IN-SITU DISCRIMINATION OF GEMSTONES USING SEMI QUANTITATIVE ANALYSIS BASED ON LIBS-PCA METHOD

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For my beloved mother and father.

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ABSTRACT

Laser-induced breakdown spectroscopy (LIBS) is a flexible non-destructive method for qualitative and quantitative analysis. It has its advantages for in-situ elemental analysis applicable to any material. LIBS system was optimized with fundamental 1064nm of Nd:YAG laser and the beam was collimated with plano-convex, convex, and focusing lenses. It aims to identify and classify the elemental differences in the spectrum of gemstones. Gemstone's relative composition was determined using stoichiometric formula. LIBS is performed using 300mJ of Nd:YAG laser and a USB2000+ spectrometer with a spectral range of 600-900nm, which then analyze using the Origin software. The lenses were placed 2cm - 6cm - 11cm respectively from the laser source. The differences in LIBS spectra lines of samples represent the elemental variations in Amethyst, Emerald, and Topaz gemstones. 80% of expected elements such as Si, O, Al, and F were identified. Discrimination in each sample is illustrated with a PCA plot, up to three PCs (principal component) referred to as scree and loadings plot of gemstones. The cluster formed shows that each gemstone has similar characteristics. The overlap cluster may be because they have a similar spectrum but are still distinct in features. LIBS-PCA technique is one of the methods that can be used to highlight spectral differences to identify various gemstones and discriminate real from imitated ones. It could identify, discriminate effectively, and classify gemstones with even minor differences for various samples.

ABSTRAK

Spektroskopi kerosakan akibat laser (LIBS) ialah kaedah kuasi tidak musnah yang fleksibel untuk analisis kualitatif dan kuantitatif. Ia mempunyai kelebihannya untuk analisis unsur in-situ yang boleh digunakan untuk sebarang bahan. Sistem LIBS telah dioptimumkan dengan asas 1064nm laser Nd:YAG dan pancaran disatukan dengan kanta plano-cembung, cembung dan fokus. Ia bertujuan untuk mengenal pasti dan mengklasifikasikan perbezaan unsur dalam spektrum batu permata. Komposisi relatif batu permata ditentukan menggunakan formula stoikiometrik. LIBS dilakukan menggunakan 300mJ laser Nd:YAG dan spektrometer USB2000+ dengan julat spektrum 600-900nm yang kemudiannya menganalisis menggunakan perisian Origin. Kanta diletakkan 2cm - 6cm - 11cm masing-masing dari sumber laser. Perbezaan pada garis spektrum dalam sampel spektrum LIBS mewakili variasi unsur dalam batu permata Kecubung, Zamrud dan Manikam. 80% unsur jangkaan seperti Si, O, Al, dan F telah dikenalpasti. Diskriminasi dalam setiap sampel digambarkan dengan plot PCA sehingga tiga komponen utama yang dirujuk kepada plot scree dan pemuatan batu permata. Kelompok yang terbentuk menunjukkan setiap batu permata mempunyai ciri-ciri yang serupa. Kelompok bertindih mungkin kerana mereka mempunyai spektrum yang sama tetapi masih berbeza dari segi ciri. Teknik LIBS-PCA adalah salah satu kaedah yang boleh digunakan untuk menyerlahkan perbezaan spektrum untuk mengenal pasti pelbagai batu permata dan membezakan yang nyata daripada yang meniru. Ia boleh mengenal pasti, mendiskriminasi dengan berkesan dan mengklasifikasikan batu permata dengan perbezaan kecil walaupun untuk pelbagai sampel.

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LIST OF SYMBOLS AND ABBREVIATIONS

Al	-	Aluminium
B	-	Boron
Ca	-	Calcium
El	-	Element
F	-	Fluorine
Fe	-	Ferum
Mw	-	Molecular weight
Na	-	Sodium
n	-	Number of element
O	-	Oxygen
OH	-	Hydroxide
%	-	Percentage
CCD	-	Charge Couple Device
EDX	-	Energy Dispersive X-Ray
FOC	-	Fiber Optic Cable
GIA	-	Gemological Institute of America
LASER	-	Light Amplification by Stimulated Emission Radiation
LIBS	-	Laser Induced Breakdown Spectroscopy
Nd:YAG	-	Neodymium-doped Yttrium Aluminum Garnet

NIST - National Institute of Standard Technology

PCA - Principal Component Analysis

LIST OF APPENDICES

LIST OF PUBLICATIONS

1. Saufi, N.M. *et al.* (2022). Element Identification of Different Gemstones by Using LIBS-PCA Method. In: Mustapha, A.B., Shamsuddin, S., Zuhaib Haider Rizvi, S., Asman, S.B., Jamaian, S.S. (eds) Proceedings of the 7th International Conference on the Applications of Science and Mathematics 2021. Springer Proceedings in Physics, vol 273 (pp 155-163). Springer, Singapore. https://doi.org/10.1007/978-981-16-8903-1_16.

