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Chemical Analysis of Thermoluminescent Colorless Topaz Crystal Using Laser-Induced Breakdown Spectroscopy

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Abstract: We present results of calibration-free laser-induced breakdown spectroscopy (CF-LIBS) and energy-dispersive X-ray (EDX) analysis of natural colorless topaz crystal of local Pakistani origin. Topaz plasma was produced in the ambient air using a nanosecond laser pulse of width 5 ns and wavelength 532 nm. For the purpose of detection of maximum possible constituent elements within the Topaz sample, the laser fluences were varied, ranging 19.6–37.6 J·cm^{−2} and optical emission from the plasma was recorded within the spectral range of 250–870 nm. The spectrum obtained has shown the presence of seven elements viz. Al, Si, F, O, H, Na and N. Results shows that the fluorine was detected at laser fluence higher than 35 J·cm^{−2} and plasma temperature of >1 eV. Al and Si were found as the major compositional elements in topaz crystals. The ratios of concentrations of Al and Si were found as 1.55 and 1.59 estimated by CF-LIBS and EDX, respectively. Furthermore, no impurity was found in the investigated colorless topaz samples.

Keywords: CF-LIBS; energy-dispersive x-ray; topaz crystal; topaz plasma; laser fluence

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1. Introduction

Topaz is a popular silicate mineral (Al₂SiO₄ (F,OH)₂) and is naturally found in a wide range of colors and colorless forms. Compared to other existing commercial materials, topaz is the hardest material, physio-chemically resistant to weathering, and possesses thermoluminescent characteristics [1]. Natural colorless topaz is largely utilized in jewelry, and the irradiation process is commonly employed to artificially induce colors in it [2]. In the jewelry industry, artificial methods are employed to induce colors in topaz, which include (i) irradiation with neutron, electrons and gamma rays followed by low-temperature annealing, (ii) colored metal oxide coating and (iii) heat treatment in different chemical atmospheres [3,4].

The thermoluminescent property makes topaz potentially an important candidate for its use as a thermoluminescent dosimeter (TLD) [5]. This property is exhibited by the insulators or semiconductors in which ionizing radiations are absorbed and remain trapped within the localized defects for a sufficiently long time. On thermal heating thermally heated, these materials emit the previously absorbed radiations and show a thermoluminescence character. The radiation trapping defect-sites in such crystals either could be due to the presence of extrinsic impurities or intrinsic defects such as lattice vacancies and interstitials [6]. High-energy TLD based on topaz crystals has been developed previously [7–11]. The response of fabricated TLD strongly depends on the concentration of transition metals

(Ti, V, Cr, Mn, Fe, and Cu), present as impurities in the topaz crystals or intrinsic defects, such as lattice vacancies and interstitials [3,6]. The concentration of these elemental impurities defines the performance of TLD; therefore, precise measurement of these impurities is crucial. The techniques of X-ray powder diffraction (XRD), energy-dispersive X-ray (EDX), X-ray fluorescence (XRF), inductively coupled plasma mass spectrometry (ICP-MS), atomic absorption spectroscopy (AAS), and Raman spectroscopy are applied for trace element detections in a material.

Laser-induced breakdown spectroscopy (LIBS) is a powerful alternative analytical method having with few advantages over the conventional analytical techniques, such as simultaneous identification of elements, the requirement of nominal or no prior sample preparation, in situ analysis, the capability of analyzing liquid, gas and solid samples, fast response, identification of lighter elements, element identification in real time and low detection limit down to ppm or even better [12]. This method is straightforward, utilizing plasma from the probed sample, irradiated by a laser pulse of sufficient fluence. The characteristic spectral emission from the plasma gives elemental identification within the sample [13]. From the very first robust demonstration of the LIBS instrumentation on the surface of planet Mars [14], in order to carry out a qualitative analysis of minerals found on the Mars planet by Vadillo and Laserna in 1996, LIBS has had been established as a sensible route for qualitative and quantitative analysis for elemental and compositional analysis [15]. Later on, LIBS was used to investigate a variety of geo-materials [16–19]. This technique was also employed to identify emerald produced by different synthetic processes [20]. Similarly, several LIBS applications for terrestrial and extra-terrestrial geomaterials have been reported to date [21,22].

