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Nanoparticles Enhanced Laser-Induced Breakdown Spectroscopy for Characterisation and Discrimination of Gemstones

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Abstract. Laser-induced breakdown spectroscopy (LIBS) is an excellent technique for rapid on-site investigations that attracts interest from diverse research areas. Gemmology is no exception. The application of LIBS for gemstone characterisation is limited due to ineffective ablation and crack formation, even more so with cost-effective, non-gated LIBS systems. Nanoparticle-enhanced LIBS (NELIBS) has proven to improve the effectiveness of LIBS by minimizing sample damage and enhancing the spectral features. Therefore, this study is dedicated to exploring the advantages of NELIBS, for characterising Sapphire and Opal and discrimination based on spectral differences. Our objective is to explore enhancing spectral features and performing discriminant analysis using the PLS-DA algorithm. Nanoparticles (NPs) were deposited in two layers by sequentially drying two drops (2μL) of a colloidal solution of 20nm gold nanoparticles (AuNPs) on the sample surface. Targeted areas were shot with 3 pulses of Nd:YAG laser (~350mJ, 10ns, 1064nm, 1Hz) for collecting NELIBS spectra with the OceanOptics HR4000 spectrometer. The procedure was repeated without NPs for comparative analysis with conventional LIBS (CLIBS). Results have shown a significant enhancement in spectral features, i.e., the emergence of several new spectral lines of major gemstone elements in the UV-Vis regions of the NELIBS spectra, while the CLIBS spectra were devoid of any meaningful spectral information. The PLS-DA model was trained and validated using a 4-fold cross-validation approach. The model discriminated gemstones with 99.48% accuracy at the 4th fold and exhibited a mean cross-validation accuracy of 98.97%. This preliminary investigation demonstrates the effectiveness of NELIBS for characterization and the potential for onsite identification of gemstones.

1 Introduction

Laser-Induced Breakdown Spectroscopy (LIBS) has proven to be useful for a wide variety of applications [1–6]. Herman and Senesi provide their in-depth analysis of LIBS as a geochemical tool for this century [7]. This is because of its simplicity, versatility, and immense potential, which is yet to be realized, especially for geochemical investigations. LIBS offers an attractive set of features for application in gemmology. It is a rapid and non-destructive method for studying gemstones [8]. It can do simultaneous multi-elemental analysis in a single laser shot. This makes LIBS an invaluable tool for identifying different types of natural gemstones but also for authentication, i.e., discriminating between original and artificial replicas [9]. Its ability to detect light elements, require minimal sample preparation, and offer portability for in-field analysis makes it particularly suitable for studying geological materials, including gemstones. However, when it comes to transparent or semi-transparent samples, the ineffective laser-sample coupling renders the performance rather inefficient. The high refractive index causes laser energy to absorb beyond the superficial layer, resulting in cracks and irreparable damage to the sample.

It is proven that a layer, of nanoparticles, NP, on the target surface can enhance the signal intensity by several folds and minimize sample damage [10], particularly for semi-transparent and transparent samples [11]. Moreover, Khan et al. [12] have reported an improvement in the sensitivity and repeatability of measurements with Cu nanoparticles.

The method of enhancing laser-induced breakdown spectroscopy with nanoparticles is referred to as nanoparticle-enhanced laser-induced breakdown spectroscopy and is represented by the acronym NELIBS. In this technique, a layer of nanoparticles, usually Au or Ag, is deposited on the sample surface simply by pouring a drop of colloidal solution. Due to faster evaporation at the boundary, the drop of colloidal solution leaves a ring of NPs on the sample surface, which leads to inhomogeneous NP distribution and is commonly referred to as the “coffee ring” effect. Sànchez-Aké et al. [11] have attempted to address this

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issue of non-uniform distribution by depositing a layer of Au on a glass substrate, but it adds complexity to the procedure. Therefore, deposition drying with a drop of NP colloidal solution is usually preferred, and the central region of the ring is used where the NP distribution is relatively homogeneous [13].

