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Nanoparticles Enhanced LaserInduced Breakdown Spectroscopy of Gemstones

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Abstract: Nanoparticle is a tiny particle that scales in size from 1 to 100 nanometers, which are invisible to the naked eye, can have significantly different physical and chemical properties than their larger material counterparts. With global industrial revolution, nanoparticles have been widely used across variety of industries sector, pharmaceutical purposes,cosmetics, and environmental preservation. Laser Induced Breakdown Spectroscopy (LIBS) is a persuasive elemental analysis method. This study will apply high energetic laser pulse using Nd:YAG laser of 1064nm and HR4000 spectrometer to determine the mineral composition in gemstones spectroscopically. Spectral lines observation in this LIBS spectrum will be used to identify heavy metal elements. The laser-induced breakdown spectroscopy identifies the existence of organic and non-organic elements for instance Ca, Si, Al, C and other materials in gemstones. We can enhance the performance of LIBS as an analytical to obtain the chemical composition and validatethe presence of various elements through LIBS spectra of gemstones by covering the target surface with nanoparticles.

Keywords: LIBS, Nanoparticles, Gemstones, NELIBS

1. Introduction

Nanoparticles are known as fine particles which are invisible to the naked eye that can have extensively different optical, physical and chemical characteristics than their bigger material counterparts. Because of their remarkable capabilities, NPs are small enough to capture electrons and create quantum effects. Metal nanoparticles and their surface plasmon resonance properties are broadly used throughout laser spectroscopy since they allow absorption of the incident electromagnetic field distribution, resulting in centralised Surface Plasmon Resonance (SPR) [1]. LIBS is a type of Atomic Emission Spectroscopy (AES) that uses a high-energy laser pulse to excite an optical sample. The interaction of the laser and the sample generates plasma, and the light emitted by the plasma provides spectral signatures of chemical composition in various materials [2]. LIBS provides a number of benefits, including quick reaction and hardly any sample processing methods, the ability to use calibration-free

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techniques, dynamic set up, multi elemental analysis, and limit of detection (LOD) in the ppm range. The variations of line intensity, background noise intensity, signal-to-background ratio (SBR), detection sensitivity and detection of limit (LOD) are usually affected by LTS) [3]

However, LIBS works poorly with semitransparent materials, like many of the gemstones, because of inefficient ablation. Moreover, the laser induced damage also occurred on the uncovered sample surface. Due to this, the detection limits of LIBS get lower than the covered surface sample. A way to overcome this problem and enhance the efficiency of LIBS is covering the ablation site with a thin layer of nanoparticles. It is expected to improve the laser energy coupling with the sample surface and enhance the ablation. The fast explosion of the NPs and the plasma induction allow the ablation and the transfer in the plasma phase of the portion of sample surface where the NPs were placed. Consequently, a better emission spectrum would be obtained that would carry significant information about sample and help with determining the elemental composition and discrimination or identification of gemstones.

Enhance LIBS spectra of gemstones and observe the functionality on detecting the compositions of gemstones. In this project, we will study the enhancement of spectral features in LIBS spectra of four (04) semi-transparent gemstones i.e., Amethyst, Emerald, Tourmaline and Sapphire. The LIBS spectra of gemstone without NPs and with Au NPs will be obtained and compared respectively Using the Atomic Spectral Database National Institute of Standards and Technology (ASD-NIST) [5], the strong persistent lines of spectra under investigation were identified in the recorded spectrum. LIBS experimental setup will be prepared with optimal alignment of optical components.

2. Materials and Methods

Four gemstones that are used in this study are difficult to ablate by conventional LIBS for being semi-transparent. The impurities sticking to the sample surface may affect the interpretation of spectral lines recorded in the LIBS spectra. Therefore, each gemstone was cleaned by an ultrasonic bath before performing LIBS. For the LIBS experiment, we use gold (AuNPs). Because of the huge surface area and excellent conductivity, gold nanoparticles are frequently employed in biotechnology and biomedicine. For nanoparticles, we used 20nm Gold (AuNPs) from Sigma Aldrich. Because of the huge surface area and excellent conductivity, gold nanoparticles are frequently employed in biotechnology and biomedicine. In solution, unaggregated gold nanoparticles will appear red. If such particles aggregate, the solution will turn blue/purple and can eventually become clear with black precipitates

The schematic diagram of the experimental setup is shown in Fig. 1. It includes a second harmonic Nd:YAG laser (532 nm, 6 ns duration, energy up to 1000 mJ), a spectroscopic system consisting of a OceanOptics HR4000 spectrometer (200-1100nm) . The sample will be placed on a z-translation stage that could adjust the sample height in relation to the laser direction. To avoid the breakdown on the sample surface, the laser will be focused 5 mm beyond the sample with a plano convex lens with a focal length of 100 mm. The laser spot size will be approximately 1.5 mm in diameter throughout this experiment.

