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Investigation of matrix effects on laser-induced plasmas

TESI DI LAUREA MAGISTRALE IN
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Author: **Lorenzo Bonelli**

Student ID: 10769638
Advisor: Prof. Christoph Gerhard
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Abstract

This thesis investigates and characterizes matrix effects in Laser-Induced Breakdown Spectroscopy (LIBS), with particular focus on how crystal structure and material phase influence plasma properties.

To this end, different structural forms of SiO_2 and Al_2O_3 were studied. For SiO_2 , α -crystalline quartz and amorphous fused silica (Infrasil) were analyzed, while for Al_2O_3 the comparison involved α -crystalline sapphire and ceramic polycrystalline alumina. These materials were selected to isolate the role of structural order and phase composition in plasma formation and evolution.

LIBS measurements were performed under controlled experimental conditions, and the acquired spectra were analysed using the Calibration-Free LIBS (CF-LIBS) approach. By systematically varying the gate width and the delay time, the temporal evolution of the plasma temperature $T(t)$ and electron number density $n_e(t)$ was reconstructed.

Comparing the plasma parameters obtained for the different material structures enabled assessing the time-dependent contribution of matrix effects and their correlation with crystallinity and material phase.

This work contributes to a deeper understanding of the physical origin of matrix effects in LIBS and provides insights to improve the robustness of CF-LIBS quantitative analysis.

Keywords: LIBS, CF-LIBS, matrix effects, plasma diagnostics, laser–matter interaction, laser–plasma interaction, LTE.

Abstract in lingua italiana

Questo lavoro di tesi è volto allo studio e alla caratterizzazione degli effetti di matrice nella tecnica Laser-Induced Breakdown Spectroscopy (LIBS), con particolare attenzione all'influenza dell'ordine cristallino e della fase dei materiali sulle proprietà del plasma.

A tal fine sono state studiate differenti forme strutturali di SiO_2 e Al_2O_3 . Per SiO_2 sono stati analizzati quarzo α cristallino e silice fusa amorfa (Infrasil), mentre per Al_2O_3 il confronto ha coinvolto zaffiro (α - Al_2O_3 monocristallino) e allumina policristallina ceramica. Questi materiali sono stati selezionati per isolare il ruolo dell'ordine strutturale e della composizione di fase nella formazione e nell'evoluzione del plasma.

Le misure LIBS sono state eseguite in condizioni sperimentali controllate e gli spettri acquisiti sono stati analizzati mediante l'approccio Calibration-Free LIBS (CF-LIBS). Variando sistematicamente il tempo di ritardo e la larghezza del gate, è stata ricostruita l'evoluzione temporale della temperatura del plasma $T(t)$ e della densità elettronica $n_e(t)$.

Il confronto dei parametri di plasma ottenuti per le diverse strutture dei materiali ha permesso di valutare il contributo tempo-dipendente degli effetti di matrice e la loro correlazione con la cristallinità e la fase del materiale.

Questo lavoro contribuisce a una comprensione più profonda dell'origine fisica degli effetti di matrice in LIBS e fornisce indicazioni per migliorare la robustezza dell'analisi quantitativa CF-LIBS.

Parole chiave: LIBS, CF-LIBS, effetti di matrice, diagnostica del plasma, interazione laser-materia, interazione laser-plasma, LTE.

Contents

Abstract	i
Abstract in lingua italiana	iii
Contents	v
Introduction	1
1 Laser-Induced Breakdown Spectroscopy	3
1.1 Experimental principle of LIBS	4
1.2 Physical processes involved in LIBS	5
1.2.1 Laser-matter interaction and ablation	6
1.2.2 Laser-plume coupling and plume expansion	7
1.2.3 Optical emission and radiation transport	8
1.3 Influence of experimental parameters	11
1.3.1 Laser parameters and breakdown threshold	11
1.3.2 Temporal parameters: delay time and gate width	12
1.4 Spectral features and line broadening mechanisms	13
1.4.1 Line intensity and self-absorption	14
1.4.2 Stark effect and other broadening mechanisms	15
1.5 Introduction to LIBS data analysis	16
2 CF-LIBS	19
2.1 Physical principles of CF-LIBS	19
2.1.1 Forward model and spectral matching	20
2.1.2 Multi-elemental equilibrium plasma model	20
2.1.3 Charge neutrality and choice of unknowns	21
2.2 Physical assumptions	21
2.2.1 Stoichiometric ablation	22

2.2.2	Accuracy of spectroscopic data	22
2.2.3	Spatial homogeneity and inhomogeneous models	22
2.2.4	Local thermodynamic equilibrium (LTE)	23
2.2.5	Optical thinness and self-absorption	23
2.3	Saha–Boltzmann equation	25
2.3.1	Boltzmann distribution and Boltzmann plot	25
2.3.2	Ionization balance and Saha–Eggert equation	26
2.3.3	Saha–Boltzmann plot	27
2.3.4	Practical considerations for regression-based diagnostics	27
2.3.5	Beyond the optically thin approximation	27
2.4	Loop scheme and procedure	28
2.4.1	Initialization and line selection	28
2.4.2	Outer iteration loop: parameter estimation	29
2.4.3	Inner loop: spectral synthesis and mismatch evaluation	29
2.4.4	Stopping criteria and consistency checks	30
2.5	Experimental constraints and uncertainty sources	30
2.5.1	SNR, averaging, and impact on minor/trace elements	31
2.5.2	Temporal gating and choice of acquisition window	31
2.5.3	Line measurement: integration, Voigt fitting, and instrumental broad- ening	32
2.5.4	Pre-processing and instrumental corrections	33
2.5.5	Uncertainty propagation: closure, self-absorption, and plasma size .	34
2.6	Motivation	35
3	Matrix effects	37
3.1	Conceptual framework: where matrix effects enter the LIBS chain	37
3.2	Material-driven origins of matrix effects	38
3.2.1	Optical properties and laser–solid coupling	38
3.2.2	Thermophysical properties and ablation efficiency	38
3.2.3	Microstructure and surface condition: roughness, porosity, and grain boundaries	38
3.2.4	Plasma-stage matrix effects: shielding, inhomogeneity, and self- absorption	39
3.3	How experimental parameters modulate matrix effects	39
3.3.1	Laser fluence and irradiation regime	39
3.3.2	Ambient gas and confinement	39
3.3.3	Temporal gating and choice of the analysis window	40

	Contents	vii
3.4	Sample set and complementary characterization (XPS)	40
3.4.1	Sample set	40
3.4.2	Material properties relevant to matrix effects	40
3.4.3	XPS: surface composition and contamination	40
3.5	Implications for the present thesis and link to the Results chapter	43
4	Results and analysis	45
4.1	Cleaning analysis	45
4.2	Fluence analysis	46
4.3	Line selection	46
4.4	Data acquisition	48
4.5	Temporal sampling	48
4.6	Plasma length	49
4.7	Results	49
4.8	LTE screening	51
4.9	Discussion	51
4.9.1	Fit model and statistical metric.	52
4.9.2	Electron density evolution	53
4.9.3	Temperature evolution	54
4.9.4	SiO ₂ : quartz vs Infrasil	54
4.9.5	Al ₂ O ₃ : sapphire vs alumina ceramic	55
4.9.6	Neutral-to-ionic line statistics	55
4.10	Initial Temperature analysis	56
4.10.1	SiO ₂	57
4.10.2	Al ₂ O ₃	59
5	Conclusions	61
5.1	Main findings	61
5.2	Implications for CF-LIBS practice	63
5.3	Outlook and future developments	63
5.3.1	Extending the material set to disentangle optical and thermophys- ical drivers	63
5.3.2	Improved initial-temperature experiments and explicit temperature-dependent material properties	64
5.3.3	Towards more predictive modelling and improved robustness	65
	Bibliography	67

A	Appendix A: Experimental apparatus	71
A.1	CORALIS system overview	71
A.2	LIBS excitation source	71
A.3	Sample chamber and positioning system	73
A.4	Optical emission collection and spectrometer	74
A.5	Detection system and timing control	74
A.6	Control software and data handling	74
A.7	Operating conditions	75
	List of Figures	77
	List of Tables	79
	List of Symbols	81

Introduction

Laser-Induced Breakdown Spectroscopy (LIBS) is an atomic emission spectroscopy technique based on the generation of a transient plasma by laser ablation. The interaction between a high-energy laser pulse and the sample surface induces rapid vaporization and ionization of matter, producing a microplasma whose optical emission carries information on the elemental composition of the target. Under suitable conditions, LIBS can therefore provide both qualitative identification and quantitative determination of the sample constituents.

In recent years, interest in LIBS has increased due to its versatility, minimal or no sample preparation, and fast acquisition. Nevertheless, quantitative analysis remains *challenging*. In LIBS, sampling and excitation are intrinsically coupled: the plasma is generated directly from the material and acts simultaneously as the radiation source and as an absorbing and emitting medium. As a consequence, the measured spectral signal depends not only on elemental concentrations, but also on plasma properties and on the laser-matter interaction, which is governed by the material thermophysical and optical properties in addition to its chemical composition.

This scenario leads to the so-called matrix effects. In LIBS, matrix effects denote all variations of the analytical signal that arise from changes in plasma formation and evolution and are not solely determined by the analyte concentration. Differences in thermal transport, optical absorption, and structural order can affect ablation efficiency and plasma conditions, ultimately influencing line intensities, line shapes, and their temporal evolution. Therefore, materials sharing the same empirical formula but exhibiting different crystal structure or phase may produce systematically different LIBS spectra and plasma parameters.

Within this framework, Calibration-Free LIBS (CF-LIBS) was introduced to mitigate matrix effects by relying on a physics-based description of plasma emission [1]. Under suitable assumptions, CF-LIBS enables quantitative analysis without external calibration curves by retrieving key plasma parameters directly from the measured spectra and using them to infer elemental concentrations.

The interest in LIBS, and especially in CF-LIBS, has grown substantially over the last decade [2], and several strategies have been proposed to improve analytical accuracy [3]. However, a systematic investigation aimed at isolating and quantifying the contribution of crystal structure and material phase to matrix effects in LIBS is still limited.

To this end, this thesis aims to disentangle the role of chemical composition from that of structural order and phase by studying materials with the same empirical formula but different structural forms [4]. The comparison is performed for SiO_2 between α -crystalline quartz and amorphous fused silica (Infrasil), and for Al_2O_3 between α -crystalline sapphire and ceramic polycrystalline alumina. This approach minimizes compositional variability and focuses on how structural differences affect plasma generation and dynamics.

The main objective is to reconstruct the temporal evolution of the plasma temperature $T(t)$ and the electron number density $n_e(t)$ and to compare these quantities across the investigated materials in order to identify systematic trends. By varying the detection delay and the gate width, different stages of plasma evolution are probed, enabling a time-resolved characterization of plasma parameters.

The thesis is organized as follows. Chapter 1 introduces the principles of LIBS from both an experimental and physical point of view along with spectra diagnostic tools. Chapter 2 presents the CF-LIBS methodology adopted in this work, including the underlying assumptions, the numerical procedure, and the uncertainty sources relevant to quantitative analysis. Chapter 3 discusses matrix effects in LIBS and summarizes the material properties relevant to laser–matter interaction. Finally, in Chapter 4 the experimental results are presented and discussed, highlighting the influence of crystallinity and phase on plasma evolution and on CF-LIBS robustness.

1 | Laser-Induced Breakdown Spectroscopy

Laser-Induced Breakdown Spectroscopy (LIBS), also referred to by some authors as Laser-Induced Plasma Spectroscopy (LIPS), is an analytical technique employed for the characterization of matter. The method relies on the interaction between a pulsed laser beam and the material under investigation. When the laser irradiance exceeds a given threshold, this interaction may result in the formation of a laser-induced plasma (LIP). The plasma emits electromagnetic radiation during its evolution, and this emission constitutes the measurable signal in LIBS experiments. Then the emitted light is collected by a spectrometer and analysed. Subsequently, the analytical information is encoded in the spectral distribution of the radiation, since each chemical element is associated with a characteristic set of emission wavelengths that can be regarded as a spectral fingerprint.

LIBS belongs to the broader class of Atomic Emission Spectroscopy (AES), as the detected signal originates from radiative de-excitation processes involving atoms and ions within the plasma. Therefore, each element is characterized by a specific set of emission lines, which enables a qualitative identification of the species present in the sample. Nevertheless, the scope of LIBS is not restricted to qualitative analysis. By adopting appropriate analytical strategies and under suitable experimental conditions, it is also possible to extract quantitative information from the recorded spectra. Among the available approaches, calibration-free LIBS (CF-LIBS), which will be discussed in detail in chapter 2, represents one of the most commonly adopted methods, although alternative quantitative techniques can also be applied.

One of the main practical features of LIBS is that little to no sample preparation is required, which allows the technique to be considered as a direct analysis method. Furthermore, the amount of material ablated during a single laser shot is typically limited, so that the technique is often described as quasi-non-destructive. These characteristics are particularly relevant when dealing with delicate, valuable, or non-replaceable samples.

LIBS can be applied to samples in solid, liquid, or gaseous states, provided that suitable

experimental configurations are adopted. The capability of performing remote or stand-off measurements has enabled its use in contexts where direct access to the sample is not possible. A notable example is represented by planetary exploration missions [5], in which LIBS has been successfully employed for the remote analysis of extraterrestrial materials. More generally, this versatility has led to the adoption of LIBS in a wide range of fields including materials science, the nuclear industry [6], industrial quality control [7], environmental studies [8], and cultural heritage research [9].

In the following sections, LIBS will first be introduced from a schematic point of view, focusing on its basic components and their typical experimental implementation. The physical processes governing plasma formation and emission will then be outlined. Analytical methodologies will not be discussed in detail within this chapter, as they will be specifically addressed in chapter 2.

1.1. Experimental principle of LIBS

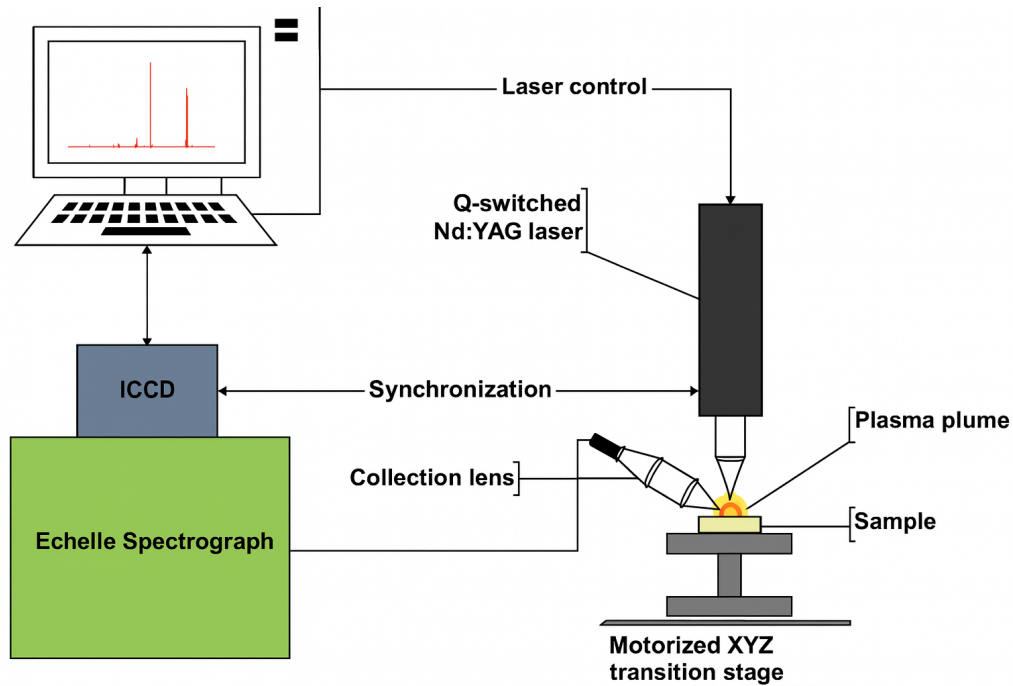


Figure 1.1: Schematic representation of a typical LIBS experimental setup [10].

The fig. 1.1 schematically illustrates a typical LIBS experimental setup. This system is required to perform two main operations. The first one is the emission of a pulsed laser beam onto the sample surface, while the second one concerns the collection of the emitted radiation for spectral analysis. The latter can be performed with both spatial resolution,

by selecting different positions on the sample, and temporal resolution, by controlling the time window during which the spectrometer acquires the signal.

The laser source is generally a Q-switched solid-state Nd:YAG laser operating at a wavelength of 1064 nm. The laser pulse is directed towards the sample and focused by means of an optical system based on lenses. The characteristics of this optical arrangement determine the laser spot size on the surface and, consequently, the irradiance delivered to the material.