When the sample is irradiated with a laser in the presence of a deposited layer of metallic NPs, the laser primarily interacts with the NPs through surface plasmon resonance. It explodes the NPs layers and couples laser energy to the superficial layers of the sample evaporating them into plasma [14]. It minimizes the damage and effectively avoids the internal cracking of transparent and semi-transparent samples. NELIBS has received considerable interest from scientists in recent years for enhancing quantitative investigations for a variety of samples [15–18].

The enhancement of spectral features [12] is attractive for classification and authentication applications. It motivated us to study the effectiveness of NELIBS with AuNPs for the characterization and discrimination of sapphire and opal gemstones by enhancing the spectral features that were hard with the conventional LIBS technique. We employed a cost-effective LIBS system in its simplest configuration and reported a significant outcome in spectral feature enhancement and discrimination using PLS-DA.

2 Methodology

2.1 Sample Preparation

Gemstone samples were acquired from a reputed gemstone dealer in the local market. Before being exposed to laser pulses, the sample surface was wipe-cleaned using isopropyl alcohol. Distinct sites on the sample surface were cleaned with NELIBS and CLIBS. With the help of a micropipette, two layers of gold nanoparticles (20 nm, ~6.54E+11 particles/ml, Sigma Aldrich) (AuNPs) were sequentially deposited on the sample surface to have a sufficient number of nanoparticles at the ablation site. Each layer is a drop of 2µL volume; after pouring the first drop onto the sample surface, it was left for 30 minutes to air dry in the laboratory environment. The second layer was deposited similarly and dried before subjecting it to NELIBS.

2.2 Experimentation

The LIBS system utilised in this project consisted of an Nd:YAG (350 mJ, 1064 nm, 1 Hz, ~10 ns) laser aligned orthogonally to the sample surface. With the help of a converging lens (*f* = 10 cm), the laser was loosely focused onto the sample surface to a 2 mm spot size to irradiate a sufficient number of nanoparticles for significant signal enhancement [13]. The emission from the resulting laser-induced plasma was collected by a 600µm fibre and delivered to an HR4000 spectrometer to resolve this radiation into its constituent wavelengths and display the spectrum on a laptop screen. The parameters for spectra collection were controlled using Spectrasuite software (OceanOptics, Inc.).

The spectrometer covered the wavelength range from 197 nm to 1100 nm, however, our region of interest was within the UV-Vis (220 nm–530 nm) region. The spectrometer showed reasonable sensitivity in this region, and it was sufficient to observe distinctive spectral signatures of the major elements of gemstones i.e., Al and Si. The schematic of the experimental setup is illustrated in Fig. 1.

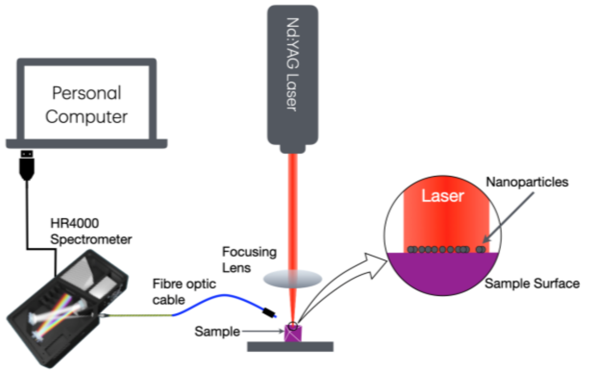

Fig. 1. Schematic illustration of the experimental setup.

3 Results and Discussion

Nanoparticles play a crucial role in enhancing LIBS performance by the surface plasmon resonance (SPR) phenomenon. The collective oscillations of electrons on the surface of NPs are called surface plasmons. The electromagnetic field of the laser governs these oscillations, causing surface plasmon resonance (SPR) with the laser field. This results in efficient laser energy absorption by NPs, rapidly heating them [13]. This energy is effectively coupled to the sample surface underneath NPs [10, 19]. This causes material to evaporate from highly localized regions on the sample surface, minimizing sample damage and preventing internal cracking. The ablated material forms an excited plasma plume, that emits significantly strong spectral lines upon de-excitation.