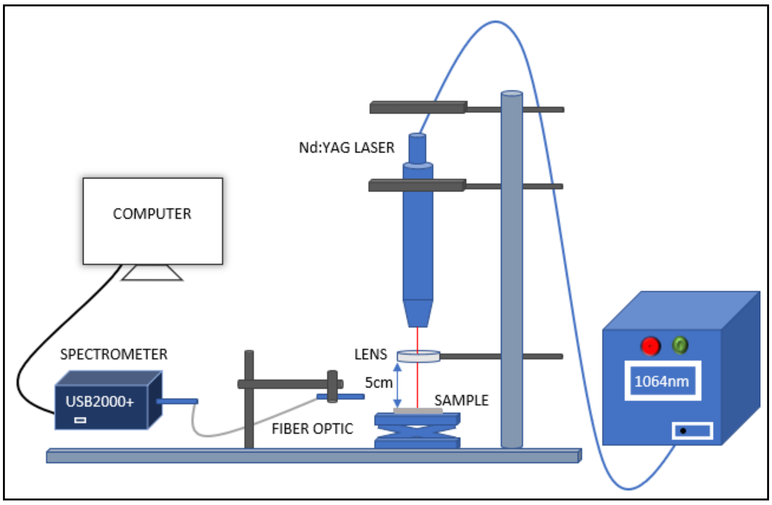


Figure 1: Schematic Diagram of the LIBS Experimental setup

The procedure of spectrum collection is need to start with recording spectrum from a thin layer of NPs. Then, placing a drop of nanoparticles on the desired location. Each emission spectra will be collected in a single shot. A series of laser beams were blasted at the sample before each LIBS measurement to maintain the surface conditions consistent across tests. In the instance of NELIBS, a drop of metallic colloidal solution will be placed on the treated sample surface with the help of a micropipette. The sample with a covered surface will be ablated with a laser for three shots. Each spectrum that was produced in the computer will be collected and tabulated. From each spot, at least 3 spectra will be recorded and then averaged into one. After that, all spectra collected from one sample will be averaged into one spectrum. Afterwards, repeat step 2 until 4 using only NPs. Then, continue the process with different types of gemstone.

3. Results and Discussion

3.1 LIBS Spectra of Tourmaline

From the Figure 2, it clearly shows the spectral mean intensity of Tourmaline sample covered by NP layer is higher than the mean intensity of Tourmaline without NP layer. The layered gold nanoparticles onto the Tourmaline surface and using a 1064 nm laser with 50 mJ pulse energies were exploited to enhance the sample spectral lines intensity.

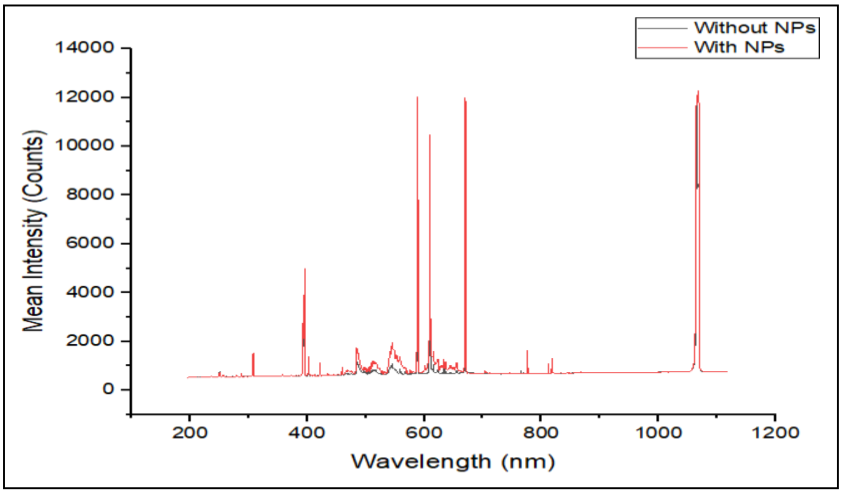
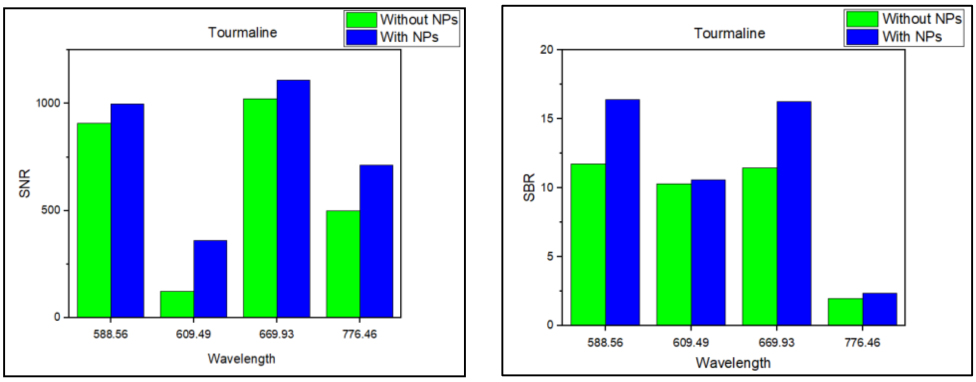