The sample is typically mounted on a movable stage, which allows the irradiation spot to be changed within successive laser shots. This approach is adopted to limit the effects of crater formation and to enable surface or near-surface analysis. Depending on the specific experimental configuration, the sample chamber can be filled with a selected background gas or operated under controlled pressure conditions.

The radiation emitted by the plasma is collected by a system of lenses and collimators and then transported to the spectrometer through an optical fiber. To achieve high spectral resolution over a broad wavelength range, an Echelle spectrometer is commonly employed. Time-resolved detection is instead achieved by using an Intensified Charge-Coupled Device (ICCD).

The synchronization between the laser system and the detection unit is a critical aspect of the experimental setup. The characteristic timescales of plasma evolution, for nanosecond laser pulses, are typically on the order of hundreds of nanoseconds. As a consequence, the delay between the laser pulse and the opening of the ICCD gate, as well as the gate width itself, must be accurately controlled, often with sub-nanosecond precision.

This section has outlined the general structure and functioning of a LIBS setup. The specific experimental apparatus employed in this work is described in detail in chapter A. The discussion will now move to the physical processes occurring during a LIBS measurement.

1.2. Physical processes involved in LIBS

Before introducing the physical description, it is important to underline that several phenomena take place during a LIBS measurement. As schematically shown in fig. 1.2, the process involves laser-matter interaction, material ablation, ionization, plume dynamics, shock wave formation, absorption, emission, and radiative transport. Therefore, it is evident that a fully self-consistent first-principles description of the entire process is not feasible. Nevertheless, each stage of the evolution can be described by appropriate physical models, which allow the underlying mechanisms to be discussed in a coherent

manner.

In the following, the discussion is restricted to solid targets irradiated by nanosecond laser pulses. Although LIBS can also be performed on liquids and gases, and with picosecond or femtosecond laser sources, this thesis focuses exclusively on solid samples and nanosecond pulses. For this reason, a more general description goes beyond the scope of this thesis.

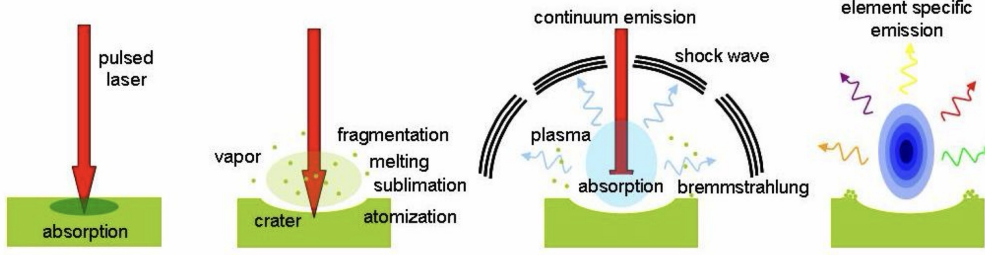


Figure 1.2: Schematic representation of the physical processes occurring during a LIBS measurement.

1.2.1. Laser–matter interaction and ablation

The first phenomenon involved is the transfer of energy from the laser pulse to the sample. A key parameter describing this interaction is the laser irradiance. The average irradiance can be expressed as

$$I_L \propto \frac{\Phi_p}{\tau_p}, \quad (1.1)$$

where Φ_p is the pulse fluence and τ_p is the pulse duration. This relation shows that both the energy delivered per pulse and the pulse duration contribute to the heating of the material.

Once the laser radiation enters the sample, its propagation along the optical axis can be described by the Lambert–Beer law [7]

$$I_L(z, t) = I_L(0, t) (1 - R_s) e^{-\mu z}, \quad (1.2)$$

where R_s is the surface reflectivity and μ is the optical absorption coefficient of the material. This expression is written in a one-dimensional geometry along the z direction, since the optical penetration depth, which can be approximated as $\delta \sim \mu^{-1}$, is typically much smaller than the laser focal spot diameter.

Assuming that the absorbed optical energy is fully converted into heat, the temperature evolution inside the material can be described by the one-dimensional heat conduction

equation with the laser acting as a source term [7]

$$\rho c_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial z} \left(k \frac{\partial T}{\partial z} \right) + \mu I_L(z, t), \quad (1.3)$$

where ρ is the mass density, c_p the specific heat, k the thermal conductivity, and $\mu I_L(z, t)$ represents the volumetric power density deposited by the laser.

When the temperature exceeds the phase transition threshold, material removal occurs in the form of vapour and particulates. The mass removal rate can be described as [11]

$$\dot{m} = \frac{\rho d_T}{\tau_p}, \quad (1.4)$$

where d_T is the effective thermal penetration depth and τ_p is the laser pulse duration. The ablated material subsequently undergoes ionization, leading to plasma formation.

1.2.2. Laser–plume coupling and plume expansion

During the initial stages of mass emission, ionization of the ablated material is strongly influenced by Inverse Bremsstrahlung (IB) absorption. In this process, laser energy is transferred to free electrons, enhancing collisional processes and promoting further ionization. The IB absorption coefficient can be written as [12]

$$\alpha_{\text{IB}} \propto \frac{n_e^2 \sqrt{\omega^2 - \omega_p^2}}{T_e^{3/2} \omega^3}, \quad (1.5)$$

where n_e is the electron density, T_e the electron temperature, ω the laser angular frequency, and ω_p the plasma frequency

$$\omega_p = \sqrt{\frac{n_e e^2}{m_e \varepsilon_0}}. \quad (1.6)$$

At the early stages of plasma formation, the electron density is relatively low, such that $\omega_p \ll \omega$, resulting in an efficient IB absorption. However, as the electron temperature and density increase, the condition $\omega_p \approx \omega$ may be approached, leading to a reduction of the absorption coefficient. This effect, known as plasma shielding, becomes significant when the electron density approaches the critical value

$$n_c = \frac{\varepsilon_0 m_e \omega^2}{e^2}. \quad (1.7)$$

During and after the laser pulse, the plasma plume expands and its evolution can be

described by hydrodynamic equations expressing the conservation of mass, momentum, and energy. In one-dimensional form, these equations read [7]

$$\left\{ \begin{array}{l} \frac{\partial \rho}{\partial t} = - \frac{\partial(\rho v)}{\partial z}, \\ \frac{\partial(\rho v)}{\partial t} = - \frac{\partial}{\partial z} (P + \rho v^2), \\ \frac{\partial}{\partial t} \left[\rho \left(E_{int} + \frac{v^2}{2} \right) \right] = - \frac{\partial}{\partial z} \left[\rho v \left(E_{int} + \frac{P}{\rho} + \frac{v^2}{2} \right) \right] + \varepsilon_{abs} - \varepsilon_{rad}, \end{array} \right. \quad (1.8)$$

where ρ is the mass density, v the expansion velocity, P the pressure, E_{int} the specific internal energy, and ε_{abs} and ε_{rad} represent volumetric power densities associated with laser absorption and radiative losses, respectively.

After the laser pulse, the plasma expands and cools freely. This expansion can be approximated by the Sedov–Taylor law [13]

$$R(t) \propto \left(\frac{E}{\rho_{ext}} \right)^{1/5} t^{2/5}, \quad (1.9)$$

where E is the released energy, ρ_{ext} the density of the surrounding medium, and R the radius of the shock front.

Between plasma formation and its decay at later times, there is a temporal window in which the plasma can be assumed to be in local thermodynamic equilibrium (LTE). A commonly used criterion to assess LTE conditions is the McWhirter criterion [11]

$$n_e \geq 1.6 \times 10^{12} T^{1/2} (\Delta E)^3, \quad (1.10)$$

where n_e is expressed in cm^{-3} , T in Kelvin, and ΔE (in eV) is the largest energy gap among the considered transitions. Although more refined LTE criteria exist [14], this relation provides a useful reference and will be adopted throughout this thesis.

1.2.3. Optical emission and radiation transport

Within a laser-induced plasma, optical radiation can be emitted and absorbed through three main mechanisms:

- *free–free* interactions involving unbound electrons, producing Bremsstrahlung continuum emission;

- *free-bound* recombination of free electrons with ions, also contributing to the continuum;
- *bound-bound* radiative transitions between discrete energy levels, producing atomic or ionic emission lines.

These processes are described through emission and absorption coefficients for both continuum and discrete radiation.

The continuum emissivity and absorption coefficient can be expressed as the sum of free-free and free-bound contributions [11, 15]

$$\varepsilon(\lambda)_{\text{cont}} = \frac{16\pi e^6}{3c^2 \sqrt{6\pi m_e^3 k}} \frac{n_e n_i}{\lambda^2 \sqrt{T_e}} \left[\xi(T_e, \lambda) \left(1 - \exp\left(-\frac{hc}{\lambda k_B T_e}\right) \right) + G_{\text{ff}}(\lambda, T_e) \exp\left(-\frac{hc}{\lambda k_B T_e}\right) \right], \quad (1.11)$$

$$\alpha(\lambda)_{\text{cont}} = [\alpha(\lambda)_{\text{ff}} + \alpha(\lambda)_{\text{fb}}] \left(1 - \exp\left(-\frac{hc}{\lambda k_B T_e}\right) \right), \quad (1.12)$$

where n_i is the ion density, k_B is the Boltzmann constant, ξ is the Biberman factor (involved also in the complete formula of α_{fb}), and G_{ff} is the Gaunt factor (involved also in the complete formula of α_{ff}). The full expressions of α_{ff} and α_{fb} are not reported here for brevity and can be found in [15].

For bound-bound transitions $u \rightarrow l$, the emissivity and absorption coefficient are given by [3]

$$\varepsilon_{ul}(\lambda, x) = \frac{hc}{4\pi\lambda_0} A_{ul} n_u(x) L(\lambda, x), \quad (1.13)$$

$$\alpha_{ul}(\lambda, x) = \frac{\lambda_0^4}{8\pi c} A_{ul} \frac{g_u}{g_l} n_l(x) \left(1 - \frac{n_u(x)g_l}{g_u n_l(x)} \right) L(\lambda, x), \quad (1.14)$$

where A_{ul} is the Einstein coefficient, n_u and n_l are the density of the upper and lower level respectively, g_u and g_l are the degeneracy of the upper and lower level respectively, $L(\lambda, x)$ is the profile line and λ_0 is the specific wavelength of the transition. In approximation of a Lorentzian shape we have [2]:

$$L(\lambda) = \frac{2}{\pi} \frac{\Delta\lambda_0}{4(\lambda - \lambda_0)^2 + \Delta\lambda_0^2} \quad (1.15)$$

The propagation of radiation through the plasma is governed by the radiation transport equation (RTE) [3]

$$\frac{dI(\lambda, x)}{dx} = \varepsilon(\lambda, x) - \alpha(\lambda, x) I(\lambda, x), \quad (1.16)$$

whose formal solution over a path length L_p is

$$I(\lambda, L_p) = \int_0^{L_p} \varepsilon(\lambda, x) \exp\left(-\int_x^{L_p} \alpha(\lambda, x') dx'\right) dx. \quad (1.17)$$

For a homogeneous plasma, both ε and α are independent of x , and the intensity reduces to [3]

$$I(\lambda) = \frac{\varepsilon(\lambda)}{\alpha(\lambda)} [1 - \exp(-\alpha(\lambda)L_p)]. \quad (1.18)$$

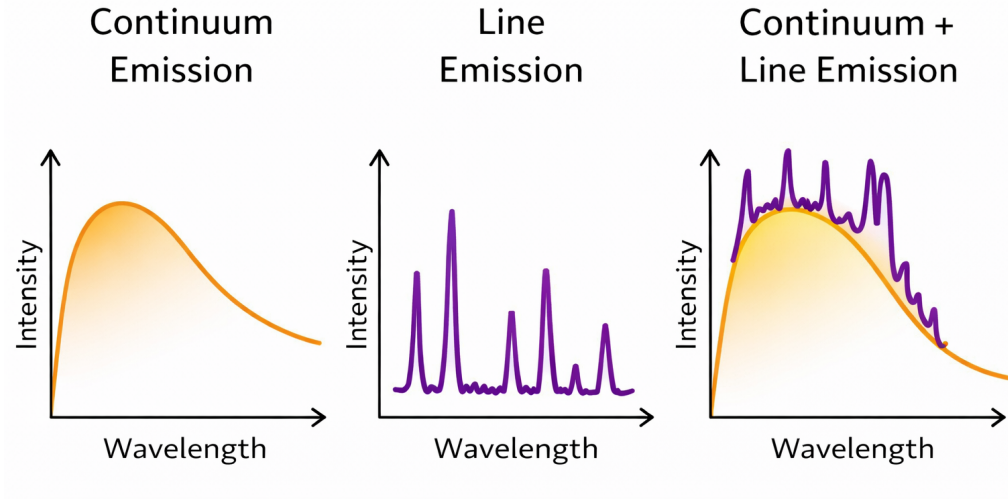


Figure 1.3: Schematic representation of the superposition of continuum emission and line radiation.

The total emission can be regarded as the superposition of continuum radiation and line emission, as schematically shown in fig. 1.3. Away from spectral lines and under LTE conditions, the continuum approaches a blackbody-like distribution modulated by the optical depth [3]

$$I(\lambda) = B(\lambda) [1 - \exp(-\alpha_{\text{cont}}(\lambda)L_p)], \quad (1.19)$$

where $B(\lambda)$ is the Planck spectral radiance.

In the vicinity of a spectral line, assuming LTE and optically thin conditions at line centre,

the line intensity can be written as [3]

$$I_{ul}(\lambda) = \frac{hc}{4\pi\lambda_0} A_{ul} N_0 g_u L_P \frac{\exp\left(-\frac{E_u}{k_B T}\right)}{U(T)} L(\lambda), \quad (1.20)$$

where N_0 is the total number density of the emitting species and

$$U(T) = \sum_i g_i \exp\left(-\frac{E_i}{k_B T}\right) \quad (1.21)$$

is the partition function. When the plasma is not optically thin, the more general expression in eq. (1.18) must be used to account for saturation and self-absorption effects.

1.3. Influence of experimental parameters

Several experimental parameters can be adjusted during a LIBS measurement. In particular, the irradiation delivered to the target can be modified by tuning the laser pulse energy and the number of pulses, while the temporal acquisition parameters can be controlled through the ICCD delay and gate width. In addition to these settings, the intrinsic shot-to-shot variability that characterizes LIBS measurements must be taken into account. For this reason, spectra are typically averaged over multiple laser shots acquired at different positions on the sample surface.

This averaging procedure reduces the sensitivity to local surface heterogeneities and leads to an overall improvement of the signal-to-noise ratio (SNR). To this aim, the motorized stage holding the sample exposes a different surface position to the laser at each shot, and the corresponding spectra are subsequently averaged. In the present work, $N = 100$ individual spectra were acquired and averaged for each measurement.

1.3.1. Laser parameters and breakdown threshold

One of the key parameters in LIBS experiments is the laser irradiance delivered to the sample. This quantity determines whether the material reaches the energy threshold required for plasma formation. The breakdown threshold depends on several factors, including the material properties, the surrounding atmosphere, the initial temperature, the laser wavelength, the pulse duration, and the focal spot size. As a consequence, an *a priori* calculation of the required irradiance is generally not possible. Instead, a trial-and-error procedure is commonly adopted, starting from values reported in the literature and progressively adjusted to obtain a stable plasma with a sufficiently high SNR.

During the optimization of the laser irradiance, potential damage to the sample must also be considered. In particular, brittle materials such as glasses can undergo cracking or other forms of mechanical damage due to thermal stress induced by intense laser irradiation.

The most direct parameter that can be varied is the laser pulse energy. Increasing the pulse energy generally enhances laser–matter and laser–plume interactions, resulting in a denser and more emissive plasma. However, this approach cannot be pursued arbitrarily, as excessive pulse energies may lead to significant thermal shock or irreversible damage to the sample.

As an alternative to generating a very intense plasma with a single laser shot, a multi-pulse approach can be employed. In this configuration, several consecutive laser pulses are delivered to the same location, and the plasma emission is analysed after the last pulse. This method can enhance laser–plasma coupling and improve plasma stability. On the other hand, repeated irradiation modifies the surface conditions, and cumulative effects such as crater deepening may occur.

Overall, both the laser pulse energy and the number of pulses represent important parameters that must be carefully tuned. A trade-off is required in order to achieve stable plasma conditions while minimizing unwanted side effects and damage to the sample.

