Elemental Analysis of Black Tourmaline Found in the Mines of Astak Valley, Gilgit-Baltistan (GB), by Using Calibration Free Laser Induced Breakdown Spectroscopy (CF-LIBS)

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Abstract

This study comprises compositional analysis of Black Tourmaline collected from the mines of Astak valley, Gilgit-Baltistan of Pakistan. The quantitative analysis were performed by using Calibration-Free Laser Induce Breakdown Spectroscopy (CF-LIBS). The high intense Nd: YAG laser focused on the surface of black tourmaline and produced plasma plume. Plasma cooldown with in few micro second, the optical emission spectra were noted in this process and recorded by using spectrometer. Optical emission spectral lines given information about the major and trace elements found in Black Tourmaline. This sample composed of Ca, Al, Mn, Ti, Fe, Li, Cr, K, B, Pb. Ba, and Si. The nature of Black Tourmaline found in the mine of Astak valley, Gilgit-Baltistan is unique than other 36 types found in different regions of the world, it belongs to Schorl species of tourmaline.

Keywords: Laser, Black Tourmaline, Plasma, Astak Valley, Calibration-Free.

1. INTRODUCTION

Tourmaline is types of gems have four species (Schorl, Elbaite, Liddicoate, Dravite) found in various part of the world in versus colors. It is a crystalline form of boron silicate mineral compounded with elements such as aluminum, iron, sodium, magnesium, and lithium and potassium etc. [1]. Most commonly Tourmaline are found in black color, sample used for this study is given in Fig. 01. Tourmaline also exist in colorless to brown, orange, red, green, blue, yellow, pink, and violet or hues in between, that is bi-color or tri-color which are used for decoration pieces as well as in jewelries [2]. Tourmaline are found in different countries such as United States, Afghanistan, Tanzania, Russia, Namibia, Mozambique, Pakistan etc. The hardness

by Mohs scale is 7.0 - 7.5, the specific gravity 2.9 -3.2 for black and brown usually [3]. Piezoelectricity is $1.928\times10^{-7}Cm^{-2}$ and pyro-electricity is $-4.0\times 10^{-3}\ Cm^{-2}K^{-1}$, the cleavage is poor crystal system trigonal with reflective index of 1.61 - 1.67 [4][5]. Details of Black Tourmaline use for elemental analysis are given in Table. 01. The general chemical formula for tourmaline is $XY_3\ Z_6\ TO_{18}\ (BO_3)\ V_3\ W$, where (X = Na, K, Ca); (Y = Al, Cr, V, Fe, Mg, Zn, Cu, Li, and Ti); (Z = Al, Cr, Fe, V, Mg); (T = Si, Al, B+3); (B = B+3); and (V = OH , O); (W = OH, F, O) [5].

Tourmaline is supper group minerals on behalf of larger numbers of species under that classification. Overall it is compost of complex boron aluminum cyclo-silicate mineral given in above general equation [5]. The concentration of the trace elements found in tourmaline are Cu, Ga, Sr, Sn, Zn and Pb proved to be the most useful discrimination for Paraiba tourmaline geographic origin determination. Different tourmaline in the word have different concentration of trace and major elements which paly fundamental role in their color and features [6].

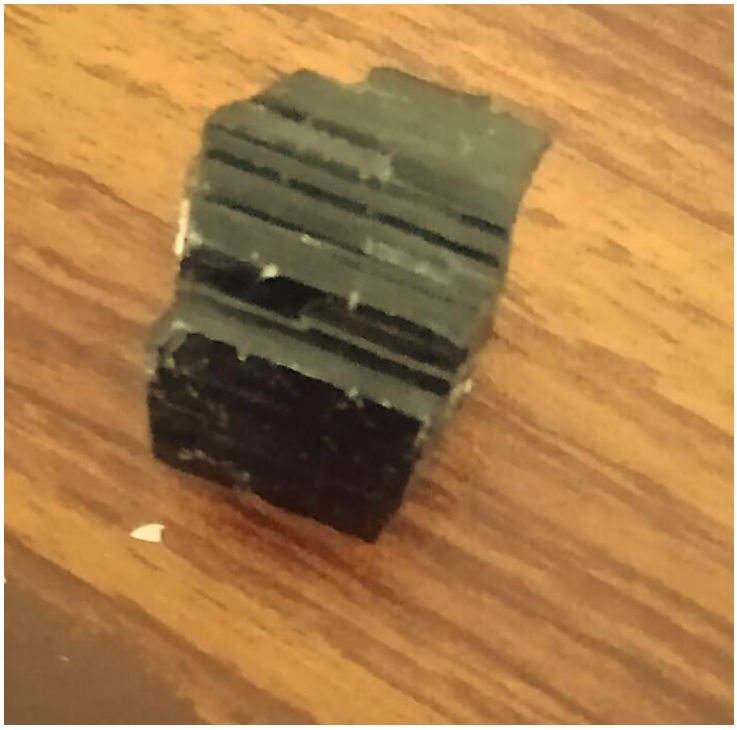

Fig. 01. *Sample (Black Tourmaline).*

Table. 01. Detail information about Tourmaline.

Sample	Reflective index	Hardness	Specific gravity	Piezo-electricity cm^{-2}	Pyro-electricity cm^{-2}
Black Tourmaline	1.61 - 1.67	7.0 - 7.5	2.9 - 3.2	1.929×10^{-7}	-4.0×10^{-3}

The Laser Induce Breakdown Spectroscopy (LIBS) is a technique used with wide applications after 1999, particularly in quantitative analysis of metallic alloys, biological material, , geological samples, cultural heritage, coal and combustion products extraterrestrial objects and other filed of life [7].