Figure 2: The spectra produce by NELIBS and LIBS on Tourmaline

Figure 3 (a) and (b) show the comparison of two signal to noise ratio (SNR) value and two signal to background ratio (SBR) respectively. The SNR value at wavelength 588.56 nm, 609.49nm, 669.93 nm and 776.48 nm show all four blue columns that represent Tourmaline with NPs are higher than the green column which represent the Tourmaline without NPs. By monitoring the first and third peak from Tourmaline at 588.56 nm and 669.93 nm, SBR blue column higher than the green column. The second and fourth wavelength at 776.46 nm shows slightly different among the column without NPs and without NPs. In general, larger values of SNR and SBR represent enhancement of the LIBS signal that would lead to better detecting ability of the instrument [6].



(a) (b)

Figure 3: SNR of a NELIBS and LIBS on Tourmaline

3.2 LIBS Spectra of Sapphire

The figure below shows the LIBS and NELIBS spectrum of two samples of Sapphire. The black line represents Sapphire spectrum obtained without NP layer, and the red line represents Sapphire spectrum with a layer of NPs on its surface. The results indicated that the detection ability of nanoparticles enhanced LIBS spectral intensities in comparison when the NP layer was absent.

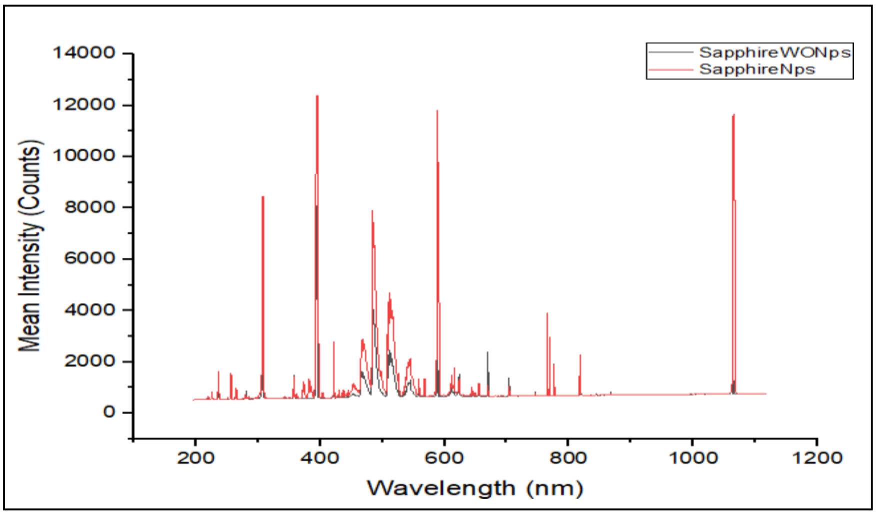
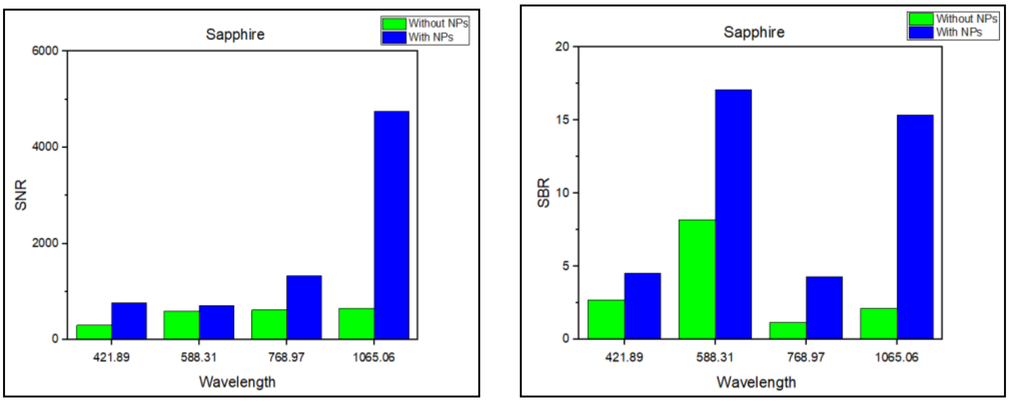