1.3.2. Temporal parameters: delay time and gate width

As illustrated in fig. 1.4, since the plasma evolves over time, the recorded spectra strongly depend on the chosen ICCD delay and gate width. At early times, the emission is dominated by a strong continuum contribution, which is followed by ionic emission, then atomic emission, and, at latest stages, by molecular bands. In most LIBS applications, the delay time is selected to be longer than the characteristic duration of the continuum emission in order to improve spectral contrast.

The choice of delay and gate width depends on the type of plasma to be investigated, whether predominantly ionic or atomic. These parameters are influenced by several factors, including the laser settings, the target material, the ambient atmosphere, and the plasma dynamics. Consequently, even in this case, their optimal values cannot be determined analytically in advance and must be identified experimentally.

Nevertheless, empirical guidelines can be used to define reasonable starting values. For inorganic materials, such as glasses, typical values are $t_{\text{gate}} \approx 700$ ns and $t_{\text{delay}} \approx 300$ ns. For organic materials, which often exhibit longer-lived plasma components or pronounced molecular emission, larger values are generally required, for example $t_{\text{gate}} \approx 1000$ ns and

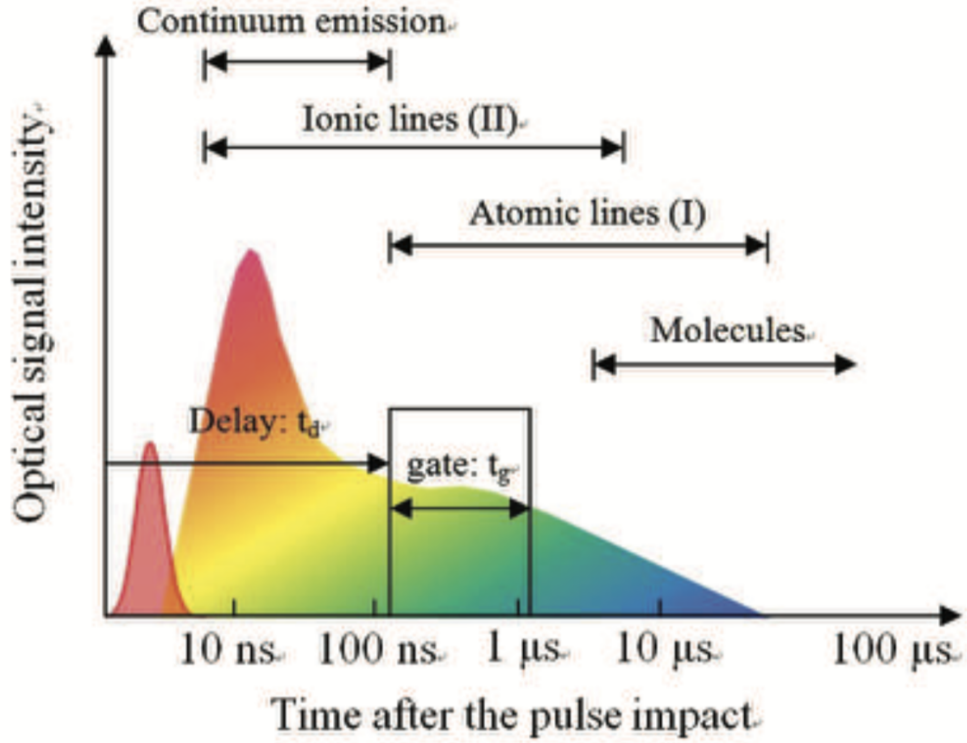


Figure 1.4: Temporal evolution of plasma emission features [7].

$t_{\text{delay}} \approx 500 \text{ ns}$. As a general procedure, in particular when exploring plasma dynamics, the empirical relation

$$t_{\text{gate}} \approx 0.5 t_{\text{delay}} \quad (1.22)$$

can be adopted as a guideline. This relation is supported by several LIBS studies reported in the literature [16] and provides a useful reference for parameter selection.

1.4. Spectral features and line broadening mechanisms

If the aim of the analysis is purely qualitative, LIBS spectra can be interpreted by identifying the characteristic emission lines associated with the elements present in the sample. In this case, the mere presence or absence of specific spectral lines is sufficient to confirm the occurrence of a given element. When quantitative information is required, however, more advanced approaches must be adopted, such as calibration-free LIBS (CF-LIBS), which will be discussed in chapter 2. This necessity arises from the fact that several physical effects simultaneously influence the recorded spectra, and these effects must be properly accounted for in order to extract reliable quantitative information.

1.4.1. Line intensity and self-absorption

A first key aspect to be considered is that the intensity of an emission line is not directly related to the apparent height of the corresponding spectral peak. As shown in eq. (1.20), the emitted line intensity depends on several parameters, including the Einstein coefficient of the transition, the plasma temperature, the population of the excited state, and the degeneracy of the involved energy levels. As an illustrative example, some spectra discussed in this thesis exhibit very intense calcium emission lines, in particular the Ca II ionic lines at 393.37 nm and 396.85 nm. The prominence of these peaks does not imply that calcium is the most abundant element in the sample. On the contrary, its concentration can be well below 1%, demonstrating that higher peak intensities do not necessarily correspond to higher elemental abundances.

A second important aspect concerns the assumption of an optically thin plasma. Under this hypothesis, re-absorption of emitted photons within the plasma is considered negligible. In practice, this condition is often not fulfilled, especially for strong resonance lines or transitions involving low-lying energy levels. In order to account for these effects, more refined plasma descriptions must be introduced. An example is the inhomogeneous plasma model schematically illustrated in fig. 1.5.

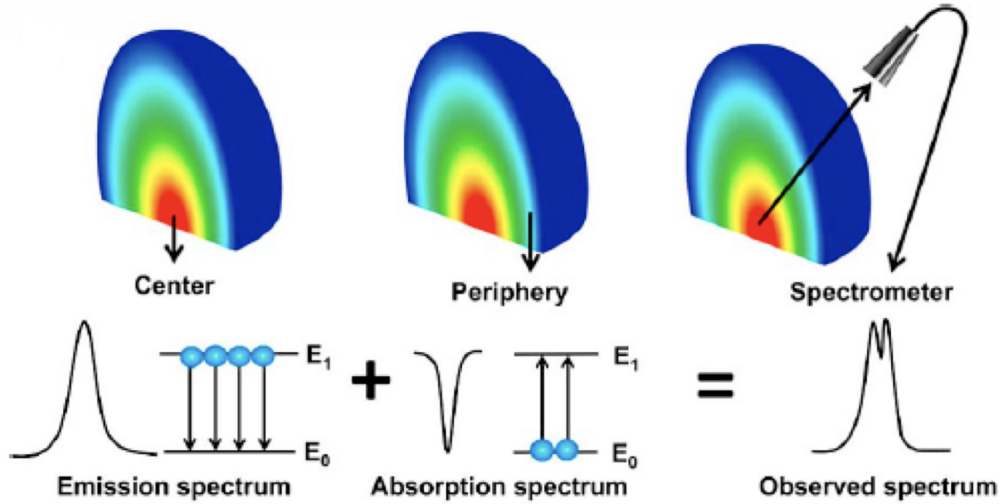


Figure 1.5: Schematic representation of an inhomogeneous plasma model [3].

In this approach, the plasma is described as being composed of two or more regions characterized by different temperatures and densities, and therefore by different emission and absorption probabilities. Although the use of such refined models increases both the analytical and numerical complexity of the problem, it enables the description of

self-absorption and self-reversal effects, which cannot be captured within a homogeneous plasma approximation.

Beyond refined modelling, several methods have been developed to evaluate, compensate for, or even exploit self-absorption effects [3]. Examples of compensation techniques include escape factor methods and line-shape-based procedures. Conversely, if self-absorption is intentionally exploited, approaches such as line-shape analysis or curve-of-growth methods can provide valuable information on parameters such as the effective plasma length, instrumental broadening, and characteristics of the inhomogeneous plasma model [3].

Despite their potential, for a first-level analysis it is generally preferable to avoid spectral lines that are strongly saturated or affected by self-absorption. Such lines typically correspond to transitions originating from the ground state or from low-lying energy levels, which are highly populated. By selecting transitions involving higher excited states, the effects of self-absorption can be largely minimized. In CF-LIBS this strategy is commonly adopted in the initial analysis, while self-absorption effects can subsequently be exploited through curve-of-growth methods.

1.4.2. Stark effect and other broadening mechanisms

When analysing LIBS spectra, emission lines are never observed as infinitely narrow features. Their finite width results from several broadening mechanisms acting simultaneously within the plasma:

- *Natural broadening*, associated with the finite lifetime of excited states. An order-of-magnitude estimate is given by $\Delta E \sim \hbar/(2\tau)$, where τ is the upper-level lifetime (often $\tau \approx 1/A_{ul}$). In LIBS plasmas, this contribution is usually negligible compared to other broadening mechanisms.
- *Doppler broadening*, which has a Gaussian profile and arises from the thermal motion of the emitting species. The Doppler width scales as $\Delta\nu_D \propto \sqrt{T/M}$, where T is the plasma temperature and M is the emitter mass.
- *Instrumental broadening*, typically approximated by a Gaussian profile and determined by the finite resolution of the spectrometer.
- *Collisional broadening*, and in particular *Stark broadening*, caused by the electric microfields generated by electrons and ions in the plasma. This contribution has a Lorentzian line shape.

In a laser-induced plasma, Stark broadening is generally the dominant broadening mechanism. Doppler and instrumental contributions can nevertheless be estimated independently, as they both exhibit Gaussian profiles. As a result, the observed line shape is commonly described by a Voigt profile, corresponding to the convolution of a Gaussian and a Lorentzian component. By fitting the experimental line profile, the Gaussian contribution (Doppler plus instrumental) can be separated from the Lorentzian contribution, which is mainly associated with Stark broadening as shown in fig. 1.6

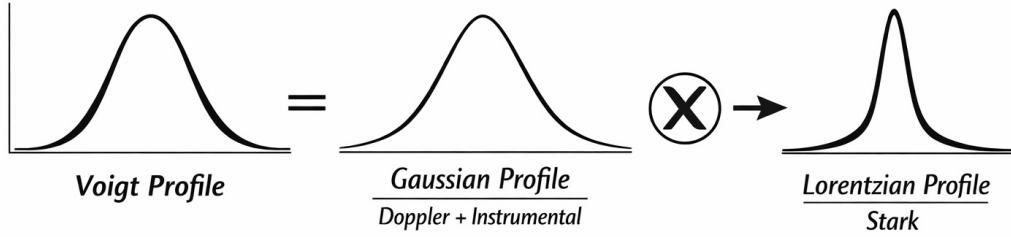


Figure 1.6: Deconvolution process.

The Stark full width at half maximum ($\text{FWHM}_{\text{Stark}}$) provides a direct estimate of the electron density. In particular, it can be related to the electron density through [17]

$$n_e = \frac{\Delta\lambda_{1/2}}{2w(T)} 10^{16} \text{ cm}^{-3}, \quad (1.23)$$

where $\Delta\lambda_{1/2}$ is the measured Stark width and $w(T)$ is a line-dependent Stark parameter, tabulated in the literature.

1.5. Introduction to LIBS data analysis

The interpretation of LIBS spectra can be approached at different levels of complexity, depending on the analytical objective and on the quality and stability of the acquired data. At a qualitative level, elemental identification is typically achieved by comparing the measured emission lines with spectral databases and reference atlases. In many practical applications, this approach is sufficient to determine the presence or absence of specific elements in the sample.

Quantitative analysis, however, is considerably more challenging. The measured spectral intensity is not solely determined by elemental concentration, but also depends on plasma parameters such as temperature, electron density, degree of ionization, optical thickness, and spatial and temporal inhomogeneities. In addition, instrumental effects (spectral resolution, detector response, collection geometry) further influence the observed signal.

As a result, a direct proportionality between line intensity and elemental abundance cannot be assumed in general.

Several strategies have been developed to extract quantitative or semi-quantitative information from LIBS spectra. Empirical approaches rely on calibration curves constructed from reference samples with known composition, relating integrated line intensities or intensity ratios to elemental concentrations. While effective in controlled conditions, these methods require representative standards and are sensitive to matrix effects and variations in plasma conditions [8].

Alternative approaches [1] aim to reduce the dependence on external calibration by exploiting physically motivated models of plasma emission. In this framework, the plasma is described through a set of macroscopic parameters (such as temperature and electron density), and the measured spectrum is interpreted using atomic physics and radiative transfer relations. Assumptions such as local thermal equilibrium and optical thinness are often invoked to simplify the treatment, although their validity must be carefully assessed for each experimental configuration.

More recently, advanced data analysis techniques based on multivariate statistics and machine learning [2] have also been applied to LIBS spectra. These methods can capture complex correlations within the spectral data and may offer improved robustness against experimental variability. However, their interpretability is often limited, and their performance depends strongly on the availability and representativeness of training datasets.

Within this broad landscape of LIBS data analysis methodologies, physically based approaches play a central role when quantitative accuracy and transferability across different samples and experimental conditions are required. The following chapter focuses on one such approach, Calibration-Free LIBS (CF-LIBS), which aims to determine elemental composition directly from the measured emission spectrum by explicitly modelling and simulating plasma properties and radiative processes.

2 | CF-LIBS

As discussed in the previous chapter, LIBS spectra allow to obtain qualitative information on the elemental composition of a sample. However, achieving a reliable quantitative analysis requires the use of dedicated techniques and physically grounded models capable of accounting for the complex phenomena occurring within the laser-induced plasma.

In particular, the most relevant plasma parameters—namely the electron density n_e and the plasma temperature T —strongly influence the emitted spectrum through their effect on both emission and absorption coefficients. As a consequence, without an accurate determination of these parameters, any quantitative interpretation of LIBS spectra would be inherently unreliable.

A commonly adopted approach for quantitative LIBS analysis is conventional calibration-based LIBS (CC-LIBS), which relies on calibration curves. In this framework, reference samples with known composition are analysed and used to establish a relationship between spectral intensity and elemental concentration. This strategy requires the availability of suitable standards and presupposes prior knowledge of the sample composition. Moreover, calibration curves are generally material-dependent, which limits their transferability and reduces the reproducibility of measurements performed on different matrices.

These limitations motivate the adoption of more refined analysis strategies. In this chapter, the Calibration-Free LIBS (CF-LIBS) approach is introduced and discussed from a physical perspective. CF-LIBS aims to retrieve elemental composition directly from the measured emission spectrum by explicitly modelling plasma properties and radiative processes, while also highlighting the assumptions and limitations inherent to this methodology.

2.1. Physical principles of CF-LIBS

Calibration-free LIBS can be formulated as an inverse problem: starting from the measured emission spectrum, one seeks the plasma parameters and elemental composition that reproduce the observed line intensities and profiles within a physically consistent

framework. In practice, this is achieved by iteratively computing synthetic spectra from an assumed plasma state and adjusting the unknown parameters until agreement with the experiment is reached. The present section introduces the core ingredients of this approach: (i) a forward model for spectral emission and detection and a metric to quantify the mismatch between computed and measured spectra; (ii) an equilibrium description of a multi-element plasma that relates the elemental abundances to the populations of atomic, ionic, and molecular species; and (iii) a convenient parametrization of the unknowns in terms of T , n_e , and the elemental fractions.

2.1.1. Forward model and spectral matching

The basis of CF-LIBS is a forward simulation of the laser-induced plasma (LIP) emission, as introduced in the previous chapter. Although a full, time-dependent, and spatially resolved simulation of plasma formation and evolution is computationally demanding, CF-LIBS does not require such a comprehensive description. Instead, it relies on modelling the dominant spectroscopic processes—namely emission, absorption, line broadening, and instrumental detection—which provide sensitivity to the key plasma parameters (n_e and T).

The computed spectrum is compared with the measured one by minimizing a χ^2 metric [16]:

$$\chi^2 = \sum_i \frac{|I_{\text{meas}}(\lambda_i) - I_{\text{comp}}(\lambda_i)|^2}{I_{\text{comp}}(\lambda_i)}. \quad (2.1)$$

By adopting a suitable iterative loop scheme, the difference between measured and computed spectra can be progressively reduced until convergence is achieved.

2.1.2. Multi-elemental equilibrium plasma model

The underlying mathematical framework assumes a multi-element plasma in equilibrium, where the total number density associated with element A can be written as [16]

$$n_A = \sum_{z=0}^{z_{\text{max}}} n_A^z + 2 \sum_{z=0}^1 n_{A_2}^z + \sum_{B \neq A} \sum_{z=0}^1 n_{AB}^z. \quad (2.2)$$

Here, n_A^z and $n_{A_2}^z$ are the number densities of atomic and homonuclear diatomic species of charge state z , respectively, while n_{AB}^z denotes the number density of heteronuclear diatomic species formed through chemical reactions with element B . The factor 2 accounts for the two atoms contained in each homonuclear molecule. The sums include all species

of significant abundance up to the maximum charge state $z_{\max}$.