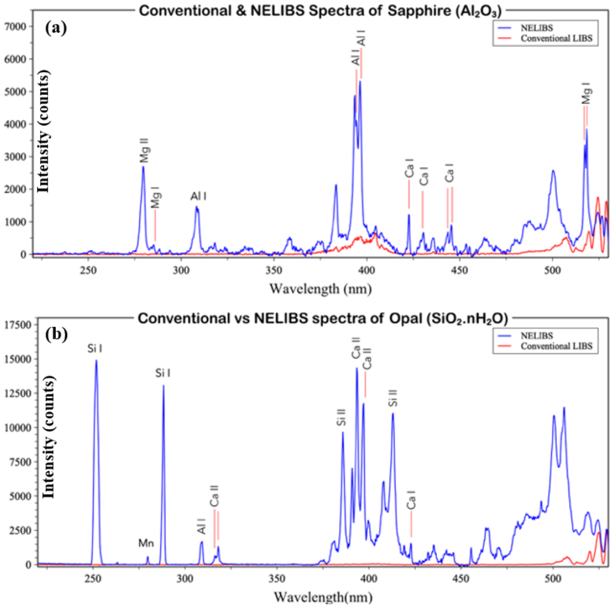

Fig. 2. Comparison between conventional and NELIBS spectra of two gemstones (a) Sapphire, and (b) Opal.

Table 1. Elements identified in Gemstones using NELIBS and wavelengths of corresponding spectral lines

	Element	Wavelength (nm)
Sapphire	Al I	308.22, 309.27, 394.40, 396.15
	Ca I	422.68, 430.25, 443.51, 445.49
	Mg I	285.21
	Mg II	279.55
Opal	Al I	308.215, 309.27
	Ca I	422.68
	Ca II	315.88, 318.93, 393.37, 396.85
	Mn I	279.48
	Si I	251.6, 288.16
	Si II	385.6, 413.07

The resonance of the electromagnetic field of the laser with the surface plasmons of NPs causes a strong coupling between laser energy and NPs. Most of the laser energy is absorbed by NPs, instantly heating them and their surroundings. NPs transfer this energy to the sample surface, causing localized evaporations, confined to regions equivalent to the size of NPs [13]. The evaporated target material appears in the form of excited plasma and emits characteristic spectral lines, as shown in Fig. 2. The comparison between the CLIBS and NELIBS spectra of sapphire and opal shows clear differences.

Several prominent atomic and ionic lines of major elements of gemstones, i.e., Al for Sapphire and Si for Opal, in addition to impurities or minor elements, Ca, Mg, Al, and Mn, cause specific physical properties and give different colours to the gemstones. The emission lines are identified using the Atomic-Spectral Database compiled by the National Institute for Science and Technology (ASD-NIST) [20] and verified using published literature [14, 21].

CLIBS spectra are almost void of any significant spectral features. It is evidence of ineffective laser-sample coupling that has led to inefficient ablation and hence near-to-no significant spectral emissions.

The spectral lines were found and counted by using the "find_peaks" method in the "SciPy" library for Python [22]. To find peaks, we used "prominence" as the key parameter. It identifies a data point as a peak if it has a certain local prominence as defined by the user. In the case of the Sapphire spectra, the value of prominence was set to 140 counts and 205 counts for Opal, to accommodate the maximum prominent peaks and avoid the identification of noise points as peaks at the same time.

The algorithm identified 40 and 43 prominent spectral lines in the NELIBS spectra of Sapphire and Opal, respectively, as indicated by a red spot in the four subplots in Fig. 3. The majority of these spectral lines can be easily attributed to Al and Si elements, which are the major elements for sapphire and opal gemstones, respectively, in addition to the minority elements Mg, Ca, and Mn in these gemstones.

