Charge State	Total number of lines identified for sample no			
		1	2	3	4
Si	I	33	32	34	35
	II	19	20	19	18
Mn	I	14	13	14	11
	II	12	12	11	13
Fe	I	45	44	42	43
	II	27	26	28	27
Mg	I	13	12	14	13
	II	16	14	16	15
Al	I	15	16	14	14
Ca	I	29	31	27	30
	II	26	25	24	22

separation pilot plant. Table 3 shows the total number of lines used for mineral identification in these sand samples. The Fig. 3(a)-3(f) show the comparison between the LIBS spectra, recorded at the same laser power, of sand sample from Sitakunda (Latitude: N 22° 36' 15.1" & Longitude: E 91° 41' 9") (red curves) and garnet (black curves). To maintain a plausible homogeneity in measurements and to avoid matrix effect, plural number of the LIBS spectra were collected at different space points within the sample pellet and finally averaged. The average spectra were used for further analyses and investigations. For further comparison, LIBS spectra of a non-arable soil sample collected from an arbitrary location (Lat N 22° 36' 15.1" & Long E 91° 41' 9") at University of Dhaka were obtained (green curves in Fig. 3(a)-3(f)) and also overlaid in each of the spectral

window shown in the figure. Although the LIBS spectra within the broad spectral region 200-to-960 nm were recorded for all the samples under investigation, the spectra of some selective windows within 250-to-430 nm region are analyzed and illustrated in Fig. 3 as the highest intensity emission lines of the common elements of garnets lie within these spectral windows. The analyses of LIBS spectra of both the sand and soil samples revealed the presence of the common elements which are the constituents of garnet (Mg, Al, Fe, Mn, Ca, Si). However, one can easily observe from the comparison that the LIBS spectra of the sand samples are characterized by the remarkably large magnitudes of the emission intensity of the common elements of garnet, the relative intensities of some lines approached to the intensities of the analogous lines of the laboratory grade garnet. This finding suggests that the sand samples contain a significant proportion of the common constituents of garnet. To substantiate the presence of garnet quantitatively, the intensity of Mg, Al, Fe, Mn and Ca atomic emission lines in sand samples from four different locations around Sitakunda were estimated, then compared with those of the respective lines in garnet and the corresponding intensity ratio is compiled in Table 4. One can easily notice from Table 4 that, for sand samples, the common elements of the garnet yielded the average intensity ratio with a maximum magnitude of about 0.99 to the minimum magnitude of about 0.25. These findings suggest that the sand samples under study contain a significant proportion of garnet. To this end, the variation of the sand samples to garnet intensity ratio ($I_{\text{sand}}/I_{\text{garnet}}$) for the common elements such as Mg, Al, Fe, Mn and Ca atomic lines is likely to be associated with the presence of various types of garnet in different concentration. The average intensity ratio of sand sample to that of corresponding atomic emission lines of garnet is found to be about 0.57, which is certainly a large value that indicates the substantial presence of garnet in the

sand samples. On the other hand, the average intensity ratio of the specific lines associated with the common elements of garnet estimated for soil sample with respect to the laboratory grade garnet is found to be substantially lower ($I_{\text{soil}}/I_{\text{garnet}} < 0.3$) for almost all the atomic emission lines, indicating that this soil sample does not contain significant amount of garnet mineral (Table 4).

Table 4: Comparative intensity analysis of sand and soil samples with garnet.