LIBS utilizes calibration [23], calibration-free [24], and multivariate methodologies [25] to perform quantitative analysis of samples under investigation. In the calibration method, for the reference elements, calibration curves are drawn, and LIBS signals of different elements are compared with the corresponding curves. However, a running error due to the matrix effect and the appearance of several calibration curves in the case of multiple elements analysis makes this approach rather less attractive [26,27]. On the other hand, in the case of calibration-free analysis, both the intensity of the spectral lines and calculated plasma parameters, the temperature (T_e) and density (n_e), are used in the plasma model for quantification and in this procedure, uncertainties of matrix effect are ruled out [28,29]. In multivariate analysis, statistical and mathematical approaches are adopted for quantification and classification purposes [30].

Calibration-free laser-induced breakdown spectroscopy (CF-LIBS) has made possible to quantify the major and minor constituting elements of alexandrite crystal, and lighter element, like beryllium (Be), which were not easily detectable by several other techniques [31]. This technique is now frequently used to determine the number of trace elements and concentration of Cu and other elements in copper-rich minerals [32,33].

Topaz is technologically an impressive material for the scientific application, although the scientific community did not pay too much attention to explicitly explore it. Rossi et al. [34] studied colored topaz of Siberian origin using CF-LIBS and compared the results with electron microprobe analysis-wavelength dispersive spectrometry (EMPA-WDS) and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). For the major elements Si, Al, Be and B, the results were in close agreement. However, in this study, fluorine, present in considerable amounts in all-natural topaz, was not detected. This may be because of the low laser pulse energy used in order to avoid surface damage. The detection of fluorine and its compounds is very important since they are being employed in fire extinguishers, pharmaceutical and agrochemical products, dental care products, polymers, etc. This gives an impression to develop a superior analytical method to provide a fast and precise quantitative detection of fluorine and its compounds for a thorough investigation. The direct determination of fluorine with the LIBS is a challenging task owing to the fact of its low excitation efficiency. Based on elemental and molecular band emission criteria, many research groups have attempted to detect and quantify fluorine

using LIBS and chemometric techniques [35–38]. Contrary to the molecular band emission, LIBS analysis shows some strong spectral lines that may be employed for the detection of fluorine but with relatively weak emission intensity. in the spectral region between 623 and 780 nm.

This work aims to investigate the existence of impurities, if any, in the colorless topaz crystal that may help in the future to establish the role of impurities in the TL character of topaz. Another objective is to detect fluorine in topaz with LIBS. This study can help in the development of topaz crystals as a TLD and understanding the mechanism of its TL response. In the present work, results of a spectroscopic study of natural colorless topaz crystal collected from the Skardu region of the northern part of Pakistan are presented. The CF-LIBS approach, together with optimized plasma parameters, has been employed to determine the elemental composition in natural topaz. Both qualitative and quantitative analysis was performed, and the results were compared with the EDX. The plasma parameters were studied to search for an optimum value suitable for the possible detection of fluorine.

2. Materials and Methods

2.1. Geology of Sampling Area

Colorless topaz crystals were collected from the Nyit Bruk mine located in the Shigar Valley, situated at a distance of around 32 km from the Skardu Gilgit Baltistan region of Pakistan. The valley is known for its diverse reserves of minerals and gemstones [39]. This area comprises of two tectonic plates: (i) Karakorum plate and (ii) the Kohistan- Ladakh island arc (KLIA) with the intervening northern or Shyok Suture Zone. These plates largely contain metasediments and meta igneous rocks along with pegmatitic dikes belonging to the Karakorum Metamorphic Complex [40,41].

2.2. Sample Characteristics

Ten pieces of natural colorless topaz crystal were collected from the Nyit Bruk mine. Samples were of smaller size with few millimeter dimensions. Topaz crystals were washed multiple times and then dried for the purpose of removing surface impurities. Since LIBS is a minimally destructive technique and removes mass of only micro Gram-per pulse, so just small spots were recorded on the surface of crystals after the laser ablation. A photograph of the topaz crystals used in this study is shown in Figure 1.

Figure 1. Photograph of the investigated natural colorless topaz crystals collected from Nyit Bruk mine Skardu.

2.3. Experimental Arrangement

Details of the experimental setup used for the current study can be found elsewhere [42]. Briefly, a high-power Q-switched Nd:YAG laser (Brilliant-Quantel, Lannion, France), pulse width 5 ns and wavelength 532 nm, was used to produce a microplasma on the surface of the topaz crystal. The laser was capable of delivering maximum pulse energy of 500 mJ at 532 nm wavelength. The target was mounted on a rotatable stage to prevent crater formation and to provide a fresh surface to each laser shot. The spot size of the laser beam on the target surface was 0.10 ± 0.01 cm. The laser energy was

