Chapter 2.
Optimization of the LIBS Experiments for Glass Sample Analysis

Abstract

Spectroscopy of laser induced plasmas (OES-LIP) are widely studied for the elemental analysis of a variety of samples. Generally, plasma consists of free electrons, ions and atoms, and overall it is electrically neutral. Plasma formed from the single pulse causes high ionization in the beginning followed by the formation of neutral atoms and molecules through the process of electron-ion recombination. This very dynamic nature of weakly ionized transient plasma necessitates the temporal investigations to obtain the optimum LIBS signal and the same has been critically evaluated on various glass samples. In addition to this, other parameters like laser pulse energy, laser wavelength, lens-to-sample distance (LTSD), number of laser pulses etc. are optimized to get a quality LIBS spectrum.
Chapter 2

2.1 Introduction

Laser Induced Breakdown Spectroscopy (LIBS) is an emerging technique for the elemental analysis of variety of samples [1-3]. A high intense laser beam is focused on the target material to form the plasma. The plasma produced in LIBS is weakly ionized which consist of electrons, ions and atoms. The emission spectrum of this plasma is recorded and analyzed for elemental characterization.

Elemental analysis of glass materials is vital in many areas including forensic [4-6], archeological studies [7,8], industry [9,10] and nuclear waste management [11,12]. Well established techniques such as Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), Atomic Absorption Spectrometry (AAS), X-Ray Fluorescence (XRF), etc. are used for the elemental analysis of glass samples [1]. LIBS can also be used to investigate material composition and is an important method for the efficient analysis of given material because of its minimal destruction and ability for simultaneous multi-elemental detection [1-3]. Although the conventional wet chemistry methods can provide precise results of the material composition, their use is limited to laboratory environments. Therefore, a technique that can perform under extreme conditions such as nuclear power plants [11,13,14], hazardous environments [15], planetary explorations [16,17], etc. is in great demand and LIBS can be a viable technique to monitor the compositions in several such situations. X-ray based methods for elemental analysis is very attractive in glass industry but they can predict better results for major and minor components and the trace analysis of light elements (Li, B, etc) is further difficult by these methods [18].

Analytical performances of LIBS to determine the composition of the material is influenced by many experimental parameters. Unlike other analytical techniques, LIBS is not a complex set-up with respect to the ease of performing the experiments and the components that it involves. Hence, the method is considered as a simple for the elemental analysis as it consists of a laser, spectrograph and suitable optics. Because of this, the method is flexible to use both in laboratory as well as for field applications without making major changes in its design. However, the performance of the method can be improved many fold with hyphenated approaches (LIBS-Raman, LIBS-LIF, etc.) and with suitable sample preparation methods [19]. By using these approaches, the accuracy and precision of the technique would be better than the normal LIBS and hence there is a continued efforts to simplify the hyphenated LIBS systems to use it as mainstream technique [20]. To be specific, one needs to optimize, the
Despite all the improvements in LIBS technology, the methods/approaches like DP/MP-LIBS, MA-LIBS, RE-LIBS, etc. increases the cost and complexity of LIBS system because of the necessity of the additional components. LIBS technique is appreciated mainly for its
fast and in situ or remote measurements and this unique characteristic makes the technique stands out over other well-established analytical techniques for elemental detection. Hence, there is a significant scope even for the conventional LIBS combined with advanced chemometrics approaches which is simple, cost effective and provide more accurate results about the sample composition. In view of this, the conventional LIBS system is standardized by optimizing several parameters and the same is elaborated in the next section of this chapter. In addition to the optimization of LIBS, an overview of samples procured/prepared for the analysis is also presented followed by a detailed discussion on instrumentation.

2.2 Materials and Methods

The effect of experimental parameters have been studied on standard reference materials (SRM), soda lime, rare earth (RE) -doped phosphate, borosilicate and iron-phosphate (IP) glasses using LIBS system. The details of glass synthesis and their composition are as follows.

2.2.1 Standard References Materials (SRM)

Standard reference materials (SRMs) are the certified materials with known composition and are procured from NIST (National Institute of Standards and Technology, Dept. of Commerce, USA). The base matrix of NIST SRM 610 and SRM 612 has 72% SiO₂, 14% Na₂O, 12% CaO and 2% Al₂O₃. NIST certifies the presence of more than 24 elements in NIST SRM 610 and SRM 612 whose concentration approximately ranges from 200 ppm to 500 ppm and 16 ppm to 79 ppm respectively.

2.2.2 Soda-lime Glass

The soda-lime glass studied here is a normal glass slide used in laboratories for basic experiments and it is not a certified material. According to the supplier/distributor’s information the material is soda-lime, further the exact composition of the oxides/elements present in it is unknown.

2.2.3 Rare Earth (RE) Doped Phosphate Glass

Glass samples were prepared based on the compositions (1-X)NaH₂PO₄.2H₂O + (X)RE₂O₃, where X=1,2,5,10 mol% and RE= samarium (Sm), thulium (Tm) and ytterbium (Yb). Calculated quantities of the precursors (NaH₂PO₄.2H₂O 99.9%, RE₂O₃ 99.99% from Sigma Aldrich) are mixed well using an agate mortar and melted inside an alumina crucible by
heating the mixture inside a muffle furnace (MTI XT 1500) at 900 °C for one hour. The well homogenized melt was transferred onto a preheated ceramic plate of 1 mm thickness that has appropriate shapes molded on it. The obtained glass specimens are annealed at 500 °C to achieve thermal homogeneity.