LIBS is the emerging analytical technique because of its unique advantages like as real-time and in situ detection, remote sensing capability, fast multi-elemental analysis and directly analysis of any types of materials. This method is also been used in biological and medical testing, industrial and medical testing, environmental production, sea and space exploration, geological and resources exploration, artifacts and jewelry identification, etc. [7, 8, 9].

This analytical technique used best for elemental analysis which can be divided in to two parts. First technique operate on separated minerals i.e. bulk non-position sensitive techniques which is based on the classical wet chemical methods, Atomic Emission Spectroscopy (AES), and Atomic Absorption Spectroscopy (AAS), X-ray Fluorescence (XRF), X-ray Diffraction (XRD), and Raman spectroscopy are commonly used techniques used for elemental analysis [10,11]. The second technique based on a minerals in situ with in a rock beam position-sensitive techniques, where a focused beam is place on a define position on a material surface, like as SIMS, LA-ICP-AES, LA-ICP-OES, PIXRE, Optical Microscopy (OM), Transmission Elemental microscopy (TEM) and scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) [12, 13, 14]. Laser Induced Breakdown Spectroscopy (LIBS) was found as a valuable tool for the gemstone analysis, particularly in the study of provenance for gems and to discriminate between different minerals pulse [3]. LIBS is effective and non-distractive research technique. Which is used in industry, diagnostic of environment and biomedical research. LIBS technique is based on the optical emission spectra generated by plasma of any kind of samples. Creation plasma depend upon the power of laser beam normally focus on target surface that may be solid, liquid or gas. This emission spectra help out to determine the fingerprint of the samples and stoichiometry [8]. Additionally, LIBS is a powerful alternative method as compere to conventional analytical techniques. Like as simultaneous identification of elements, no prior sample preparation, in situ-analysis, fast response , determination of rare elements, elemental identification in real–time and low detection down to ppm [1].

Quantitative analysis carried out using two basic methods first one is calibration curve method (CCM) or standard of internal plasma parameters. In this method matrix matching and

references samples is mandatory which can be overcome second method that is calibration free laser induce breakdown spectroscopy (CF-LIBS), used as alternative methods of CCM in which the line intensity, and plasma parameters are also used for quantitative analysis of the sample. The potential and limitation of the technique are stoichiometric ablation validity of Local Thermodynamic Equilibrium (LTE), homogeneity of spectral plasma and thickness of plasma [15]. This plasma temperature can't calculated accurately by CF-LIBS, that is why CF-LIBS provide quantitative estimation of the major elements more accurately than the trace ones [7]. Now it's clear that the compositional analysis is based on the plasma temperature and the spectral line in CF-LIBS [16]. The one calibration free laser induce breakdown spectroscopy (OL-CF-LIBS) is used for single spectral line for the detection of concentration of marital. Boltzmann plot required at least three optical thin lines, plasma temperature and electron density play important role in CF-LIBS analysis. Electron density value can deduce using stark broadening of spectral lines or by using Saha-Boltzmann equation [11]. Both the plasma temperature and concentration can be calculated by Boltzmann plot methods [17].

The main objective of this research is to determine the major and trace elements of black tourmaline collected from Astak mines. The comparative study of tourmaline of other countries or regions with black tourmaline of Astak mines on the bases of their nature and characterization of the elemental composition.

2. MATERIALS AND METHODS

2.1. Sampling and Geography of the Mine Area

The gems known as black tourmaline sample was collected from the Astak mine located in Karakorum Range at a distance of 80 km from Skardu Gilgit-Baltistan, Pakistan. On geological aspect this valley is known as the valley of gemstones and minerals. The Karakorum plate and the Kohistan-Ladakh island arc are two plates which comprises this area [10]. The latitude and longitude of Astak mines are 35º44'32" north, 75º2'33"east. Black tourmaline sample shown in Fig. 1, collected from the Astak mine, size of samples are few cm. Wash the sample for multiple times to remove the impurities of birthplace from the surface of the samples.

2.2. Experimental Setup

Schematic diagrams of the experimental setup is shown in Fig. 02. Experimental setup consist of Q-switch neodymium doped Yttrium Aluminum Garnet (Nd: YAG) laser (Brilliant-b Quantal France), has the pulse rate of 5 ns with reparation rate of 10 Hz used as excitation source.

This laser provided various energies of 400 mJ, 200 mJ, and 90 mJ at first harmonic, that is 1064 nm, second harmonic is 532 nm and the third harmonic 355 nm generated respectively. For this experiment, the laser of 532 nm was used to generate plasma on the surface of the sample, with certain energy of 110 mJ laser energy with delay of 2 ms. A converging lens of 10 cm focal length was use to focus the laser beam on the sample surface of sample. High intensity laser produce a spot sized diameter on the surface of sample approximately 0.05 mm there used a spectrometers (Avantes, Holland) covering the wavelength of 220nm to 950 nm (resolution of 0.06 nm) to collected the emitted light through a collimating lens (0 degree to 45 degree field view) normally place to laser produce plasma plume expansion. A rotator is used to rotate the sample to avoid from the deep craters on samples and also to maintain the homogeneous production of plasma. Spectrums cover 220 – 950 nm wavelength. The first spectrometer covers 220 – 340 nm, range of seconds 340- 440 nm, third dictator cover 440-580 nm, range of four one is 580 -680nm, 680- 750 nm cover at range in fifth while the six one cover range of 750-950 nm. The emission spectra was record by a Q-switch Nd-YAG laser is synchronized with spectrometer of 5 ns pulse, the generated plasma emitted spectral lines during the cooling process. The distance between the convex lens and the target material maintained at less than 10cm in order to avoid air breakdown.