CHAPTER 1

INTRODUCTION

1.1 Background of study

Gemstones trade statistics from globalEDGE [1] stated that Precious Stones and Metal were listed in top 10 import goods in Malaysia. World Integrated Trade Solution [2] shows the data of Malaysia Stones;precious and semi-precious, dust and powder, of diamonds exports by country in 2019. The import and export trade flow stated that the value is 6.4 Billion USD. The record indicated that,gemstones were among the most popular item in the Malaysia trade market.

Laser-Induced Breakdown Spectroscopy (LIBS) is a fast, easy-to-carry, and in situ atomic spectroscopy technique. With LIBS,sample preparation is not required, it is less work and take a shorter time to record the data [3] also, it can measure the concentration of major and trace elements in the different forms of samples such as air, liquid and solid [4]. It is a quasi non-destructive method that allows for future reanalysis [5] and uses a high-energy laser pulse as a source to form a high temperature of micro plasma at the surface of the target sample. It is considered an accurate inspection technique as it is repeatable and a number of tests are usable to relate between the data [6].

LIBS forming a specific spectrum contains information about the concentrations of naturally occurring elements, and the sample’s ratio of some isotopic and atomic structure [7]. From that, the purity of the gemstones can be determined. Principal component analysis (PCA) is a statistical method that can be used to summarize the content or information of a large data into a simple form for data visualization and analysis [8]. The smaller data indices are really important in observing the trends, jumps, and clusters. The measured data can be properties of samples, chemical compounds or reactions. Combining LIBS and PCA allows the discrimination of elements to be done in a simpler form.

The gemstones can be categorized into different species, groups, and its variations. For the past few decades, there has been no scientific grading system for gemstones. The gemstones are graded using the naked eye by assuming with 20/20 vision. In the early 1950s, the Gemological Institute of America (GIA) developed a system used in diamond grading. The GIA system included main innovations such as introducing 10x magnification as the standard for grading clarity [9]. With modification, these categories can be helpful in understanding the grade of all gemstones.

The price and value of gemstones are based on factors characteristics and quality of the stone [10]. Thus, some of the jewellery or gemstones were sold at a really expensive price but with low quality. With certain treatment (such as surface coating, irradiation, and heat treatment), the purity of the gemstones cannot be identified with the naked eyes as its appearance is mostly captivating. That is why it is still in high demand even though it is imitated. Meanwhile, some diamonds, rubies, sapphires, and emeralds still maintain their standard from other gemstones [11] where the quality and price are reasonable.

1.2 Problem statement

Nowadays, it recorded increasing quantities of various doped and synthetic gem materials in the jewellery market. Identifying the element, characteristics, and quality of the gemstones is usually the conventional method that needs laboratory work. It is also time-consuming, and the sample must be prepared first. The common issues are copied items similar to those of valuable untreated and natural gemstones. This approach led to a late determining the quality of the gemstone element and was unfairly used in the jewellery market. Accuracy of gemstone identification and complete information plays an important role in the jewellery market to maintain the trade value of natural gemstones and the satisfaction among consumers who are purchasing the gemstones.

High technology analytical techniques now make identifying elements and trace elements of the gemstone possible to be done where decades ago, it was only determined by guessing [12]. Hence, the LIBS-PCA method offers a much easier, flexible, and applicable in any field of study and industry. The quasi non-destructive technique is harmless for both operator and sample [13] and left only a small tiny burn spot that barely seen with naked eye. The samples are not destroyed and can be used repeatedly.