The number densities of neutral diatomic molecules formed by chemical reactions between elements A and B can be obtained from the Guldberg–Waage law of mass action [16]:

$$\frac{n_A^0 n_B^0}{n_{AB}^0} = \frac{(2\pi\mu_{AB}k_B T)^{3/2}}{h^3} \frac{Q_A^0 Q_B^0}{Q_{AB}^0} \exp\left(-\frac{D_0}{k_B T}\right), \quad (2.3)$$

where Q_A^0 and Q_B^0 are the partition functions of neutral atoms A and B , Q_{AB}^0 is the partition function of the corresponding diatomic molecule, k_B the Boltzmann constant, D_0 is its ground-state dissociation energy, and $\mu_{AB} = m_A m_B / (m_A + m_B)$ is the reduced mass.

2.1.3. Charge neutrality and choice of unknowns

Assuming charge neutrality, the electron density can be expressed as [16]

$$n_e = \sum_A \sum_{z=0}^{z_{\max}} z n_A^z. \quad (2.4)$$

It is often convenient to replace the set of elemental densities $\{n_A\}$ with the atomic fractions C_A , defined as

$$C_A = \frac{n_A}{n_{\text{tot}}}, \quad n_{\text{tot}} = \sum_A n_A. \quad (2.5)$$

A plasma containing M elements can then be parametrized by $M - 1$ independent atomic fractions (since $\sum_A C_A = 1$), together with n_e and T . Therefore, the set of unknowns typically includes T , n_e , and $M - 1$ independent values of C_A .

To constrain these quantities from the spectrum, at least one suitable line per element is required for composition, while additional lines are needed to determine T (as discussed in section 2.3) and to ensure internal consistency of the model.

2.2. Physical assumptions

The calibration-free approach was originally formulated under a set of simplifying assumptions. The seminal work by Ciucci et al. [1] discusses five hypotheses that still define the baseline CF-LIBS framework and that are routinely re-examined in modern implementations. In the following, these assumptions are outlined together with their practical implications for quantitative analysis.

2.2.1. Stoichiometric ablation

CF-LIBS assumes that the elemental composition of the plasma reflects that of the bulk material. Close to the ablation threshold (see section 1.3.1), this condition may be compromised by selective or incomplete material removal. In most practical LIBS measurements, the laser fluence is set well above threshold (often by two to three orders of magnitude) to generate a stable and sufficiently emissive plasma, which generally improves stoichiometric transfer.

Since the plasma composition cannot be measured directly, stoichiometric ablation is usually checked through the repeatability of line ratios and reconstructed compositions over multiple shots and different positions. Common mitigation strategies include discarding the first pulses on each spot (surface cleaning and signal stabilization), rastering the beam to limit crater-induced fractionation, and averaging over repeated acquisitions. When systematic drifts in line ratios persist, the retrieved composition should be regarded as an effective composition of the ablated mass, and the role of matrix effects must be considered explicitly.

2.2.2. Accuracy of spectroscopic data

CF-LIBS relies on spectroscopic parameters such as transition probabilities A_{ul} , statistical weights g_u , line positions, and level energies. Uncertainties in these inputs propagate to the inferred temperature and elemental fractions. The accuracy has considerably improved thanks to updated databases and dedicated measurements, but the sensitivity to atomic data remains a limiting factor for some elements and transitions.

In practice, robustness is improved by adopting a consistent data source (or a documented hierarchy of sources), selecting well-characterized and well-resolved transitions, and using multiple lines per element. Blends, misassignments, or inaccurate parameters typically appear as outliers in Boltzmann or Saha–Boltzmann regressions and can be rejected based on residuals. When feasible, the uncertainty associated with A_{ul} and with instrumental corrections (e.g. response function and baseline subtraction) should be reflected, at least qualitatively, in the uncertainty discussion for T and C_A .

2.2.3. Spatial homogeneity and inhomogeneous models

Early CF-LIBS formulations commonly adopted a homogeneous, 0D plasma description. Real LIBS plasmas are spatially inhomogeneous, with temperature and electron density varying across the plume. This limitation can be mitigated by using inhomogeneous

descriptions (e.g. multi-zone or core-shell models). As schematically illustrated in fig. 1.5, the plasma may be represented as a set of regions characterized by different values of T and n_e . A two-zone model often yields a substantial improvement at moderate computational cost, whereas adding more zones typically leads to diminishing returns [16].

From a practical perspective, inhomogeneity becomes evident when different subsets of lines (e.g. spanning different upper-level energies or self-absorption sensitivities) return inconsistent temperatures, or when a single set of plasma parameters cannot reproduce both weak and strong transitions simultaneously. A common strategy is therefore to start from a homogeneous model and introduce a minimal inhomogeneous description only if systematic mismatches remain after line selection and self-absorption screening.

2.2.4. Local thermodynamic equilibrium (LTE)

LTE requires that collisional processes establishing excitation and ionization equilibria are sufficiently fast compared to radiative processes. This assumption is central to CF-LIBS, since it justifies the use of Boltzmann and Saha relations during the acquisition gate and supports the interpretation of line intensities in terms of a single temperature.

LTE can be preliminarily assessed using the McWhirter criterion (eq. (1.10)); however, this condition alone does not guarantee the establishment of LTE in transient and spatially inhomogeneous plasmas. In practice, LTE validity is further evaluated through internal consistency checks, such as the linearity of Boltzmann or Saha-Boltzmann plots, the agreement between temperatures derived from different sets of spectral lines, and the absence of systematic trends in the spectral fitting residuals.

At early times, when the emission is dominated by continuum radiation, the LTE assumption is often not fulfilled. A straightforward mitigation strategy consists in increasing the acquisition delay and properly adjusting the gate width, so as to probe later stages of plasma evolution, where equilibrium-based diagnostics are more reliable.

Partial relaxations of the LTE hypothesis have been explored in advanced approaches, such as self-calibrated LIBS [2]; however, these methodologies fall beyond the scope of the present thesis.

2.2.5. Optical thinness and self-absorption

In its simplest form, CF-LIBS assumes that the plasma is optically thin at the wavelengths of the selected transitions. Under this condition, self-absorption is negligible and the radiative transfer equation (eq. (1.16)) reduces to the optically thin expression for line

emission (eq. (1.20)). This assumption is frequently violated for strong resonance lines or transitions originating from low-lying levels. For this reason, many workflows either avoid strongly self-absorbed lines in the initial analysis or explicitly include self-absorption in the forward model, potentially exploiting it to constrain plasma properties [16].

Optical-thickness effects can be identified through distorted line shapes (e.g. self-reversal), anomalous ratios within a multiplet, or the inability of an optically thin model to reproduce weak and strong transitions simultaneously. A first mitigation is line selection: preference is given to weak, non-resonant lines and to transitions less sensitive to re-absorption, while lines originating from low-lying levels are treated with caution. When this is not sufficient, self-absorption can be addressed either by correcting measured line integrals or, more generally, by fitting the spectrum with the full radiative transfer equation (eq. (1.16)). In such cases, the plasma size (or effective path length) becomes a key parameter, since it directly controls the optical depth and, in turn, the observed line radiance.

An example of the impact of self-absorption on line radiance is reported in fig. 2.1.

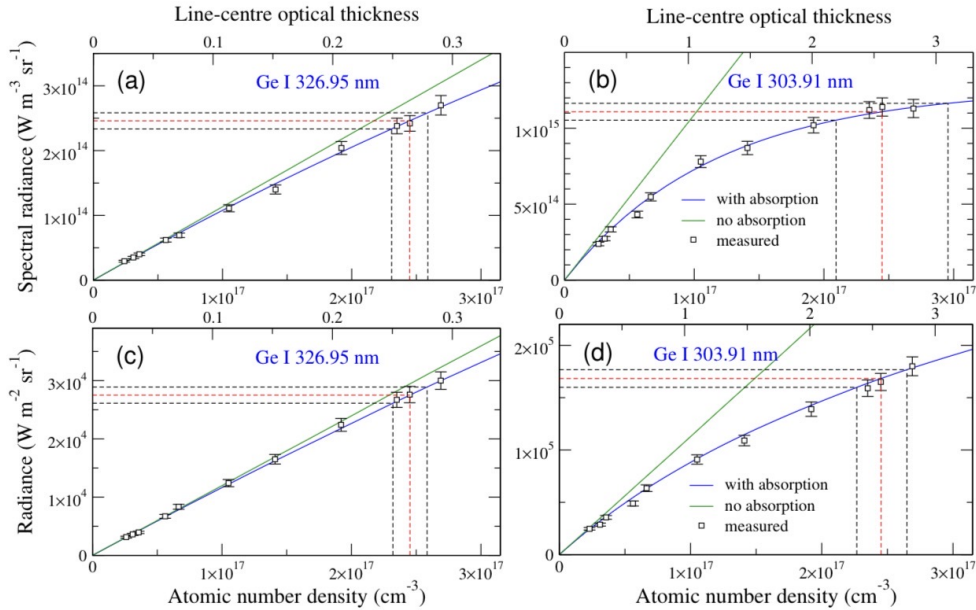


Figure 2.1: Line-centre spectral radiance (a,b) and line-integrated radiance (c,d) as functions of the Ge atomic number density and τ_0 (secondary x-axis) for weakly (a,c) and strongly (b,d) self-absorbed lines. The measurement was performed in argon on a Si/Ge thin film with a compositional gradient. The curves compare calculations for a uniform LTE plasma including (blue) and neglecting (green) self-absorption [16].

Overall, these assumptions define the domain of validity of the simplest CF-LIBS formulations. When one or more conditions are not met, the forward model can be refined (e.g. by adopting inhomogeneous plasma descriptions or by explicitly solving the radiative transfer equation), at the cost of increased complexity and computational effort.

2.3. Saha–Boltzmann equation

This section summarizes the spectroscopic relations commonly used in CF-LIBS to estimate the plasma temperature under LTE. The key idea is to relate measured line intensities to level populations through Boltzmann and Saha equilibria. In practical implementations, these relations are embedded in an iterative scheme because ionic lines explicitly depend on the electron density n_e (typically obtained from Stark broadening) and because optical-thickness effects may require additional modelling choices.

2.3.1. Boltzmann distribution and Boltzmann plot

Under LTE conditions, the population density of an excited level u is given by the Boltzmann distribution:

$$n_u = N_0 \frac{g_u}{U(T)} \exp\left(-\frac{E_u}{k_B T}\right), \quad (2.6)$$

where N_0 is the total number density of the considered species, g_u and E_u are the statistical weight and energy of the upper level, respectively, $U(T)$ is the partition function, and k_B is the Boltzmann constant.

If the plasma is optically thin at line centre, n_u can be substituted into the line emissivity (eq. (1.13)), leading to the optically thin line intensity (eq. (1.20)). Experimentally, the quantity extracted from the spectrum is the line-integrated signal (area under the line), which can be written as

$$S_{ul} = F \int I_{ul}(\lambda) d\lambda, \quad (2.7)$$

where F represents the instrumental response of the optical system.¹

Combining the above relations and taking the logarithm, one obtains the Boltzmann-plot form:

$$\ln\left(\frac{S_{ul}\lambda_0}{A_{ul}g_u}\right) = \ln\left(C \frac{N_0}{U(T)}\right) - \frac{E_u}{k_B T}, \quad (2.8)$$

where C groups constants and instrumental factors, and λ_0 is the transition wavelength.

¹In practice, F may depend on wavelength; when the response is not flat over the spectral interval of interest, a wavelength-dependent correction should be applied before constructing intensity ratios or regression plots.

eq. (2.8) can be cast into a linear regression form $y = mx + q$ by defining

$$y = \ln\left(\frac{S_{ul}\lambda_0}{A_{ul}g_u}\right), \quad x = E_u, \quad m = -\frac{1}{k_B T}, \quad q = \ln\left(C \frac{N_0}{U(T)}\right). \quad (2.9)$$

A plot of y versus x therefore yields a straight line (Boltzmann plot), whose slope provides an estimate of the plasma temperature for the considered species (fig. 2.2).

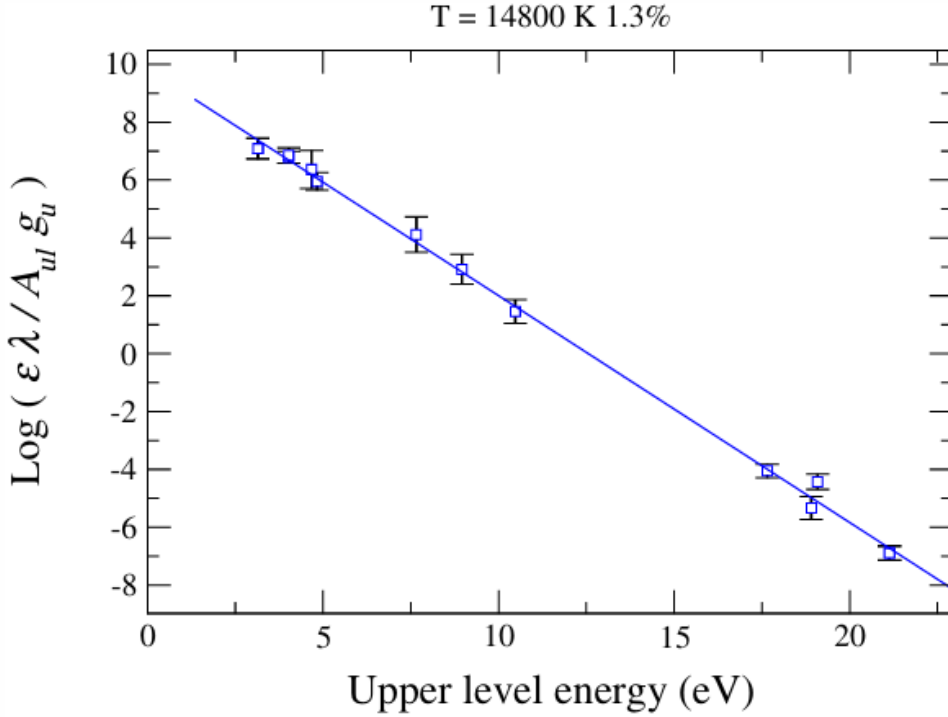


Figure 2.2: Example of a Boltzmann plot.

2.3.2. Ionization balance and Saha–Eggert equation

Laser-induced plasmas commonly contain both neutral and ionized species. In this case, the ionization balance must be described through the Saha–Eggert equation [18]:

$$\frac{N_0^{II}}{N_0^I} = \frac{2}{n_e} \frac{U^{II}(T)}{U^I(T)} \exp\left(-\frac{E_{\text{ion}}}{k_B T}\right) \frac{(2\pi m_e k_B T)^{3/2}}{h^3}, \quad (2.10)$$

where E_{ion} is the ionization energy, N_0^{II} and N_0^I are the number densities of singly ionized and neutral species, respectively, and $U^{II}(T)$ and $U^I(T)$ are the corresponding partition functions.

2.3.3. Saha–Boltzmann plot

Combining eq. (2.6) and eq. (2.10), and applying the logarithm, one obtains the Saha–Boltzmann relation:

$$\ln\left(\frac{S_{ki}^{II}\lambda_0^{II}}{A_{ki}^{II}g_k^{II}}\right) - \ln\left(\frac{2(2\pi m_e k_B T)^{3/2}}{n_e h^3}\right) = \ln\left(C \frac{N_0^I}{U^I(T)}\right) - \frac{E_k^{II} + E_{\text{ion}}}{k_B T}, \quad (2.11)$$

where the notation $k \rightarrow i$ is used for ionic transitions to emphasize that ionic energy levels differ from the neutral ones.

A linear regression in the form $y^* = mx^* + q$ can again be performed by defining

$$y^* = \ln\left(\frac{S_{ki}^{II}\lambda_0^{II}}{A_{ki}^{II}g_k^{II}}\right) - \ln\left(\frac{2(2\pi m_e k_B T)^{3/2}}{n_e h^3}\right), \quad x^* = E_k^{II} + E_{\text{ion}}. \quad (2.12)$$

With these definitions, neutral and ionic lines can be placed on the same plot. Since y^* depends on both T and n_e , an independent estimate of n_e is required and the temperature determination typically proceeds iteratively: n_e is first estimated (e.g. from Stark broadening), a temperature is then obtained from the regression, and the procedure is repeated until the update of T becomes negligible.

2.3.4. Practical considerations for regression-based diagnostics

In practice, the quality of Boltzmann and Saha–Boltzmann plots is strongly influenced by line selection and by how S_{ul} is extracted. Reliable regressions require isolated lines, consistent background subtraction (to remove continuum emission), and avoidance of severely blended or saturated transitions. Moreover, deviations from linearity often indicate either residual self-absorption, inaccurate spectroscopic parameters, or departures from LTE over the selected acquisition window.