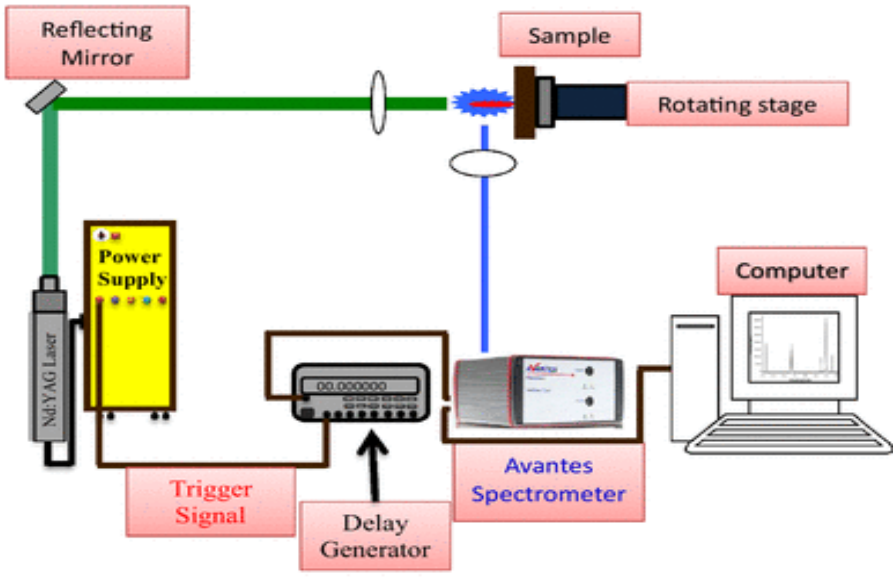

Fig. 02. Schematic diagrams of the experimental setup.

2.3. Quantitative Analysis

The three basic assumption for quantitative analysis of gems by using single laser induce breakdown spectroscopy (SL-CFLIBS) or calibration free laser induce break down spectroscopy (CF-LIBS) are as;

i. Local thermodynamic equilibrium
ii. Optical/ theoretical thin plasma.
iii. Stoichiometric ablation.

The Boltzmann plot method and shah-Boltzmann plot method used to determine the temperature of electrons relative to the absorbed spectral lines [18, 19].

Variety of lasers are given as the ranging from UV excimer laser to infrared solid state lasers. Various properties of laser are: Highly instances, plasma formation, high power density, power density, and the several nanosecond laser pulse etc. [20].

Black Tourmaline samples of few cm thickness focused by the second harmonic laser (532nm) to generated plasma by 80 mJ pulse energy. The nature of created plasma determine composition, crystal pin, optical reflection, optical transmissibility, and surface shape etc. [21]. During the recombination of plasma the large acquisition delay time to measure small molecules gives the quantitative analysis of sample [19, 22]. The sample surface must be clean by washing or firing few laser shots of low energy. Optical emission plasma were collected by a collimating lens with the help of optical fiber (core diameter 600 lm), transmitted these emission to a broadband mono-chromatic to recorded the plasma emission [15].

The focus single Nd: YAG laser produce plasma on the surface of gems at energy level of (20-120) mJ and delay time of (2 -5) μs. The emission lines were compared with NIST data base to identify the elemental composition of gems [23].

The plasma temperature can be calculated from the intensity of the emission neutral lines or determine by using H-alpha line. All the plasma parameters calculated by using NIST database. The intensity of emission lines, the electron temperature and the density of the electron numbers are depend upon the external magnetic field [24]. The speed of the plasma plum is greater with the axial direction then radical direction. Decreasing in the magnetic field acts as a retarding medium and slows down the growth of the plasma plums, and thus varies during the expansion of beta plums [25].

2.4. Optical Thin Plasma

Intensity ratio of two continuous neutrals or ionized lines used for the conformation of optical thin conditions. The optical thin conditions of black tourmaline can be determine by a pair of lines at 612.22 nm and 616.22nm, experimental and theoretical vales are 0.99 and 0.50 respectively. Both values are nearly close to each consider as optical thin [10].

$$\frac{I_{ki}}{I_{nm}} = \frac{A_{ki}\ g_k\ \lambda_{nm}}{Anm\ g_n\ \lambda_{ki}}\ exp(\frac{|E_k - E_{ni}|}{k_b\ T}) \qquad 01$$

Where A_k is transition probability, I_k is intensity λ_{ki} is wavelength of first line and k_l is second one where g is the weight of transformation from k to i. K_b is Boltzmann constant.

In present study all condition for optical thin conditions were fulfilled for optical thin condition for spectral lines of different elements present in black tourmaline [25].

The values required for theoretical values calculation are been collected from NIST data base (NIST Atomic Spectra Data Base line from 2019), compared with experimental value both values are approximately equal to each other confirmed optical thin, fulfil the base of calibration-free techniques [18].

2.5. Electron Number Density

Local thermodynamic equilibrium status was verified using Mc Whitter's Criteria equation. The neutral lines of the Ca-I line at 610.27nm ΔE= 2.91eV is the energy different between two states. Using standard the plasma temperature of black tourmaline is 8500K which need to calculate the local thermodynamic equilibrium [10] the value of electron density N_e in $cm^{-3} \geq 1.4\times10^{16}$

$$Ne\ \geq\ 1.6\ \times\ 10^{12}\ \times \Delta E^3\ \times T_e^{\frac{1}{2}} \qquad 02$$

N_e is the electron density ΔE is difference in energy level between two states and T is the plasma temperature in kelvin (K) [17]

$$N_e cm^{-3}\ \approx\ 10^{12}\ \frac{\Delta\lambda}{2\omega}. \qquad 03$$

The experimental value estimated by full width at half maxima call as stark broadening equation (FWHM) Δλ where the $\Delta\lambda = (\Delta\lambda_{\text{observed}} - \Delta\lambda_{\text{spectrometer}})$ this relation support to determine the concentration of species founds in sample. The lines are called self-absorption when plasma light is re-absorbed by the same types of elements that emitted light along optical length thus flattening line or in extreme cases, creating a dip in the line center [17].