varied from 154 to 295 mJ by changing the delay time of the Q-switch and measured by an energy meter (Nova-Quantel, Cournon-d'Auvergne, France). The laser radiation was focused using a convex lens with a focal length of 10 cm. Plasma from a topaz target was produced for fluence values ranging from 19.6–37.6 J·cm^{−2}. The corresponding laser intensity range was from 1.0×10^9 to 1.9×10^9 W/cm². Radiations from the topaz plasma were routed to a spectrometer through an optical fiber (high—OH, core dia. 600 μm) with a collimating lens (0–45° field of view) positioned normal to the direction of the expansion of the plasma plume. A set of four spectrometers (Avantes, Apeldoorn, Holland) with a resolution of 0.06 nm, covering the wavelength range of 250–870 nm, was employed to record the spectra. Background signal was subtracted from original emission signal with the help of the AVASOFT 8.1.5 software. The gate delay and gate width were set at 2 and 10 μs, respectively, from the onset of firing the laser shot. The schematic arrangement of the LIBS setup used in the current experiment is given in Figure 2.

Figure 2. Schematic arrangement of the laser-induced breakdown spectroscopy (LIBS) detection system employed to perform the experiment.

2.4. Theoretical Background

CF-LIBS methodology [28] can be employed for quantitative analysis subject to the conditions that plasma is; (a) at local thermodynamic equilibrium (LTE), (b) optically thin, and (c) of stoichiometric ablation. The existence of LTE is an essential condition in the CF-LIBS method, and to accomplish this condition, atomic states should be populated and depopulated predominantly by electron collisions instead of radiation. This could happen if the electron number density (n_e) is sufficiently high. For a high collision rate, the required minimum value of n_e is given by the McWhirter criterion [43]:

$$n_e \geq 1.6 \times 10^{12} (T_e)^{\frac{1}{2}} (\Delta E)^3, \quad (1)$$

where T_e and ΔE are electron temperature, and the energy difference between the states expected to be in LTE, the McWhirter criterion for LTE in transient and inhomogeneous plasma is necessary, but not sufficient condition. In order to check the existence of LTE, Cristoforetti et al. [44] have suggested another criterion. According to them, in time duration of the order of atoms/ions relaxation time, the diffusion length (D_λ) should be ten times less than the characteristic variation length (d) of electron number density and temperature in the plasma. Generally, the value of $d \approx fu/(dT(x)/dx)$ is considered as plasma diameter or fraction of it. In this expression, $T(x)$ is electron temperature at position x in

plasma, and $dT(x)/dx$ shows the variation in temperature with position within the plasma. D_λ (cm) can be estimated from the following expression:

$$D_\lambda = 1.4 \times 10^{12} \times \left(\frac{(k_B T)^{3/4}}{n_e} \right) \times \left(\frac{\Delta E}{M_A f_{12} < \bar{g} >} \right)^{1/2} \times \exp \left[\frac{\Delta E}{2k_B T} \right] \quad (2)$$

where ΔE (eV), $k_B T$ (eV), n_e (cm^{-3}), M_A , f_{12} , and $< \bar{g} >$ are upper-level energy, plasma temperature, electron number density, atomic mass, oscillator strength and gaunt factor, respectively.

To verify the condition of optically thin plasma, the intensity ratio method can be used given by the following expression [45]:

$$\frac{I_1}{I_2} = \frac{\lambda_2 A_1 g_1}{\lambda_1 A_2 g_2} \exp \left[-\frac{E_1 - E_2}{k_B T} \right] \quad (3)$$

where I_1 and I_2 are experimentally measured intensities of the selected lines having wavelengths λ_1 and λ_2 , whereas A_1 , A_2 , g_1 , g_2 , E_1 , E_2 , k_B and T are the transition probabilities, statistical weights and upper-level energies corresponding to lines 1 and 2, Boltzmann constant and temperature, respectively. The values of the upper energy level of a couple of selected lines could be either the same or very close to each other. The intensity ratio can be estimated with the help of Equation (3) by inserting the values of atomic parameters of selected pairs of atomic emission lines.

For quantification of multi-elemental materials, the plasma plume should represent the sample composition (stoichiometric ablation) and is possible for the laser intensity of $10^9 \text{ W} \cdot \text{cm}^{-2}$ at the target surface [46]. Using a laser intensity $>10^9 \text{ W} \cdot \text{cm}^{-2}$ can fairly justify the condition of stoichiometric ablation.

