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LIBS Principles, Advantages, Applications, Outline of Nanostructure Enhanced LIBS (NELIBS)

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Abstract:

Laser-induced Breakdown spectrographic (LIBS) analysis that may be a more cost effective and easy to implement technique, is setting out to dominate in qualitative and quantitative analyses of the assorted parts of the frequent system. It is predicated on the interaction of a laser pulse that solely lasts some nanoseconds with the sample to be analyzed. LIBS technique has many benefits for example: remotely measurement, it can be applied on all types of materials in solid, liquid, or evaporated state, fast real time analysis, no need to previous sample preparation, also it may be transportable to be used in any space .So, there are many applications in different fields that LIBS applied such as industrial, spatial, agriculture, biomedical, and archeological fields. Nanoparticles LIBS is a recent and a promised technique, exceedingly applied to achieve more higher efficient than that obtained in the conventional LIBS analysis.

Keywords:

LIBS, Plasma, Ablation, Spectroscopy, Nanotechnology and NELIBS.

1. Introduction:

LIBS (laser-introduced Breakdown Spectroscopy) is classified as the atomic emission spectrographic analysis method [1]. It exhibits a real timed quantitative and qualitative analysis for any sample with elementary chemical composition (solid, liquid, vaporized) [2, 3]. This LIBS technology has many advantages that make this technique more adaptive to any sort of scenario such as harsh industrial measurements, laboratory analysis, and field direct analysis [1]. Actually, in terribly different fields, LIBS technology is delivered to meet the requirements detection and analysis such as the analysis of additionally significant metallic trace components [2, 6, and 7], metallic alloys [7, 8], in environmental measurements [4, 9-13], in food industry [16, 17], within the medical field [18], in the biological field [5], archaeological measurements [15, 16]. Furthermore, moveable instruments LIBS are developed, which enable onboarded portable spectral LIBS in situ analysis on the Mars planet instead of previously brought the Martian soil to the Earth [19, 20].

2. The principles of LIBS technique:

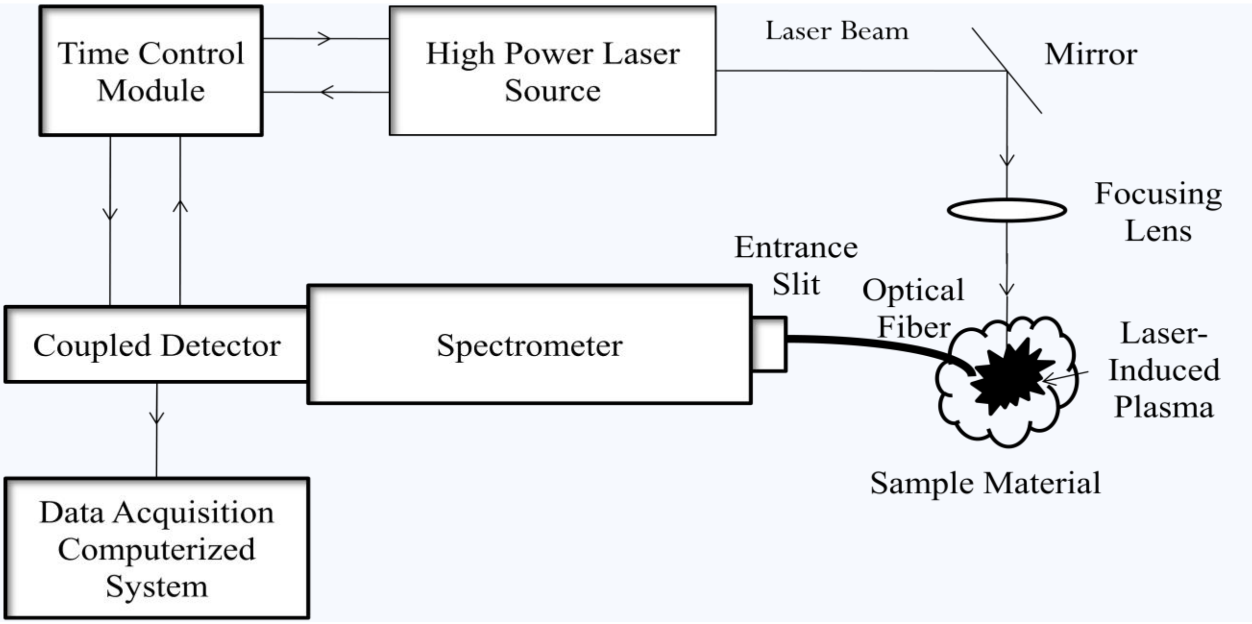

Fig.1: Basic LIBS arrangement model.