Figure 4: The spectra produce by NELIBS and LIBS on Sapphire

The Figure 5 (a) shows the SNR comparison between Sapphire with NP layer and without NP layer on its surface. From the graph, there are four main spectral lines that need to focus for further discussion, 421.89 nm, 588.31 nm and 768.97 nm. 1064 nm is the laser wavelength used for this experiment. We can see that all the blue columns are taller than the green columns which represent SNR values of Sapphire with nanoparticles layer is significantly better than otherwise. Figure 4.4 (b) shows the SBR comparison between two different samples of Sapphire. The sample with NPs from wavelength of 588.31

nm is relatively higher than the green column and the stability of detection signal of nanoparticles were superior to those without nanoparticles layer [6].



(a) (b)

Figure 5: (a) SNR of a NELIBS and LIBS on Sapphire, (b) SBR of a NELIBS and LIBS on Sapphire.

3.3 LIBS Spectra of Emerald

The spectra produced by NELIBS and LIBS on Emerald are shown in Figure 6. The spectrum were recorded using HR4000 Spectrometer and stated in a graph below. The result that we can state from the figure above is LIBS spectral line of Emerald without NPs have lower intensity than the one covered with NPs. From the graph, there are many prominent lines and peak that can be analysed for determining its wavelength and intensity.

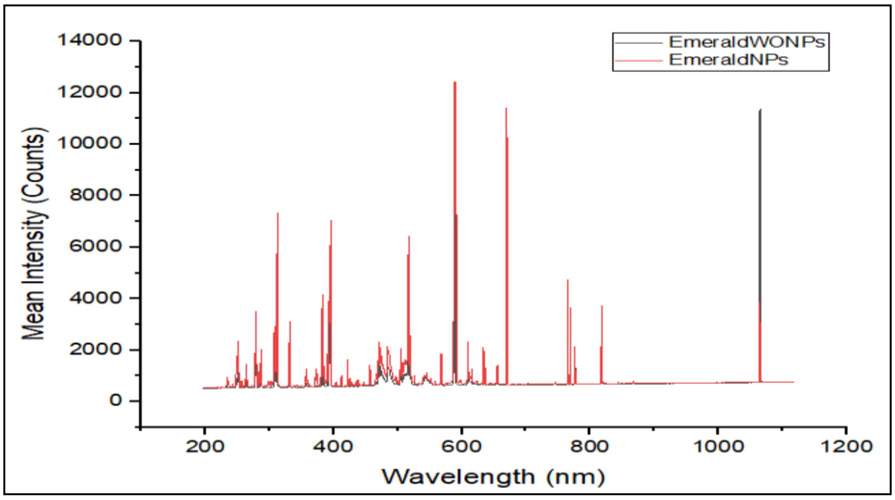


Figure 6: The spectra produce by NELIBS and LIBS on Emerald

SNR and SBR comparison value of Emerald spectra with and without NP layer are shown in the figure above respectively. Green bars represent the values without NP layer while blue bars are for Emerald with nanoparticles layer on its surface. Both wavelength at 669.93 nm of SNR and SBR graph are the highest signal value. Meanwhile, the blue bars are higher than their green counterparts. The higher the SNR and SBR value, the better is the output signal.