In the CF-LIBS technique, the atomic number density of neutral species can be found by using the following equation [28,29]:

$$N_x^i = \frac{I \lambda U_x^i(T_e)}{A_{bi} g_b} \left(4 \times 10^{14} \right) e^{\left(\frac{E_b}{k_B T_e} \right)} \quad (4)$$

where, λ , I , $U_x^i(T)$, T_e , E_b , A_{bi} and g_b are wavelength, intensity, the partition function of the neutral species, electron temperature, upper-level energy, transition probability and statistical weight, respectively. The Saha equation given by the expression below is used to calculate the density number of ionized species [47]:

$$N_x^{ii} = 2(N_x^i)(n_e^{-1}) \left(6.04 \times 10^{21} \right) \left(T_e^{\frac{3}{2}} \right) \left(\frac{U_x^{ii}(T_e)}{U_x^i(T_e)} \right) \left(\frac{-\chi_i}{k_B T_e} \right), \quad (5)$$

where, N_x^i , $U_x^{ii}(T_e)$, χ_i are number density of neutral atoms, partition functions of ionized atoms at calculated plasma temperature, and ionization potential. Aggregate relative atomic number density of elements is obtained by adding neutral and ionized atomic number densities obtained from Equations (4) and (5):

$$N_x = N_x^i + N_x^{ii} \quad (6)$$

The weight of each element in the multi-elemental sample can be estimated by multiplying the relative atomic number density of each element with their corresponding atomic weight ($WA_x \times N_x$) and weights so obtained were summed together ($SH_x WA_x \times N_x$). Relative weight percentages of each element in the sample are then estimated as follows:

$$\text{Weight percentage}_x = \frac{WA_x \times N_x}{SH_x (WA_x \times N_x)} \times 100 \quad (7)$$

3. Results and Discussion

3.1. Qualitative Analysis

At low fluence values, only a few low-intensity lines of neutral atoms were present. In order to detect the emission lines of different elements present in the topaz, the laser fluence was optimized. These lines were recognized through a comparison of the experimentally observed wavelength lines to the available online database, managed by the National Institute of Science and Technology (NIST), USA [48]. At higher fluence $37.6 \text{ J} \cdot \text{cm}^{-2}$, the maximum number of emission lines were present in the spectra. To clearly understand and classify the emission lines, the spectrum was broken into smaller parts, which are displayed in Figure 3.

Figure 3. Optical emission spectra from laser-induced plasma of natural colorless topaz crystal obtained in the spectral range of (250–870) nm at a laser fluence of $37.6 \text{ J} \cdot \text{cm}^{-2}$.

The neutral atoms lines are represented by I and those of ionized atoms by II. The lines identified show the presence of aluminum, silicon, oxygen, nitrogen, hydrogen, sodium and fluorine in the topaz crystals. The spectrum is comprised of ten Si-I and four Si-II lines, thirteen Al-I and six Al-II lines, fifteen N-I and five N-II lines, three O-I and a single line of each H, F-I and Na-I, and gives a clear manifestation of the chemical composition of topaz. For the laser ablation in the ambient air, there is a great possibility for nitrogen in the spectra, as observed previously using the same spectrometer [49]. The possible reasons for the Na line in the spectra at a higher laser fluence value of $37.6 \text{ J} \cdot \text{cm}^{-2}$ could be either due to; (i) small impurities in topaz crystals or (ii) contamination from human touch and experimental atmosphere.

Fluorine detection with the LIBS in solid samples is a challenging task. The strongest and the most persistent emission lines of neutral fluorine within the spectral range of 200–900 nm are laying at around 685 and 703 nm [36]. The upper energy levels of transition for these lines are at 14.5 and 14.7 eV, respectively. To be able to observe the fluorine emission line, we worked with the plasma produced at a higher laser fluence beyond $33.1 \text{ J}\cdot\text{cm}^{-2}$. The emission line of neutral fluorine at 685.46 nm was appeared at $35.4 \text{ J}\cdot\text{cm}^{-2}$, showing an increase in intensity as fluence reaches $37.6 \text{ J}\cdot\text{cm}^{-2}$ (see Figure 4).

Figure 4. Emission line spectra in the region of interest showing the appearance of the F-I line at 685.46 nm from topaz plasma induced at fluence values in the range of $28.5\text{--}37.5 \text{ J}\cdot\text{cm}^{-2}$.

It is noteworthy to mention that the strong emission line at 703.97 nm could not be assigned to F-I because this line was initially present at low fluence, and it resembles more closely the Al-II line.

Further, to observe the effects of plasma parameters on emission lines, both electron temperature (T_e) and electron number density (n_e) were determined. The emission of the F-I line around 685.46 nm became possible for $T_e \geq 11,975 \text{ K}$ and $n_e \geq 2.74 \times 10^{17} \text{ cm}^{-3}$ suggesting some threshold or minimum values of plasma parameters to possibly detect F-I lines. However, these values are annexed to this particular experiment and may vary otherwise.