The pulsed (nanosecond or picoseconds or femtosecond) laser interaction with the sample material to be investigated is the limestone of the LIBS analysis. Figure1: represents a basically LIBS arrangement model. Actually, there are more developed LIBS technique devices all over the world [21, 28]. The laser irradiance (power per unit area, in LIBS, in order of GW.cm-2) is concentrated on the surface of the sample that induced a major energy deposit during a short time on a surface [21, 22]. This abrupt heating of the materials then results in ablation and vaporization of the material. The resulting vapor absorbs a part of the laser radiation; it heats up and ionized which leads to Plasma generation containing excited electrons, atoms and ions. [21, 23].Quantum physics relations ruled this interaction between the laser and the matter that describe how photons absorbed or emitted by atoms. If an associated electron absorbs a photon, the electron reaches a quantum mechanical state of upper energy level. The electron tends towards the lowest attainable energy levels (degeneration process); the electron emits a photon (atom relaxation).

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These emissions are the spectral emission lines found within the LIBS spectra, its characteristics and related energy levels are well known for each atom [25].

Throughout the propagation within the encompassing atmosphere, atoms and ions emit photons with wavelengths related to the emitting atomic elements. Therefore by assembling this radiation from the plasma and then analyze its spectrum. It is attainable to determine the elements within the plasma and thus within the analyzed sample, from the created emission line databases [5, 12].Then, this radiation will be collected by using an associated optical fiber connected to a spectrometer which linked to a specific detector. This setup enables to record time spectra with the wavelength vary from near ultraviolet (UV) to near infrared (IR) through visible.

- **There are three main physical phases steps of LIBS mechanism:**

a. ***Laser interaction with matter phase***, where the energy will move from the laser to the sample material which in turn leads to evaporate the sample material;
b. ***The plasma creation phase***, which is formed by the interaction between this atomic vapor and the laser pulses, then its spatial and temporal will be developed;
c. ***The large spectral emission phase***, by which the detection and the analysis process of the signal can be accomplished [22, 24].

There are several environmental Parameters that influence on the characteristics and lifetime of the plasma, and by controlling these parameters, the modification of the LIBS spectral emission analysis can be occurred. Basically, the LIBS spectrographic analysis is characterized by a pulsed laser, a focusing lens, signal collecting system, optical fiber, spectroscope, and a computer.

The Laser source is the major instrument in the LIBS setup. It provides the sufficient energy for induced plasma generation and then the plasma aspects can be specified. The important laser associated parameters are the laser wavelength pulse width, pulse energy, and the pulse repetition rate [21, 26, and 28]. Indeed, the pulsed laser energy is mainly based on the laser wavelength and the laser pulse width. Clearly, by controlling these parameters related to every application requirements, the LIBS efficiency can be enhanced. Nanoseconds pulsed laser is the more commonly used for LIBS analysis [21]. The parameters related to laser energy that interacted with the material sample are *fluence* (energy per unite space, J /cm2) and *irradiance* (energy per unit space and time, W/cm2). The ablation phenomenon (erosion, fusion, sublimation, etc.) have a specific fluence threshold. So, the applicable laser should have certain fluence at which the ablation of the sample will be started. As a result, any change of these laser parameters i.e. laser wavelength (λ), energy (E), pulse length (τ) will affect the plasma generation and hence LIBS signal. So, the Characteristics and nature of the laser-induced plasma are powerfully influenced by the laser parameters. Additionally, the absorption process of the laser energy within the sample material depends upon the material properties, and its encircling atmosphere.