### 2.2.4 Borosilicate Glass

Mn doped glass samples were prepared in Nuclear Recycle Board, BARC, Tarapur, India. To prepare these glasses, an appropriate amount of analytical reagent grade chemicals like silicon oxide, titanium oxide, iron oxide, boric acid, sodium nitrate and manganese nitrate were weighed and thoroughly mixed. The moisture content in the mixtures was removed on exposing it under the IR lamp. The mixture is then melted in the furnace at 1000° C and later the melt liquid is transferred to a preheated (at 550° C) graphite mold. The samples were removed from the mold and cooled down to room temperature. The final concentrations of doped element, Mn in the glass matrix were about 0.77%, 3.87%, 7.74% and 11.61%. A blank (without doping) sample was also prepared along with doped samples.

### 2.2.5 Iron Phosphate (IP) Glass

The iron-phosphate glasses are prepared by melting the desired amount of raw materials in an electrical muffle furnace. Qualitative and quantitative analysis of Chromium (Cr), Strontium (Sr) and Titanium (Ti) will be studied in iron phosphate glass matrix using LIBS system. Glass samples were prepared based on the compositions X[K2Cr2O7 + SrTiO3] + (1-2X)[(0.80) NaH2PO4.2H2O + (0.20)Fe2O3] where X = 0.0, 0.8, 1.6, 2.4 and 3.2 mol.%. Appropriate amount of raw materials were weighed and mixed in an agate mortar. The raw materials were ground for 1 h and melted in an electrical muffle furnace at 950°C for 1 h. The hot molten liquid is annealed for 2 h by pouring into a pre-heated brass mould kept at 400 °C to remove the thermal stress. Thereafter the glass samples are allowed to cool down slowly to room temperature.

### 2.3 Instrumentation

#### 2.3.1 Major Components of LIBS

By focusing a pulsed laser beam on a sample surface with sufficient energy can generate enough intensity to create the plasma [31]. Hence, laser source of any wavelength (UV, VIS or NIR) which has intensity above the threshold (10⁸ W/cm² to 10¹⁰ W/cm²) value of the
material can be used in LIBS experiments. Q-switched CO\textsubscript{2} laser, excimer lasers (XeCl, KrF and ArF) and fiber lasers are among the few lasers commonly employed in LIBS experiments. Although a variety of laser sources are available for the LIBS studies, the Q-switched Neodymium-doped Yttrium Aluminium Garnet; Nd:Y\textsubscript{3}Al\textsubscript{5}O\textsubscript{12} (Nd:YAG) solid state laser is widely used. In Q-switched lasers, very narrow and intense laser pulses are produced with the help of a pockel cell. These lasers are generally pumped by Xe-Arc flash lamps and give the emission at 1064 nm (fundamental wavelength). However, one can obtain the lower wavelengths of second (532 nm), third (355 nm) and fourth (266 nm) harmonics using BBO or KDP nonlinear crystals. These lasers come with a variety of specifications for example; the pulse energies: 20 mJ to 3 J and repetition rate: 1 Hz to 50 Hz.

Pulse duration, another laser property, also influences the plasma in LIBS experiments. Besides the wide use of nanosecond pulsed lasers, femtosecond sources can be also employed in LIBS experiments; energy deposited per pulse by these lasers is extremely high due to the narrow pulse duration. Different processes take place at different pulse durations; in nanosecond lasers thermally induced process is dominant, whereas, femtosecond pulsed lasers causes multiphoton absorption [32]. Although femtosecond laser sources induce, high irradiances they have lower ablation threshold energies when compared to nanosecond lasers. Chapter 1, section 1.1.2 gives more discussion on laser matter interaction with respect to pulse duration.

Spectrograph is another major component in LIBS experimental setup in which the emitted radiation is dispersed. Besides, a variety of spectrographs such as Czerney-Turner spectrograph, narrow band-pass filters, Paschen-Runge spectrometer, the echelle spectrometer is commonly employed in LIBS studies. Emissions from the LIBS plasma cover from UV to NIR regions of the electromagnetic radiation in which the signature of both atomic and ionic states of the elements are present. Therefore, a spectrometer that can cover this entire region enables the simultaneous detection of multiple elements. Further, it is very essential for a spectrograph to have both high resolving power and broad spectral range. Although the Czerney-Turner and the Paschen-Runge spectrometers are widely used in LIBS, they make use of single dispersing element [32]. Czerney-Turner spectrometers consists of a narrow slit, spherical mirrors, a plane grating and the detector. The emitted radiation from the plasma enters the spectrometer through the slit and falls on a mirror. The radiation incident on the mirror is directed towards the plane grating where the grating spatially disperses the incident light into different spectral components. These diffracted spectral components are
further falls on second spherical mirror. This mirror finally directs the light towards the detector where the spectral components are spatially separated on it. In case of Paschen-Runge spectrometers, the concave grating is used as dispersing element [32]. The dispersed light falls on detectors arranged at different spectral regions. However, both these spectrometers are not capable enough to have both broad spectral coverage and high resolution. In addition to this the other arrangement of narrow bandpass optical filters coupled with photodiode do not detect atomic/ionic emission lines simultaneously.