1.3 Research objectives

Some objectives are outlined to ensure all the processes led to the success of this research. The objectives of this research are:

i. to optimize laser-induced breakdown spectroscopy using Nd:YAG laser with collimated beam by plano-convex, convex and focusing lens
ii. to identify the elemental spectrum using spectral lines in LIBS spectra of gemstones and discriminate the gemstones using Principal Component Analysis (PCA) method
iii. to determine the relative composition of different types of gemstones by Stoichiometric formula

1.4 Scope of study

This research is focused on the discrimination of gemstones and identifying natural from imitating ones. The gemstones used in this research are Amethyst, Sapphire, Topaz, Tourmaline, and Emerald. Fundamental, 1064nm of Nd:YAG laser ablated the samples, and emission spectra were collected spectrometers in the wavelength range of 600-900 nm. Identifying spectral lines using NIST atomic spectral database [14]. The spectra were subjected to PCA with three PCs (principal component) used for visual observation of the discriminability of the data. The element content and identification of spectral lines were verified by EDX analysis and compared with their theoretical composition from the molecular formula and calculated stoichiometric proportion. PCA is a technique considered a classical properties extraction and representation of data as it can visualize the data more straightforwardly.

1.5 Significance of study

Detecting the element in determining the impurities content in gemstones is very important. The LIBS-PCA is a recommended method to detect and analyze the element in the gemstones based on their expected element from the molecular formula. The setup enables the element detection in a wide range of emission spectrum between 600 nm up to 900 nm. This range offers element detection even with low concentrations. Different lenses in the setup enable a clear and sharp laser beam for easier ablation of gemstones. PCA method shows the cluster of the element [15] with minimal information loss and high interpretability. The technique can be used on a portable device for the element identification of gemstones.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter discusses the Laser-Induced Breakdown Spectroscopy (LIBS) as the elemental identification method. Principal Component Analysis (PCA) method is commonly used as a data visualisation in a more straight forward form to classify gemstones. Electron Dispersive X-ray Spectroscopy play a role in element verification between expected and experimental data.

2.2 Laser induced spectroscopy

2.2.1 Laser

Laser stand for Light Amplification by Stimulated Emission of Radiation [16]. It is a device that amplifies the light emit by stimulating atoms or molecules. Stimulated emission of radiation amplifies the intensity of light. It can generate light in the form of a laser beam. This light emits at particular visible, ultraviolet (UV) and infrared (IR) wavelengths. Laser beams form monochromatic (single color) rays, coherent (same frequency and waveform), and collimated (in the same direction) [17].

When the laser was invented in 1960, it was once called an optical maser or infrared maser (Microwave Amplification by Stimulated Emission of Radiation) [18]. Then, officially known as laser in 1965. Laser brought a revolution and a future influence in spectroscopy, optical technology, and various sciences and technology fields. A few types of laser, such as Gas Laser, Solid-State Laser, Dye Laser [19] and Laser Diode, classify based on their amplifying medium.

Solid state laser mixes solid such as crystal or glass with rare earth elements as a source of optical gain. The most common solid-state lasers are ruby laser and Nd:YAG laser (Figure 2.1). The mixed element is usually neodymium, chromium or ytterbium. It optically pumps with a flash lamp (pump source) and may generate high output power between a few milliwatts and kilowatts. Flash lamps generate a high light pulse to the laser medium [20] that will form photons. The optical resonator builds up with the highly reflective mirror and partially reflective mirror. High reflective mirror bounces the photon back toward electron which then leading to photon amplification in an optical resonator [21]. The number of photons increasing until reach population inversion allows them to pass through the partially reflective mirror as laser output.

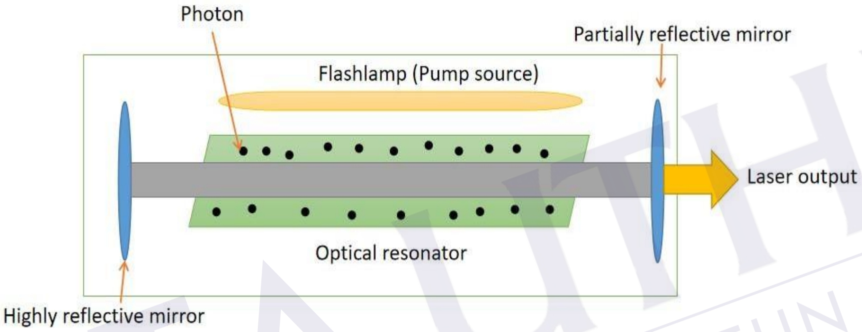

Figure 2.1: Schematic diagram of Nd:YAG laser

2.2.2 Spectroscopy of laser induced plasma

Spectroscopy is the process of separating light (also known as electromagnetic radiation) into its wavelengths, referred to as a spectrum [22]. In classical spectroscopy, a prism and photographic plates were employed; however, diffraction gratings were used in modern spectroscopy to disperse the light form. The energy levels of electrons in atoms and molecules are quantized, and electromagnetic radiation can only be absorbed and emitted at particular wavelengths [23]. As a result, spectra are not smooth but punctuated by absorption or emission lines [24].

