RESEARCH

Effect of laser polarization on atomic and ionic emissions in Laser-Induced Breakdown Spectroscopy (LIBS)

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Abstract

Laser-Induced Breakdown Spectroscopy (LIBS) is attracting a great deal of interest in qualitative and quantitative analysis of materials. Close observation reveals that developments in the science that underpins LIBS as an analytical technique are limited to either signal enhancement strategies or newer data analysis techniques that facilitate better interpretation of raw LIBS data. Developments related to the excitation part of LIBS have been restricted to the effects of laser beam characteristics or the effect of ambient experimental conditions. The influence, if any, of the polarization state of the excitation laser has largely remained unexplored. We address this lacuna by probing the influence of different polarization states of the excitation laser on LIBS spectra of metals (copper and silver) and non-metals (polyethylene) by analyzing the polarization-dependent behavior of both atomic and ionic emission lines. Our observations open the possibility of tackling the problem of relatively faint emissions from ionic species in the plasma by appropriately manipulating the polarization state of the incident laser beam; this may lead to easy-to-implement improvement in the performance of LIBS instruments.

Graphical abstract
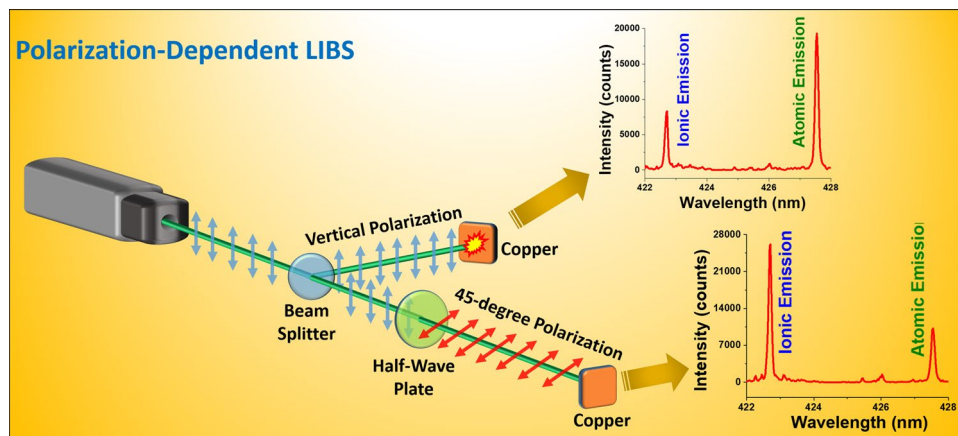
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1 Introduction

Laser-Induced Breakdown Spectroscopy (LIBS) has become an established technique for qualitative and quantitative materials analysis [1, 2] based on elemental composition. It finds ready application in trace element detection [3, 4]. The wide acceptance of LIBS in material analysis is centered on its ease of applicability in in-situ analysis, stand-off capability, trace level of detection, and universal applicability, with only very marginal (microscale) destruction of the sample. The technique uses a focused laser beam to create microplasma on a surface by ablating the material under study [5, 6]. Laser-induced excitation of plasma, followed by its de-excitation, results in the emission of characteristic lines of the elemental constituents present in the sample, either in the atomic or ionic state. Small molecular species in the sample can also contribute to the emission process. Collection and analysis of the signal emitted reveal the corresponding elements that are present in the sample, making it possible to decipher the sample's elemental composition [7], to detect the presence of 'foreign' elements in trace amounts [8], and, in a more general sense, for material identification and classification [9, 10]. Reported applications of LIBS have invariably focused on developing signal collection strategies to meet the requirements of a specific application and, of course, to increase the sensitivity of measurements [11–13]. Recently, much attention has been paid to signal analysis, with novel combinations used to different statistical tools and multi-variate data analysis methods [14, 15].

The discussion on theoretical, experimental, and analytical facets of LIBS has focused majorly on the optimization of signal collection, which in turn helps to retrieve corresponding elemental information. For experimental systems with a gated detector, parameters like gate width, gate delay, and other acquisition parameters have also been studied [16, 17]. Although the physics of the excitation part of the technique in terms of excitation laser wavelength, laser energy, laser pulse width, and laser repetition rate, and the consequent parameters like laser spot size, peak power, and fluence at the sample surface are reported, other important parameters like polarization of the laser beam are under-discussed. However, the comparison of laser-induced ablation using nanosecond and femtosecond lasers has been made [18, 19]. Although the primary objectives of LIBS are different, all these optimization procedures mentioned as a part of the experiments effectively aim to improve the ability of the system to efficiently ablate and collect signals from the sample to detect the trace elements present in them. Hence, it is important to induce and collect as many signals as possible with available instruments for useful sample analysis. Especially for LIBS, where multi-elemental analysis is performed most of the time, different atoms and their ions behave differently to the excitation. In calibration-free approaches in trace element detection, it is important to collect comparatively weak emissions from ionic species in plasma and the emissions from atomic species. The parameter optimization ultimately aims to improve this signal gathering. However, an important parameter has attracted hardly any attention throughout the recent development of LIBS is the excitation laser beam's polarization state, which constitutes the focus of the present work. The article aims to evaluate the effect of laser beam polarization in the excitation-emission process of different types of samples and to find whether it can be applied as a signal enhancement strategy in future experiments.

The excitation laser used in LIBS may have one of many polarization states. In conventional LIBS systems, in general, linearly polarized lasers are used. It can also be elliptically polarized, circularly polarized, or even unpolarized beam. The linearly polarized beam may have the polarization vector in the vertical or horizontal state or any direction [20]. We have already noted the paucity of information on the influence of polarization of the exciting laser beam on LIBS spectra; existing reports are confined to the effect of polarization state on the photoionization process in general [21, 22], probing changes in plasma emission when switching from linearly to circularly polarized excitation beam [23], and the polarization characteristics of the emitted radiation [24]. In the work we report here, we systematically measured LIBS spectra using laser excitation in each possible polarization state.