Echelle spectrographs coupled with gated detectors (ICCD) employed in LIBS provide both high resolution and broad spectral range [31,32]. Unlike the above discussed spectrometers, echelle spectrometers use an assembly of grating and a prism as two orthogonally set dispersing elements. Echelle spectrometers have high resolution due to the large blaze angle and large number of groves per millimeter on an echelle grating. Another dispersing element, prism used in this spectrograph prevents the overlap of higher order diffraction. An arrangement of prism and echelle grating shifts the order of diffraction orthogonally. Finally, the spectral components spread out in both vertical and horizontal directions providing two-dimensional view (echellogram) of the spectral lines as a function of diffraction order (Figure 2.1)

![Echellogram showing: (a) unequal distribution of diffraction orders due to single prism and grating and (b) equal distribution of diffraction orders due to dual prism and grating [33]](image)

However, the use of single prism and grating produce the uneven distribution of diffraction orders. The performance of echelle reduces due to these uneven distributions, which causes the formation of ghost lines. This problem is prevented by using the dual order prism and a grating in place of single prism and single grating system. The ease of calibrating these systems and non-movable components inside them increased the reliability of these systems.
The optical signals generated in LIBS are converted into electrical signals by means of electro-optical devices. The photodiodes, photodiode arrays, photomultiplier tubes (PMT) and the charge coupled devices (CCD) are the detectors employed for such purposes. Since the LIBS plasma is transient in nature and the signal-to-noise ratio (SNR) of spectral lines is optimum only at certain detection window. Hence, the gated detectors must be used in LIBS to record the optimum signals. For this reason, intensified versions of photodiode arrays [34] and CCD [35] are used in LIBS. CCDs consist of light sensitive elements known as pixels through which the photons falling on them is converted into electrons. The shift registers used in these integrated circuits collects the electrons and fed to the amplifiers through which the incoming charge-packets are converted to output voltage. This voltage is finally processed and the spectrum can be seen on the computer monitor. A detector coupled with the spectrograph must also have high quantum efficiency in the broad spectral range so that the signal-to-noise ratio is optimum. Therefore, in LIBS, the echelle spectrographs coupled with intensified CCDs have multiple advantages than other systems. The more elaborated discussion on LIBS instrumentation are available in literatures [3,31,32].

2.3.2 LIBS Experimental Setup

![Figure 2.2: Schematic diagram of the LIBS setup with (a) 355 nm (third harmonic) as the excitation wavelength (b) 532 nm (second harmonic) as the excitation wavelength](image)

A Q-switched Nd:YAG laser (Spectra Physics PRO 230-10) with its optical emission at 355 nm was used as a source to generate the plasma on the target material. This laser source has a pulse duration 6 ns, repetition rate 10 Hz and a maximum laser energy 400 mJ. A mirror with high damage threshold at the said wavelength was kept at 45° to the incident laser beam to reflect it towards a Pellin-Broca prism. This prism helps us to separate out the fundamental (1064 nm) and second harmonic (532 nm) wavelengths from the third harmonic (355 nm)
laser light which will be then directed towards the sample. A neutral density filter is used to fine tune the energy of the laser light to be deposited on the target material.

Table 2.1: Details of the LIBS system components

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Instrument</th>
<th>Additional information</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Nd:YAG laser</td>
<td>Spectra Physics PRO 230-10 Wavelength 355 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Average laser energy 400 mJ Repetition rate 10 Hz Pulse duration 6 ns Laser beam diameter 8 mm</td>
</tr>
<tr>
<td>2</td>
<td>Nd:YAG laser</td>
<td>Quantel Qsmart-450 Wavelength 1064 nm and 532 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Average laser energy 450 mJ at 1064 nm and 225 mJ at 532 nm Repetition rate 10 Hz Pulse duration 6 ns Laser beam diameter 6 mm</td>
</tr>
<tr>
<td>3</td>
<td>Focusing optics</td>
<td>Spherical lens Diameter 2.5 cm, focal length 20 cm, BK7</td>
</tr>
<tr>
<td>4</td>
<td>Translation stage</td>
<td>HOLMARC Optomechanic Pvt Ltd. Moves 0.3125 µm each step, Speed 6 mm/s</td>
</tr>
<tr>
<td>5</td>
<td>Spectrograph</td>
<td>Andor Mechelle-5000 Echelle type spectrograph</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Resolution 0.05 nm Blazed for 575 nm Broad operational spectral range</td>
</tr>
<tr>
<td>6</td>
<td>Optical fiber</td>
<td>Andor Core diameter 50 µ</td>
</tr>
<tr>
<td>7</td>
<td>Digital storage oscilloscope</td>
<td>Textronix TDS 2024B Four channel oscilloscope</td>
</tr>
<tr>
<td>8</td>
<td>Computer</td>
<td>Microsoft Windows XP Profession al version 2002, Service Pack 3, 1 GB RAM, 2.01 GHz Processor speed</td>
</tr>
</tbody>
</table>