Laser spectroscopy can form either an absorption, spontaneous or stimulated emission (Figure 2.2). For absorption emission, the atom from the ground state absorbs the energy from the photon and excites it to a higher energy state. In spontaneous emission, the atom is already at a higher energy state. But it may decay and move to the ground state releasing energy in the form of photons. Spontaneously, the photon is emitted in a random direction. Meanwhile, in stimulated emission, the incoming photon with a specific frequency interacts with the atom causing it to move to the ground state and forming a new photon in the same phase, energy and frequency.

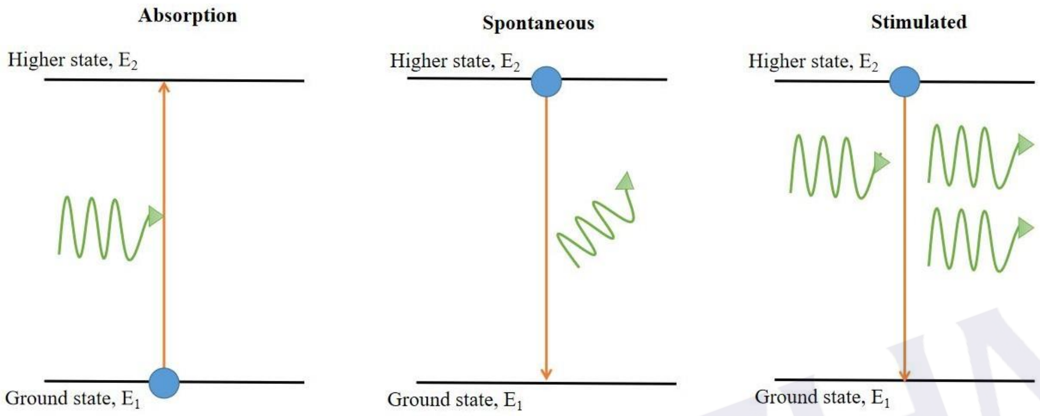

Figure 2.2: Emission of laser spectroscopy

LIPS (Laser Induced Plasma Spectroscopy) is an analytical technique that uses high energy pulsed laser plasma and ion stimulation to analyze atomic emission [4]. A little portion of the sample can interact with the laser beam to produce an emission spectrum for measurement. The spectrum included elements that may be used to determine the sample's composition [4]. Figure 2.3 depicts the three primary LIPS processes: laser interaction with the material, particle removal (ablation), and plasma formation (breakdown). Beginning with energy reflection (Figure 2.3 a) or absorption (Figure 2.3 b), it eventually transformed into sample vaporisation [4].

The vapour on the surface shrank in size as the intensity increased. Figure 2.3 c shows how the scattering and absorption of the laser beam had a considerable heating effect that resulted in the creation of plasma [25]. A quick growth of photo-ablated pieces is what defines the transformation state of laser plumes (Figure 2.3 e). Cluster formation and accumulation of polyatomic particles take place throughout the cooling process. (Figure 2.3 f). After some time, the ablated material is deposited around the hollow together with molten material (Figure 2.3 g). The sample's characteristics and the laser's parameters, such as wavelength and pulse width, have an impact on the shape and size (Figure 2.3 h) [4].