The existing reports on polarization-dependent LIBS primarily investigate how the polarization properties of LIBS emission signals and continuum background help to suppress the influence of continuum emission in the output spectra (polarization-resolved LIBS: PR-LIBS) [25–28]. The optimizations in the said are reported with different angles of incidence, fluence, collection angles, etc. [25, 26]. The effect of excitation laser polarization is reported in terms of output when the polarization changed from s-polarized to p-polarized [25]. However, the primary concern is the behavior of continuum emission at different polarizations.

In the current article, we investigate how the atomic/ionic emissions from metallic and non-metallic samples behave at different polarizations of excitation laser based on the absolute intensity variations observed, without any influence from continuum emissions, by using a gated detector to capture constituent emissions selectively.

2 Methodology

2.1 Experimental

The experimental system used in our studies comprises a lab-made LIBS set-up in back-collection geometry, as shown in Fig. 1. A nanosecond Nd: YAG pulsed laser operating in its second harmonic mode is used as the laser source (Q-Smart 450, Quantel). The pulse width is typically 6 ns, the repetition rate is 10 Hz, and the maximum energy at 532 nm output is 225 mJ. For data acquisition, we use a high-resolution Echelle spectrograph (Mechelle, ME5000, and Andor, Ireland) coupled to an Intensifier Charge Coupled Device (ICCD) (Andor iStar, DH734-18U-03PS150 Andor, Ireland). The output from the laser source is incident on a high energy threshold 532 nm beam splitter (non-polarizing, 50:50 splitting) kept at 45° to the incident beam; this reflects the laser beam towards a UV-grade quartz lens (2.54 cm aperture, 10 cm focal length) which focuses the beam on to the sample kept on a translation stage. Before the beam splitter, a half-wave plate and a quarter-wave plate were introduced one at a time according

to the demand of the experimental procedure, as discussed in the following section. The emitted signals from the sample are collected using the same lens. This attributes an incident angle of 0° with the surface normal of the sample. They are collimated onto the second lens of the same material and dimensions (with a 5 cm focal length), which focuses the signal onto an optical fiber cable (200-micron core diameter). The optical fiber carries the signal into the spectrograph-ICCD system; the ICCD is gated with the laser. The control of the experiment, recording, and storing of the data is performed using a computer (Intel Core Duo, Speed 3 GHz, 4 GB RAM, 520 GB memory). Figure 1 is a schematic depiction of our experimental configuration in the present work.

The samples used for the present series of experiments are 99.9% pure copper metal, silver metal, and a polyethylene strip (non-metallic sample) mounted on a clamp fixed onto the translation stage. During data acquisition, the translation stage moves in the X and Y directions to ensure that a fresh sample surface is irradiated at each signal acquisition. As copper is widely used as one of the standard samples for LIBS experiments, this enabled us to optimize our

Fig. 1 Experimental system for LIBS experiment
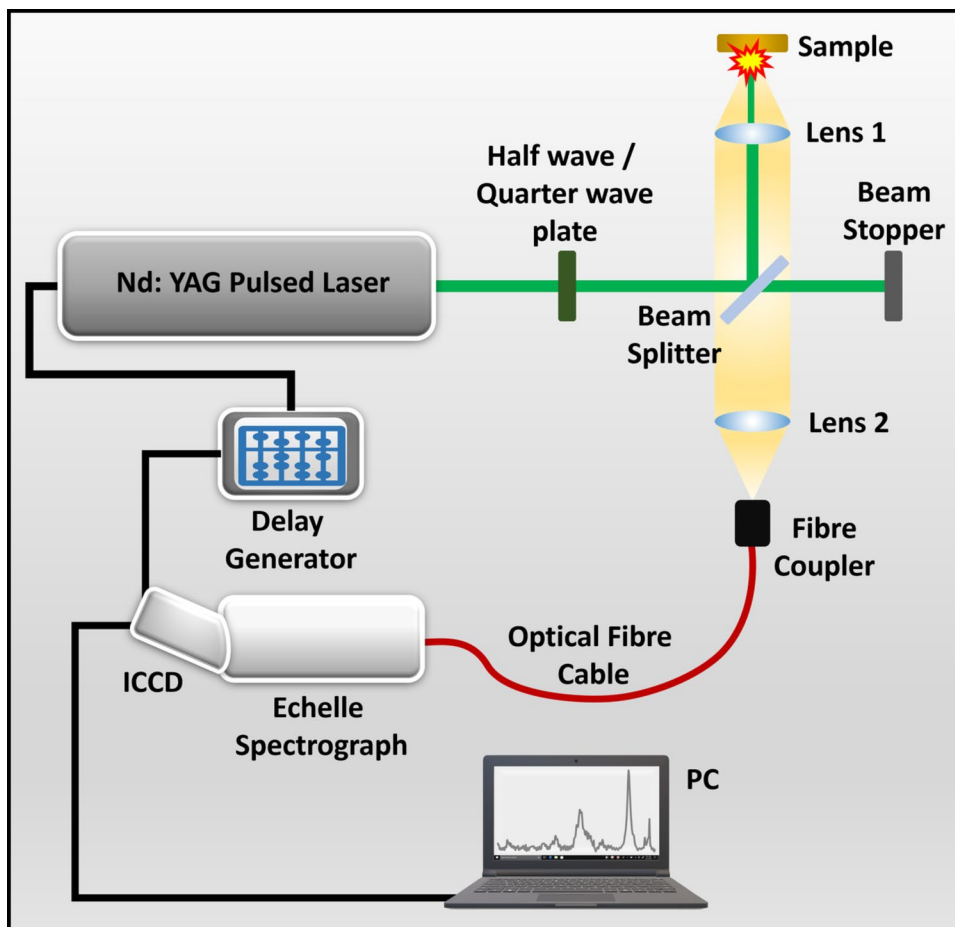
measurements: 900 ns and 6 microseconds are used as the gate delay and gate width, respectively [17].

Before any experiments, the polarization direction of the excitation laser beam was established, which we take as the default direction of polarization in the entire experiments described in the article. We use a high energy threshold reflecting type thin film polarizer; this reflects S-polarized light and transmits P-polarized light when it is kept at its specific Brewster's angle—56°. The polarization direction of the laser before the position of wave plates is also determined to be used as the reference direction of polarization along which the axes of wave plates are aligned at the beginning of the experiment.

