Effects of repetition rate on the identification of elements in gemstone using the LIBS method

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Abstract. In material science, there are several methods for detecting elemental content in a material (sample) such as X-Ray Fluorescence (XRF), (X-Ray Diffraction) XRD, (Scanning Electron Microscope) SEM, (Transmission Electron Microscope) TEM), etc. Non-metallic samples such as gemstone can be detected by XRF and XRD methods. But in this method, the sample must get special treatment such as being crushed and converted into powder form. In this study, LIBS was used to identify elements in a gemstone. The laser-induced breakdown spectroscopy (LIBS) method is an alternative method for solving deficiencies in the previous study. The results show the same elements contained in the gemstone can clearly be detected. The elements are also confirmed by using the standard technique of X-ray fluorescence and the result revealed that the elements are consistent as in the case of the LIBS technique.

1. Introduction

The gemstone is one of the mineral resources owned by Indonesia. Color in gemstones is caused by light of specific wavelengths being absorbed inside the stone. Such absorption is a characteristic of the gemstone material, the molecular structure, and extraneous impurities or inclusions within the crystalline structure [1]. There are several methods for analyzing elemental content in gemstone such as X-Ray Fluorescent (XRF). This method requires that the sample get special treatment first as it is crushed into powder form. The weakness of the XRF method is that the sample cannot be reused because it has already become another form. To overcome these weaknesses, the Laser Induced Breakdown Spectroscopy method was used in this study. With the LIBS method, spectrums will emerge that indicate the characteristics of a particular element. One of the advantages of this method is that no special treatment is needed in the sample preparation [2].

2. Method

One method that can be used in identifying elemental content in the gemstone is the laser induced breakdown spectroscopy (LIBS) method. This method is used because it can be done quickly and without treating the sample specifically. The advantage of this method is that when you get results you can match them directly to an online database [3-4]. The laser used in this study was pulse Nd:YAG laser with a wavelength of 1064 nm, energy of 45 mJ, and a pulse width of 7 ns. The repetition rate of the laser was set at 10 Hz, 15 Hz, 20 Hz. The environmental pressure used corresponds to atmospheric pressure. The experimental set up used in this study are shown in Fig. 1. The laser beam is fired on the sample surface through reflection from a silver mirror and then focused through a focusing lens with a focal length of 30 mm. A luminous plasma was then produced due to the interaction of the laser with the sample target. Plasma was then captured by optical fiber and sent to an optical multichannel analyzer (OMA). OMA converted the captured plasma into a spectrum graph. Spectrum is characteristic of the elements in the sample. The peak intensity of the spectrum was matched with the National Institute of Standards and Technology (NIST) database to obtain the elemental content contained in the sample [5].

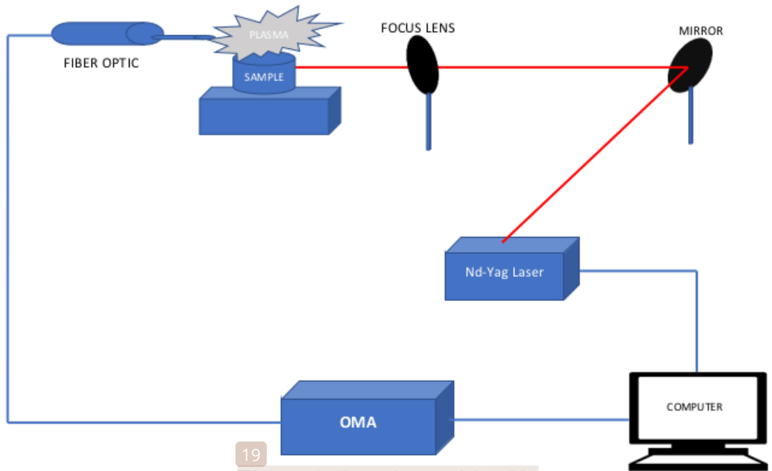
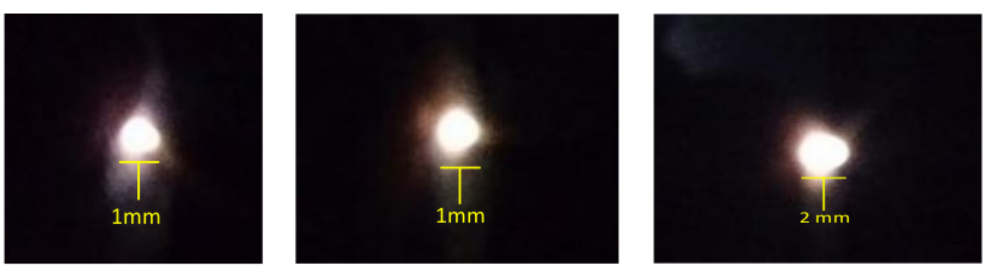