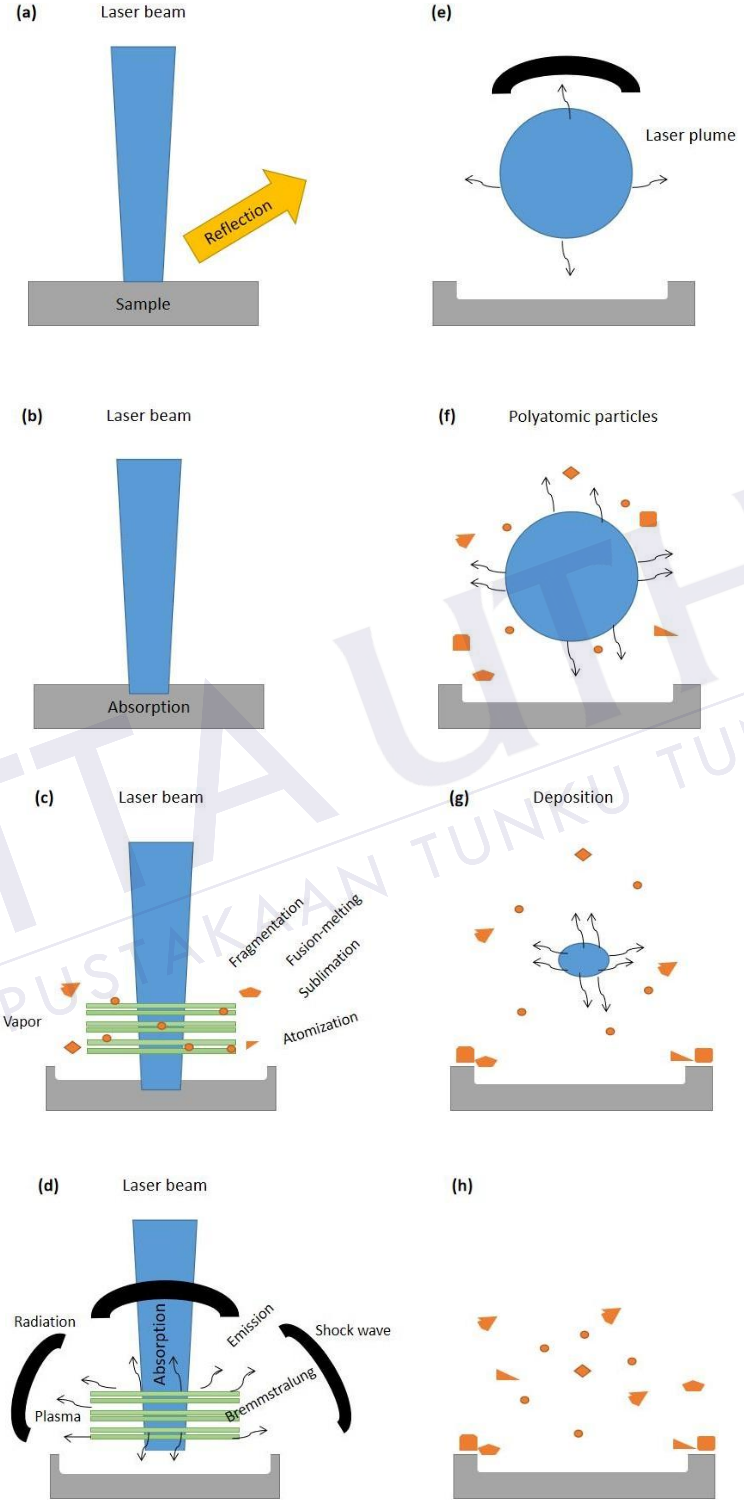

Figure 2.3: Schematic of the main processes in LIPS [4]

2.2.3 Laser induced plasma

Plasma used to be known as a hot-ionized gas. It was the fourth state of matter or material after solid, liquid, and gas [26]. When charged particles are created, light is re-radiated, laser light is absorbed, and plasma is visible as a spark. High ionization and absorption by gases commonly transparent to light will cause the breakdown [27]. During the breakdown peak, laser irradiance occurred in two stages. (1) The development of the first ionization and the avalanche that followed, with the breakdown increasing ionization. (2) Multi-photon ionization occurs when an atom absorbs many quanta in a row and generates an ion-electron pair [28].

Strong absorption happens when the laser irradiation exceeds the threshold value. However, if it is less than that, no significant attenuation occurs. The breakdown occurs when there is a rise in energy sequence during light transmission, and laser irradiance increases [29]. With the presence of a breakdown, time taken for laser to transmit are faster than the initial laser profile without breakdown [27].

A plasma plume forms when a high-energy laser beam ablates on a solid sample, which causes the sample's surface to vaporize or melt [30]. Evaporation and ionization of materials emit photons of matter particles. Less evaporation is produced if quick pulses are utilized with appropriate power. Strong molecule emission bands are mixed with the atomic line emission as interference in LIBS spectra [31]. The effective spectrum enhancement methods can improve plasma radiation intensity under a limited laser pulse [32-33].

The heat conduction of the sample influences the temperature. Due solid block samples' various heat transmission methods, the laser–solid interactions are divided into surface absorption and volume absorption [34]. Volume absorption is defined when the heat conduction depth is minor compared to the optical penetration depth [35]. The plasma slowly penetrates the sample to accelerate quenching after the laser ablates at the same spot. This condition is quite challenging to the stability of LIBS spectra.

During the decay or cooling of plasma, condensation or particle production occurs [22]. It begins when the plasma temperature reaches the material's boiling point and ends when the material's condensation temperature is reached. Significant thermal stresses within the material cause it to break into irregularly shaped particles and exfoliate (removing the outer layer) [36].

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