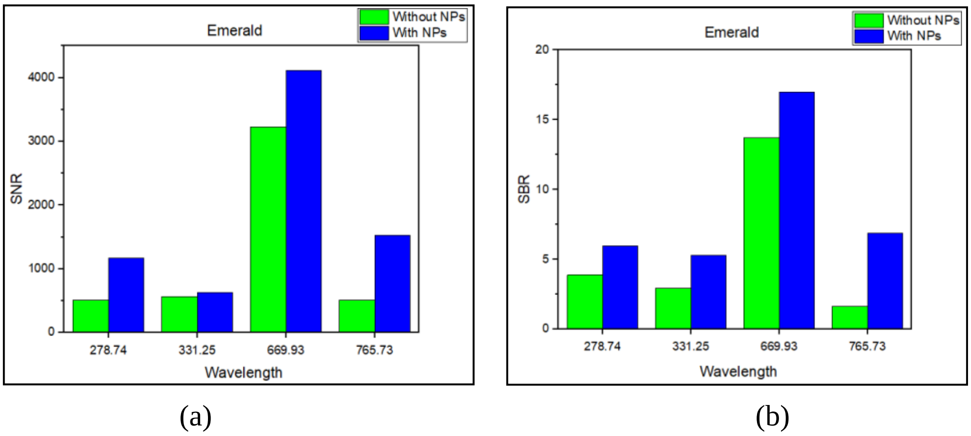


Figure 7: (a) SNR of a NELIBS and LIBS on Emerald, (b) SBR of a NELIBS and LIBS on Emerald.

3.4 LIBS Spectra of Amethyst

The spectra produced by NELIBS and LIBS on Amethyst are shown in Figure 8. It clearly shows the spectral mean intensity of Amethyst sample covered by NP layer is higher than the mean intensity of the sample without NP layer. Gold nanoparticles are layered onto the Amethyst surface and exploited to enhance the sample spectral lines intensity after three pulses of 50 mJ energy and 1064 nm Nd:YAG laser.

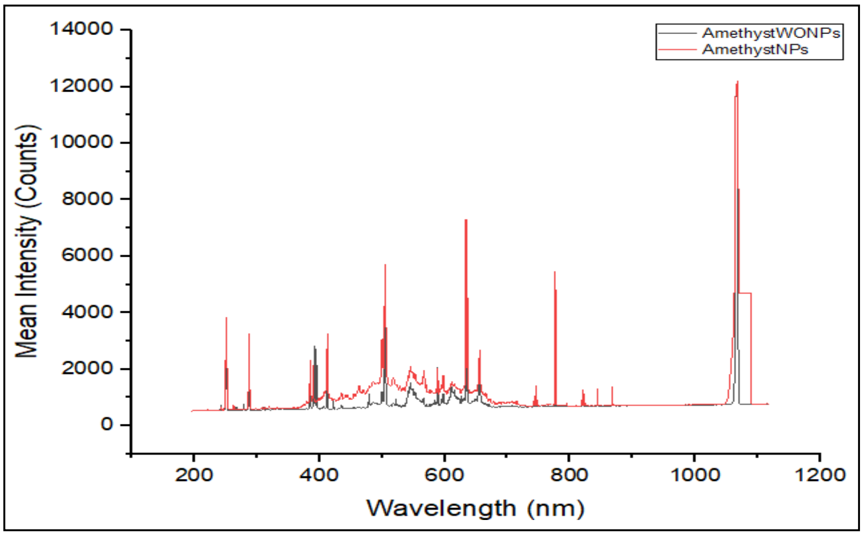
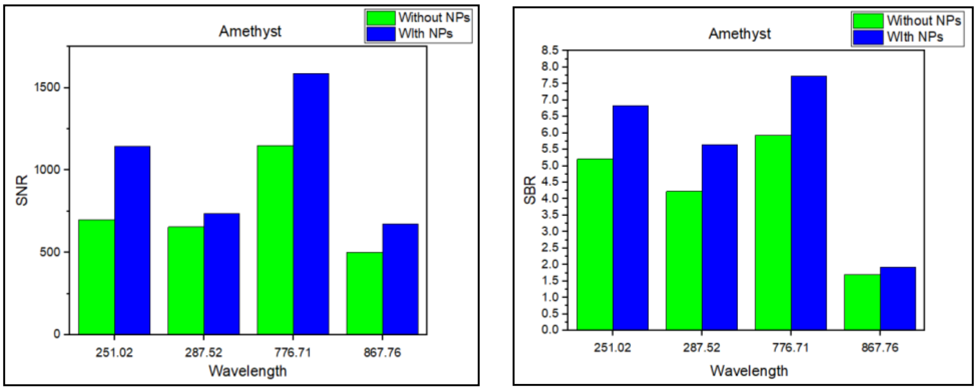


Figure 8: The spectra produce by NELIBS and LIBS on Amethyst

Figure 9 (a) shows the comparison of two signal to noise ratio (SNR) values, one with and the other without NPs. Meanwhile, the comparison of two signal to background ratio (SBR) showed in Figure 4.8 (b). From the graph, there are four wavelengths that need to focus for further discussion, 251.02 nm, 287.52 nm, 776.71 nm, and 867.76 nm. All blue bars that represent Amethyst covered with NPs drop are higher than the green bars. Resulting in, larger values of SNR and SBR demonstrating better detecting ability of instrument and enhancement of LIBS spectral intensities with nanoparticles.