The cf-LIBS is best techniques of analyze both qualitatively and quantitatively. This has been met under two conditions which are local thermodynamic equilibrium (LTE) and optical thin

condition (OTC). Elemental analysis of Black Tourmaline was carried out by using calibration free technique. Elemental composition can be calculated by using Boltzmann equation.

$$FC^z = \frac{U^z(T)\, I_k}{g_k A_k}\, e^{\frac{E_k}{TK_B}} \qquad 04$$

Were F, is ablated factor related to mass, C^z is elemental composition of neutral atoms I_k is the intensity of spectral line, g_k is statistical weight of upper level A_k is transition probability, U(T) is partition function, E_k is upper energy level, T is electron temperature eV and K_b is constant of Boltzmann [26]. All these parameters were taken from NIST database, which is necessary for the compositional analysis. The concentration of neutral elements found within the sample can be calculated by putting values in equation 4. The concentration of ionized elements determine by using equation called Saha-Boltzmann given as in equation 5.

$$n_e \frac{C^{z+1}}{C^z} = \frac{(2Tm_e K_B)^{\frac{3}{2}}}{h^3}\, \frac{2U_{z+1}}{U_z}\, exp\left[-\frac{E_{ion}}{TK_B}\right] cm^{-3} \qquad 05$$

Mentioned relation is the ratio concentrations the neutrals and ionized elements which are denoted as C^z and C^{z+1} respectively. The contribution of all elements present in any samples can be calculated by the sum all neutral atoms and the sum of all charge atoms written as in equation 6.

$$C_T = C_Z + C_{Z+1} \qquad 06$$

Now it's easy to determine the percentage weight of each elements presents in black tourmaline using relation given in equation 7.

$$C_{\%} = \frac{C_{element}}{C\ (Sum\ of\ all\ elements)} \times 100\% \qquad 07$$

All require values were taken from NIST database on the bases of requirements of relation, the energy and temperature both are in eV. Calculated concentration of all elements given in Table 4.5.

Quantitative analysis can be performed with LIBS provided the laser-generated plasma is stomata-metric, optically thin and self-absorbing, and meets LTE standards. The selection of spectral lines also plays an important role in the quantitative analysis of LIBS. The line was selected according to following criteria:

1. To minimize self-absorption effects, resonance lines should be avoided and for high concentration elements, transitions below 6000 cm^{-1} for quantitative analysis can also be avoided.

2. Spectral lines less than 291006 s^{-1} should also be excluded as the corresponding time is close to the time of plasma conversion
3. For all elements, high intensity spectral lines should be avoided as these lines tend to be overpopulated [27].

3. RESULTS

LIBS is fast, remote, and analytical technique, by which elemental compositions of Black Tourmaline were investigated. The second harmonic Nd: YAG laser of 532 nm with pulse energy of 130 mJ was used and recorded that the spectrum of samples taken from Astak mine Roundu Gilgit Baltistan of Pakistan. This Black Tourmaline is composed of Calcium, Magnesium, Aluminum, Titanium, Sodium, Silicon, Carbons, Iron, and Lead.

Plasma is a high energy source which is an electrically neutral conducting gaseous mixture having a significant concentration of cations and electrons. As an electrical conductor it can be heated inductively by coupling with an oscillating magnetic field. The temperature of the plasma may be of the order of 5,000 to 8,000 K. The plasma based AES in principle, is similar to the flame photometry; the only difference being that flame is replaced by much more energetic atomization-excitation processes using plasma. In emission work, the argon plasma is frequently employed [28]. The Ca ionic emission intensity from a hard stone sample is much stronger than the corresponding neutral emission intensity, and the reverse is true for a soft sample containing Ca, due to the lower plasma expansion speed as a consequence of weak repulsive force provided by the soft target. Therefore, the ratio between the Ca emission intensities of the ionic line and neutral line may be used to estimate the sample hardness [29].

Fig. 03 (a) and (b) give the emission spectrum of Black Tourmaline collected from the mine of Astak valley. The emission spectrum have a wide range of wavelength 220 nm to 440 nm. The absorption spectrum of 220 nm to 440 nm revealed that the Black Tourmaline sample collected from Astak valley is composed different elements in major and trace amount. This shows multiple intense peaks, the highest peak of neutral lead observed at 249.67 nm, neutral silicon at 288.15 nm, Mg I at 285.21 nm, and Aluminum at 309.251 nm. In this gem sample, calcium, titanium, manganese, magnesium and iron are also present. The concentration of iron, aluminum, Couper, carbon, magnesium, titanium and manganese are in small amount.