Figure 1. Experimental Set-Up

3. Results and discussion

3.1 Visual analysis

Figure 2 shows the plasma photographs obtained with the variation of the repetition rate of 10 Hz, 15 Hz, and 20 Hz, respectively, tested on agate stone samples. The colors formed from the three variations emit white light. Plasma arises from the presence of particles that have been affixed. Laser pulses will interact with the sample and lubricate the surface of the sample, due to ablation, particle emissions can occur, this emission can be seen as plasma. It can be seen that the higher the repetition rate is given, the greater the diameter of the plasma formed. This result confirmed and has a similar pattern with the previous paper [6,7]. The bigger the diameter of plasma in the higher repetition rate is because much more materials are ablated by the laser bombardment.



(a) (b) (c)

Figure 2.Plasma photograph taken from the concrete sample with pulse repetition rate variation (a) 10 Hz (b) 15 Hz (c) 20 Hz

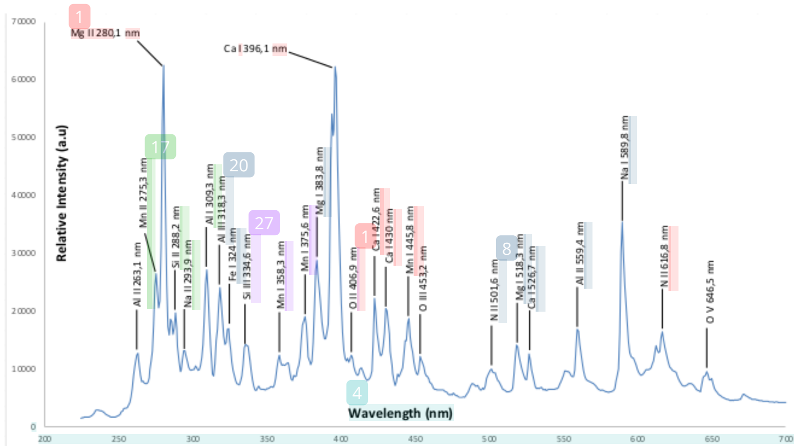


Figure 3. The emission spectrum of elements obtained from the Gemstone taken by using a 10 Hz repetition rate of pulse laser

3.2 Spectrum and element analysis

Figure 3 shows the emission spectrum obtained from a gemstone sample with a repetition rate of 10 Hz. Spectrum data show that the wavelengths that appear are the wavelength of Al II 263.1 nm, Mn II 275.3 nm, Mg II 280.1 nm, Si I 288.2 nm, Na II 293.9 nm, Al I 309.3 nm, Al III 318.3 nm, Fe I 324 nm, Si III 334.6 nm, Mn I 358.3 nm, Mn I 375.6 nm, Mg I 383.8 nm, Ca I 396.1 nm, O II 406.9 nm, Ca I 422.6 nm, Ca I 430 nm, M I I 445.8 nm, O III 453.2 nm, N II 501.6 nm, Mg I 518.3 nm, Ca I 526.7 nm, Al II 559.4 nm, Na I 589.8 nm, N II 616.8 nm, OV 646.5 nm. Those elements represent the elements contained in the Agate stone sample.