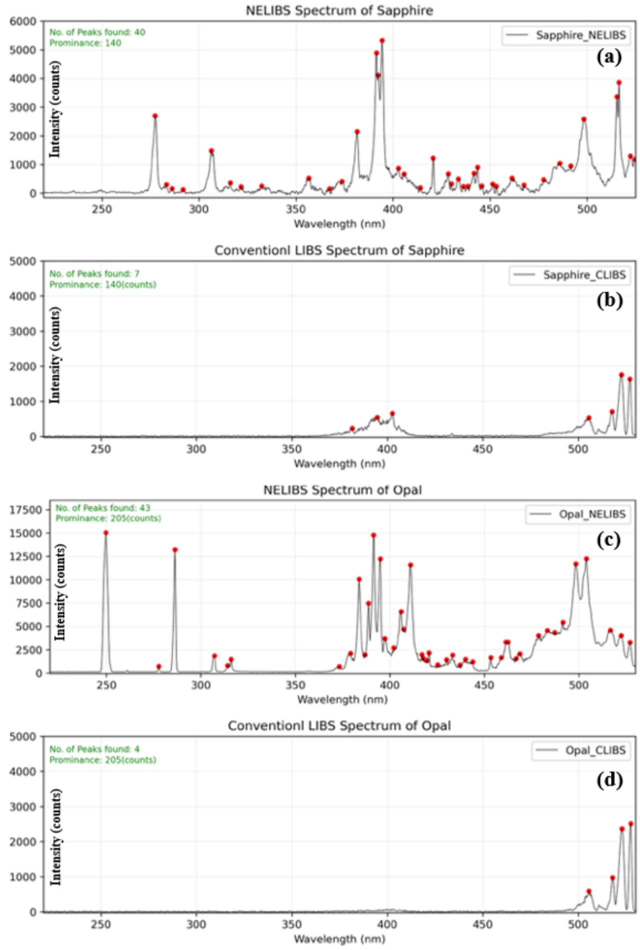

Fig. 3. Spectral lines identified by the "find peaks" algorithm using Python high-level programming language, (a) NELIBS Spectrum of Sapphire, (b) Conventional LIBS Spectrum of Sapphire, (c) NELIBS Spectrum of Opal, and (d) Conventional LIBS Spectrum of Opal.

On the other hand, the "find_peaks" algorithm has identified 7 and 4 peaks, respectively in the CLIBS spectra of Sapphire and Opal in Fig. 3 (b) and (d). These peaks cannot be confidently attributed to any of the primary components.

The bar graph in Fig. 4 gives a comparison between the number of spectral lines found in the CLIBS and NELLIS spectra of sapphire and opal gemstones. The differences are well observed, especially since the number of spectral lines based on the NELIBS technique was more than five times higher if compared with the diagnosed number of spectral lines based on the CLIBS technique.

3.1 Partial Least Square - Discriminant Analysis (PLS-DA)

Gemstone discrimination is an important application. The present work attempted it using partial least squares discriminant analysis (PLS-DA). The model was trained on the labelled dataset consisting of 10 instances of NELIBS spectra of Sapphire and Opal samples, each instance having 1184 features. The model was trained and validated using a 4-fold cross-validation approach.

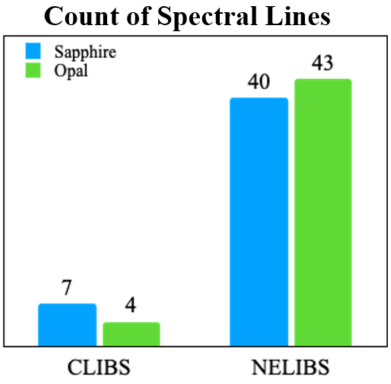

Fig. 4. Number of spectral lines in CLIBS and NELIBS spectra of Sapphire and Opal Gemstones.