The analysis starts by acquiring the LIBS spectra of samples by introducing wave plates in the laser path before the beam splitter to induce changes in the inherent polarization state and the polarization direction of the laser beam. The half-wave plate induces a change of 2θ if the axis of the half-wave plate is oriented at θ angle concerning the direction of polarization of the incident beam. On the other hand, a quarter-wave plate changes the polarization state of the linearly polarized laser beam. If the axes of the half-wave plate are oriented at 45° to the polarization direction of the incident beam, the transmitted beam will be circularly polarized. If it is at any angle from 0° to 45°, the corresponding transmitted beam will be elliptically polarized.

The first set of experiments in this part of our work investigated the changes observed in copper LIBS spectra when the polarization direction of the linearly polarized excitation laser beam is altered from the inherent direction. A laser energy of 5.7 mJ is applied before the focusing lens. The experimental parameters optimized for the experiment are tabulated in Table 1. For every 20° rotation of the polarization angle concerning the original direction ranging from 0° to 180°, 5 spectra are acquired. Correspondingly, by introducing the quarter-wave plate in the laser path, five spectra of copper are acquired by keeping the axes of the same at 0, 20, 45, 70, and 90° to the polarization direction of the

Table 1 Experimental parameters used for this study

Parameter	Value
Laser wavelength	532 nm
Laser energy	5.7 mJ
Repetition rate	10 Hz
Gate delay	900 ns
Gate width	6 µs
Exposure time	0.5 s
Number of accumulations	10
The number of spectra recorded	5 (averaged for analysis)

laser. Similar procedures were repeated for other samples, including silver metal and polyethylene, to compare how the results vary when metallic and non-metallic samples are considered.

The second part of the experiment is to rule out the possibility of any external factors that might induce changes in the LIBS spectra other than the polarization state and the polarization direction of the excitation laser beam. Several measurements were carried out to monitor changes due to possible pulse-to-pulse variations in the laser energy during the acquisition. Another potential factor is changes in energy and beam characteristics of the excitation beam, perhaps caused by wave plates in the beam path. To monitor this, the beam characteristics of the excitation beam are measured after the wave plates for different orientations of the wave plates concerning the polarization direction of the beam. We used the moving-slit method, where a slit of fixed width is mounted with a high energy threshold laser power meter in the same base mount. At different orientations of the wave plates that result in different polarization directions in the case of the half-wave plate and different polarization states in the case of a quarter-wave plate, the laser beam profile is plotted using the set-up, and the beam width is determined. In addition, the maximum energy obtained at each stage of the laser beam is also estimated from the plots, as all the measurements are performed at the same input laser energy of PE. All measurements are performed at a fixed position of ~70 cm from the laser head. We also made measurements with different experimental geometries, specifically with different excitation-collection angles, to explore whether our results on polarization-dependent LIBS showed any variations.

2.2 Data analysis

All measurements taken under each of the experimental conditions outlined above were subjected to analysis that involved careful tracking of changes in intensities of dominant emission lines in the LIBS spectra, including both atomic as well as ionic lines, and determining the mean values and the standard deviation of absolute intensity values among each series of experimental runs.

The LIBS spectra of samples under each experimental condition were carefully analyzed using Origin software (OriginLab Corporation, USA). The data pre-processing steps, like background removal, etc., were not required since the gated detector in the system captures signals without the background continuum. The absolute intensity values of selected atomic and ionic lines from the analyzed samples for each of the polarization conditions (five trials) were noted, and the corresponding plot of variation of intensity with change in polarization of the laser was plotted by

calculating the mean and standard deviation of the obtained intensity values.

3 Results and discussion

3.1 Observations

Typical LIBS spectra obtained from the pure copper sample, silver sample, and polymer (polyethylene) sample, along with major emission lines recorded in the experimental system without the wave-plates in the optical path of the laser beam, are represented in Fig. 2.

The atomic emission lines from copper considered in our study include those at 427.51, 515.32, 521.82, 809.26 nm, and the ionic emission lines at 393.32, 397.43, and 422.79 nm. The results we obtained on how the atomic lines vary in intensity are shown in Fig. 3.

Figure 3 depicts typical variations in the atomic emission line intensities of copper spectra with the orientation of the polarization direction to the characteristic direction of polarization of the laser. The energy levels are represented in upper-level configuration-Term-J order [29]. From Fig. 3, it can be inferred that the atomic emission from the copper sample seems to be influenced by the polarization direction of the excitation laser. The maximum intensity is observed when the polarization direction of the beam is along the inherent direction of polarization of the laser (vertical). As the polarization direction is gradually altered from vertical to horizontal, the corresponding intensity decreases from maximum to minimum. As the data points are averages of five trials, the possibility of a random variation is negligible; the plot of standard deviation at each polarization angle reveals the rigidity of the trend observed in all emission lines considered. Due to the limitation of the experiment in terms of the ambient air environment around the plasma, the standard deviation among the trials is slightly on the higher side. Still, the trend in average variation is evident in Fig. 3 and the following figures depicting the intensity changes. All the atomic emission lines in Fig. 3 show the same behavior trend. The vertically polarized laser beam induces the highest emission intensity in the LIBS spectra of copper.

The behavior exhibited by the ionic emission lines from the sample concerning the change in orientation of laser beam polarization is completely different from that observed in the case of atomic emission lines. The results obtained in the case of ionic emission lines are depicted in Fig. 4, from which it can be noted that the maximum intensity exhibited by the ionic emission lines in the LIBS spectra of copper is not when the direction of polarization of the excitation laser is vertical, as in the case of atomic emission lines. As the plots suggest, the maximum intensity is neither when it is vertical nor when it is horizontal, but at an orientation of around 45° concerning the initial direction of polarization of the laser (in the presented data, readings are at intervals of 20° from 0° to 100°). This behavior is surprising and warrants further study to elucidate the physics underpinning it. Nevertheless, our observations point to a potential method of enhancing ionic emissions in LIBS spectra which are usually very weak compared to atomic emissions.

The observations made in our polarization-dependent LIBS measurements differ significantly from those expected from conventional LIBS. A representation of the composite averaged spectra of copper recorded at different polarization angles (0°, 40°, and 100°) of the excitation laser beam is shown in Fig. 5a, along with the stalked pattern observed from the 422.79 nm and 427.51 nm in Fig. 5b.