The major issues concerned to the LIBS technique are:

(1) The laser interaction with matter: The laser ablation process can be considered as a photochemical process in which the photons of the laser radiation are firstly absorbed by the sample material. This absorption related to the incident laser wavelength and also the sample optical properties. Under the effect of the thermal and photochemical impact, the sample energy state can be altered.

The degree of the laser illumination and the laser wavelength strongly affect on the ablation process [21, 26]. So, for a given laser energy (E), the laser with matter interaction surface (A), and the laser pulse width (τ), the laser illumination (I) is outlined as [25]:

$$\boldsymbol{I = \frac{E}{A.\tau}}$$

(2) The laser wavelength: plays a vital role in LIBS technique where it affects on: (a) The degree of the incident laser material absorbance and in turns chiefly affects on the laser ablation. (b) The generation of the laser induced plasma and its properties. Also, the laser absorption process is mainly based on the sample material nature. Conductive materials have high ability to absorb electrons (high optical absorbents). However, dielectric materials are less optical absorbents and will be entirely transparent for UV or visible light [21, 26].

(3)The laser pulse width: or the laser pulse period, for example (nanosecond, picosecond, femtosecond) pulse width. Consequently, the time period of the plasma (plasma lifetime) will alter related to the pulse width of applied laser for instance, in the case of nanosecond pulse laser, the plasma is formed as a result of the laser interaction with the matter, followed by an extra interaction between the laser and the plasma which in turns leads to generate an excited plasma.

But, for femtosecond pulse laser, the laser will be applied for a short period before the generation of the plasma, and there is no laser-plasma interaction, and it is a fast transition from the vaporization state to the plasma generation (short plasma). And so, the sample material nature specifies which of the applied laser pulse width can be used. Actually, for solid material, the short pulse width laser can be utilized for small crater diameter [13, 21, and 26].

(4)The pulsed laser energy: is based on the laser spot size (laser diameter) incident on the sample material, and on the pulse width. Therefore, in the LIBS setup, the focusing tool is more important for obtaining high laser irradiance [21, 26].

(5)The Sample material and its surrounding environment: have a huge influence either on the ablation process or on the plasma generation and its properties [12]. This atmospheric conditions such as, the ambient gas pressure and the gas nature also should deeply study to clarify the interaction of the laser induced plasma with the close gas molecules and to discover LIBS application in any atmospheric conditions like LIBS applications in Space field [21, 26]. The plasma is generated by the sample material laser absorption process and then developed by the interaction between the plasma and the close gas according to the plasma spectrum intensity and at a certain optimized pressure. Then, under this pressure degree, the plasma will cool quickly by free expansion within the gas (not preserved by collision). On the contrary, at higher pressure, the plasma energy will dissipate to the surrounding gas by the collision and thermal effect. Eventually, by decreasing the pressure, the degree of the plasma volume will be increased, and hence its density will be decreased [21, 27].

(6)The LIBS collecting system: in the most LIBS arrangement, when the laser focused on the sample surface by a collection of lenses, the plasma signal (a three-dimensional radiant object, powerfully heterogeneous) is generated and gathered by a lens that provides a picture of the plasma to the spectrometer through its entrance with an explicit magnification or reduction. Setup of these lenses is so easy to use; however, causes chromatic aberrations (different focal points relied on the incident wavelength). These chromatic aberrations can be solved by using wide range spectrometer or by using the optical fibers or by using a group of mirrors which makes a multiple of reflections then direct light to the spectrometer. Setup adjustment of these mirrors should be more accurate to avoid geometric aberration (the paraxial optical rays are far away from an optical axis and do not focus at the same place) that leads to form blurred image [21, 26].

(7)The LIBS optical fibers: are usually used to gather light from the plasma to the spectroscope and infrequently to transfer the laser. Fused silica fiber is the most commonly used in LIBS. Fiber diameters are ranging from 50 μm to 1mm and it may be crystalline or photonic fibers. Vital plasma signals like shock waves could be detected by a specific optical fiber [21].