Elements with charge state	Observed wavelength (nm)	Ratio of the intensity of Sitakunda a sand to garnet $I_{\text{sand}}/I_{\text{garnet}}$	Ratio of the intensity of Dhaka University campus soil to garnet $I_{\text{soil}}/I_{\text{garnet}}$
Mg I	285.07	0.59	0.15
Mg II	279.375	0.32	0.14
Mg II	280.116	0.42	0.15
Al I	308.059	0.51	0.13
Al I	309.082	0.59	0.15
Al I	394.293	0.99	0.42
Al I	396.047	0.89	0.41
Ca I	422.57	0.71	0.19
Ca I	428.215	0.36	0.20
Ca I	430.698	0.73	0.18
Ca II	330.538	0.30	0.14
Ca II	393.217	0.74	0.42
Ca II	396.726	0.68	0.41
Si I	288.03	0.71	0.32
Si I	252.734	0.84	0.18
Si I	252.277	0.93	0.18
Si II	334.064	0.92	0.29
Fe I	301.916	0.39	0.09
Fe I	305.613	0.33	0.06
Fe I	342.644	0.30	0.14
Fe I	344.006	0.68	0.25
Fe II	277.837	0.44	0.14
Mn I	402.947	0.32	0.24
Mn I	403.286	0.25	0.17
Mn II	257.418	0.55	0.16
Mn II	260.501	0.25	0.09
Mn II	261.015	0.36	0.06

Alvey *et al.* (Alvey *et al.* 2010) used the LIBS technique to discriminate six common garnet types. However, since most garnets in the sand are found as mixtures of more than one type, the present approach is preferable for predicting the presence of a mineral in the sand. The process is easier because minimal sample preparation is needed whereas identifying garnet mineral using a petrological microscope is time-consuming and cumbersome (Reddy *et al.* 2012, Cheepurupalli *et al.* 2012). In addition, LIBS is also suitable for measurements in remote or harsh environments, by means of portable LIBS set up (Yamamoto *et al.* 1996).

The study of beach sands by using the LIBS technique for detecting the presence of garnet is the first step to use LIBS for geological exploration of minerals in Bangladesh.

It should be noted that this method is not applicable for distinguishing the presence of Magnetite (Fe_3O_4), Ilmenite (FeTiO_3) and Rutile (TiO_2) in sand samples. The high intensity of the Fe line in sand samples can be linked either with the presence of magnetite or ilmenite. Likewise, the intensity of the Ti line in the sand samples could be originated from either Ilmenite or Rutile. Therefore, from Fe and Ti atomic line intensity comparison, we cannot distinguish between the presence of magnetite, ilmenite and rutile in sand samples. In this case, LIBS followed by a suitable statistical analysis would be the appropriate approach for obtaining conclusion on the applicability of LIBS technique to heavy minerals and identifying these heavy minerals in beach sands.

CONCLUSION

In this work, a simple and rapid method of detecting the presence of a garnet mineral in beach sands of Bangladesh by LIBS technique has been demonstrated. The LIBS spectra of garnet are obtained and the emission lines of the common elements were identified. The

elemental spectral information obtained from a laboratory grade garnet sample was used as reference lines to identify the presence of garnet in the sand samples collected from different locations around Sitakunda, Chattagram, Bangladesh. Since intensity of spectral lines is directly proportional to the concentration of an element, from spectral intensity analysis, we found a significant proportion of garnet in sand samples as manifested by a significantly large magnitude of the intensity ratio of a specific set of atomic lines of sand samples to that of garnet. To the best of our knowledge, this is the first time LIBS technique has been used to trace and identify the mineral constituents in the sand samples from Bangladesh. This comparatively easy and rapid detection technique for the presence of garnet has great potentiality of use in future heavy mineral exploration and for mapping of the relative concentration of minerals along the coastal belt in Bangladesh.

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REFERENCES

- Abdellatif, G. & H. Imam. 2002. A study of the laser plasma parameters at different laser wavelengths, *Spectrochim. Acta, Part B*, **57**: 1155-1165.
- Alam, M., M. Chowdhury, M. Kamal, S. Ghose, M. Islam, M. Mustafa, M. Miah & M. Ansary. 1999. The 226Ra, 232Th and 40K activities in beach sand minerals and beach soils of Cox's Bazar, Bangladesh, *J. Environ. Radioact.*, **46**: 243-250.
- Alvey, D. C., K. Morton, R. S. Harmon, J. L. Gottfried, J. J. Remus, L. M. Collins & M. A. Wise. 2010. Laser-induced breakdown spectroscopy-based geochemical fingerprinting for the rapid analysis and