Figure 5a clearly highlights the difference in the behavior of atomic and ionic lines upon changes in the polarization direction of the beam. The 422.79 nm line (Cu II) has the maximum emission intensity at around 40° orientations of the polarization direction. In contrast, the 427.51 nm (Cu I) line has the maximum for 0° and orientation, further depicted in Fig. 5b. An additional observation here
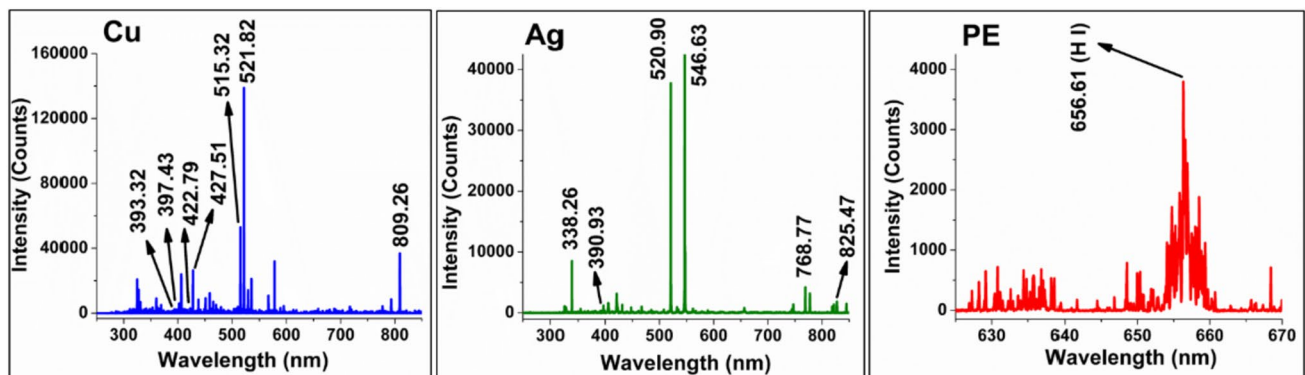
Fig. 2 LIBS spectrum of copper, silver, and polyethylene (PE) samples acquired using the experimental system (Fig. 1). The excitation laser was linearly polarized for all three samples
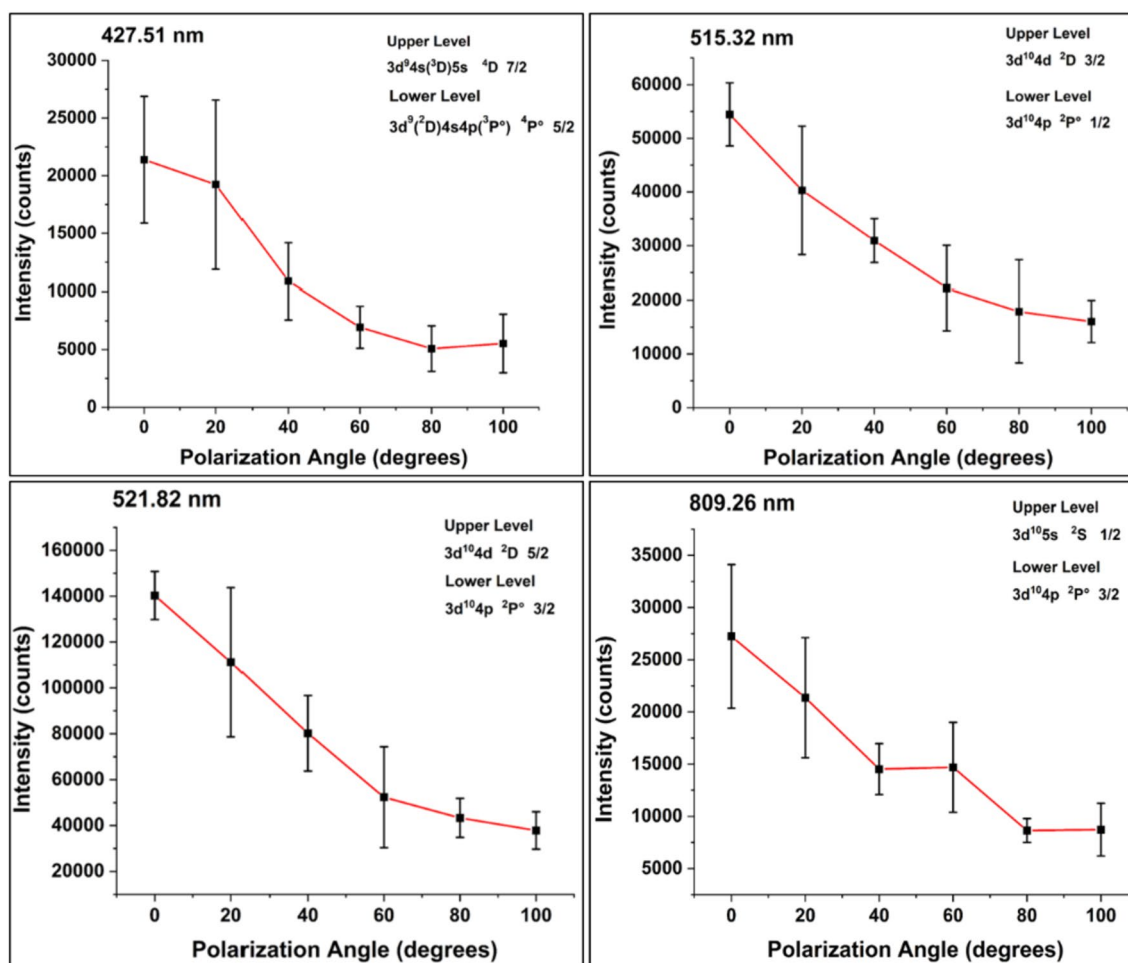
Fig. 3 Variation in absolute intensities of atomic emission lines in LIBS spectra of copper with the orientation of polarization direction of a linearly polarized excitation laser beam

is the difference in emission intensity of the two adjacent emission lines (atomic and ionic) in the same LIBS spectra. Suppose any external factors were causing the intensity changes. In that case, all the emission lines should follow a similar pattern. However, the composite spectra depicted in Fig. 5a and b show markedly different trends for the two adjacent emission lines. Precisely, a 3.13-fold increase in the intensity can be observed in the ionic emission line when the polarization direction is changed from 0° to around 45°. In contrast, the same polarization change causes a reduction of 1.89-fold for the atomic emission line intensity. The results obtained here indicate that the polarization-induced changes seen in emission line intensity can be used for enhancing the signals from ionic species in plasma in trace element analysis using LIBS without losing many signals from atomic species.