(a) (b)

Figure 9: (a) SNR of a NELIBS and LIBS on Amethyst, (b) SBR of a NELIBS and LIBS on Amethyst.

3.5 Elemental Identification of Tourmaline

The spectra were collected over the range from wavelength 300.00-845.90 nm. Referring to NIST database, eight elements were identified including Aluminium (Al), Chromium (Cr), Calcium (Ca), Lithium (Li), Sodium (Na), H-alpha (H-α) and Oxygen (O). It could be seen that the spectral intensities of Tourmaline with NPs were taller compared without NPs spectral intensities. Tourmaline is a wide variety of coloured gemstone that compounded with elements that are stated in Figure 4.9 [7]. The result indicated that NPs are favorable to enhance the element signal of LIBS and Na I 589 nm and Li I 670.77 nm were more suitable for further analysis.

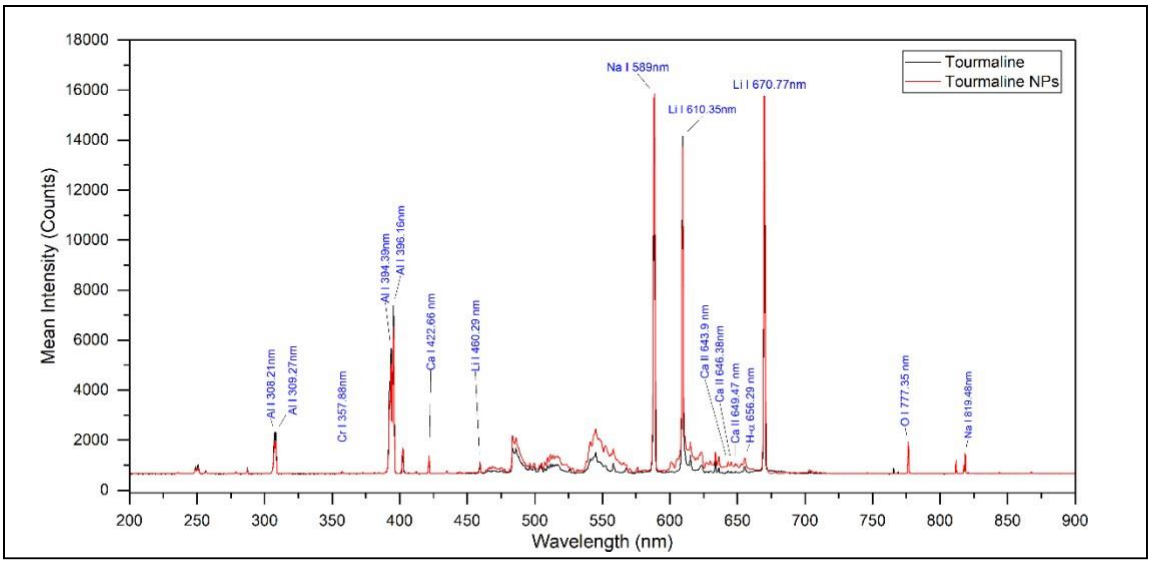


Figure 10: The sample spectral lines of Tourmaline.

3.6 Elemental Identification of Sapphire

From figure 4.10, there are eleven spectral lines were identified by using the NIST database. Aluminium (Al), Chromium (Cr), Calcium (Ca), Lithium (Li), Sodium (Na), and Oxygen (O) are including. Presence of Al and O justify that Sapphire are formed from aluminium oxide (Al2O3) combined with other elements [8]. Strong absorption lines are present for the pure sodium atom at 589 nm [9]. The result of spectral intensities recorded specify that nanoparticles are applicable to enhance elemental identification of LIBS.