3.2. Quantitative Analysis

For quantitative analysis, the CF-LIBS method [28] was used by strictly considering the conditions that plasma was; (a) at LTE, (b) optically thin, and (c) of stoichiometric ablation. To verify the validity of these conditions and subsequently use CF-LIBS methodology to determine the elemental concentration, the measurement of plasma parameters is described below.

3.2.1. Electron Temperature

Boltzmann plot method was employed to make an estimation of the electron temperature using the expression [50]:

$$\ln\left(\frac{I_{\lambda}^{ba}\lambda}{hcA_{ba}g_{ba}}\right) = \ln\left(\frac{N(t)}{U(t)}\right) - \frac{E_{ba}}{kT_e}, \quad (8)$$

where I_{λ}^{ba} , λ (nm), A_{ba} (s^{-1}), g_{ba} , $N(t)$, $U(t)$, E (eV) and T_e are the integrated line intensity, wavelength, transition probability, statistical weight of upper-level (b), total number density, partition function, the energy of the upper-level, Boltzmann constant, and electron temperature, respectively. By plotting $\ln\left(\frac{I_{\lambda}}{hcA_{ba}g_{ba}}\right)$ against the upper-level energy E , the electron temperature was calculated from the slope $-1/kT_e$ with a propagation error of about $\pm 5\%$. The error is mainly due to uncertainties of transition probabilities and integrated intensities of the spectral lines. For the Boltzmann plot, selected Al-I lines and their relevant spectroscopic parameters are listed in Table 1.

Table 1. Spectroscopic parameters of Al-I lines used to draw the Boltzmann plot.

Element	Wavelength λ (nm)	Transition Probability A (s^{-1})	Statistical Weight (k)	Upper-Level Energy E_k (cm^{-1})
Al-I	256.85	1.92×10^7	4	38,929.41
Al-I	257.60	3.60×10^7	6	38,933.97
Al-I	265.29	1.42×10^7	2	37,689.41
Al-I	266.07	2.84×10^7	2	37,689.41
Al-I	308.26	5.87×10^7	4	32,435.45
Al-I	309.26	7.29×10^7	6	32,436.80

The quantitative results are affected by the uncertainties in line intensities and broadening arising from self-absorption in the plasma. Intensities of identified lines of different elements in the spectrum have been corrected using the method described by Sun et al. [51] for the purpose of minimizing uncertainties and self-absorption. An internal reference line with negligible self-absorption of each species in the spectrum was selected, and the self-absorption coefficient for the reference line f_{λ_R} was assumed to be unity. A criterion for the selection of a reference line is to select the line with low transition probability A_{ba} or a high upper-level energy E_b . Al-I line at 265.29 nm was selected as the reference line, and the self-absorption coefficient f_{λ} of other spectral lines was calculated by using the following expression:

$$f_{\lambda} = \frac{I_{\lambda}^{ba} A_{mn} g_{mn}}{I_{\lambda_R}^{mn} A_{ba} g_{ba}} \exp\left[-\frac{E_m - E_b}{k_B T_e}\right] \quad (9)$$

where λ_R , $I_{\lambda_R}^{mn}$, A_{mn} , and g_{mn} are the wavelength, spectral line intensity, transition probability, and statistical weight of standard reference line related to the transition between energy levels m and n , while I_{λ}^{ba} , A_{ba} and g_{ba} are the spectral line intensity, transition probability and statistical weight of other spectral lines related to the transition between energy levels a and b . E_m and E_b are the upper-level energies of the internal reference line and other spectral lines, respectively and T_e is the electron temperature previously obtained from the Boltzmann plot without correction for self-absorption. Intensity correction was done by dividing the experimentally observed intensity of a line by the self-absorption coefficient f_{λ} as follows:

$$I_{\lambda_{corrected}}^{ba} = \frac{I_{\lambda}^{ba}}{f_{\lambda}} \quad (10)$$

After self-absorption correction, the intensities values were used in Equation (8), and the Boltzmann plot was re-plotted. T_e was obtained from the slope of the Boltzmann plot, and the process was repeated until a negligible difference in the temperature reached up, and a best-fit to the line was obtained. The Boltzmann plots for $37.6 \text{ J}\cdot\text{cm}^{-2}$ without and with self-absorption correction are shown in Figure 5a,b, respectively. With self-absorption correction, an excellent linear fit was obtained with an R^2 value of 99.9%, and the T_e values were $10,724 \pm 536 \text{ K}$ and $12,660 \pm 633 \text{ K}$ without and with correction of self-absorption, respectively. The correspondence T_e plot with self-absorption correction for the different fluence values is shown in Figure 5c. As expected, T_e values were increased by increasing the laser fluence.