Similar studies were conducted using other samples, counting silver and polyethylene. A comparison of the behavior of atomic emissions from silver metal and

polyethylene is shown in Fig. 6 using our measurements of the behavior of copper atomic emission lines for reference.

All the spectral line data depicted in Fig. 6 show a similar trend in variation of the absolute intensity values from the atomic species with the polarization direction changes. Similar to the results obtained for copper, the emission in maximum for 0° configuration of polarization direction for all samples, with the minimum obtained for around 90° configuration. A comparison of ionic emissions from copper and silver is shown in Fig. 7.

Though the maximum intensity values for ionic emissions are less than those for atomic emissions, both indicate a similar trend in the emission intensity variation. Both samples showed maximum intensity around 45° orientations of the polarization axis of the excitation laser beam.

We also carried out experiments using circularly and elliptically polarized beams. These were realized by replacing the half-wave plate with a quarter-wave plate in the optical path (Fig. 1). The observed behavior of both atomic and
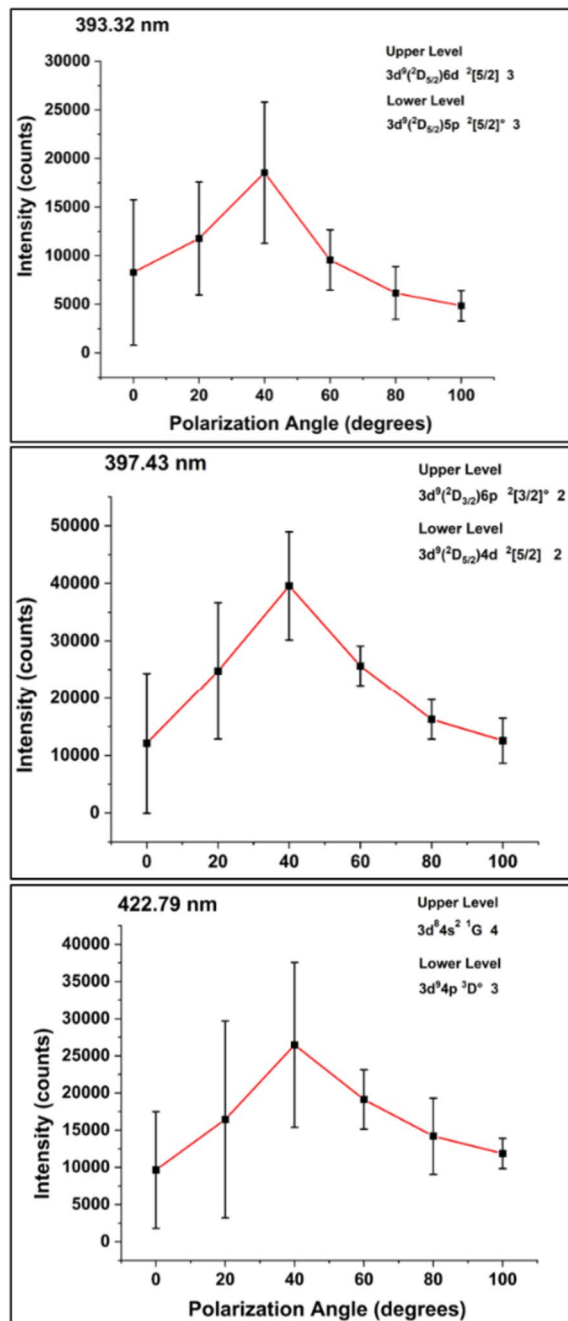
Fig. 4 Variation in absolute intensities of ionic emission lines in LIBS spectra of copper with the orientation of polarization direction of the linearly polarized excitation laser beam

ionic emission lines in the LIBS spectra of copper concerning the change in the excitation laser beam's polarization state is represented in Figs. 8a and b.

The response of atomic emission to the different polarization states of the excitation laser is such that when the polarization state is linear (when the orientation of axes of the quarter-wave plate to reference direction is 0° or 90°), maximum emission is obtained. The least emission is when the polarization state is exactly the circular polarization (when axes of the quarter-wave plate are oriented at 45° concerning the reference).

The response of atomic emission to the different polarization states of the excitation laser is such that when the polarization state is linear (when the orientation of axes of the quarter-wave plate to reference direction is 0° or 90°), maximum emission is obtained.

The least emission is obtained when the polarization state is circular (when the quarter-wave plate's axes are oriented at 45° concerning the reference).

Analysis of the behavior of ionic emission lines as a function of change in the polarization state of excitation also reveals the same trend, as depicted in Fig. 8b. Here also, the maximum emission from the sample can be observed at 0° and 90° orientations of axes of the quarter-wave plate concerning the reference line.

According to the plot, the minimum emission is at a 45° orientation, the same as in the case of atomic emission. It can be concluded here that there is no change in the behavior of atomic and ionic emission lines while changing the polarization state of an excitation laser beam. The maximum intensity is obtained when the polarization state is linear and vertical, as in the case of conventional LIBS.

To check whether the LIBS signal collection angle influences the polarization effects observed in the current study, a comparison of emission line intensity patterns at different polarization directions was performed by collecting the signal at different angles (back-collection and oblique collection) concerning the direction of laser incidence. For comparison, the experimental arrangement (Fig. 1) was modified by ensuring that the laser incidence and collection of signals from the sample surface were at an oblique angle (~60°) to the surface normal of the sample, as shown in Supplementary Figure S1. The analysis results for the polarization dependence with the system with oblique incidence and collection angle are shown in Supplementary Figure S2.