2.3.5. Beyond the optically thin approximation

The optically thin approximation is introduced here for clarity, as it yields closed-form relations and straightforward linearization. It is not, however, a strict requirement for CF-LIBS. When self-absorption cannot be neglected, one may either apply suitable corrections to the measured line integrals or estimate T and n_e by fitting the spectrum through the full radiative transfer equation (eq. (1.16)). Extended formulations have been proposed to mitigate optical-thickness effects, such as the columnar-density Saha–Boltzmann approach [18]. Although relevant, these advanced models are beyond the scope of this thesis and

will not be discussed further.

2.4. Loop scheme and procedure

A typical CF-LIBS iterative workflow is illustrated in fig. 2.3.

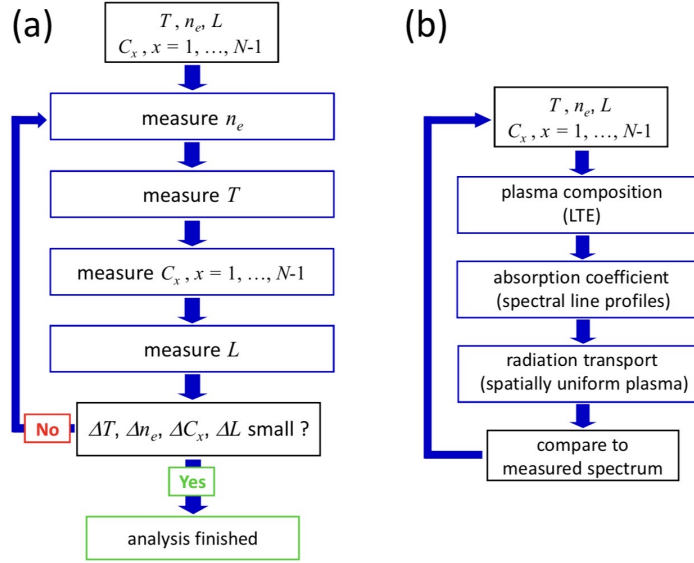


Figure 2.3: Algorithm of calibration-free LIBS analysis: (a) principal iteration loop with successive estimates of electron density, temperature, elemental fractions, and plasma diameter. Each estimate is obtained through the calculation loop (b) by varying the target parameter [16].

As discussed in section 2.1, CF-LIBS is formulated as a self-consistent inverse problem: the set of unknown parameters (typically T , n_e , the elemental fractions C_A , and, when required, an effective plasma size or path length) is adjusted until the forward model reproduces the measured spectrum within a prescribed tolerance (e.g. via eq. (2.1)). In practice, this is implemented as an outer iteration loop, coupled to an inner spectral synthesis loop.

2.4.1. Initialization and line selection

The analysis starts by identifying a set of suitable spectral lines for the species expected in the sample. When the material class is known (e.g. metals, ceramics, organics) and prior information on major constituents is available, this information can be used to guide the selection. Otherwise, preliminary line identification is performed directly on

the measured spectrum. In both cases, transitions are selected to minimize ambiguities due to line blending and to limit optical-thickness effects (see section 2.2.5).

2.4.2. Outer iteration loop: parameter estimation

Given an initial guess for the unknown parameters, the outer loop proceeds through the following steps:

1. **Electron density.** Estimate n_e from Stark broadening by fitting selected line profiles with a Voigt function and attributing the Lorentzian contribution to Stark broadening (eq. (1.23)). This step is performed first because the Stark width depends primarily on n_e and only weakly on T .
2. **Temperature.** Estimate T using a Boltzmann plot (eq. (2.8)) when only neutral lines are employed, or a Saha–Boltzmann plot (eq. (2.11)) when ionic lines are included, as described in section 2.3. Since the Saha–Boltzmann formulation depends explicitly on n_e , temperature estimation is naturally embedded in a sub-iteration until the regression becomes stable.
3. **Elemental fractions.** Update the elemental fractions by comparing measured and computed line integrals for the identified species within the adopted plasma model and radiative transfer framework.
4. **Plasma size/path length (when required).** When self-absorption is explicitly modelled through the radiative transfer equation, an effective plasma size (often expressed as a plasma diameter or path length) must be estimated. This can be achieved either using calibration information obtained under similar laser conditions or by exploiting pairs of transitions characterized by significantly different optical thickness, as illustrated in fig. 2.4.

2.4.3. Inner loop: spectral synthesis and mismatch evaluation

For a given parameter set, the inner loop computes a synthetic spectrum by evaluating the emission and absorption coefficients, applying the selected line-shape model (including the instrumental response), and solving the radiative transfer equation when required (eq. (1.16)). The agreement between computed and measured spectra is quantified through the chosen mismatch metric (e.g. eq. (2.1)). At each iteration, LTE can be screened (e.g. via eq. (1.10)) and absorption coefficients can be recomputed consistently (eq. (1.14)).

2.4.4. Stopping criteria and consistency checks

Convergence is reached when parameter updates between two successive outer iterations become sufficiently small and when the spectral residuals do not show systematic structures across the selected spectral windows. Additional consistency checks include: (i) linearity of Boltzmann or Saha–Boltzmann regressions (section 2.3); (ii) stability of T and n_e when changing the subset of diagnostic lines; and (iii) the absence of clear signatures of self-absorption (e.g. self-reversal or anomalous multiplet ratios) in the lines used for the final estimates (see section 2.2.5).

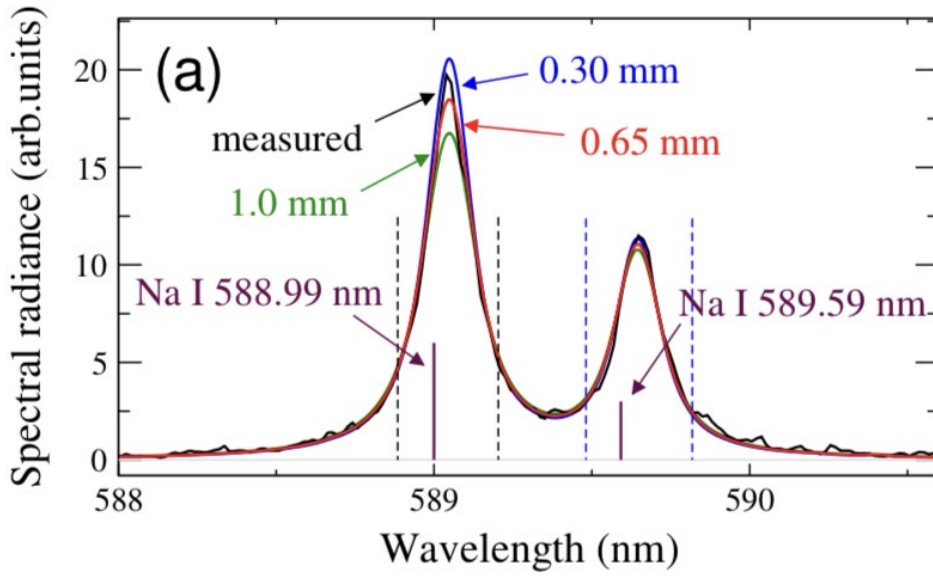


Figure 2.4: Measured spectrum and spectral radiance computed for different values of plasma size [16].

2.5. Experimental constraints and uncertainty sources

The CF-LIBS framework infers plasma parameters and elemental fractions from the measured spectrum through an inverse procedure constrained by a forward emission model. The accuracy of the retrieved quantities, however, depends not only on the physical assumptions discussed in section 2.2, but also on the experimental acquisition settings and on the processing steps used to extract line intensities and widths. This section summarizes the main experimental constraints and the dominant uncertainty sources, with particular emphasis on the factors that limit the quantification of minor and trace elements.

2.5.1. SNR, averaging, and impact on minor/trace elements

A well-known limitation in quantitative CF-LIBS arises from the *closure* condition, $\sum_A C_A = 1$: inaccuracies in the major constituents can propagate to the remaining fractions. Nevertheless, closure alone is generally insufficient to explain the large errors often observed for low-abundance species. In most practical cases, the dominant contribution is the limited signal-to-noise ratio (SNR) of weak analytical lines.

This limitation is closely linked to the plasma conditions required by CF-LIBS. In order to operate within a regime where LTE-based relations can be applied, one typically targets relatively high electron densities. Under these conditions, continuum emission (Bremsstrahlung and radiative recombination) increases and may obscure weak lines if not properly handled. The dependence of continuum emissivity on plasma parameters is recalled in eq. (1.11), while the superposition of continuum and line radiation is schematically illustrated in fig. 1.3.

From an experimental standpoint, SNR can be improved by increasing the gate width, thereby collecting a larger number of photons. In addition, SNR can be increased by averaging spectra acquired over repeated shots and different positions on the sample surface, as already adopted in this work (section 1.3). For uncorrelated noise, the improvement scales approximately as

$$\text{SNR} \propto \sqrt{N}, \quad (2.13)$$

where N is the number of averaged spectra. This procedure is particularly relevant for high-resolution spectrometers (e.g. echelle systems), where the combination of high spectral resolution and broad spectral coverage can reduce the detected signal per spectral channel.

When extensive averaging is employed, it is important to prevent systematic modifications of the laser–material interaction due to repeated irradiation of the same location (e.g. crater growth and “cannon” effects). A standard mitigation strategy is to use a motorized stage to distribute laser shots over multiple sites on the sample surface.

2.5.2. Temporal gating and choice of acquisition window

Time-resolved detection is essential in LIBS because the plasma evolves rapidly after breakdown. As shown in fig. 1.4, early emission is dominated by continuum, followed by ionic and then atomic emission at later times [7]. In CF-LIBS, the acquisition window must be selected to (i) reduce continuum background and (ii) ensure that the plasma properties do not vary significantly within the observation interval, so that equilibrium

relations (Boltzmann/Saha) provide a meaningful description.

A practical stationarity requirement can be expressed as

$$\frac{\Delta T}{T} \ll 1, \quad \frac{\Delta n_e}{n_e} \ll 1, \quad (2.14)$$

where ΔT and Δn_e denote the variations of the plasma parameters within the gate width t_{gate} [16]. This condition limits the extent to which t_{gate} can be increased to improve SNR.

The selection of t_{delay} (gate delay) and t_{gate} (gate width) therefore results from a compromise between signal accumulation and temporal stability. A commonly reported guideline is [16]

$$t_{\text{gate}} \simeq \frac{t_{\text{delay}}}{2}, \quad (2.15)$$

which is consistent with the empirical rule already introduced in section 1.3.2 (see eq. (1.22)).

Finally, LTE must be assessed within the selected window. A standard screening criterion is the McWhirter condition eq. (1.10). Measurements acquired far outside an LTE-like interval—for instance at very early times dominated by continuum emission—cannot be interpreted within standard CF-LIBS formulations. In practice, t_{delay} and t_{gate} are tuned to operate in a time region where line emission is sufficiently strong while LTE conditions remain plausible.

2.5.3. Line measurement: integration, Voigt fitting, and instrumental broadening

The extraction of n_e , T , and elemental fractions relies on robust estimates of line integrals and line widths. The measured spectrum can be interpreted as the superposition of a slowly varying background (continuum and baseline) and discrete line emission (see fig. 1.3). For a given transition, the experimental observable entering Boltzmann and Saha–Boltzmann plots is the line-integrated signal S_{ul} (eq. (2.7)), which is obtained after background subtraction:

$$S_{ul} = \int_{\lambda_1}^{\lambda_2} [I_{\text{corr}}(\lambda) - I_{\text{base}}(\lambda)] d\lambda, \quad (2.16)$$

where $I_{\text{base}}(\lambda)$ represents the estimated baseline and $I_{\text{corr}}(\lambda)$ is the spectrum corrected for instrumental effects (section 2.5.4). Baseline removal is typically performed by fitting a local background (e.g. polynomial or spline) in a window around the line. The key requirement is that the procedure preserves the line wings, since distortions directly affect

both the integrated area and the extracted width.

For electron-density estimation, Stark broadening is retrieved from the Lorentzian component of a Voigt fit, as discussed in section 1.4.2 and illustrated in fig. 1.6. The measured line shape is commonly modelled as a Voigt profile, i.e. the convolution of a Gaussian component (Doppler + instrumental) and a Lorentzian component (dominated by Stark broadening):

$$V(\lambda) = [G(\lambda; \Delta\lambda_G) * L(\lambda; \Delta\lambda_L)]. \quad (2.17)$$

If Doppler and instrumental broadenings are both approximated as Gaussian contributions, their FWHM values combine as

$$\Delta\lambda_G \simeq \sqrt{\Delta\lambda_{\text{inst}}^2 + \Delta\lambda_D^2}, \quad (2.18)$$

where $\Delta\lambda_{\text{inst}}$ is the instrumental FWHM and $\Delta\lambda_D$ is the Doppler FWHM. The Lorentzian width $\Delta\lambda_L$ is then associated, to first order, with the Stark width used in eq. (1.23) to estimate n_e [17].

Accurate knowledge of $\Delta\lambda_{\text{inst}}$ is therefore essential: it is typically determined using narrow reference lines (e.g. calibration lamps) and propagated through the Voigt deconvolution. Underestimation of $\Delta\lambda_{\text{inst}}$ leads to an overestimation of the Lorentzian/Stark contribution (and thus of n_e), whereas overestimation of $\Delta\lambda_{\text{inst}}$ biases the inferred Stark width in the opposite direction.

2.5.4. Pre-processing and instrumental corrections

A meaningful comparison between measured and computed spectra requires correction of the raw signal for instrumental effects. In particular, the wavelength-dependent response of the optical chain (collection optics, fiber coupling, spectrometer throughput, detector sensitivity) must be taken into account, since CF-LIBS relies on radiance comparisons across broad spectral intervals [16]. This is consistent with the instrumental factor F introduced in the definition of the line-integrated signal (eq. (2.7)).

A compact correction model can be written as

$$I_{\text{corr}}(\lambda) = \frac{I_{\text{raw}}(\lambda) - I_{\text{dark}}(\lambda)}{R(\lambda)}, \quad (2.19)$$

where $I_{\text{dark}}(\lambda)$ accounts for the electronic background acquired with the same exposure time, and $R(\lambda)$ is the apparatus response function. The latter is typically measured using radiometric standards (e.g. deuterium and tungsten lamps), although broadband

calibration is particularly demanding for echelle spectrometers due to the strong spectral variation of lamp emission and instrument throughput [16].

Additional pre-processing steps include wavelength calibration, outlier removal (e.g. cosmic rays), and normalization conventions consistent with the forward model. Response correction and baseline subtraction should be applied consistently before extracting line integrals used in Boltzmann/Saha–Boltzmann plots (section 2.3) or before comparing measured and computed spectra in the χ^2 minimization (eq. (2.1)).

2.5.5. Uncertainty propagation: closure, self-absorption, and plasma size

A quantitative CF-LIBS result should be accompanied by an uncertainty discussion grounded in the dominant error sources. A useful starting point is the propagation of errors from inferred atomic number densities to elemental fractions. Applying standard error propagation to $C_A = n_A / \sum_j n_j$ yields [16]

$$\frac{\Delta C_A}{C_A} = \sqrt{(1 - C_A)^2 \left(\frac{\Delta n_A}{n_A} \right)^2 + \sum_{j \neq A} C_j^2 \left(\frac{\Delta n_j}{n_j} \right)^2}. \quad (2.20)$$

This relation shows that closure does not automatically imply that minor/trace fractions are dominated by major-element uncertainties. In practice, large errors for low-abundance species are frequently driven by limited SNR and by the difficulty of extracting reliable line integrals in the presence of strong continuum emission [16].

When self-absorption is significant, uncertainty can increase further because the relation between measured intensity and optical thickness is nonlinear. For a homogeneous plasma, an error-propagation analysis leads to the following expression for the relative uncertainty on the atomic number density [16]:

$$\frac{\Delta n_A}{n_A} = \sqrt{\left(\frac{\Delta \tau_0}{\tau_0} \right)^2 + \left(\frac{\Delta A_{ul}}{A_{ul}} \right)^2 + (1 - e^{-\tau_0}) \left[\left(\frac{\Delta w_{sd}}{w_{sd}} \right)^2 + \left(\frac{\Delta L_p}{L_p} \right)^2 \right]}, \quad (2.21)$$

where τ_0 is the line-centre optical thickness, w_{sd} is the spectral line width, and L_p is the effective plasma size/path length. The factor $(1 - e^{-\tau_0})$ ensures that the optically thin limit is recovered, where uncertainties associated with line width and plasma size vanish [16]. This term also clarifies why, when optical thickness is explicitly modelled through eq. (1.16), the estimation of L becomes directly coupled to the uncertainty on

composition.