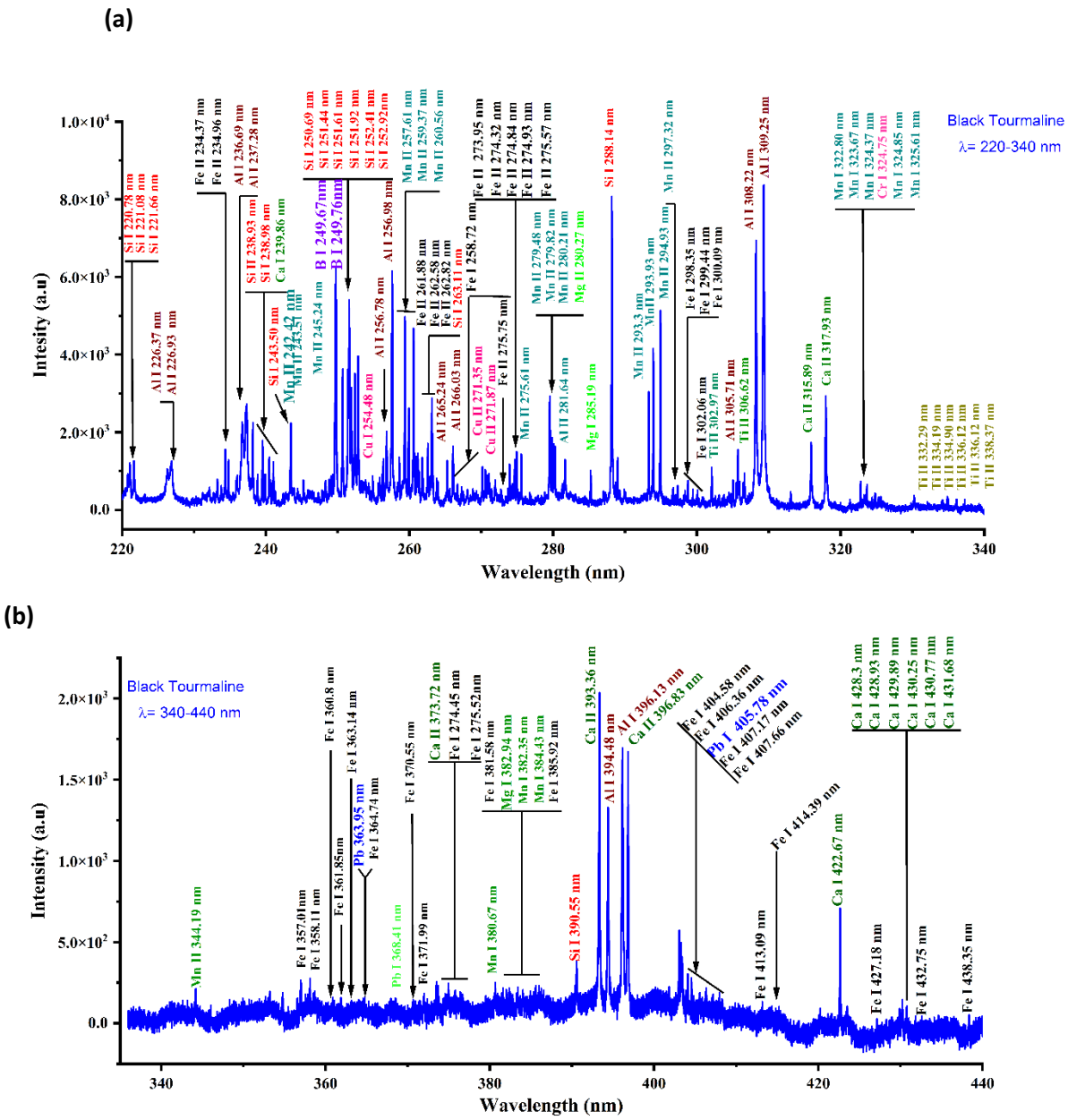

Fig. 03. *Optical Emission Spectrum of Black Tourmaline sample representing the spectral line of all the identified elements exist in the range of a) 220-340 nm and b) 340-440 nm.*

Fig. 04 (a) and (b) are the emission spectrums of Black Tourmaline ranging from 440 nm to 680 nm, collected from Astak mine Roundu. This spectrum revealed the composition of the sample. Some elements in major and trace amount were observed between 440 nm to 680 nm. The spectral lines with highest intensities are sodium, calcium and lithium at the lines of 588.98 nm, 610.27 nm and 670.77 nm respectively. The neutral and ionized elements Ti, Sr, Fe,B, and Ba also observed in Black Tourmaline.