Figure S2 shows a similar pattern for atomic emission lines as obtained in the previously employed back-collection geometry, where maxima are for 0° and 180° orientations (vertical), and the minimum is observed for 90° orientations (horizontal). For ionic lines, a similar pattern was identified as in the back collection geometry case. However, it was not so clear-cut primarily because the overall collection efficiency at the oblique collection angle is significantly reduced; this is reflected in the distinctly lower intensity levels depicted in the figure. Nevertheless, the observed pattern suggests maxima around 45° and 135°, similar to the observations in back-collection geometry.

In our experimental runs, we took cognizance of potential influences from other experimental parameters, like laser energy and laser beam characteristics (due to the presence of wave plates). These may influence the excitation-emission
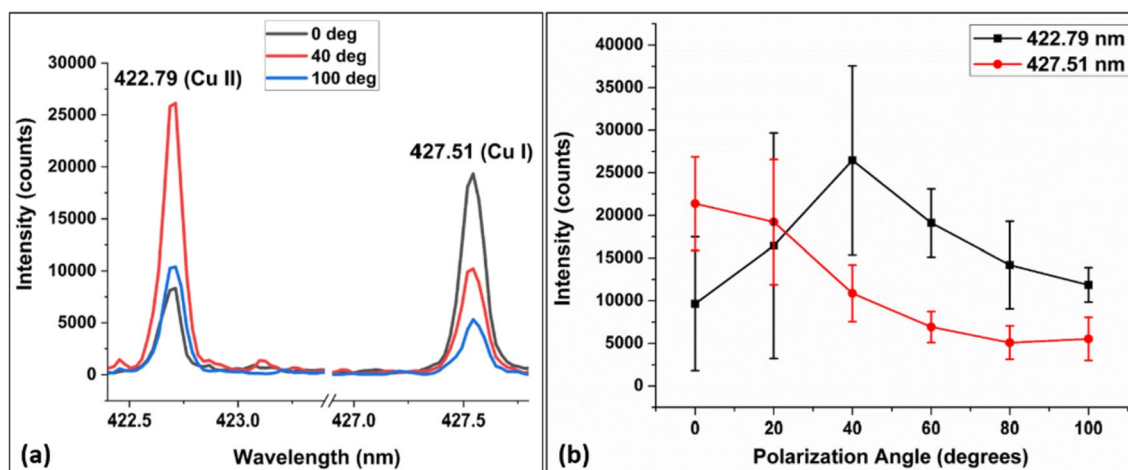
Fig. 5 **a** Comparison of emission intensities from atomic (427.51 nm) and ionic (422.79 nm) species from copper plasma concerning the polarization angle of the excitation laser beam, and **b** stalked plot of the intensity variations for the two emission lines with polarization angle

process. The laser beam characteristics recorded in the presence of wave plates positioned at different orientations concerning the reference direction of polarization are represented in supplementary Figures S3a and b, respectively. Figure S3(a) shows that the beam shape and width remain essentially unaltered when the polarization angle is at 0°, 90°, and 180° as in the initial polarization direction condition.

The maximum power after the wave plate also remains constant at these positions, revealing that the presence of a half-wave plate in the optical path before the excitation part does not influence other factors like laser energy or laser beam shape.

Observations from Figure S3b suggest that the presence of a quarter-wave plate also does not influence the laser beam energy or beam characteristics. There are no evident changes in the beam profile of the excitation laser, even if the quarter-wave plate is introduced in its path. Measurements were performed at three different angles of orientation of the quarter wave plate's axis concerning the laser beam's linear polarization direction. The 0° orientation corresponds to linear polarization (same as the inherent polarization direction of the laser), and the 45° orientation corresponds to circular polarization at the measurement spot. The shape of the beam and the maximum power remain at almost equal values for all conditions, confirming that the observed polarization dependence of LIBS spectra is unlikely to have been caused by any changes in the laser beam characteristics in the presence of wave plates.

Similarly, the changes in energy of the excitation laser beam have also been monitored in the presence of a half-wave plate and a quarter-wave plate at different orientations. The results are shown in supplementary Figures S4a and S4b.

For a fixed laser energy (4.3 ± 0.1 mJ) measured before the wave plates, the variations in energy after the wave plates are noted in 5 trials, with an interval of 30 s between trials. Figure S4a represents the variations in energy when the axis of the half-wave plate is oriented at 0, 40, and 80° concerning the default direction of the beam, which shows no variations in energy that can influence the excitation process. Similarly, readings on laser energy are noted for different orientations of a quarter-wave plate, where similar results in the case of the half-wave plate are obtained. The results confirm that the energy changes do not cause emission changes due to the presence of wave plates at different orientations. To check whether the reflective element-beam splitter (non-polarizing type/ UV-fused silica) used in the optical system (50:50 splitting for 45° AOI in Fig. 1) has any dependence on the polarization of the incident laser beam, the laser energy after the beam splitter was also monitored at different polarizations, where similar results as in Figure S4 were obtained.