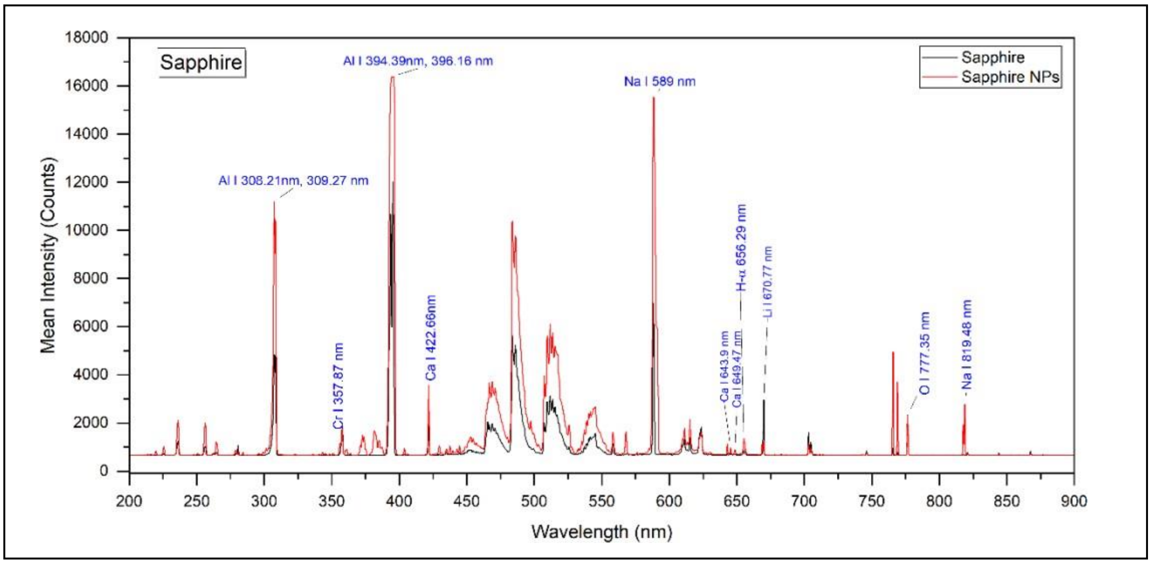


Figure 11: The sample spectral lines of Sapphire.

3.7 Elemental Identification of Emerald

There are twenty (20) prominent lines that can be found from the spectrum and it consists of Beryllium (Be), Silicon (Si), Aluminium (Al) and Oxygen (O) elements. Beryllium is an element with a hardenability of 7.5-8 upon this Mohs scale, and its wavelength is 249.467 nm. Due to tiny levels of chromium, emerald is a variant of the mineral beryl (Be3Al2(SiO3)6) it is green in colour [10]. These superior results justify that NP layer played a significant role in LIBS enhancement.

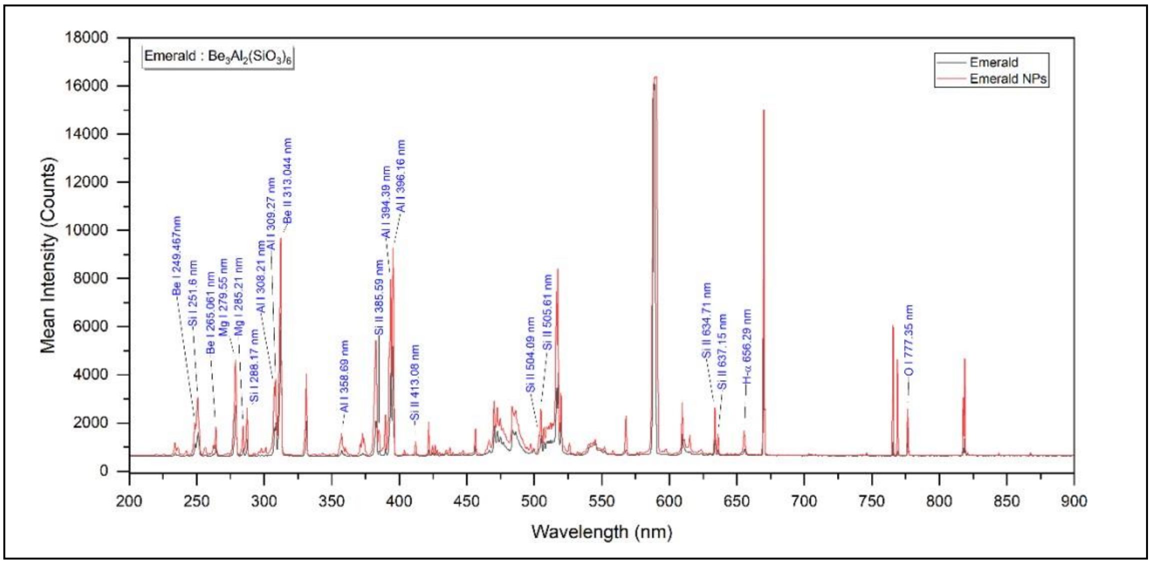


Figure 12: The sample spectral lines of Emerald.