The original data had only 3 spectra per sample because NPs ablate away after the first two laser shots. Therefore, the analytical efforts in this paper only consider the spectra obtained with the first three laser shots. New instances of the data were generated by scaling and adding Gaussian noise to the existing data. It is a rather small dataset that lacks diversity and robustness for training a discrimination and prediction model. It may lead to overfitting and less than optimal performance [23, 24]. An efficient characterization plan was considered to overcome this issue in future extensive investigations.

The PLS-DA algorithm provided by scikit-learn machine learning library for Python was used in this project. Since the model was trained and validated using a four-fold Cross-Validation approach which means, the data is divided into four subsets, three of which were used as training sets and one as the test set. The process is repeated until the model's performance has been tested on all subsets and the overall performance is averaged over all iterations. The performance of the PLS-DA model improves over each iteration of validation, at the fourth fold of cross-validation, the accuracy is 99.49%, while the mean cross-validation accuracy is 98.97%. As shown in Fig. 5, in the PLS-DA classification plot, there is a clear separation between the components of opal and sapphire with no overlapping.

PLS-DA was not tested on CLIBS data since there were no significant spectral signatures of major gemstone elements in the spectral region of interest.

4 Conclusion

In this paper, the characterisation of sapphire and opal gemstones was presented using nanoparticle-enhanced laser-induced breakdown spectroscopy (NELIBS) and compared with conventional laser-induced breakdown spectroscopy (CLIBS). Several key observations have emerged. NELIBS revealed significant spectral features, surpassing those found in the CLIBS spectra of sapphire and opal gemstones. CLIBS spectra lacked distinct spectral signatures, while NELIBS spectra exhibited prominent spectral lines corresponding to major and minor/impurity elements in sapphire and opal gemstones.

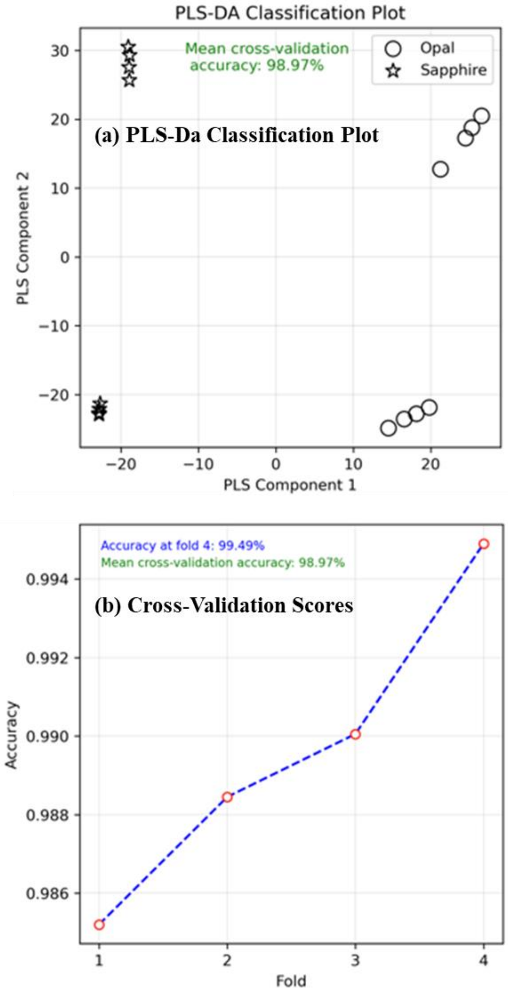

Fig. 5. PLS-DA classification of gemstones based on dataset from NELIBS spectra.

Additionally, the Partial Least Squares-Discriminant Analysis (PLS-DA) classification plot demonstrates a clear separation between the two gemstone classes. Remarkably, the model achieved near-perfect accuracy (99.49%) in four-fold cross-validation, with an average cross-validation accuracy of 98.97%. These findings underscore the efficacy of NELIBS for the characterization and classification of gemstones.

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