(8)LIBS detection system: includes a spectrometer, and a detector. *A spectrometer* is an instrument that diffracts collected light from the plasma. It may work at one or more wavelength of interest. ”Ladder spectrometer” is firstly used spectrometer for LIBS applications since the 90s [28-29]. Czemy-Turner spectrometer is now the most commonly used in LIBS analysis, which formed of an entrance slit, two mirrors, and a diffraction grating. After entering the light through the entrance slit, first mirror collimates and reflects light to different angles based on their wavelengths, then second mirror direct the light on the focal plane where the detector is located. The applicable *detector* type relied on the LIBS application that is used for [21].It can be described by (1) spectral range: that defines the emission lines (wavelength range) that can be detected, (2) brightness: that determine the maximum light flux that can be transmitted through the detector, (3) resolution: that defines the ability of the detector to differentiate between two adjacent wavelength lines [21, 26].The choose of the detector is related to the combined spectrometer in LIBS system , and it can detect single or more wavelengths. Photodiodes or photomultiplier tubes are commonly used in the case of single wavelength detection. CCDs (Charged Coupled Device) or CCD camera can be utilized for several lines simultaneous detection. Data acquisition of the detection is usually offset by 1 or 2 µsec related to the plasma generation to cancel the background effect. Micro-Channels Plates (MCP) can be used to amplify the signal after specific delay, which helps to determine a signal window for acquisition process [21].

3. LIBS Advantages and constraints:

There are tremendous advantages of LIBS technique : (1) it permits a synchronous multi-elemental analysis (2) high selectivity, (3) high sensitivity , (4) remotely i.e. non-contact measurement, (5) fast technique (typically from a few second to a few minutes), (6) all chemical elements can be detected at the same time, with a specific detection limit for every element to specify ppm (particle per minute) for each element [1, 30],(7) solids, liquids, gases and aerosols can be analyzed,(8) LIBS instrumentation may be completely moveable system or transportable in vehicle or may be absolutely robotized based on the applications.(9) higher detection limit compared to that for other analytical techniques (ranging from ppm to the hundred ppm), (10) no need to sample preparation [19, 20, 30].

LIBS also have some limitations: (1) LIBS system integration in the field may be hard, (2) LIBS system optics may be damaged as a result of using high power laser if the fluence is just too sturdy, (3) plasma production is a random process which based on many conditions such as surface condition of the sample.

4. LIBS Applications:

- **LIBS Applications in the industry field:**

It is a major application for LIBS [37,38] because it is a fast and remotely analytical measurement .Many samples can be analyzed in severe and dangerous medium ; such as remote explosives detection by using LIBS [48]. In Metaleorgy field application, the compositions of many alloys can be detected by using LIBS, and also the impurities in any sample can be discovered [42, 51-53]. In the nuclear field application, LIBS can be utilized for remote detection of the nuclear radiation from nuclear reactors to avert hazardous radiation grades [49, 50].The impurities in the solar cell construction can be detected and analyzed by using LIBS which leads to fulfill higher efficiency solar cells [55].In geology field application, LIBS can detect and measure different concentrations of metal elements in the rocks [39, 40]. Finally, venomous elements such as; heavy elements in the waste of the industry [54] can be detected by using LIBS which leads to recycle or hoard these elements and consequently reduce the environmental pollution.

- **LIBS Application in the space field:**

Newly, a hybrid LIBS-Raman spectrometer, which onboarded the Martian spacecraft, performs a spectral analysis for Martian geological samples [41, 56].

- **LIBS Applications in the agricultural, and food industry field:**

LIBS is commonly used in the agricultural, and food industry field [11, 32, 33] such as; (1) external added sugar in honey can be detected [34], (2) soil fertility can be defined, and the phosphorus concentration in the soil sample can be detected [35, 36].

- **LIBS Applications in the biomedical field:**

Recently, chemical compositions of human biological samples for examples; tissues, bones, and fluids can be detected and analyzed by using LIBS [43]. Also, toxic components and mineral percentages in bones, teeth, nails, or tissues can be precisely measured by LIBS [43, 44]. LIBS can help to detect cancer and provide a surgical device that leads to simultaneously detect and destroy tumor cells [45]. Moreover, it is possible to classify pathogenic viruses and bacteria by applying LIBS [46, 47]. In Nanotechnology field, LIBS can a very useful way for monotone element analysis (18, 21, and 30).