ND filter helps the user to fix the incident energy just above the ablation threshold of the sample under study. A 20 cm bi-convex lens focuses laser beam on to the target mounted on XY-translation stage. The collection optics consists of UV grade quartz lenses and mirrors which was placed at 45° with respect to the incident laser beam. The characteristic emission received by the collection optics is sent to the echelle spectrograph. This spectrograph is
coupled with an intensified charged coupled device (ICCD) system (Andor Mechelle ME5000-DH734-18U-03PS150) and is used to acquire the LIBS spectrum. The echelle spectrograph in the present experimental setup can register the spectrum from 250 nm to 850 nm with the wavelength resolution of 0.05 nm. The spectrograph consists of an echelle grating (52 lines/mm which is blazed at 575 nm with a slit width of 10 µm), which has very high spectral dispersion ($\lambda/\Delta\lambda$). The synchronization between detector and Nd:YAG laser helps to obtain LIBS spectrum with maximum signal to noise ratio (SNR). A NIST certified Deuterium–Quartz–Tungsten–Halogen [Ocean Optics, USA] and Hg–Ar [Ocean Optics, USA] lamps are used to calibrate the echelle-spectrograph-ICCD system. The details of instruments used and their respective parameters are presented in Table 2.1. A computer is used to control the detector gating, translation stage motion and to visualize the recorded spectrum. Experimental setup presented in the Figure 2.2 (a) was used to study the rare earth doped phosphate glasses and borosilicate glass samples. However, the LIBS setup shown in Figure 2.2 (b) was used to study the iron-phosphate glass samples. Schematics shown in Figure 2.2 (a) and (b) differ in the laser sources used for the experiments. Laser source (Quantel-450) depicted in Figure 2.2 (b) has same parameters as that of in Figure 2.2 (a) except the wavelength (second harmonic, 532 nm) and the diameter (6 mm) of the laser beam.

2.4 Critical Experimental Conditions

The spectra recorded in the LIBS experiment depends on several parameters. Laser properties such as energy, wavelength, repetition rate and pulse duration play crucial role to obtain a good spectrum. Apart from this, the spot size, ambient conditions and the detection window also influence the LIBS measurements. Appropriate detector systems are equally important in LIBS setup in which the spectrum recorded using instruments like spectrographs coupled with photomultiplier tubes, CCD, ICCD, etc. have varying responses in different wavelength regions and resolution. The effect of pulse duration is already discussed in the Chapter 1 where the effect of pulse duration on irradiance, ablation efficiency and laser-matter interactions are discussed.

Experiments carried out in ambient conditions showed that atmospheric/surrounding gas, temperature and pressure influence the plasma formation. The plasma formed in ambient gas of He, Ar and air differ significantly with respect to electron temperature and electron density [36]. The parameters such as mass, density, thermal characteristics and ionization potential
are responsible for the variation in plasma formation. For example, the plasma emission of Iron is 10 times greater at 1 atm of He gas than in air and Ar under the same pressure [37]. Effect of atmospheric pressure influence the strength of the signal and the weak plasma emission is evident under low-pressure (<10 Torr) condition. The weak plasma confinement degrades the plasma at such conditions. Conversely, it has been also demonstrated that the increased plasma confinement is evident on increasing the ambient pressure [38]. This creates the hot and dense plasma due to the high pressure in the surroundings causing the intense and long duration plasma emission.

LIBS is capable enough to provide the best results even when the spectra are recorded at high sample temperatures. Under such condition, the plasma is assumed to be optically thin and in local thermodynamic equilibrium (LTE). Yun et al have carried out the analysis of molten glass samples in which the LIBS spectra were recorded at 1200 ºC [39]. The emission line intensity was investigated with respect to increase in sample temperature from room temperature to 1200 ºC. The LIBS intensity for various constituents of borosilicate glass matrix (Ca, Al, Si and Ti) were analyzed and an increase in the emission intensity was observed. The same authors quantified the analyte of interest in glass and no significant change in the analytical performance of LIBS was observed even when the samples are studied at high temperature [40]. Lopez-Moreno et al. have carried out the quantitative analysis of steel slag samples at 850 ºC [41]. The correlation coefficient of 0.98 and 0.99 were obtained for the intensity ratios of Mg/Ca and Si/Ca respectively. These results demonstrated that the analytical performance of LIBS is almost similar even when the sample temperature is high.

### 2.4.1 Temporal Study of LIBS Plasma

The optimum LIBS signal must have better signal to noise ratio and also it must be free from background continuum. The plasma is formed immediately after the laser pulse absorption but vanishes completely in few microseconds (µs) to milliseconds (ms). A schematic diagram of the temporal evolution of LIBS plasma immediately after laser absorption is shown in (Figure 2.3). The time scale for all these phenomena such as laser pulse absorption, plasma formation and plasma decay is so short that the gated detectors such as ICCD are indispensable to find the optimum LIBS signal. During this plasma formation and decay (Figure 2.3), the spectral line profile is mainly affected by the transient nature of the LIBS plasma. The background continuum arising from bremsstrahlung and recombination is
dominant at early stage of the plasma and in the present study, this continuum persists until few hundreds of nanoseconds. In Figure 2.3 the terms, $t_d$ and $t_b$ represents the gate delay and gate width (integration time) respectively.

**Figure 2.3:** Illustration of the variation of Optical signal intensity with respect to time after the laser pulse is absorbed by the sample in LIBS. Inset: Si (I) at 100 ns and Si(I) at 1000 ns

The time between laser pulse absorption to opening of the detector window is known as gate delay ($t_d$) whereas the gate width ($t_b$) is duration in which the plasma emission is collected. The emission line profile of Si (I) at 100 ns and 1000 ns gate delay are also shown in the inset of the Figure 2.3. The Si (I) emission line is seen broad at 100 ns where as it becomes sharp and narrow at 1000 ns. The noise free, narrow spectral lines observed near 1000 ns are not affected by bremsstrahlung and recombination radiations and hence such lines are suitable for the quantitative analysis.