The uncertainty on τ_0 can be related to the uncertainty on the measured intensity through an *error growth factor* [16]:

$$\frac{\Delta\tau_0}{\tau_0} = g(\tau_0) \frac{\Delta I}{I}, \quad g(\tau_0) = \frac{1}{\tau_0} \frac{f(\tau_0)}{f'(\tau_0)}, \quad (2.22)$$

where $I = f(\tau_0)$ denotes the functional dependence of intensity on optical thickness and $f'(\tau_0) = \partial I / \partial \tau_0$. For line-centre intensity measurements and negligible apparatus broadening, the growth factor reduces to [16]

$$g_0 = \frac{1 - e^{-\tau_0}}{\tau_0 e^{-\tau_0}}. \quad (2.23)$$

For increasing τ_0 , the growth factor can become large, motivating the common CF-LIBS practice of prioritizing weak, non-resonant transitions and avoiding strongly self-absorbed lines in the initial analysis (see also section 2.2.5).

Overall, the dominant uncertainty sources in CF-LIBS typically include: (i) limited SNR for weak lines (especially for minor/trace elements), (ii) departures from LTE within the selected gate window, (iii) residual self-absorption and uncertainties on L and w_{sd} when optical thickness is significant, (iv) spectroscopic-data uncertainties (notably A_{ul}), and (v) instrumental corrections (apparatus response and instrumental width). Their relative importance depends on the material class, on plasma conditions, and on the adopted modelling level (optically thin vs. full radiative transfer).

2.6. Motivation

Throughout this chapter, it has been shown that CF-LIBS can, in principle, be applied to a wide range of materials. In the context of this thesis, the method is employed to investigate matrix effects and their influence on quantitative LIBS analysis.

This approach is particularly well suited for this purpose because the laser-induced plasma is strongly affected by intrinsic material properties, such as thermal conductivity, reflectivity, and band-gap energy. These properties govern the laser-matter interaction and the subsequent ablation process, ultimately influencing plasma formation and evolution. As a result, variations in material properties lead to changes in key plasma parameters, notably the temperature T and the electron density n_e .

In the following chapter, these matrix-dependent effects will be analysed by applying

the CF-LIBS framework to different classes of materials. The results will highlight how material properties influence plasma conditions and, consequently, the reliability and limitations of calibration-free quantitative analysis.

3 | Matrix effects

Matrix effects are a major limitation of quantitative LIBS and, more generally, of any approach that attempts to relate spectral intensities directly to elemental concentrations. In LIBS, sampling, vaporization, excitation, and emission occur within the same transient event (laser ablation and plasma formation). As a consequence, the measured signal depends not only on the amount of a given element, but also on the physical properties of the target and on the plasma conditions generated during the interaction. This is why calibration curves are typically matrix-dependent and why quantitative CC-LIBS requires reference standards that closely match both the elemental composition and the host matrix.

Calibration-free LIBS (CF-LIBS) was introduced to reduce the dependence on empirical calibration by extracting plasma parameters and composition through a physically constrained plasma model [1]. However, CF-LIBS does not eliminate matrix effects: material properties still influence ablation efficiency and plasma formation and therefore indirectly affect the inferred temperature T and electron density n_e , as well as the validity of key assumptions (LTE, optical thinness, homogeneity).

3.1. Conceptual framework: where matrix effects enter the LIBS chain

A useful way to organize matrix effects is to follow the causal chain of the measurement: (i) laser energy coupling into the solid, (ii) ablation and mass removal, (iii) plasma formation and evolution, (iv) emission and radiation transport, (v) collection optics and instrument response. A change in target properties may affect one or more of these stages and ultimately modify the detected spectrum even at fixed elemental composition. In particular, the first stages (energy coupling and ablation) set the initial conditions for plasma evolution; therefore, matrix effects are often more pronounced at early times, whereas at later times the plasma dynamics are increasingly governed by expansion and cooling in the ambient gas.

3.2. Material-driven origins of matrix effects

3.2.1. Optical properties and laser–solid coupling

The fraction of laser energy effectively deposited into the target depends on optical constants (refractive index, absorption coefficient) and on the local surface condition. In the simplest picture, reflectivity and absorption determine the penetration depth and the spatial distribution of deposited energy, as discussed in the context of Lambert–Beer absorption in solids (see eq. (1.2)). As a result, even for nominally identical chemical composition, different structural states (e.g., crystalline vs. amorphous) may lead to different coupling efficiency and different effective irradiance at the onset of ablation.

3.2.2. Thermophysical properties and ablation efficiency

Once energy is deposited, the conversion into ablated mass is strongly controlled by thermophysical properties such as density ρ , thermal conductivity k (and, more generally, thermal diffusivity), and phase-change energetics. The heat conduction model introduced in eq. (1.3) highlights that different k and ρ values alter both the spatial extent of the heated region and the timescale for heat dissipation. For the same incident fluence, these differences translate into changes in ablation rate and mass removed per pulse. Since the early plasma density is directly linked to the amount of ablated material, thermophysical matrix effects naturally propagate into different n_e and T at early delays.

3.2.3. Microstructure and surface condition: roughness, porosity, and grain boundaries

Beyond bulk thermophysical constants, microstructure can induce both systematic and statistical effects. Surface roughness and porosity locally modify incidence angles and field enhancement, leading to variations in breakdown and ablation thresholds. In polycrystalline ceramics, grain boundaries and residual defects act as preferential sites for energy absorption and fracture-driven material removal. These mechanisms increase shot-to-shot variability and may alter the particle-to-vapour balance of the plume. In this work, statistical effects are mitigated by averaging spectra acquired over many positions ($N = 100$), so that the focus is placed on systematic differences between materials.

3.2.4. Plasma-stage matrix effects: shielding, inhomogeneity, and self-absorption

Material-dependent ablation conditions affect the plasma not only through the initial mass vaporization but also through optical thickness and spatial gradients. A denser or larger plume can enhance laser–plasma interaction (shielding) and modify the subsequent heating phase, which changes the initial plasma state and the temporal evolution of emission. In addition, if the plasma becomes optically thick in strong transitions, self-absorption alters line intensities and may bias both CC-LIBS and CF-LIBS analyses; this is particularly relevant when strong resonant lines are used or when the plasma size/density increases [3].

3.3. How experimental parameters modulate matrix effects

Material-driven matrix effects are always observed through the filter of experimental parameters. For this reason, it is important to clarify which parameters can amplify or partially mask them.

3.3.1. Laser fluence and irradiation regime

Fluence (controlled by pulse energy, spot size, and pulse duration) determines whether the interaction occurs close to the ablation/breakdown threshold or well above it. Near threshold, small differences in optical and thermophysical properties lead to large relative changes in ablation yield, so matrix effects tend to be enhanced. At higher fluence, plasma generation is more robust, but the experiment may enter regimes where continuum emission and plasma shielding become more important, which can reduce spectral contrast and complicate quantitative analysis.

3.3.2. Ambient gas and confinement

The ambient gas composition and pressure influence plume expansion, shock dynamics, cooling rate, and collisionality. Although they are held constant in the experimental set-up used in this thesis (see chapter A), they set the background against which material differences manifest in $T(t)$ and $n_e(t)$.

3.3.3. Temporal gating and choice of the analysis window

Delay time and gate width select different phases of plasma evolution. Early delays are typically affected by intense continuum and strong gradients, while later delays emphasize atomic emission under cooler and more expanded conditions. Since the CF-LIBS framework relies on assumptions such as LTE and quasi-stationarity within the selected gate (see section 2.5), the choice of the temporal window is crucial, as it affects both the sensitivity to matrix effects and the robustness of inferred plasma parameters.

3.4. Sample set and complementary characterization (XPS)

3.4.1. Sample set

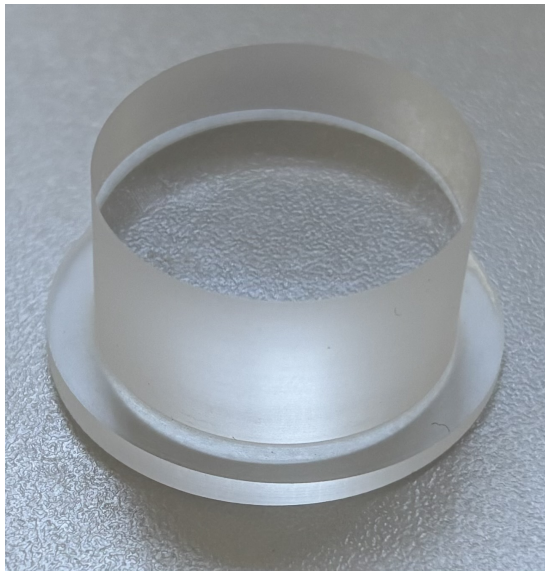
The materials investigated in this thesis are: *Sapphire* (fig. 3.1a), a single-crystal α -Al₂O₃ with corundum structure; *Alumina* (fig. 3.1b), a high-purity sintered aluminum oxide ceramic (99.9% Al₂O₃) and therefore polycrystalline; α -*Quartz* (fig. 3.1c), a crystalline (single-crystal) SiO₂ sample; and *Infrasil* (fig. 3.1d), fused silica, i.e. amorphous SiO₂ glass.

3.4.2. Material properties relevant to matrix effects

The table 3.1 summarizes the key properties that control laser coupling and the conversion of deposited energy into ablated mass: refractive index (affecting Fresnel reflection), bulk absorption at the laser wavelength, thermal conductivity (controlling heat dissipation), density (affecting mass loading for a given ablated volume), and band-gap energy (relevant for defect-mediated coupling in the NIR). For birefringent crystals (Quartz and Sapphire), refractive index and thermal conductivity can be anisotropic; therefore, values are reported when available along directions parallel/perpendicular to the crystalline *c*-axis. For Alumina, *n* and μ are not listed because, in polycrystalline ceramics, the laser-matter coupling and the optical losses are typically dominated by scattering rather than by linear bulk absorption [19].

3.4.3. XPS: surface composition and contamination

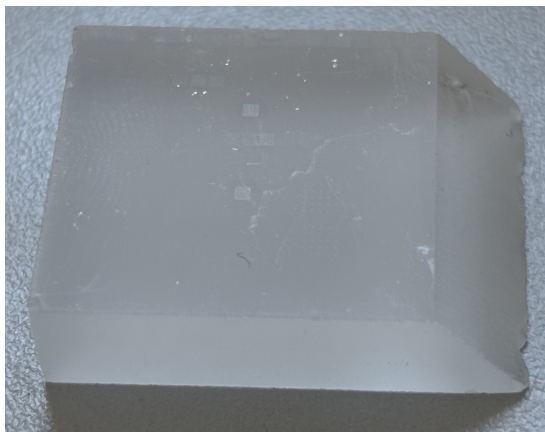
X-ray photoelectron spectroscopy (XPS) provides surface-sensitive elemental composition and can highlight the presence near-surface contaminants and minor species that may



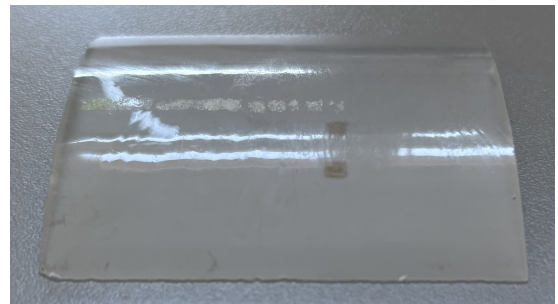
(a) Sapphire



(b) Alumina



(c) Quartz



(d) Infrasil

Figure 3.1: Photographs of the samples used in this work.

contribute to early-time LIBS spectra (especially during the first shots or at early delays). Table 3.2 reports the mean atomic concentrations (and standard deviations) obtained from multiple spots on each sample.

The presence of carbon is interpreted as adventitious/surface contamination rather than bulk composition, which is expected given the high surface sensitivity of XPS. For the alumina ceramic sample, Na, Mg, and K are detected at the surface at the percent level; this is consistent with the fact that ceramic processing and handling can introduce surface-enriched impurities. These impurities may introduce defect states and locally modify the effective optical response compared to the ideal bulk value. Therefore, compared to single-crystal LIBS spectra, they may contribute with additional weak lines, even if their bulk

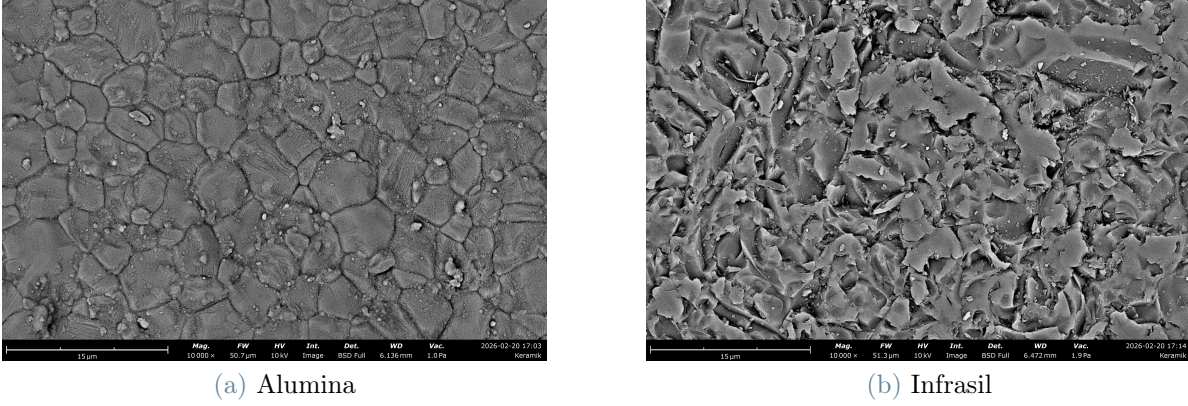


Figure 3.2: SEM images highlighting microstructural features: (a) Alumina (polycrystalline grains), (b) Infrasil (amorphous glassy morphology).

Table 3.1: Selected properties relevant to matrix effects at room temperature.

Property	Quartz	Infrasil	Sapphire	Alumina
n (@1064 nm)	$n_{ord} = 1.5341509$	1.4498251	$n_{ord} = 1.7544854$	—
	$n_{extra} = 1.5429237$		$n_{extra} = 1.7466254$	
μ (@1064 nm) (ppm cm ⁻¹)	0.25–4	300	11	—
k (W m ⁻¹ K ⁻¹)	$\parallel c$: 11.7; $\perp c$: 6.5	1.38	$\parallel c$: 35.1; $\perp c$: 33	30
c_p (J kg ⁻¹ K ⁻¹)	744	772	753	768
ρ (g cm ⁻³)	2.65	2.203	3.99	3.95
E_g (eV)	9.47	9.0	8.8	8.8
ε_r	$\parallel c$: 4.27; $\perp c$: 4.34	3.75	$\parallel c$: 10.55; $\perp c$: 8.6	9

Data sources: n values from manufacturer dispersion relations; c_p for Al₂O₃ from [20]; absorption values at 1064 nm discussed in [21–23]; E_g values from [24–26].

concentration is substantially lower.

Table 3.2: XPS atomic concentrations (at.%) reported as mean $\pm$ standard deviation over 12 measured spots.

Element	Infrasil	Quartz	Sapphire	Alumina
C	10.34 $\pm$ 2.65	11.95 $\pm$ 6.06	25.70 $\pm$ 4.32	14.51 $\pm$ 2.12
O	61.42 $\pm$ 2.48	59.30 $\pm$ 5.42	48.25 $\pm$ 3.02	54.05 $\pm$ 0.95
Si	28.24 $\pm$ 0.56	28.75 $\pm$ 1.00	—	—
Al	—	—	26.05 $\pm$ 1.32	28.73 $\pm$ 0.70
Na	—	—	—	1.56 $\pm$ 0.43
Mg	—	—	—	0.57 $\pm$ 0.15
K	—	—	—	0.58 $\pm$ 0.08

3.5. Implications for the present thesis and link to the Results chapter

The core goal of this thesis is to quantify how matrix-dependent material properties influence the time evolution of the plasma parameters inferred by CF-LIBS. The experimental strategy is to keep the instrumental configuration fixed and to compare material pairs with identical nominal chemical composition but different structural states. For SiO_2 , the comparison between fused silica (amorphous) and quartz (crystalline) isolates the role of amorphous vs. crystalline order on laser coupling, ablation efficiency, and plasma evolution. For Al_2O_3 , the comparison is between sapphire (single crystal) and sintered alumina ceramic.