- discrimination of minerals: the example of garnet, *Appl. Opt.*, **49**: C168-C180.
- Boyain-Goitia, A. R., D. C. Beddows, B. C. Griffiths & H. H. Telle. 2003. Single-pollen analysis by laser-induced breakdown spectroscopy and Raman microscopy, *Appl. Opt.*, **42**: 6119-6132.
- Cheepurupalli, N. R., B. Anu Radha, K. Reddy, E. Dhananjayaram & A. Dayal. 2012. Heavy mineral distribution studies in different micro-environments of Bhimunipatnam coast, Andhra Pradesh, India, *IJSRP*, **2**:1-10
- Gondal, M. & T. Hussain. 2007. Determination of poisonous metals in wastewater collected from paint manufacturing plant using laser-induced breakdown spectroscopy, *Talanta*, **71**: 73-80.
- Haider, A., M. Rony, R. Lubna & K. Abedin. 2011. Detection of multiple elements in coal samples from Bangladesh by laser-induced breakdown spectroscopy, *Opt. Laser Technol.*, **43**: 1405-1410.
- Harmon, R. S., F. C. DeLucia, C. E. McManus, N. J. McMillan, T. F. Jenkins, M. E. Walsh & A. Miziolek. 2006. Laser-induced breakdown spectroscopy—An emerging chemical sensor technology for real-time field-portable, geochemical, mineralogical, and environmental applications, *Appl. Geochem.*, **21**: 730-747.
- Hoover DB, C. Williams, B. Williams, C. Mitchell. 2008. Magnetic susceptibility, a better approach to defining garnets, *The Journal of Gemmology*, **31**: 91-103.
- Khajehzadeh, N. & T. K. Kauppinen. 2015. Fast mineral identification using elemental LIBS technique, *IFAC-PapersOnLine*, **48**: 119-124.
- Manson, D. & C. Stockton. 1984. Pyrope-spessartine garnets with unusual color behavior, *Gems Gemol.*, **20**: 200-207.
- McMillan, N. J., R. S. Harmon, F. C. De Lucia & A. M. Miziolek. 2007. Laser-induced breakdown spectroscopy analysis of minerals: carbonates and silicates, *Spectrochim Acta Part B At Spectrosc.*, **62**: 1528-1536.
- McMillan, N. J., C. E. McManus, R. S. Harmon, F. C. De Lucia & A. W. Miziolek. 2006. Laser-induced breakdown spectroscopy analysis of complex silicate minerals—beryl, *Anal. Bioanal. Chem.*, **385**: 263-271.
- Morel, S., N. Leone, P. Adam & J. Amouroux. 2003. Detection of bacteria by time-resolved laser-induced breakdown spectroscopy, *Appl. Opt.*, **42**: 6184-6191.
- Reddy, K., D. D. Varma, E. D. Rao, B. Veerananarayana & T. L. Prasad. 2012. Distribution of heavy minerals in Nizampatnam-Lankavanidibba coastal sands, Andhra Pradesh, East coast of India, *J Geol Soc India*, **79**: 411-418.
- Rusak, D., B. Castle, B. Smith & J. Winefordner. 1997. Fundamentals and applications of laser-induced breakdown spectroscopy, *Crit. Rev. Anal. Chem.*, **27**: 257-290.
- Samuels, A. C., F. C. DeLucia, K. L. McNesby & A. W. Miziolek. 2003. Laser-induced breakdown spectroscopy of bacterial spores, molds, pollens, and protein: initial studies of discrimination potential, *Appl. Opt.*, **42**: 6205-6209.
- Sriramadas, A. 1957. Diagrams for the correlation of unit cell edges and refractive indices with the chemical composition of garnets, *Am. Mineral*, **42**: 294-298.
- Yamamoto, K. Y., D. A. Cremers, M. J. Ferris & L. E. Foster. 1996. Detection of metals in the environment using a portable laser-induced breakdown spectroscopy instrument, *Appl Spectrosc.*, **50**: 222-233.

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