Figure 5. Boltzmann plots drawn using Al-I lines at laser fluence $37.6 \text{ J}\cdot\text{cm}^{-2}$: (a) without and (b) with correction for self-absorption in the intensity of the spectral lines (c) variation of electron temperature with the laser fluence ranging ($19.6\text{--}37.6$) $\text{J}\cdot\text{cm}^{-2}$.

3.2.2. Electron Number Density

Stark broadened line profiles of well isolated spectral lines were used to determine n_e using the following simplified expression [43,52]:

$$n_e = \frac{1}{2} \Delta\lambda_{\frac{1}{2}} \times 10^{16} \quad (11)$$

where ω is Stark parameter, and its value was taken from the literature [53] $\Delta\lambda_{\frac{1}{2}}$ denotes full width at half maximum (FWHM) of Stark broadened line and its value was taken from Lorentzian fit made to the selected lines and a representative of Al-I line at 396.17 nm, is shown in Figure 6a. The value was corrected for instrumental width of 0.06 nm. The average value of n_e was obtained using the lines of Al-I at 257.60 and 396.17 nm, Si-I at 288.21 nm and N-I at 746.68 nm. The dependence of n_e on laser fluence is given in Figure 6b. The increase in n_e with laser fluence could be due to the coupling of more energy to the surface. Energy coupling leads to plasma heating and increases ionization, well consistent with the previous observation [54]. The average value of n_e calculated for the laser fluence $37.6 \text{ J}\cdot\text{cm}^{-2}$ was $3.08 \times 10^{17} \text{ cm}^{-3}$.

3.2.3. Local Thermodynamic Equilibrium (LTE)

LTE condition was verified using the McWhirter criterion given in Equation (1) [43]. For the Si-I line at 288.20 nm, the energy difference between states is $\Delta E = 4.3 \text{ eV}$. McWhirter criterion suggests that for plasma temperature of 12,660 K, a value of $n_e (\text{cm}^{-3}) \geq 1.4 \times 10^{16}$ would be required for LTE to existing. The McWhirter criterion was also verified for various

spectral lines of identified minor and major elements in emission spectra and the results indicated the existence of LTE condition.

In order to check the existence of LTE, another criterion suggested by Cristoforetti et al. [44] was also verified. For the calculation of diffusion length (D_λ), values of f_{12} , and $\langle \bar{g} \rangle$ were obtained from the NIST database and Cristoforetti et al., respectively [44,48]. For the selected emission lines of Si and Al, the calculated values of D_λ given in Table 2, were found to be 10 times less than the assumed characteristic variation length (d) of 2 mm. This result further validates the LTE assumption.

Figure 6. (a) Stark broadened line profile of Al-I line at 396.17 nm recorded for laser fluence of $37.6 \text{ J} \cdot \text{cm}^{-2}$ (b) Electron number density as a function of laser fluence.

Table 2. Spectroscopic parameters of the selected emission lines and calculated values of D_λ for the validation of local thermodynamic equilibrium (LTE) condition.

Element	Wavelength (nm)	Oscillator Strength f_{12}	M_A	$\Delta E(\text{eV})$	$\langle \bar{g} \rangle$	D_λ (mm)	$10D_\lambda$ (mm)
Si	288.20	1.62×10^{-1}	28.08	4.30	≈ 0.1	0.001	0.01
Al	396.19	1.16×10^{-1}	26.98	3.12	≈ 0.1	0.0006	0.006

3.2.4. Optically Thin Plasma

The intensity ratio method was used to verify the condition of optically thin plasma [45]. The two pair lines of Si-I at 250.73 and 251.65, 251.47 and 251.97 nm, and three pairs of Al-I lines at 256.86 and 257.80 nm, 265.32 and 266.10 nm, 308.37 and 309.43 nm were used. The intensity ratios calculated experimentally and theoretically using Equation (3) were 0.38 and 0.33, 1.31 and 1.35 for two pairs of Si-I lines and 0.41 and 0.36, 0.44 and 0.5, 0.57 and 0.56 for three pairs of Al-I lines, respectively. Both theoretical and experimental intensity ratios are close enough to consider that plasma was optically thin, and the self-absorption was not overwhelming. After correcting the line intensities with the help of the aforementioned self-absorption correction method using Equations (9) and (10), intensity ratios were again calculated, and results showed almost complete agreement between theoretical

and experimental intensity ratio values. This implies that the effect of self-absorption was reduced to a minimum value.