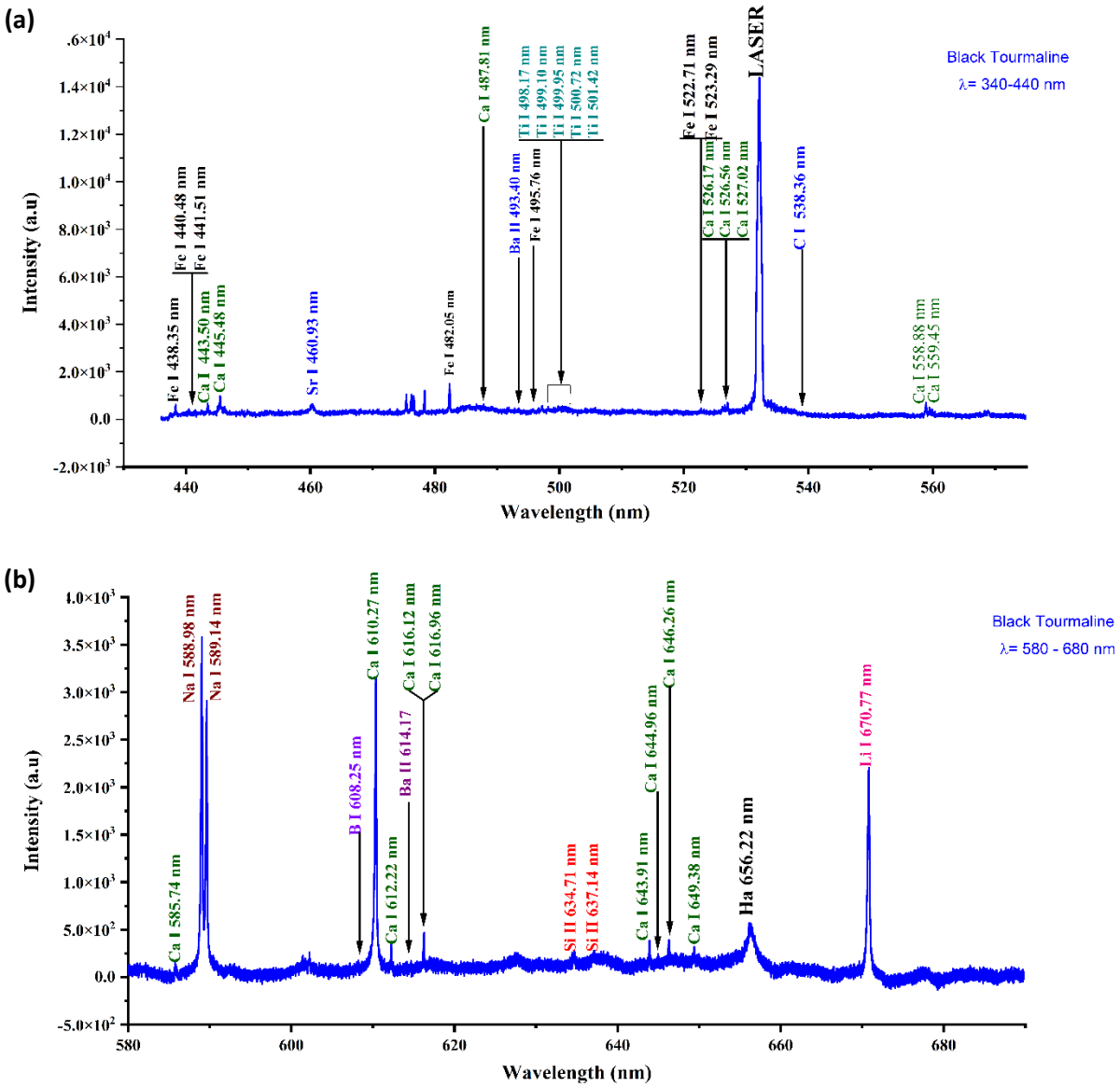

Fig. 04. *Optical Emission Spectrum of Black Tourmaline sample representing the spectral line of all the identified elements exist in the range of a) 440-560 nm and b) 580-680nm.*

Fig. 05 (a) and (b) are the emission spectrums of Black Tourmaline of wave length 680 nm to 950 nm. This identified some major and trace elements in the sample. The spectral lines with the highest intensities are neutral nitrogen at 764.83 nm, neutral potassium at 766.49 nm, and oxygen at 777.19 nm.

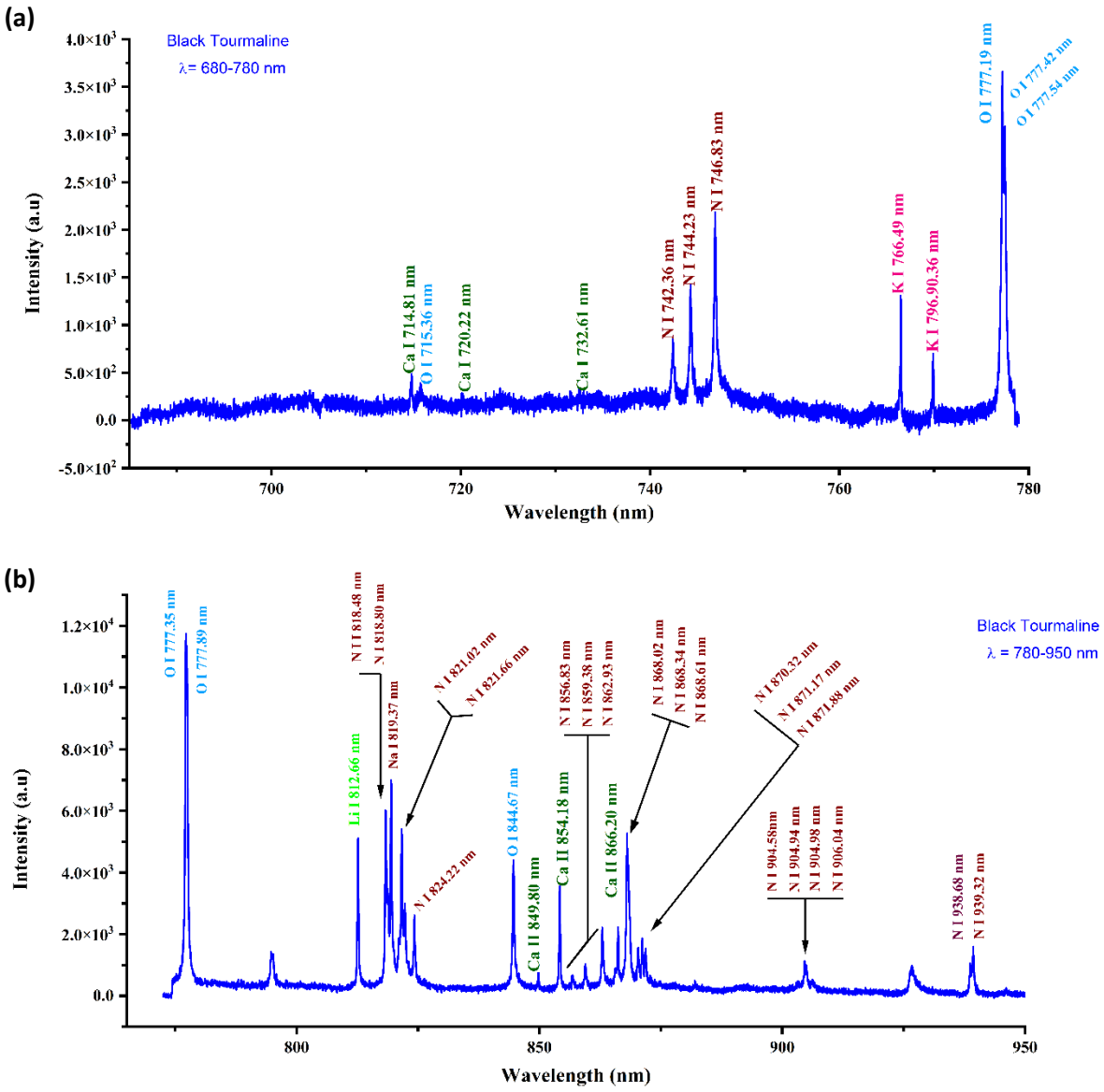

Fig. 05. *Optical Emission Spectrum of Black Tourmaline sample representing the spectral line of all the identified elements exist in the range of a) 680-780 nm and b) 780-950nm.*