In the following chapter, time-resolved LIBS spectra are analysed at different delay times to build $T(t)$ and $n_e(t)$ curves. This representation directly probes how differences in energy coupling and ablation translate into different plasma initial conditions and cooling/expansion dynamics. Since multiple mechanisms can act simultaneously and sometimes in opposite directions, a purely theoretical prediction is generally not sufficient to disentangle contributions; therefore, the interpretation is based on the experimental evolution of the plasma parameters and on the complementary XPS characterization.

4 | Results and analysis

Obtaining spectra suitable for CF-LIBS requires a careful optimization of the acquisition parameters. For this reason, two preliminary studies were carried out: (i) a surface-cleaning analysis, aimed at minimizing contamination-driven lines, and (ii) an irradiation (fluence) study, aimed at maximizing the signal-to-noise ratio (SNR) while preserving the sample integrity.

4.1. Cleaning analysis

LIBS spectra can be strongly affected by surface contamination. A common mitigation strategy consists of performing a sequence of *cleaning shots* on the same position before acquiring the spectrum used for analysis, to reduce the contribution of surface-related elements. This procedure produces a crater and progressively probes deeper layers of the material, enabling bulk-sensitive measurements thanks to tight focusing optics and the positioning accuracy of the translation stage.

The cleaning analysis was performed at fixed gating parameters ($t_{\text{delay}} = 400$ ns and $t_{\text{gate}} = 150$ ns) and fixed irradiation conditions ($E_{\text{laser}} = 8$ mJ, single pulse). For each number of shots, spectra were acquired on a set of $N = 100$ positions and averaged. The procedure was repeated on three different regions of each sample to reduce the impact of local inhomogeneities and statistical fluctuations. A characteristic contamination line (or a set of lines) was then selected; in the present case, Ca lines were used as a tracer, since they were consistently stronger for the first shots and decreased as the surface layer was removed. The same positions were irradiated repeatedly (10 iterations) to evaluate the evolution of the Ca signal with increasing number of shots (i.e. as a function of depth).

Based on the results shown in fig. 4.1, a trade-off was selected between (i) applying a sufficient number of cleaning shots to stabilize the spectra and (ii) limiting the total number of shots to avoid excessive material removal.

Throughout this work, two cleaning shots at $E_{\text{laser}} = 8$ mJ were applied at each position, followed by the acquisition shots used for plasma diagnostics and CF-LIBS analysis.

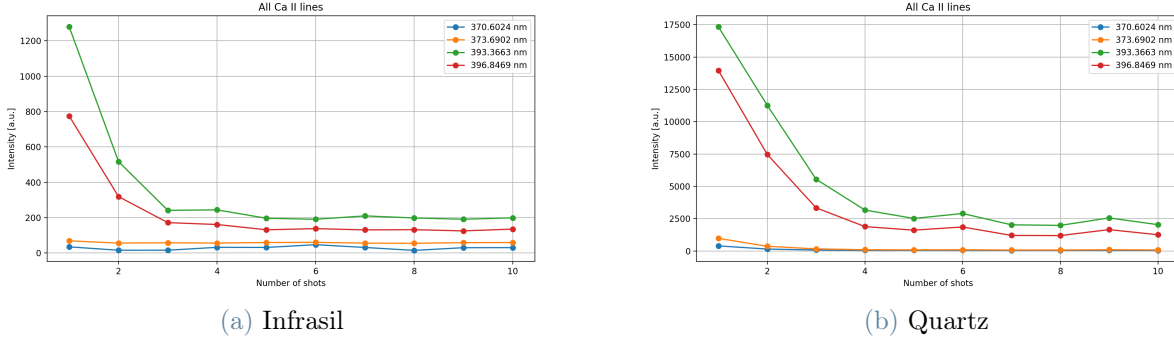


Figure 4.1: Cleaning analysis for the SiO_2 samples. The Ca-line intensity decreases as successive shots remove surface contamination and progressively probe the bulk.

4.2. Fluence analysis

The second preliminary study focused on the optimization of the irradiation conditions, namely pulse energy and number of pulses, with the dual goal of maximizing SNR and limiting sample damage. Pulse energies were explored in the range $E_{\text{laser}} = 2\text{--}22$ mJ, and the number of pulses varied from 1 to 10. Since the focusing conditions were kept fixed, varying E_{laser} corresponds to varying the fluence.

For single-shot acquisition, the SNR trend, reported in fig. 4.2, shows an initial increase followed by a degradation at higher energies. This behaviour is consistent with the growth of continuum emission (and, depending on the regime, plasma shielding), which reduces spectral contrast.

A reasonable single-shot compromise was found around $E_{\text{laser}} = 15$ mJ. However, single-shot operation resulted in less stable plasma conditions. A multi-pulse strategy was therefore tested to improve stability while preserving comparable spectral quality. In particular, a configuration with $E_{\text{laser}} = 5$ mJ and 8 pulses provided spectral characteristics similar to the 15 mJ single-shot case, with improved repeatability.

In the following, to increase both SNR and plasma stability, the configuration $E_{\text{laser}} = 5$ mJ with 8 pulses is adopted.

4.3. Line selection

A critical step for repeatable and reliable CF-LIBS analysis is the selection of suitable reference lines. In this work, the reference line for each material serves (i) as the diagnostic line for the electron-density estimate via line-shape analysis and (ii) as a stable anchor

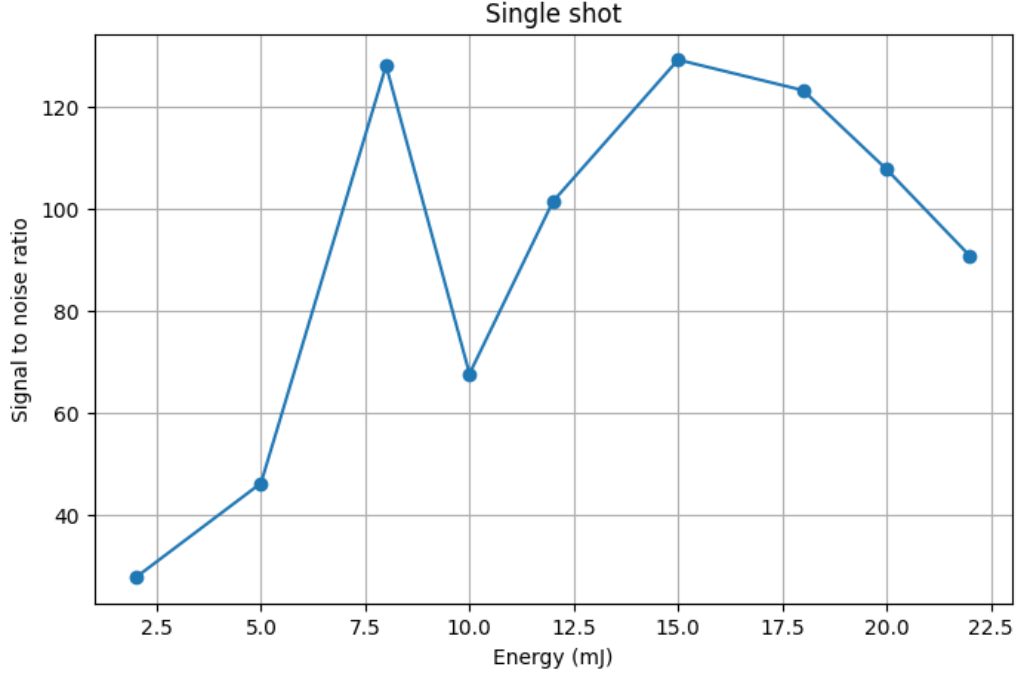


Figure 4.2: Irradiation study for single-shot acquisition: the SNR improves at moderate energies and degrades at higher energies due to the increasing continuum contribution.

for normalization of the major-element contribution. The selected transition should: (i) exhibit high SNR, (ii) be minimally affected by self-absorption, (iii) be isolated (limited blending), and (iv) be detectable across the full explored time range. In addition, the choice must account for the different temporal behaviour of atomic and ionic emission: ionic lines are typically stronger at early times, while neutral lines dominate at later times. Consequently, selecting an atomic reference line may increase uncertainty at early delays, whereas selecting an ionic line may increase uncertainty at late delays.

Line selection was guided by the lower-level energy E_l (to reduce the likelihood of strong self-absorption), previous studies on similar materials [27], and the stability/quality of the line-profile fitting. The reference transitions adopted are the Si I line at $\lambda = 390.5523$ nm (fitting showed in fig. 4.3a) and the Al II line at $\lambda = 281.6185$ nm (fitting showed in fig. 4.3b). Their spectroscopic parameters are reported in table 4.1.

Line	Wavelength (nm)	Accuracy	A_{ul} (s^{-1})	E_l (cm^{-1})	E_u (cm^{-1})
Si I	390.5523	B	1.33×10^7	15394.370	40991.884
Al II	281.6185	A	3.57×10^8	59852.02	95350.60

Table 4.1: Spectroscopic parameters of the reference lines used for plasma diagnostics and normalization.

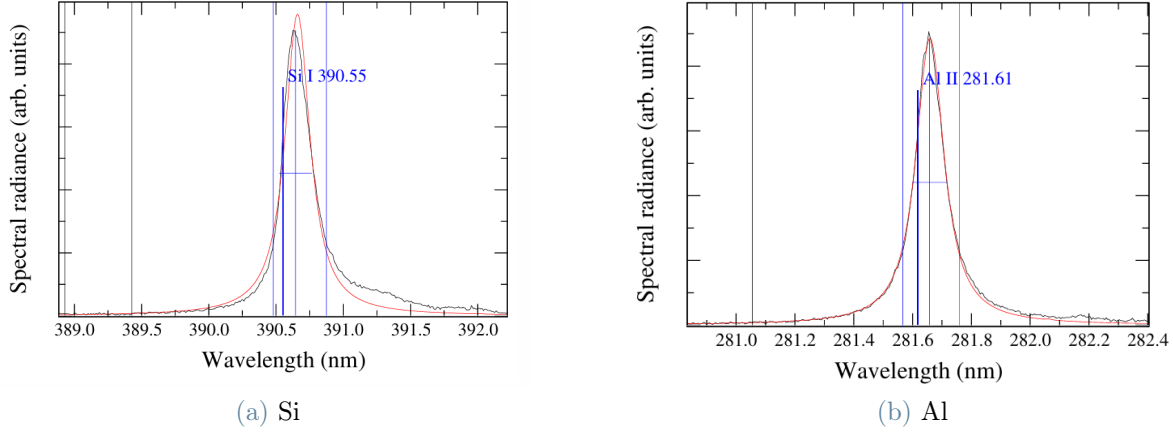


Figure 4.3: Reference lines experimental (black) and computed (red) adopted for the SiO_2 and Al_2O_3 sample sets.

These transitions combine favourable atomic-data accuracy (especially for A_{ul}) with relatively high E_l , which reduces the probability of severe self-absorption compared with resonance lines.

4.4. Data acquisition

The detection system includes two spectrometers, covering the UV range (190–430 nm) and the visible range (405–800 nm). Since the two channels cannot be acquired on exactly the same plasma event, UV and visible spectra were collected on two nearby positions under identical experimental settings and then merged into a single spectrum. The merging was performed after response correction by matching the overlap region (405–430 nm). Repeating this procedure yields a set of complete spectra (190–800 nm) suitable for CF-LIBS analysis.

In particular, the acquisition protocol consists of three spectra in the UV range and three spectra in the visible range. Each UV spectrum is merged with each visible spectrum, yielding nine possible UV–VIS combinations. Therefore, correlations among the merged spectra are expected. This strategy reduces systematic biases related to limited spectral coverage, at the cost of increased acquisition and processing time.

4.5. Temporal sampling

The temporal evolution $T(t)$ and $n_e(t)$ was reconstructed by varying delay time and gate width. The initial set of acquisition windows was chosen based on commonly used

values in the literature [7] and then refined by inspecting the data dispersion: additional time points were introduced in regions where the inferred parameters varied significantly without a clear monotonic trend. The final set of gate parameters $(t_{\text{delay}}, t_{\text{gate}})$ (in ns) is:

$$\begin{aligned} &(70, 30), (150, 100), (300, 100), (400, 150), \\ &(700, 300), (1000, 500), (1200, 600), (1500, 750), \\ &(2000, 1000), (3000, 1500), (5000, 2500). \end{aligned}$$

Since each measurement corresponds to an average over the gate width, the time associated with each point in the plots is taken as

$$t = t_{\text{delay}} + \frac{1}{2}t_{\text{gate}}.$$

4.6. Plasma length

The effective plasma size (path length, L_p) required by the analysis was estimated by fitting experimental trends obtained under similar laser and ambient conditions using reference curves. The fitted values adopted for the SiO_2 and Al_2O_3 sample sets are shown in fig. 4.4. The associated uncertainty was treated as constant within the explored temporal range.

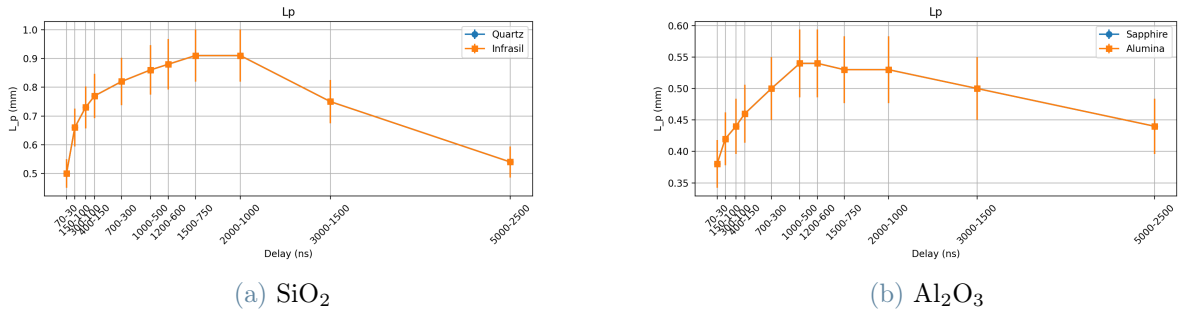


Figure 4.4: Fitted L_p values from reference curves.

4.7. Results

The inferred electron-density evolution $n_e(t)$ is shown in fig. 4.5 together with the McWhirter threshold used as a preliminary LTE screening criterion. For the Al_2O_3 sample set, the latest acquisition window (5000, 2500) was excluded because the corresponding spectra exhibited very weak emission, preventing a reliable CF-LIBS analysis.

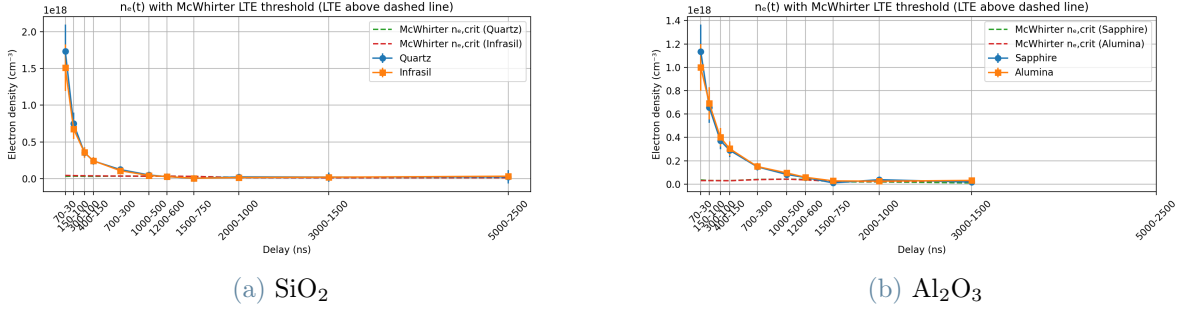


Figure 4.5: $n_e(t)$ with the McWhirter criterion. LTE is preliminarily considered plausible when the measured n_e lies above the dashed line.