3.2 Discussions

The experimental observations we report here unambiguously imply that there is an influence of the polarization of the excitation laser beam on the atomic emission line intensity of metals and non-metals in Laser-Induced Breakdown Spectroscopy. A limitation of the current work is that the experiments have been performed in ambient air, not vacuum environments. This has an effective impact on overall reproducibility among multiple trials in similar experimental conditions as the plasma dynamics in air current fluctuates. This can be clearly visible in comparatively higher error bars in observations, which is more impactful in low-intensity conditions. However, the trend in variation
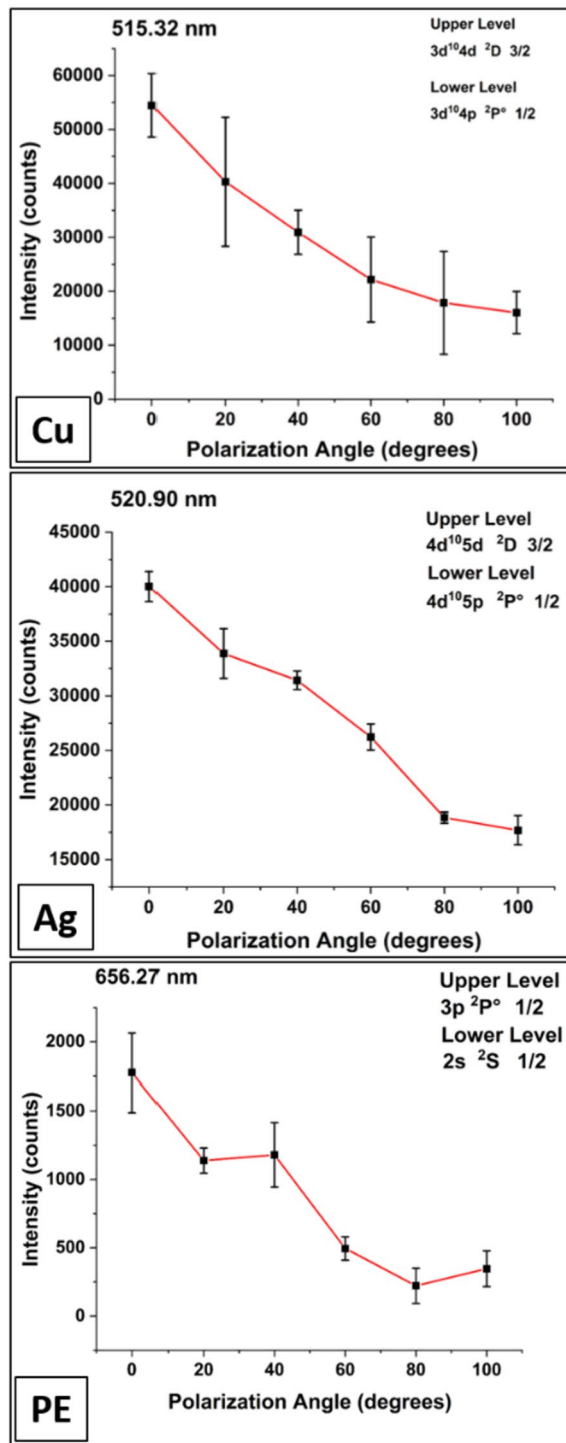
Fig. 6 Comparison of behavior of atomic emission intensities from copper (Cu), Silver (Ag), and polyethylene (PE) samples on change in polarization direction of the excitation laser beam

of emission intensities with polarization is evident in the corresponding correlation patterns. Although a theoretical clarification of the physics that underlies this observation

remains to be obtained, some possible reasons behind the observations are discussed in the following.

A possibility is that LIBS emission might have a certain emission cone depending on the direction of laser polarization (horizontal or vertical). So, the emission cone for vertical polarization may be better coupled to the detector. Therefore, the signal detected for atomic lines would be stronger at vertical than horizontal polarization. The same rationale would, of course, apply to both atomic and ionic emission lines. However, this is not reflected in the observations we report here for ionic lines. Emission cone effects can, therefore, be ruled out.

The interpretation of observations in the case of circularly or elliptically polarized laser excitation beam can proceed along the following lines. The usual Coulomb potential of an atom changes when linearly polarized light is replaced by circularly polarized light: it assumes a doughnut-like toroidal shape with a saddle point at the atomic position instead of the Coulombic singularity. For high enough values of laser intensity (high values of optical field strength), the electric field of the circularly polarized light induces atomic electrons into a circular trajectory in the plane of polarization, with the circle centered at the atomic nucleus. This is depicted in Fig. 9.

It is expected that, under these conditions, ionization would be reduced, as would excitation in the case of circular polarization. The non-localized nature of the electron density distribution under these conditions should be consistent with the notion that excitation and ionization are reduced under circular polarization, assuming that the optical field strength is kept constant, leading to reduced emission compared to the linearly polarized condition.