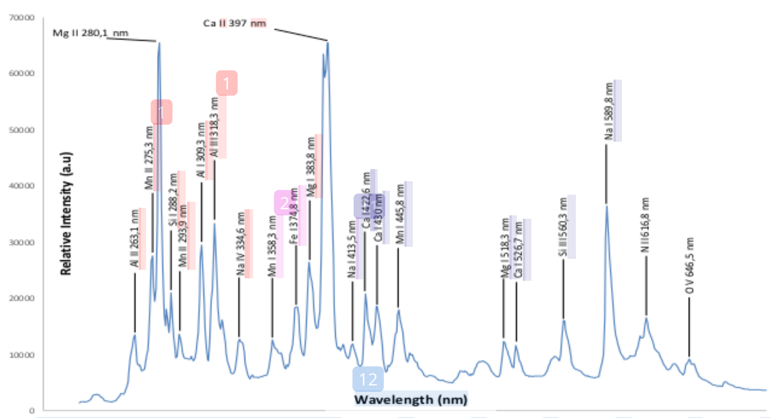


Figure 4. The emission spectrum of elements obtained from the Gemstone taken by using a 15 Hz repetition rate of pulse laser

Figure 4 is a graph of the emission spectrum obtained from gemstone agate stone sample with a repetition rate of 15 Hz. The spectrum data show that the wavelengths that appear are the same with Fig

4, namely the wavelength of Al II 263.1 nm, Mn II 275.3 nm, Mg II 280.1 nm, Si I 288.2 nm, Mn II 293.9 nm, Al I 309.3 nm, Al III 318.3 nm, Na IV 334.6 nm, Mn I 358.3 nm, Fe I 374.8 nm, Mg I 383.8 nm, Ca II 397 nm, Na I 413.5 nm, Ca I 422.6 nm, Ca I 430 nm, MnI 445.8 nm, Mg I 518.3 nm, Ca I 526.7 nm, Si III 560.3 nm, Si III 589.8 nm, N II 616.8 nm, O V 646.5 nm.

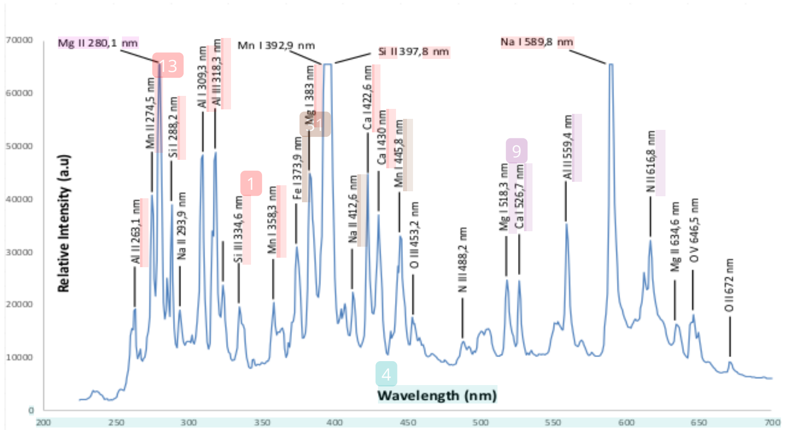


Figure 5. The emission spectrum of elements obtained from the Gemstone taken by using 20 Hz repetition rate of pulse laser

Figure 5 is a graph of the emission spectrum in a gemstone sample with a repetition rate of 20 Hz. Spectrum data show that the wavelengths that appear are the wavelength of Al 263.1 nm, Mn II 274.5 nm, Mg II 280.1 nm, Si I 288.2 nm, Na II 293.9 nm, Al I 309.3 nm, Al III 318.3 nm, Si III 334.6 nm, Mn I 358.3 nm, Fe I 373.9 nm, Mg I 383 nm, Mn I 392.9 nm, Si II 397.8 nm, Na II 412.6 nm, Ca I 422.6 nm, Ca I 430 nm, Mn I 445.8 nm, O III 453.2 nm, N III 488.2 nm, Mg I 518.3 nm, Ca I 526.7 nm, Al 559.4 nm, Na I 589.8 nm, N II 616.8 nm, Mg II 634.6 nm, O V 646.5 nm, O II 672 nm. The elements identified in Figs. 3, 4, and 5 are the same elements in the Agate stone sample. However, it should be noticed that the intensity of the emission spectrum is much higher in the case of the 20 Hz repetition rate.