3.8 Elemental Identification of Amethyst

The spectra were collected over the range of 630.92-780.50 nm. Three elements were identified based on NIST database, including Th I 633.93 nm, Rn I 655.75 nm and Th I 776.71 nm. Radon was found in Amethyst as noble gas and appears as colorless gas which may release from the surface of gemstone overtime. We can conclude that, nanoparticles can increase the intensities spectrum of LIBS and the presence of heavy metals, useful and non-beneficial elements will indeed be found

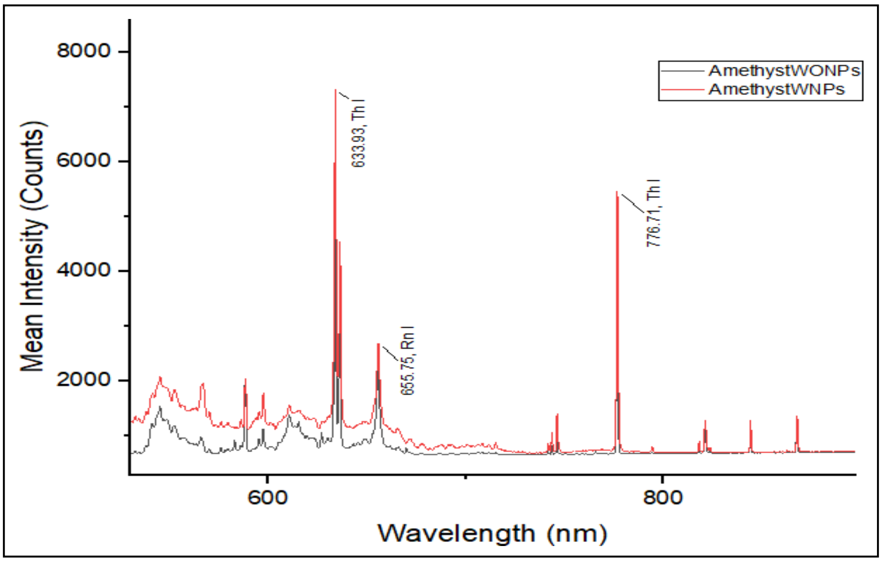


Figure 13: The sample spectral lines of Amethyst.

4. Conclusion

The performance and enhancement justification of nanoparticles have been analyzed in terms of SNR and SBR result by using spectrum data collected. The comparison of LIBS spectra with and without nanoparticles were successfully obtained. The result indicates the larger values of SNR and SBR of covered surface sample with Au nanoparticles represent better detecting ability of the LIBS instrument. The stability of detection signal of nanoparticles was superior to those without nanoparticles layer. Hence, the output spectrum that have been obtained from this experimental method conclude that Gold (Au) nanoparticles enhanced LIBS of gemstones.

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References

[1] D. Marcella, A. Rim and D. G. Alessandro, "Nanoparticle Enhanced Laser Induced Breakdown Spectroscopy (NELIBS), a first review," *Spectrochimica Acta Part B*, 2018.

[2] F. Anabitarte, A.Cobo and J.M. Lopez-Higuera, "Laser-Induced Breakdown Spectroscopy:Fundamentals, Applications, and Challenges," 2012.

[3] Jingge Wang, Xiaolong Li, Hehe Li, Xinzhong Li, Zhicong Li and et al, "Lens-to-sample distance effect on the quantitative analysis of steel by laser-induced breakdown spectroscopy," *Applied Physics,* 2020.

[4] S. Jamil, U. Liaqat, N. Ahmed, R. Ahmed, Z.A. Umar and M.A. Baig, "The role of nanoparticles concentration in the emission intensity," *Physica B: Physics of Condensed Matter* , 2021.

[5] Y. Ralchenko, "NIST: National Institute of Standards and Technology," 20 July 2009. [Online]. Available: http://physics.nist.gov.

[6] Xiaodan Liu, Fei Liu, Weihao Huang, Jiyu Peng, Tingting Shen and Yong He, "Quantitative Determination of Cd in Soil Using Laser-Induced Breakdown Spectroscopy in Air and Ar Conditions," *PubMed Central,* 2018.

[7] Wikipedia, "Wikimedia Foundation," 2022. [Online]. Available: https://en.wikipedia.org/wiki/Tourmaline .

[8] Sapphire, "Aluminium Manufacturers," 2020. [Online]. Available: https://www.aluminummanufacturers.org/aluminum-sulfate/sapphire/ .

[9] A. M. Bonch-Bruevic, T. A. Vartanyan, A. V. Gorlanov, Yu. N. Maksimo, S. G. Przhibel'sk and d V. V. Khromov, "Photodesorption of sodium from the surface of sapphire," *Zh. Eksp. Teor. F*, 1990.

[10] C. Interest, "IYPT 2019 Elements 004: Beryllium, emeralds, and NASA telescopes," 16 February 2019. [Online]. Available: https://www.compoundchem.com.