3.2.5. CF-LIBS Analysis

To quantify the elements identified in the topaz sample by CF-LIBS, the selection of emission lines was made according to the selection criteria mentioned in [28,29]. For measurement of Si concentration, Si-I lines at 250.73, 251.66, 251.97, 252.45, 252.89, 263.15, 288.21, 298.78 and 390.54 nm were selected, and for measurement of Al concentration, the Al-I lines at 257.60, 266.07 and 396.19 nm were used. The relevant spectroscopic parameters of these lines are listed in Table 3.

Table 3. Spectroscopic parameters of selected lines of Si-I and Al-I used for quantitative analysis of topaz crystals using the CF-LIBS method.

Element	Wavelength λ (nm)	Transition Probability A (s^{-1})	Statistical Weight (k)	Upper-Level Energy E_k (cm^{-1})
Si-I	250.73	5.47×10^7	5	39,955.05
Si-I	251.66	1.68×10^8	5	39,955.05
Si-I	251.97	5.49×10^7	3	39,760.28
Si-I	252.45	2.22×10^8	1	39,683.16
Si-I	252.89	9.04×10^7	3	39,760.28
Si-I	263.15	1.06×10^8	3	53,387.33
Si-I	288.21	2.17×10^8	3	40,991.88
Si-I	298.78	2.66×10^6	3	39,760.28
Si-I	390.55	1.33×10^7	3	40,991.88
Al-I	257.60	3.60×10^7	6	38,933.97
Al-I	266.07	2.84×10^7	2	37,689.41
Al-I	396.19	9.85×10^7	2	25,347.76

The number density of neutral and singly ionized atoms of Si and Al was calculated using Equations (4) and (5), respectively and the total number density of each species was obtained by summing the number density of neutral and singly ionized atoms of both of these elements. Calculated values of the number densities for each selected line of Si-I and Al-I are given in Table 4. The average number density of both the species was taken for calculating their concentration in the sample using Equation (7).

Table 4. Atomic number densities of neutral and ionized species of topaz crystals at a plasma temperature of $12,660 \pm 633$ K.

Element	Wavelength λ (nm)	Number Density of Neutral Species N_x^I (cm^{-3})	Number Density of Ionized Species N_x^{II} (cm^{-3})	Sum of Number Densities of Neutral and Ionized Species N_x (cm^{-3})
Si-I	250.73	2.29×10^{16}	3.67×10^{15}	2.66×10^{16}
Si-I	251.66	1.89×10^{16}	3.03×10^{15}	2.19×10^{16}
Si-I	251.97	2.75×10^{16}	4.40×10^{15}	3.19×10^{16}
Si-I	252.45	2.79×10^{16}	4.47×10^{15}	3.24×10^{16}
Si-I	252.89	2.87×10^{16}	4.59×10^{15}	3.32×10^{16}
Si-I	263.15	1.12×10^{17}	1.79×10^{16}	1.30×10^{17}
Si-I	288.21	4.47×10^{16}	7.16×10^{15}	5.18×10^{16}
Si-I	298.78	2.04×10^{16}	3.27×10^{15}	2.37×10^{16}
Si-I	390.55	1.28×10^{16}	2.06×10^{15}	1.49×10^{16}
Al-I	257.60	5.63×10^{16}	4.65×10^{15}	6.09×10^{16}
Al-I	266.07	7.77×10^{16}	6.42×10^{15}	8.41×10^{16}
Al-I	396.19	4.77×10^{16}	3.94×10^{15}	5.17×10^{16}

Oxygen is a constituent of topaz, but hard to determine its actual amount due to performing experiments in the ambient air. Similarly, the quantification of Na was also not performed as the detected line was a resonant line and is not allowed to use by the selection criteria. Only a single detected line of F was also not appropriate for quantitative analysis owing to high uncertainty associated with the determination of the concentration of a single line. Moreover, the upper energy level at 685.45 nm line of F-I is 14.5 eV, which is much higher than the upper-level energies of Al-I lines from 4.95 to 6.62 eV, and Si-I lines from 3.14 to 4.83 eV, thus makes it unsuitable for quantitative analysis. In the natural colorless topaz sample, the concentration of Al and Si in terms of weight percentage (Wt %) was found as 60.81 and 39.18%, respectively.