3.1. Electron Temperature

The distinct spectral line of Ca-I are selected to determine the plasma temperature because of the reach of calcium neutral lines in Black Tourmaline or by using the alpha lines, by equation 08.

$$ln\left(\frac{\lambda_k I}{g_k A_k}\right) = -\frac{E_k}{k_b T} + ln\left(\frac{FC^S}{U(T)}\right) \qquad 08$$

Compared equation 08 with equation of slope $m = -\frac{1}{k_b T}$ and calculated the temperature of Black Tourmaline as 8500 K or 0.68 eV. The electrons temperature calculated by using

transition energy levels given in Table. 02. By linear fit as shown in Fig. 06, a temperature of 8500 K was calculated with uncertainty of 10%.

Table. 0 Error! No text of specified style in document.**2** Transition Probability of Electron in Various Energy State.

Wavelength (nm)	Upper Leve → Lower level	Transition Probability×($10^7 ms^{-1}$)	G_k	E_k (eV)
429.89	4s4p → 3p4s	4.66	3	4.76
445.48	4s4p → 4s4d	8.7	7	4.68
558.88	3d4s → 3d4p	4.9	7	4.47
559.45	3d4s → 3d4p	4.8	5	4.73
585.74	3d4p → 4p	6.6	5	5.04
612.28	4s4p → 4s5s	2.87	3	3.91
616.21	4s4p → 4s5s	4.77	3	3.91
643.92	4d4s → 3d4p	5.3	9	4.45
646.25	4d4s → 3d4p	4.7	7	4.44

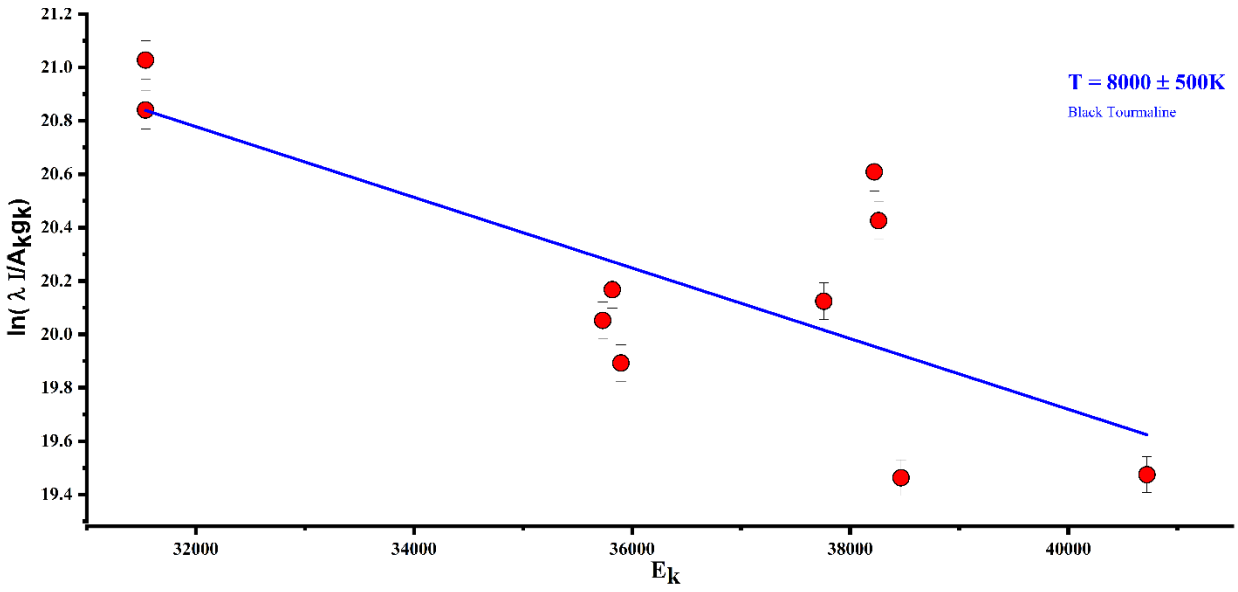

Fig. 06. *Electron Temperature of Black Tourmaline.*

3.2. Electron Number Density (n_e)

The electron number density (ne) is one of the most important parameter for quantitative analysis of sample. It can be calculated by using emission spectral line of any elements found in the sample while the line must be free of self-absorb. The most common method used for find "n_e" is stark-broadening, which is independent of neutral or ionized record lines. The formula of stark-broadening is given in equation 09.

$$N_e = \left(\frac{\Delta\lambda_{FWHM}}{2\omega_s}\right)^{1.47} \times 10^{16} \qquad 09$$

The value of broadening constant ω_s = 0.00698 nm and line profile of Ca-I is 610.27 nm. Which is optically thin, taken to estimate the electron number density. The calculated number density by experimental setup is 6.58×10^{16} cm^{-3}. The line profile is experimental values is represent by green dots, together with Voight fitting, calculated value is given in Table. 03 Graphical representation of sample shown in Fig. 07.

Table. 03 Stark-Broadening of Black Tourmaline.