The various experimental parameters have been investigated using both second harmonic (532 nm) and third harmonic (355 nm) wavelengths of the Nd YAG laser. The LIBS experimental conditions such as gate delay, gate width and detector gain have been studied using standard reference material i.e., NIST 610 glass. This material has base matrix of soda lime glass and hence the effect of these experimental conditions have been investigated with respect to major atomic and ionic emission lines of Si and Ca. Every spectrum is recorded using 532 nm laser beam as the excitation source, with an average of 115 laser pulses at irradiance of $4.42 \times 10^{10}$ W/cm$^2$. Four LIBS spectra are averaged for each gate delay, gate width and detector gain as shown in Figure 2.4 (a), (b) and (c) respectively.
Chapter 2

Figure 2.4: Variations of intensities of the 288.15 nm, 315.88 nm, 422.67 nm and 634.71 nm spectral lines at different detector parameters (a) gate delay, (b) gate width and (c) detector gain using 532 nm as irradiation source

The LIBS spectra recorded with respect to various gate delays illustrates the poor signal-to-noise ratio (SNR) near 0.1 \( \mu s \) gate delay (Figure 2.4 (a)). As the gate delay is increased, the SNR improved at 0.7 \( \mu s \) and gradually it reaches near to zero at 20.0 \( \mu s \). LIBS spectra recorded keeping 0.25 \( \mu s \) to 10.0 \( \mu s \) gate width, but the optimum SNR is found to be above 5.0 \( \mu s \) (Figure 2.4 (b)). The LIBS intensity is also verified for different detector gain where the intensity is exponentially increased (Figure 2.4 (c)) with increase in incident laser intensity. The exponential increase in the LIBS signal intensity is mainly accounted for the increased CCD clock voltages of electron multiplication register where the secondary electrons are generated through impact-ionization.

LIBS plasma of Iron Phosphate glass sample has been temporally studied using 532 nm laser source. Similar experimental conditions as that of previous one (irradiance = \( 4.42 \times 10^{10} \) W/cm\(^2\) and number of laser pulses = 115) are employed to record the LIBS spectra. The SNR versus gate delay of atomic emission lines of K, Cr, Sr and Ti at 769.89 nm, 425.43 nm,
460.73 nm and 430.59 nm demonstrated the identical behavior at different gate delays and the optimum SNR is observed at 0.7 µs (Figure 2.5 (a)). The SNR versus gate width of all these doped elements is also studied (Figure 2.5 (b)). Poor SNR is observed at shorter detection window and further, from the figure it is clear that the SNR is saturating at longer gate widths. In this experiment, the gate width of 5.0 µs is found to be suitable. Figure 2.5 (c) and (d) represents the average LIBS spectra of Iron-Phosphate glass at various gate delays and gate widths respectively. It is clear from the figures that the decrease in the emission line intensity is evident on increase in the gate delays and conversely the emission intensity is increased at higher gate widths.

![Figure 2.5](image_url)

*Figure 2.5: Variations of signal to noise ratio of 769.89 nm, 425.43 nm, 460.73 nm and 430.59 nm lines at different (a) gate delays and (b) gate widths using 532 nm as irradiation source; (c) and (d) represent the corresponding variation of LIBS spectra at different gate delays and gate widths respectively.*

The experiments were also performed using 355 nm laser beam to determine the optimum experimental conditions to record the LIBS spectra of different glass materials. Rare earth (Thulium) doped phosphate glass sample has been studied at different gate delays and gate
widths (Figure 2.6 (a) and (b)). The results observed here are similar to the one obtained with 532 nm laser source. The emission lines of Tm used for this study are 418.76 nm and 420.37 nm. The experimental parameters like gate delay and gate width are further studied on soda lime glass and borosilicate glass using 355 nm laser beam. Most of the emission lines observed in soda lime glass exhibits better SNR from 0.5 µs to 1.0 µs and the optimum gate width is found to be 5.0 µs (Figure 2.6 (c) and (d)).

Figure 2.6: Variation of signal to noise ratio of spectral lines (see the inset) at different gate delays and gate widths on Tm doped phosphate glass ((a) and (b)), soda lime glass ((c) and (d)) and borosilicate glass ((e) and (f)) using 355 nm as the irradiation source.
Similarly, LIBS spectra recorded at various gate delay and widths on borosilicate glass demonstrated similar observation as that of soda lime glass (Figure 2.6 (e) and (f)). In view of all these observations, the optimum gate delay and gate width to record the LIBS spectra of different glass samples are found to be 0.7 µs and 5.0 µs respectively. The Table 2.2 summarizes the laser parameters employed to obtain fairly good LIBS signal.

Table 2.2: Summary of experimental parameters used for the optimization of gate delay and gate width

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Samples</th>
<th>Wavelength (nm)</th>
<th>No. of laser pulses</th>
<th>Irradiance (W/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NIST 610 SRM glass</td>
<td>532</td>
<td>115</td>
<td>4.42×10^10</td>
</tr>
<tr>
<td>2</td>
<td>Iron Phosphate glass</td>
<td>532</td>
<td>115</td>
<td>4.42×10^10</td>
</tr>
<tr>
<td>3</td>
<td>Tm doped phosphate glass</td>
<td>355</td>
<td>115</td>
<td>4.56×10^11</td>
</tr>
<tr>
<td>4</td>
<td>Soda lime glass</td>
<td>355</td>
<td>230</td>
<td>9.90×10^11</td>
</tr>
<tr>
<td>5</td>
<td>Borosilicate glass</td>
<td>355</td>
<td>230</td>
<td>7.55×10^11</td>
</tr>
</tbody>
</table>