- **LIBS Applications in the archeological field:**

Occasionally, there are many obstacles and difficulties in analyzing the archeological samples by conventional techniques, such as it is prohibited to be moved or destroyed for analysis, and also it requires a sample preparation. LIBS can overcome these difficulties that faced other conventional analysis techniques based on their advantages[31]; (1) It is possible to use portable LIBS instrument (no sample movement), (2) No need to sample preparation, (3) No need to contact for analysis (no sample damage),and (4)extremely accurate results. Furthermore, the renovation of archeological parts can be accomplished by LIBS technology. Finally, the combination between LIBS with other method such as; Raman or X-ray fluorescence (XRF) can be achieved to increase the efficiency [14, 31].

5. Nanostructure Enhanced LIBS (NELIBS):

- **Nanotechnology historical brief**

Nanotechnology turned out an important issue throughout the last decade of 1980 beginning with the important paper by Eric Drexler “Molecular engineering: An approach to the Development of general capabilities for molecular manipulation” [57]. Drexler mentioned the Richard Feynman work [58] before it absolutely was printed because this work was powerfully supported the ideas introduced, and the queries displayed by the latter, clearly mentioned by the gap sentence of this paper. Regardless of the differences encompassing the attitude on nanotechnology Drexler paper, it is clear that he was one of the major founders of the nanotechnology field, and was the first person use this expression in his book “Engines of creation: The coming era of nanotechnology” [59]. Over this years, the decisive developments of scanning tunneling microscope, which in turn lead to atomic microscope discovery, quantum dots composition and their potential applications [60]. By the primary half of the 90S, the Nanotechnology future seemed too promising because some researchers were developed a new nonmaterial and their specific applications in different fields such as (energy conversion, agriculture, electronics, and chemical catalysis) [61].” Nanoscience” term became related to the expression of nanotechnology which involved the control over the nanoscale in addition to any scientific phenomenon that influence the nanoparticles characteristics. In this period, many of laboratories, institutions, and universities especially in Europe and United States were concentrated on the nanoresearches [62], and different chemical technique for nanomaterial synthesis with at least one dimension limited to less than 100nm.[63,64] were determined. In year 2001, Alan MacDiarmid represented a great part of his Nobel Prize reception session to the electrically conducting nanofibers organic polymers design and production [65]. Researchers early considered that the nanoparticles morphology, which by controlling the shapes of nanoparticles, they can enhance the nanomaterial properties. Different shapes of nanoparticles represented by the new designed nanomaterials [66, 67].

Nature itself may be a large supply of nanoparticles, which generate from several processes: photochemical reactions, volcanic eruptions, or sea water evaporation aerosols generated by shocking waves [68]. Indeed, the relationship between the nanomaterials and humanity occurred for centuries. Some bacteria [69], algae (diatoms) [70], and viruses [71] have the size less than a few nanometers.

In present day, Nanotechnology still has more interest; the real nanomaterials are now widespread and can be found in many products such as, clothes, food, and cosmetics [72]. Recently, Nanotechnology is promising in the medicine field where many studies related to nanotoxicity to control and prevent the effect of these components, have also a great interest [72].

- **NELIBS:**

Nanoparticles are the particles whose structures with the dimensions smaller than 10^{-7} m and their physical properties are so different from those of the entire material [73, 74].Metal nanoparticles have been exceedingly applied in LIBS, which create a domestic surface Plasmon Resonance (SPR), by modifying the incident light distribution. Furthermore, it can improve the optical response of the surface particles, by controlling their optical and geometry characteristics [75, 76] and therefore cause a very efficient plasma excitation [75], which in turn leads to highly enhancement in spectroscopic sensitivity and selectivity. For high enough laser irradiance, the optimum of induced electromagnetic field improvement happens at the plasma resonance frequency i.e. nanoparticles resonance frequency [77, 78]. The typical laser spot size, is in order of 1-2 mm, should be focused on the deposited nanoparticles on the surface of the sample. Nanopaticles should be pure from any impurities as possible as we can. For maximum field improvement, there are an optimal ratio between the nanoparticles diameter and the distance between them [79,80].There are a variety of application fields where the nanoparticles LIBS can be applied and the results can be enhanced in the certain order of magnitude, related to the conventional LIBS, such as; (1) analysis of metallic alloys [81], (2) detect minerals in any solution [82-84], (3) Measure the percentage of contamination for any sample [81], (4) Describe any strong binding of Lithium ions with protein for any biological samples [83], (5) gemstone elemental analysis [85-87], where the laser irradiance at resonance state to prevent any damage of the sample. A nanoparticle enhanced LIBS (NELIBS), is related to the development in nanoparticles field, is a recent and a promised field that still not optimized and needs more efforts and researches.