EDX analysis was also performed to make a comparison, and the EDX spectrum is given in Figure 7. The presence of Al, Si, O and F in the colorless topaz crystal was verified by the EDX, while N, H and Na were not detected in the sample. EDX analysis showed the concentration of Al, Si, O and F as 37.27, 23.41, 28.94 and 10.38% by weight percentage, as presented in Table 5. The concentrations of N and O were not calculated because EDX analysis showed no N in the topaz sample, and its presence in the LIBS spectrum arises from the ambient air. Since all these four elements were not quantified by CF-LIBS, so it is hard to draw a comparison of elemental concentration of these elements; however, the ratio of concentrations of Al and Si were calculated. The ratio of Al/Si for CF-LIBS and EDX was found to be 1.55 and 1.59, respectively. Results obtained by these two techniques show a reasonably good agreement and are summarized in Table 5.

Figure 7. Energy dispersive X-ray (EDX) spectrum of topaz crystals.

Table 5. Elemental compositions of different elements present in topaz crystals measured by CF-LIBS and EDX techniques.

Element	Formula (Wt. %) [55]	CF-LIBS (Wt. %)	EDX (Wt. %)	Al/Si (Formula)	Al/Si (CF-LIBS)	Al/Si (EDX)	Relative Error
Al	29.61	60.81	37.27	1.92	1.55	1.59	±2.52
Si	15.41	39.18	23.41				
O	43.02	-	28.94				
F	11.47	-	10.38				
Na	-	-	-				
N	-	-	-				
H	0.50	-	-				

4. Discussion

Qualitative results obtained with the help of the LIBS have shown the presence of all the elements in the chemical formula of topaz, $\text{Al}_2\text{SiO}_4(\text{F,OH})_2$, and additionally, N and Na were also detected. The absence of N and Na in the EDX spectrum has confirmed that the presence of N lines in the LIBS spectrum was due to air, and the Na line could possibly be due to surface contamination. These results prove the chemical purity of colorless topaz crystal. Colorless topaz crystal of Pakistani origin was developed as a TL dosimeter, and its radiation monitoring efficacy and detection efficiency were found comparable to a high-energy TL dosimeter, such as TLD-100 [7,8]. Similarly, natural colorless topaz crystals from Brazil have shown better sensitivity to ultra-violet and gamma radiations compared to colored topaz crystals [6,56]. The current study suggests that the TL response of colorless topaz crystals might be due to intrinsic defects rather than the presence of impurities [3,11]. However, we cannot rule out completely the presence of impurities in concentrations less than the detection limits of the LIBS and EDX.

Quantitative results described in Table 4 give the realization that colorless topaz crystal is free from impurity except for environmental contamination. In a CF-LIBS study made by Rossi et al. [30], the pale yellow and pale green topaz has shown the presence of Fe and Mn, which are believed to be the reason for the colors of topaz. CF-LIBS technique could quantify only two major elements of topaz, namely Al and Si, while the EDX analysis has quantified all the elements present in the chemical formula of topaz except hydrogen. Hydrogen cannot be detected with the help of the EDX due to the limitation of this technique. The ratio of weight percentage of Al to Si as measured by CF-LIBS and EDX technique was 1.55 and 1.59, respectively, as compared to 1.92 according to the chemical formula of pure topaz [55].

This study strongly validates the effectiveness of the LIBS to detect main constituents in the sample and other lighter elements, such as hydrogen. For quantitative analysis, the CF-LIBS technique has few limitations, such as unavailability of the spectral lines of some elements in the multi-elemental sample and low sampling mass (ablated mass per laser shot $\approx$ nanogram). The capability of CF-LIBS to quantify major elements in the sample is quite good proved by the analogous ratio values of Al and Si concentrations obtained by the EDX and CF-LIBS techniques.

5. Conclusions

In summary, LIBS emission spectra from topaz plasma produced at various laser fluence values showed all the constituents present in the chemical formula viz., Al, Si, O, F and H. Nitrogen and Na spectral lines were identified only for the higher fluence value $37.6 \text{ J}\cdot\text{cm}^{-2}$. EDX analysis also verified elemental composition with the exception of H, N and Na. Nitrogen lines are expected from ambient air, and the feeble Na line could possibly be from surface contamination. With the help of CF-LIBS analysis, the concentration of major elements, Al and Si, was estimated to be 60.81 and 39.18 wt %, respectively. At the same time, EDX analysis showed relative concentrations of Al, Si, O and F as 37.27, 23.41, 28.94 and 10.38 wt %, respectively. The ratio of relative concentrations of Al and Si as measured by CF-LIBS and EDX were found to be 1.55 and 1.59, respectively. This study could be beneficial in understanding the role of impurities in natural topaz and the capability of the LIBS for qualitative and quantitative analyses of gemstones and minerals.

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