2.4.2 Dependence of Laser Wavelength

The intensity of the emission line is dependent on the laser wavelength used. As discussed in the Chapter 1, the shorter wavelength or wavelength less than 1000 nm is responsible in generating the multiphoton absorption and laser wavelength greater than 1000 nm produces the collision-induced ionization [42]. Several groups have studied the effect of laser induced plasma emission intensity with respect to irradiation source. Barnett et al. have carried out detailed investigation on the influence of LIBS emission intensity with respect to second harmonic (532 nm) and fourth harmonic (266 nm) laser wavelengths [43]. The authors concluded that the spectra recorded from NIST glass samples using 532 nm laser as excitation source has greater emission intensity than the 266 nm laser excitation. Further, they also reported that the 532 nm laser is capable of producing better SNR, however, they observed better precision at 266 nm laser irradiation. Similarly, Cahoon et al. used 266 nm and 1064 nm on NIST glass samples and found that UV irradiation source removes more mass than the IR source, creating uniform craters. The analytical performances of 266 nm excitation provided better precision and they concluded that the use of this wavelength is highly suitable for forensic applications.

In the present study, all the three wavelengths viz, fundamental (1064 nm), second harmonic (532 nm) and third harmonic wavelengths (355 nm) of the Nd:YAG laser have been used to
create the plasma on NIST certified standard reference material. Experimental conditions such as gate delay (0.7 µs), gate width (5.0 µs), laser energy (20 mJ), gain (200) and number of laser pulses (115) were kept identical for the three incident wavelengths of the laser beam. Four LIBS spectra recorded at similar conditions were averaged for the analysis. Figure 2.7 (a) and (b) shows the changes in the emission intensity as a function of irradiating wavelength.

Figure 2.7: Variations in emission intensities of the LIBS of spectra of NIST 610 standard reference material: (a) Effect of irradiating wavelengths; (b) Truncated region of LIBS spectrum showing the intensity of Si (I) and Mg (II) emission lines

It is observed that, the spectral line intensity of Si (I), Si (II), Ca (I) and Ca (II) lines exhibits better response for 532 nm incident laser beam as compared to UV and IR laser beams. The experiment is repeated with soda lime glass and 15 spectra are averaged to investigate the wavelength dependence, keeping the number of laser pulses to 115 per spectrum. Figure 2.8 depicts the study in which LIBS emission intensity of atomic and ionic lines of Mg (285.21 nm and 279.55 nm), Si (288.15 nm and 634.71 nm) and Ca (422.67 nm and 315.88 nm) are more intense with 532 nm laser source as compared to 1064 nm.

Figure 2.8: The effect of fundamental (1064 nm) and second harmonic wavelength (532 nm) on LIBS emission line intensities of soda-lime glass
Chapter 2

Barnett et al. reported similar results using NIST glass samples in which 532 nm irradiation source gave higher emission intensity than 1064 nm [43]. The intermediate laser wavelengths induce the maximum breakdown threshold and hence the strength of the emission lines in LIBS spectrum is more at 532 nm [42]. In view of this, the results obtained here matches well with the literature and further it elucidate that the 532 nm laser source is effective in generating emission lines with high intensity than other wavelengths (fundamental and third harmonic sources).

2.4.3 Number of Laser Pulses

The LIBS spectra of NIST 610 glass has been recorded at 5, 10, 15, 20 and 30 accumulations. Here, 10, 20 and 30 accumulations approximately correspond to 115, 230 and 345 laser pulses respectively, which have been used for the ablation. The atomic and ionic emission line intensity of Si (288.15 nm and 634.71 nm) and Ca (315.88 nm and 422.67 nm) have been investigated. All these spectra have been recorded with 532 nm laser wavelength and the irradiance of $4.42 \times 10^{10}$ W/cm$^2$ and the spectral line intensity increases almost linearly with the increase in number of laser pulses (Figure 2.9 (a)). Although the variation in the spectral line intensity is linear at various laser pulses one can also determine the percentage relative standard deviation (RSD) of these emission lines. In view of this, Figure 2.9 (b) exemplifies the gradual decrease in the percentage RSD for LIBS spectrum recorded at more number of averaged laser pulses.

![Figure 2.9: (a) LIBS signal intensity versus number of laser pulses and (b) Percentage relative standard deviation versus number of laser pulses](image-url)

2.4.4 Effect of Laser Pulse Energy

Laser pulse energy is another significant parameter that influences the strength of the emission lines. In other words, the material ablated and the plasma formed depends directly
on the incident laser energy and is directly proportional to the emission line intensity. In this experiment, the LIBS spectra of soda lime glass has been studied and the response of five emission lines of Si (I) are investigated at 250.69 nm, 251.61 nm, 252.85 nm, 288.15 nm and 390.55 nm.

The LIBS spectra have been recorded at three different laser energies viz., 9.5 mJ, 17 mJ and 38 mJ. The emission intensity of Si (I) increased linearly with respect to increasing laser energy. Each spectrum is an average of 230 laser pulses and it is recorded at gate delay and gate width of 0.7 $\mu$s and 5.0 $\mu$s respectively. Six such spectra were recorded and they were averaged to one spectrum. Further, the percentage RSD as a function of laser pulse energy provided the essential insights of obtaining the optimum LIBS spectrum. The results obtained from Figure 2.10 (b) demonstrated the gradual decrease in the percentage RSD with respect to increase in laser energy.