The principle of atomic excitation and ionic radiation is the basis in atomic spectroscopy. Excitation occurs because the electron rises to a higher energy level, then the atom will be in the excited state. At a very fast time, the excited atom will return to the ground state. Energy absorbed during the excitation process will be released in the form of quanta. The energy quanta emitted is a characteristic of the spectrum of atoms or certain elements. The specific atomic spectrum is obtained from the following equation (Eq. 1),

$$E_2 - E_1 = h\,\frac{c}{\lambda} \qquad (1)$$

where h is the Planck constant (6.626x10-34 Js), c is the speed of light ($3x10^8$ m/s), and λ is the wavelength (nm). For example, the silica element was detected at a wavelength of 288.2 nm. The wavelength is obtained from calculations as below [8]:

$$(5.0823458 - 0.7809579)eV = 6.626x10^{-34}\,\frac{3x10^8}{\lambda}$$

$$(8.13175328 - 1.24953264)x10^{-19}Js = 6.626x10^{-34}Js\,\frac{3x10^8 m}{\lambda}$$

$$\lambda = 288.2\ nm$$

3.3 RelativeIntensity analysis

Figure 6 is a graph of the emission spectrum in a gemstone sample at intervals of (a) 200-350 nm, (b) 350-500 nm, (c) 500-650 nm, and (d) 650-700 nm. The blue line shows the spectrum at the repetition rate of 10 Hz, the red line shows the spectrum at the repetition rate of 15 Hz, and the gray line shows the spectrum at the repetition rate of 20 Hz. The peaks on the graph show how much elemental intensity is contained in the sample [9]. The results on the graph show that the relative intensity produced with a 20 Hz repetition rate is higher than that using the 10 Hz and 15 Hz repetition rates. This shows that the higher the repetition rate used, the higher the relative intensity produced. The relative intensity arises due to ablation on the surface of the sample by lasers and particles which appear in the form of plasma emissions [10].