NELIBS in Metals:

Of course, Metals are the best choice when study the basic properties of NELIBS, because metals supply a good electrical contact with and between nanoparticles and can perform an efficient laser interaction with material. The amount of ablated material is directly proportional to the applied laser electromagnetic field [88, 89]. By enhancing the laser electromagnetic field which in turns affects the seed electrons produced within the plasma. Keldysh theory [90] shows that the difference between the production of seed electrons in the conventional photoemission process (multiphoton ionization) and in the enhanced laser EM field where the tunneling emission (electron field emission) [91, 92]. Generally, the laser electromagnetic field enhancement efficiency relies on two major parameters: Irradiance of the applied laser, and nanoparticles concentration in the sample surface (i.e. nanoparticles density).

NELIBS in transparent material (such as glass):

They usually seem to be a challenge for LIBS technique because the focused laser beam can easily go through the transparent material and make poor reproductivity and cracks [93]. By using nanoparticles on the surface of the sample, the laser beam interacts with the nanoparticles instead of the direct interaction with the glass. The laser electromagnetic field enhancement leads to the electron field emission where occurred only at the contact place between the nanoparticles and the sample material, and by using much lower laser irradiance than in the case of conventional LIBS [94]. Then powerful plasma can be produced on the surface, which represents data for the elementary composition of the glass. By using NELIBS, the sample can be preserved from damage which can be much higher in the case of conventional LIBS [because NELIBS uses laser irradiance much lower than that required for conventional LIBS], so this non-destructive advantage makes this technique more adapted to invaluable transparent sample analysis such as gemstones or archeological glasses.

NELIBS in liquid solution:

Liquid solutions can be analyzed by using conventional LIBS, in the liquid state (by double pulse method) or by depositing the drying drops of the liquid solution on the non-conducting substrate. The solution analysis by the double pulse method provides up to ppm degrees [95]. The second method (drying drops of liquid solution) has not any limitation of detection, and there is no constraint in the solution amount. However, for a few amount of solution for example (a few microliters), the sensitivity will be a big problem in the conventional LIBS technique. By using NELIBS, the LIBS sensitivity can be improved to sub-ppb levels. For NELIBS There are three advantages: [1] The laser electromagnetic field enhancement, [2] The solution absorption on the nanoparticle surface, which leads to total transformation of all deposited solution to the plasma phase by only one laser pulse, which in turns leads to more powerful plasma generation rather than that generated in the case of LIBS, [3] the metals detection in the biological material, where in LIBS, not all of the ablated biological molecules will be ionized (there are atoms difficult to be ionized such as nitrogen, and carbon), which leads to promising application in medical field such as the quantitative analysis of metals in human plasma [96].

Conclusions:

LIBS is a vital analytical chemical analysis (quantitative or qualitative), which exhibits many of appealing advantages better than other conventional analytical techniques such as; remote measurement, portable, no need to sample preparation, nondestructive analytical method. There are a variety of important LIBS applications in many fields such as; industry, agricultural space, geological, archeological, and biomedical fields. Nanoparticles improved LIBS is a recently promised technique to enhance the analytical properties of the conventional LIBS such as; sensitivity, and selectivity by using a specific nanoparticles deposited on the sample surface. Therefore, additional research effort in nanoparticles improved LIBS is needed to enhance the LIBS efficiency.

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