### 2.4.5 Role of Lens-to-Sample Distance (LTSD)

The changes in the spectral line profile depend on several factors: laser pulse energy, Lens-to-Sample Distance (LTSD), optical properties of the sample, etc. The present study is focused on investigation of spectral line profile with respect to lens-to-sample distance (LTSD). The plasma formed in LIBS is not uniform spatially. The core part of the plasma consist of large number of ions and excited atoms in which the plasma temperature is maximum and the immediate next region have lesser ions and reduced plasma temperature. The outer part of the plasma is much cooler in comparison with the core part where the
neutral species dominates. A schematic representation of laser-induced plasma is shown in the Figure 2.11.

![Figure 2.11: Illustration of different regions of the laser induced plasma](image)

The emission of photons takes place when the excited atoms reach the ground state. However, the photons emitted due to the de-excitation escape from the plasma only at optically thin conditions [31]. This is possible if the incident laser beam has enough energy to ionize the material completely. In case, the outer core of the plasma has relatively large number of cooler atoms then spectral line suffers from self-absorption and hence under such circumstances the plasma is optically thick. In LIBS, concentration of the element is measured by the intensity of a spectral line to perform semi-quantitative/quantitative analysis. However, self-reversed line profiles affects in determining spectral line intensity due to the observed dip at the central frequency. This in turn will have adverse effects on quantitative analysis of analyte under investigation. As anticipated earlier, the optimum LIBS spectrum can be recorded when the plasma is optically thin and at local thermodynamic equilibrium (LTE). However, attaining this condition in the LIBS plasma requires the appropriate fluence/irradiance. In general, the ablation and plasma formation in solids takes place only when the irradiance is greater than \(10^8 \text{ W/cm}^2\) [31]. Since the irradiance and the spot size are inversely proportional, the sufficient laser pulse energy (>10 mJ) deposited on a very small spot of the order of few microns (<50 µm) helps in producing the plasma. Therefore, the laser beam has to be focused appropriately onto the target surface and to investigate this, LIBS spectra were recorded at various LTSDs.

A Q-switched Nd:YAG laser of 532 nm wavelength is focused through 20 cm focal length lens on soda lime glass sample/target. Figure 2.12 depicts the variation of lens-to-sample distance (LTSD) where initially the lens is at a position x with a distance of 19.25 cm from the target where the sample/target is fixed at one position and lens is moved away from the target. From position x the LTSD is increased 0.2 cm each time stepwise and the LIBS spectrum is recorded at each distance. This procedure is repeated until the lens reaches to the
position y, where, the LTSD is now equal to 21.05 cm. The LTSD from position x to y covered a total distance of 1.8 cm including the Rayleigh range of the focusing lens.

![Diagram showing lens-to-sample distance](image)

*Figure 2.12: Schematic diagram showing lens-to-sample distance*

Six spectral lines viz., Si (I)-288.15 nm, Si (II)-634.71 nm, Ca (I)-422.67 nm, Ca (II)-315.88 nm, Mg (I)-285.21 nm and Mg (II)-279.55 nm have been used to demonstrate similar behavior in terms of the strength of the emission line with respect to different LTSD (Figure 2.13 (a)). The LIBS spectral line intensity is near to zero at 19.25 cm and rapidly increases to maximum at 19.65 cm. After 19.85 cm the intensity slowly decreases and reaches to minimum at 21.05 cm.

![Graphs showing LIBS signal intensity and peak area](image)

*Figure 2.13: (a) Variation of LIBS signal intensity versus lens-to-sample distance; (b) Peak area of Si (I) 288.15 nm emission line (20 cm focal lens, 20 mJ laser energy, 532 nm laser, soda-lime glass)*

The experiment demonstrates the persistence of maximum emission line intensity when the LTSD is near the Rayleigh range. For the sake of completeness, one of the emission line shown in Figure 2.13(a) (i.e., Si (I) 288.15 nm) is further examined using its area under the peak. Figure 2.13 (b) illustrates the area under the peak (Lorentzian fit) for the Si (I) emission line from the LIBS spectrum recorded at various LTSD. The Figure 2.13(b) also demonstrated the similar trend as that of Figure 2.13 (a) in which the peak area was
maximum near the Rayleigh range. In Table 2.3, the details of Lorentzian fit for the Si (I) line including the peak area, full-width half-maximum (FWHM) and correlation coefficient ($R^2$) are given.

**Table 2.3**: Lorentzian fit for the Si (I) 288.15 nm line

<table>
<thead>
<tr>
<th>LTSD</th>
<th>Peak area</th>
<th>FWHM</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>19.25</td>
<td>146.180</td>
<td>0.076</td>
<td>0.688</td>
</tr>
<tr>
<td>19.45</td>
<td>4324.74</td>
<td>0.106</td>
<td>0.976</td>
</tr>
<tr>
<td>19.65</td>
<td>3776.91</td>
<td>0.081</td>
<td>0.976</td>
</tr>
<tr>
<td>19.85</td>
<td>4342.04</td>
<td>0.097</td>
<td>0.986</td>
</tr>
<tr>
<td>20.05</td>
<td>3568.29</td>
<td>0.090</td>
<td>0.990</td>
</tr>
<tr>
<td>20.25</td>
<td>3088.45</td>
<td>0.095</td>
<td>0.988</td>
</tr>
<tr>
<td>20.45</td>
<td>2725.79</td>
<td>0.080</td>
<td>0.986</td>
</tr>
<tr>
<td>20.65</td>
<td>2760.57</td>
<td>0.083</td>
<td>0.987</td>
</tr>
<tr>
<td>20.85</td>
<td>1107.56</td>
<td>0.097</td>
<td>0.911</td>
</tr>
<tr>
<td>21.05</td>
<td>146.180</td>
<td>0.076</td>
<td>0.688</td>
</tr>
</tbody>
</table>

A close look at the area under the peak of Si (I) 288.15 nm line further demonstrates the consistency of spectral line profile when recorded at lower pulse energies (Figure 2.14). The data shown in Table 2.2 is obtained from the Lorentzian fit of Si (I) emission line and the same data is collectively displayed in Figure 2.14.