Sample	Element	Expo national	ω (nm)	$\Delta\lambda_{FWHM}$
Black Tourmaline	Ca	10^{15}	6.69×10^{-3}	0.0069

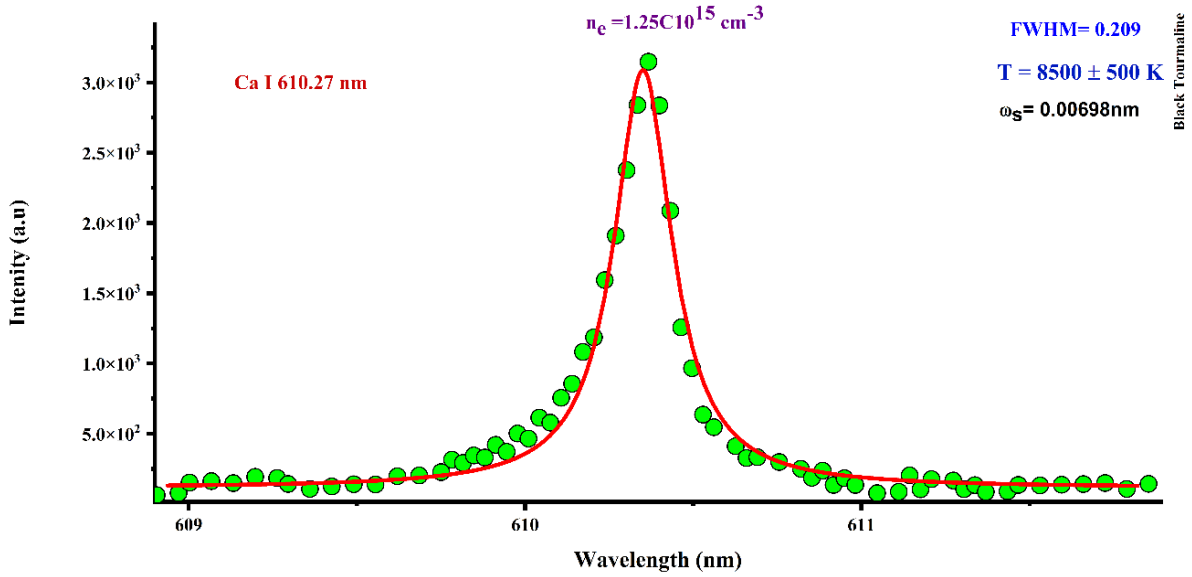

Fig. 07. *Electron Number Density of Black Tourmaline*

3.3. Optical Thin Condition

Optical thin condition of calibration-free LIBS is calculated by using relation $\frac{I_{ki}}{I_{nm}} = \frac{A_{ki}\ g_k\ \lambda_{nm}}{Anm\ g_n\ \lambda_{ki}}\ exp(\frac{|E_k - E_n|}{k_b T})$. Taken two or more lines to determine optical thin conditions, the two lines are 612.22 and 616.22 nm in equation 10, A_{ki} is transition probability, I_{ki} is intensity levels, λ_{ki} is wavelength, g_k is transformation from k to i, g_{mn} is the weight of transformation from m to n, T is temperature of electrons, and K_b is Boltzmann constant. The values of both experimental and theoretical values are given in Table. 04.

Table. 04 Intensity ratios experimental and theatrical.

Sample	Element	λ (nm)	A_k	g_k	ΔE (eV)	Expr; value($\frac{I1}{I2}$)	Theoretical Value ($\frac{I1}{I2}$)	%Error
Black Tourmaline	Ca	612.22	3.3×10^6	5	0.68	0.95	0.99	4.0%
		616.22	5.6×10^6	3	0.68			

3.4. Concentration of Elements in the Sample

Concentrations of different element found in black tourmaline were calculated by using equations 04 to 07 given in Table. 05. The exclusion lines of Ca-I lines (315.88, 317.93, 428.30, 430.24, 442.54, 445.45, 527.05, 551.56, 560.56, 610.27, 612.22, and 616.27 nm) were selected to measure the concentration of Ca. For the concentration Si-I selected line were 250.68, 251.61, 263.12 and 288.16 nm. The concentration of Na-I was determine by 588.99 and 589.59 nm lines, Li-I was calculated by 760.77nm, and of Al-I was determined by 393.40 and 396.15 lines. In the Black Tourmaline the concentration of Ca, Si, Mg, Fe, Na, Li, Al, K, B, Cu, Mn, and Pb are given in terms of weight percentage (Wt%).

Table. 05 Concentration of All Elements Present in Three Sample of Gemstones.

Element	Ca	Si	Mg	Fe	Na	Li	Al	K	B	Cu	Mn	Pb	T. Wt %
(Wt %)	1.87	14.12	0.04	30.54	15.3	9.7	17.95	7.29	2.29	0.15	0.3	0.45	100

4. DISCUSSION

This study gives the detailed information about Black Tourmaline found in the mines of Astak valley Gilgit-Baltistan. It is unique in its nature than other 36 types found in different regions of the world, it belongs to Schorl species of tourmaline. It founds in cylindrical or trigonal in shape.

Mostly Black Tourmaline are found with topaz and fluorite, or some other gems. It is composed different elements with different concentrations, which cause of its hardness, brightness and crystalline structures. Its uniqueness is because of Pb, Ti, and Cr. The major and trace elements are Si, Al, Mg, Mn, Ca, Ti, Ba, B, Li, Na, and K. Because of the beauty, uniqueness and physical arrangements of Black Tourmalines are used for decoration piece and in jewelries all over the world. Calibration-free Laser Induce Breakdown Spectroscopy (CF-LIBS) employed for the elemental analysis of major and trace elements. It is also illustrated that LIBS a more powerful technique for compositional analysis of samples such as geological samples without consuming too much time. LIBS can contemplate a simple analytic technique for the identification of elements present in the sample. It is also applied from small scale laboratories to a large scale industry.

ACKNOWLEDGEMENTS: We are thankful to National Center for Physics (NCP) Islamabad, Pakistan for the facilitation of experiment and guidance.

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