4 Conclusions

The analysis of emission intensities from atomic and ionic species in the laser-induced plasma of copper shows a pronounced dependence on the polarization state of the excitation laser light. Changes in emission line intensities of copper, silver metals, and polymer (PE) samples have been carefully monitored by us upon inducing changes in the polarization direction of a linearly polarized laser beam using a half-wave plate. The same measurements have also been made upon conversion of the polarization state from linearly polarized to circularly polarized using a quarter-wave plate. The observed emission characteristics differ for atomic and ionic emissions when the excitation beam is linearly and circularly polarized. Intriguing and potentially important differences are observed in ionic emission line intensities when laser light of different polarization directions is used for excitation; enhanced emission is obtained when the polarization angle is around 45°, which
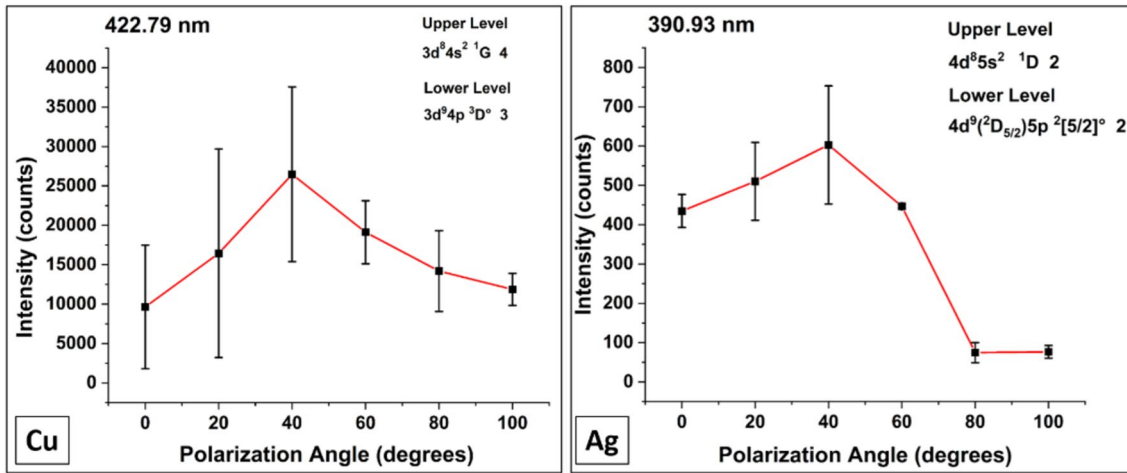
Fig. 7 Comparison of the behavior of ionic emission intensities from copper (Cu) and Silver (Ag) samples on change in the polarization direction of the excitation laser beam
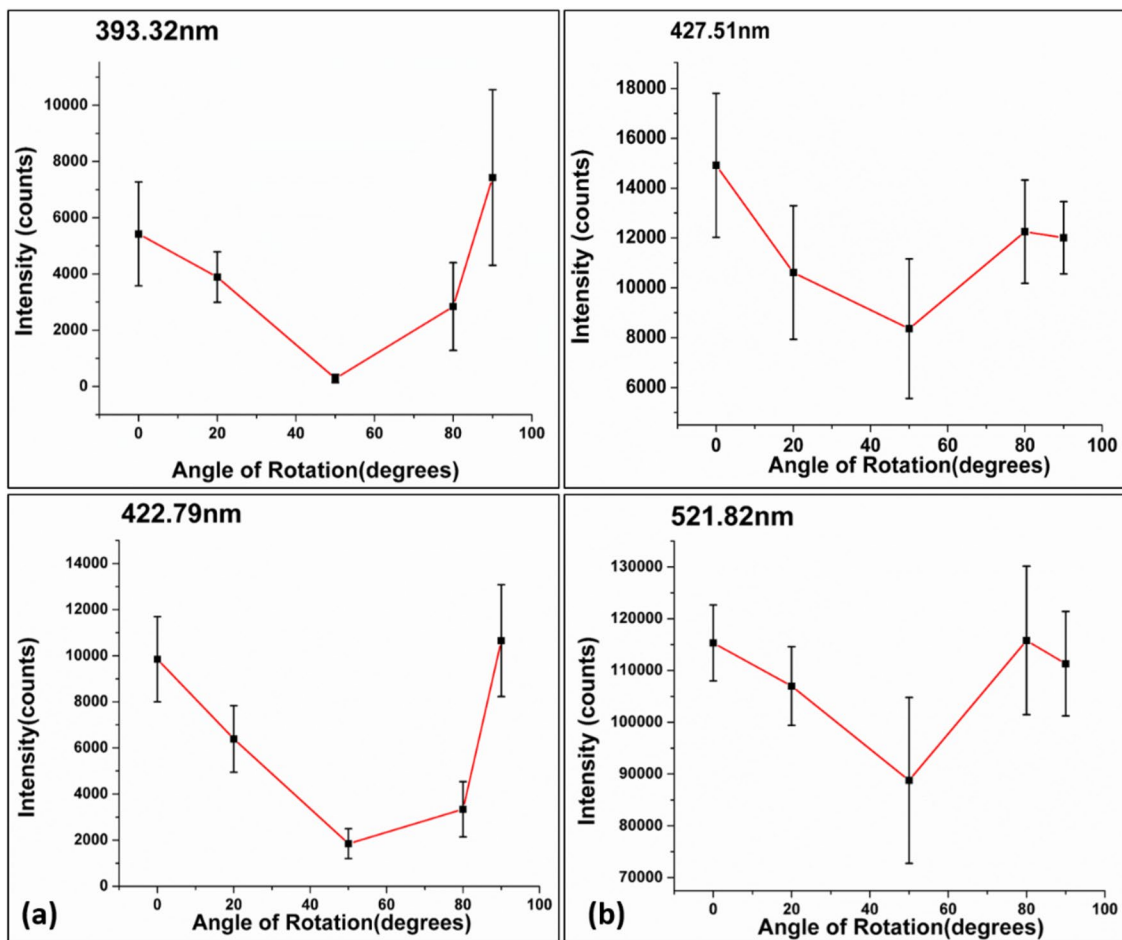
Fig. 8 Variation in absolute intensities of (**a**) atomic emission lines and (**b**) ionic emission lines in LIBS spectra of copper with the change in the polarization state of the excitation laser beam
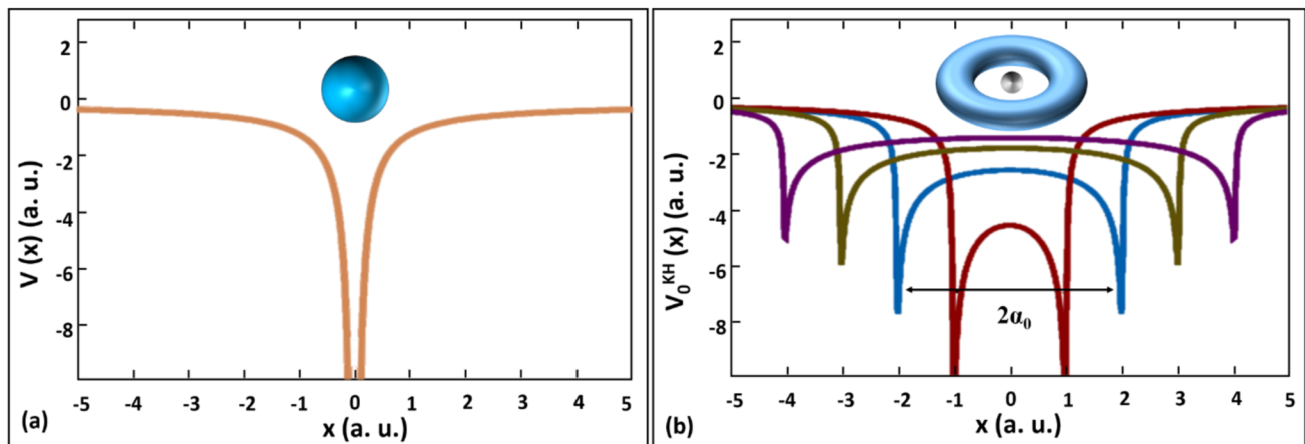
Fig. 9 Changes in the ground state potential of a hydrogen atom upon irradiation by (**a**) linearly polarized light and (**b**) circularly polarized light represented in terms of radial potential functions

has implications for enhancing signal-to-noise ratios in LIBS measurements that rely on ionic lines.

The changes in emission characteristics have been evaluated regarding emission cone dependence on polarization direction and changes in radial potential functions of atoms with different polarization states of the excitation laser beam. Further theoretical interpretations are required to develop proper insights into the physics that underpins polarization-dependent LIBS.

Data availability Not applicable.

Declarations

Conflict of interest The authors declare no competing interests.

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