*Figure 2.14*: Lorentzian fit of the emission line of Si (I) 288.15 nm at various LTSD
On close observation, it is found that the Si (I) 288.15 nm line profiles have more distortion/deviation when LTSD is 19.25 cm, 20.85 cm and at 21.05 cm which is evident from the poor coefficient of determination ($R^2$) of the Lorentzian fit. From Figure 2.14 it is evident that the $R^2$ values for the rest of the LTSDs vary from 0.97 to 0.99 and this shows that no much significant change in the line profile near the focal length of the lens. The reason for better $R^2$ value may be due to the use of emission lines whose transition takes between the two upper energy levels; here in this case the lower and upper energy levels are at 0.780 eV and 5.082 eV respectively. In other words, the transitions that originate from the ground state are more prone to have flat or self-reversed profiles [31]. Furthermore, the part of the energy deposited by the laser pulse on a surface of the glass substrate can also distribute through the bulk of the medium due to the transparent nature of the material. This might be another reason due to which the incident laser beam does not distort/deviate the spectral line profile at low laser pulse energy even though the LTSD is at the Rayleigh range.

2.4.6 Surface Morphology

The major task of the analysts in archaeology, forensics and other disciplines is to critically evaluate the chemical composition without losing/destroying much of the sample [44]. The decision to study the precious samples from these disciplines strongly depends on the amount of material consumed during the experiment. Samples relevant to such applications need to be analyzed with no/minimal destruction. One should note that ICP based methods are expensive, require rigorous sample preparation and are destructive in nature. In contrast to this, LIBS is inexpensive, require no/minimal sample preparation and more importantly it is quasi non-destructive technique. In LIBS, the focused laser beam on sample surface ablates few micrograms to nanograms of the material and the surface area that is affected by the laser pulse varies from few tens to hundreds of microns. To demonstrate this effect, the surface morphology of the laser ablation on soda lime glass has been studied.

The soda lime glass sample is mounted on XY- translational stage which is moving at a speed of 6 mm/s. Initially, the focused Nd:YAG laser (355 nm, 10 Hz, 6 ns, 35.8 mJ) beam is allowed to fall on the surface of the glass sample placed at 19.5 cm from the focusing lens and this focused laser beam creates the craters. The experiment is repeated for LTSD of 19.6 cm and 19.7 cm to monitor the damage due to the laser irradiation. The craters formed on glass surface at three different LTSD are further investigated by using the Scanning Electron Microscopy (SEM). Figure 2.15 represents the SEM (Zeiss EVO 18 Special Edition) images
of craters formed by single pulse of the Nd:YAG laser beam. An elaborate discussion about the effect of laser matter interactions on solid surface is given in Chapter 1. The craters formed by nanosecond lasers on glass are not always uniform in shape and it is mainly attributed for the laser pulse width (FWHM). The reason for this is due to the fact that the micro and nanosecond lasers interact with the material through the processes of heating, melting and vaporization.

However, the first two processes are absent in femtosecond laser pulses in which the incident laser beam causes the direct vaporization of the material. In other words, the nanosecond laser pulses are broad enough to interact with the material through thermal ablation process and cause the melting of the surrounding surface. Further, the craters are much more insignificant/negligible when the pico- or femtosecond pulses are used [32]. In such case, the interaction of laser pulse is so short that the pulse is lost before it melts/damages the surroundings. From the above experiment, it is observed that the craters formed in LIBS experiment are strongly dependent on the irradiance as well as the physical properties of the sample. Few other groups [45,46] have reported that spots created in LIBS experiments were approximately of 200 µm in size. In the present work, the craters were ranging from 25 µm to 180 µm which clearly demonstrate that LIBS is a least destructive technique. Macroscopic investigation of LIBS craters/spots shows that LIBS has potential advantages as compared to the well-established (ICP based) methods.

2.5 Conclusion

The time evolution of the LIBS plasmas on soda-lime glass, rare earth doped phosphate glass, borosilicate glass and iron-phosphate glass samples suggested that the optimum gate delay ranging from 0.7 µs to 1.0 µs and gate width of 5.0 µs to record LIBS spectra. The work
carried out here with different wavelengths viz, 1064 nm, 532 nm and 355 nm provided maximum signal intensity at 532 nm. The effect of LIBS emission line intensity on averaged number of laser pulses demonstrated the linear relationship between the two. The percentage relative standard deviation (%RSD) calculated for different numbers of laser pulses shows optimum LIBS intensity for more laser pulses. Further, linear relationship was found between the intensity of five LIBS emission lines of Si (I) and laser pulse energy. The exponential decrease in the %RSD is also found at high laser pulse energy. The effect of LIBS emission intensity with respect to LTSD showed better intensity near the Rayleigh range.
2.6 References