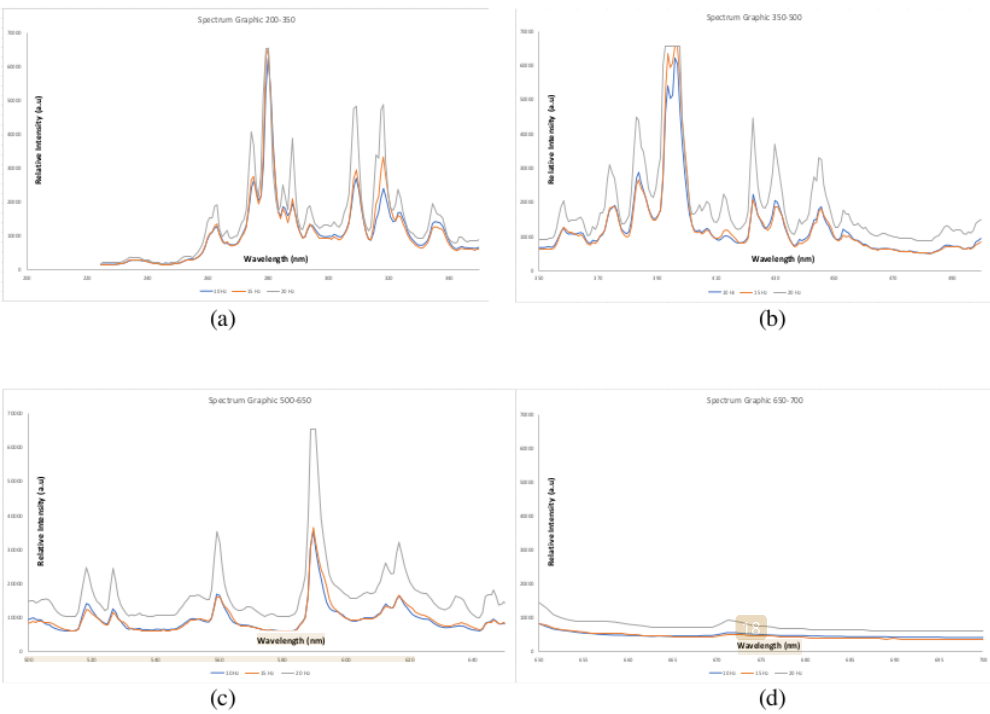


Figure 6. Emission spectrum obtained from the gemstone sample with a pulse repetition rate variation 10 Hz,15 Hz, and 20 Hz at (a) 200-350 nm, (b) 350-500 nm, (c) 500-650 nm, and (d) 650-700 nm

3.4 Identification of elements by X-Ray Fluorescence (XRF)

Table 1 shows the elements obtained from the gemstone taken by using the XRF technique. The content of the elements in gemstone according to the XRF test are Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe, Cu, Zn, Sn, Zr, Rh. The elements with the highest intensity are Si, Ca, and Fe. The elements identified by the XRF technique are the same with elements of agate stone sample taken by using the LIBS technique shown in Figs. 3, 4, and 5. This result confirmed that the LIBS technique by pulsed laser ablation is applicable for identification and analysis of elements in the stone sample especially the Agate sample. The use of LIBS is much convenient for the analysis compared to the case of XRF because the sample preparation is quite simple and the technological cost is much cheaper for the LIBS case.

Table 1. Table the elements obtained from the gemstone agate stone using X-Ray Fluorescence

No.	Component	Result	Unit	Det. limit	El. line	Intensity	w/o normal
1	Total	232	mg/cm2				232.4035
2	Mg	0.261	mass%	0.03711	Mg-KA	0.0677	0.2612
3	Al	3.95	mass%	0.01819	Al-KA	5.4191	3.9497
4	Si	11.0	mass%	0.03338	Si-KA	14.6156	11.0469
5	P	0.0778	mass%	0.00782	P -KA	0.1263	0.0778
6	S	0.160	mass%	0.00545	S -KA	0.5015	0.1597
7	Cl	0.0365	mass%	0.00604	Cl-KA	0.1689	0.0365
8	K	1.18	mass%	0.01470	K -KA	2.5896	1.1772
9	Ca	4.68	mass%	0.01320	Ca-KA	16.9287	4.6804
10	Ti	0.321	mass%	0.01698	Ti-KA	0.2891	0.3208
11	Mn	0.125	mass%	0.00815	Mn-KA	0.4065	0.1247
12	Fe	4.64	mass%	0.00740	Fe-KA	24.3363	4.6359
13	Cu	0.0095	mass%	0.00378	Cu-KA	0.0983	0.0095
14	Zn	0.0138	mass%	0.00321	Zn-KA	0.1924	0.0138
15	Sr	0.0461	mass%	0.00268	Sr-KA	2.1038	0.0461
16	Zr	0.0130	mass%	0.00298	Zr-KA	1.0373	0.0130
17	Rh	0.122	mass%	0.04782	Rh-KB1	0.5874	0.1222
18	Balance	73.3	mass%		Pd-KAC	5.5421	73.3247

4. Conclusion

The effect of laser repetition rate in the identification of elements in the gemstone Agate stone sample using the LIBS technique can be seen through the visual plasmas and their emission spectra. In visual plasma, the higher the repetition rate used, the wider the diameter of the plasma formed. Spectrum graphs produced from variations in repetition rates show differences in relative intensity. The higher the repetition rate used, the higher the relative intensity produced. Also, a comparative study was made using the XRF technique for the identification of elements. The results confirmed that the elements identified in the LIBS technique are the same as the elements obtained by the XRF technique.

5. Acknowledgment

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