The uncertainty on averaged quantities was evaluated as follows. For a set of n measurements X_i (with $X \in \{T, n_e\}$), the mean is

$$\bar{X} = \frac{1}{n_{\text{meas}}} \sum_{i=1}^{n_{\text{meas}}} X_i. \quad (4.1)$$

The variance of the mean, including correlations, is

$$\sigma_{\bar{X}}^2 = \frac{1}{n_{\text{meas}}^2} \left(\sum_{i=1}^{n_{\text{meas}}} \sigma_i^2 + \sum_{i < j} \text{Cov}(X_i, X_j) \right), \quad (4.2)$$

where σ_i is the uncertainty associated with X_i and $\text{Cov}(X_i, X_j) = \rho_{ij}\sigma_i\sigma_j$, with ρ_{ij} the correlation coefficient. Since the measurements are not strictly independent (see section 4.4), a conservative worst-case scenario was adopted by assuming $\rho_{ij} = 1$ for all pairs, which yields

$$\sigma_{\bar{X}}^2 = \frac{1}{n_{\text{meas}}^2} \left(\sum_{i=1}^{n_{\text{meas}}} \sigma_i \right)^2. \quad (4.3)$$

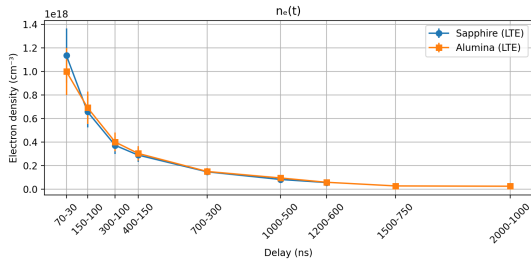
The actual uncertainty is expected to lie between the independent and fully correlated limits:

$$\frac{1}{n_{\text{meas}}^2} \sum_{i=1}^{n_{\text{meas}}} \sigma_i^2 \leq \sigma_{\bar{X}}^2 \leq \frac{1}{n_{\text{meas}}^2} \left(\sum_{i=1}^{n_{\text{meas}}} \sigma_i \right)^2. \quad (4.4)$$

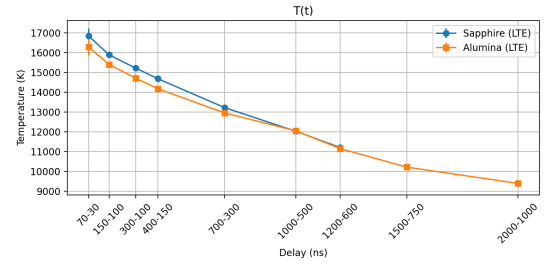
The McWhirter condition is not satisfied for all acquisition windows; therefore, a subset of the results cannot be interpreted within an LTE-based CF-LIBS framework.

4.8. LTE screening

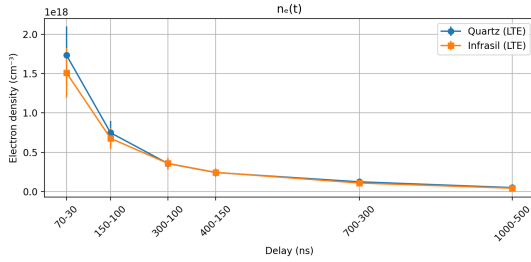
To restrict the analysis to LTE-consistent conditions, all points that do not satisfy the McWhirter criterion were removed from the dataset (both for n_e and for T). For the resulting points the linearity of Saha-Boltzmann plot was ensured. The resulting curves are shown in fig. 4.6. For most points, the uncertainty bars remain smaller than the marker size, indicating that the inferred parameters are robust even under the conservative worst-case assumption.



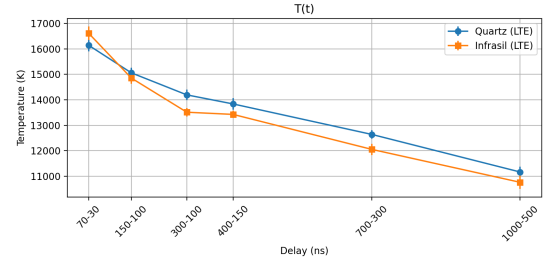
(a) $n_e(t)$ for Al_2O_3



(b) $T(t)$ for Al_2O_3



(c) $n_e(t)$ for SiO_2



(d) $T(t)$ for SiO_2

Figure 4.6: Plasma-parameter evolution after LTE screening with McWhirter criterion.

A qualitative difference in LTE persistence is already visible: depending on the material-dependent plasma dynamics, the McWhirter condition may remain satisfied over a longer or shorter temporal interval. This aspect is discussed in section 4.9, together with its connection to matrix effects.

4.9. Discussion

This section discusses the trends observed in the retrieved plasma parameters after LTE screening. Only differences larger than the estimated uncertainties are interpreted as significant. Over the investigated time window, both $n_e(t)$ and $T(t)$ exhibit a monotonic decrease (see fig. 4.6). In order to quantify the characteristic decay rates and to enable a compact comparison between material pairs, the post-screening trends are parametrized

with exponential laws. In particular, $T(t)$ typically shows two distinct slopes in semi-logarithmic representation (fig. 4.7), motivating a two-stage (piecewise) exponential description.

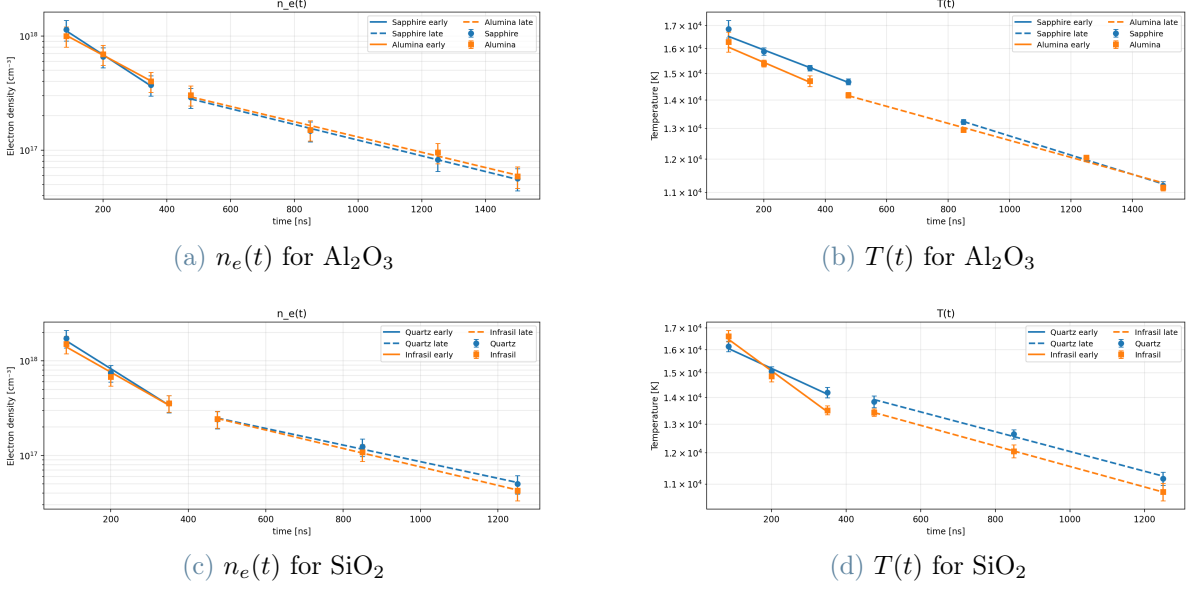


Figure 4.7: Exponential fits of the plasma-parameter evolution after LTE screening with the McWhirter criterion. Fits are performed only on the time points for which the LTE condition is simultaneously satisfied by both samples in each material pair.

4.9.1. Fit model and statistical metric.

For a generic decreasing quantity $y(t) \in \{n_e(t), T(t)\}$, an exponential decay is written as

$$y(t) = A_0 \exp\left(-\frac{t}{\tau}\right), \quad (4.5)$$

which becomes linear by taking the natural logarithm:

$$z(t) = \ln(y(t)) = b + mt, \quad (4.6)$$

with $b = \ln(A_0)$ and $m = -1/\tau$. The regression is performed in the (t, z) plane using a weighted linear least-squares procedure; uncertainties on A_0 and τ are obtained from the covariance matrix of the fitted parameters. The goodness of fit is quantified through the

reduced χ -square of the weighted $\ln(y)$ regression,

$$\chi_{\text{red}}^2 = \frac{1}{N_{\text{fit}} - \nu} \sum_{i=1}^{N_{\text{fit}}} \left(\frac{z_i - z_i^{\text{fit}}}{\sigma_{z_i}} \right)^2, \quad (4.7)$$

where N_{fit} is the number of fitted data points, ν is the number of fit parameters (here $\nu = 2$), z_i is the measured value, z_i^{fit} is the fitted value, and σ_{z_i} is the standard error of z_i . The fit intervals (and therefore N_{fit}) are selected by minimizing χ_{red}^2 over contiguous subsets within the early-time and late-time regions. As a consequence, for a given regime the number of fitted points can differ between the two samples of the same pair, depending on how long each dataset remains available under the LTE screening.

Plasma parameter	Stage	Sample	A_0	$A_{0,\text{err}}$	τ	τ_{err}	χ_{red}^2
n_e	early	Quartz	2.69×10^{18}	0.71×10^{18}	169	32	0.381
		Infrasil	2.21×10^{18}	0.58×10^{18}	187	38	0.508
	late	Quartz	6.51×10^{17}	2.28×10^{17}	494	95	0.119
		Infrasil	7.17×10^{17}	2.45×10^{17}	445	76	0.018
T	early	Quartz	16716	304	2084	335	0.661
		Infrasil	17567	341	1313	129	1.392
	late	Quartz	15867	448	3629	424	0.547
		Infrasil	15382	345	3494	386	0.002
n_e	early	Sapphire	1.58×10^{18}	0.40×10^{18}	239	61	0.067
		Alumina	1.36×10^{18}	0.34×10^{18}	289	89	0.014
	late	Sapphire	5.97×10^{17}	1.69×10^{17}	631	106	0.046
		Alumina	6.09×10^{17}	1.72×10^{17}	649	111	0.183
T	early	Sapphire	16960	244	3253	411	0.464
		Alumina	16542	369	2899	770	0.424
	late	Sapphire	16369	315	3997	272	0.462
		Alumina	15729	161	4508	199	2.572

Table 4.2: Exponential-fit parameters for $n_e(t)$ and $T(t)$. A_0 has the units of the fitted quantity (T in K, n_e in cm^{-3}); τ is in ns; χ_{red}^2 is the reduced chi-square of the weighted $\ln(y)$ fit.

4.9.2. Electron density evolution

For all investigated materials, the retrieved electron number density $n_e(t)$ exhibits a clear monotonic decrease that is well described, over the explored temporal window, by an approximately exponential decay. This behaviour is consistent with the combined effect of plume expansion (increasing the emitting volume) and electron–ion recombination

(reducing the free-electron population). Within the estimated uncertainty, no systematic differences between crystalline and amorphous/polycrystalline structures emerge for $n_e(t)$. The electron-density dynamics can therefore be considered essentially similar across the investigated materials, and the main material-dependent signatures are instead observed in the temperature evolution.

4.9.3. Temperature evolution

The temperature evolution $T(t)$ shows the most pronounced material-dependent signatures. In fig. 4.7, $T(t)$ is characterized by (i) an early-time faster decay, which is sensitive to the initial plasma conditions set by laser–material coupling and ablation, and (ii) a later-time slower decrease, which is closer to the behaviour expected for a plume whose evolution is increasingly governed by expansion and cooling in the surrounding gas. In this framework, the early- and late-time characteristic constants τ in table 4.2 provide a compact quantitative comparison of the two stages.

4.9.4. SiO₂: quartz vs Infrasil

For SiO₂, Infrasil exhibits a higher initial temperature than crystalline quartz. This trend is consistent with the heat-conduction model described by eq. (1.3): at 1064 nm Infrasil has a much larger absorption coefficient μ than quartz (hence a larger volumetric source term), and its lower thermal conductivity k reduces heat diffusion into the bulk. As a result, the energy is absorbed more efficiently and remains more spatially confined, leading to higher peak temperatures near the surface and to a shallower ablated depth [4]. Within the simplified conduction-limited scaling adopted here, the characteristic thermal penetration depth $d_T \sim \sqrt{\alpha \tau_p}$ (with $\alpha = k/(\rho c_p)$) is smaller for Infrasil; accordingly, the mass-removal rate described by eq. (1.4) is reduced. This increases the effective energy per unit ablated mass and favours a faster temperature drop. Consistently, $T(t)$ for Infrasil decreases more steeply than for quartz at early times, which is reflected by the smaller early-time τ in table 4.2.

As time progresses, recombination becomes increasingly important and the spectrum transitions from ion-dominated to neutral-dominated emission, as indicated by the increase of the neutral-to-ionic line-count ratio in fig. 4.8a. In this later stage, the temperature decrease becomes less sensitive to the details of the initial coupling and is progressively governed by plume expansion in the ambient gas. In this regime, a Sedov–Taylor-type description (eq. (1.9)) provides a reasonable qualitative framework and explains why the late-time slopes of $T(t)$ become similar for quartz and Infrasil. The matrix effect re-

mains observable mainly through the different early-time initial conditions, which shift the subsequent evolution even when the late-time decay law is comparable.

4.9.5. Al_2O_3 : sapphire vs alumina ceramic

For Al_2O_3 , the thermophysical properties reported in table 3.1 (e.g. k , ρ , c_p) are comparatively similar for sapphire and dense alumina. Therefore, the strong contrast observed for SiO_2 , where both μ and k differ substantially between amorphous and crystalline samples, is expected to be weaker here. In this case, differences in the early-time plasma conditions are primarily linked to microstructure-dependent laser–material coupling. Sapphire is an optically homogeneous single crystal, for which refraction and absorption are well-defined and scattering is minimal. Conversely, in polycrystalline alumina the optical response is affected by grain boundaries, residual porosity, and surface roughness: light attenuation and energy deposition can be dominated by scattering and local inhomogeneities rather than by a single bulk μ . These mechanisms tend to redistribute energy deposition over a broader effective interaction region and can increase particulate mass loading compared to a single crystal.

In line with this picture, the temperature decays of sapphire and alumina are broadly comparable, with only modest early-stage differences that remain within the uncertainties (table 4.2). These small deviations follow the same trend observed for SiO_2 , with the crystalline material exhibiting a larger τ than the polycrystalline one. At later times, both samples approach a similar slow-cooling behaviour, consistent with an evolution increasingly governed by plume expansion in the ambient gas. In this time window, the fit for alumina yields a larger τ ; however, the corresponding χ^2_{red} indicates that a single-exponential model provides a poorer description, and the inferred difference should therefore be interpreted with caution.

4.9.6. Neutral-to-ionic line statistics

To support the interpretation in terms of recombination and the progressive transition toward neutral-dominated emission, fig. 4.8 reports the time evolution of the ratio between the number of identified neutral and singly-ionized lines, n_I/n_{II} . The increase of n_I/n_{II} qualitatively indicates the growing relative weight of neutral emission as the plasma cools and expands. In this analysis, line counts were extracted using the same identification criteria across the full time range, so that relative trends (rather than absolute values) can be meaningfully compared.

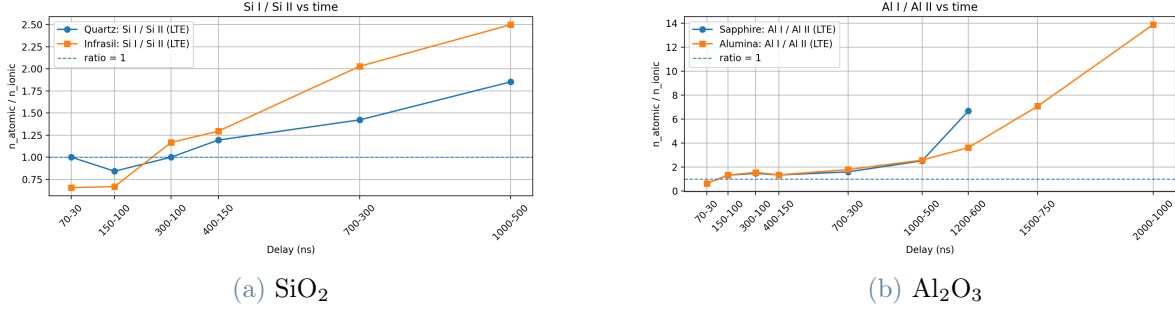


Figure 4.8: Temporal evolution of the ratio between the number of identified neutral and singly-ionized lines (n_I/n_{II}). The increase of n_I/n_{II} indicates the progressive dominance of neutral emission due to recombination as the plasma cools and expands.

4.10. Initial Temperature analysis

In addition to the room-temperature dataset, an auxiliary test was performed by varying the *initial* sample temperature prior to acquisition. The specimens were either cooled in a freezer down to approximately -10°C and measured shortly after being placed in the LIBS chamber, or heated on a heating plate up to approximately 50°C and then measured.

The full CF-LIBS workflow did not yield stable or physically meaningful quantitative results for these datasets. The primary limitation is that the sample temperature is not constant during acquisition: it can evolve significantly while spectra are recorded and averaged over multiple positions, altering laser-matter coupling and plasma formation conditions in a non-reproducible way. As a consequence, key assumptions underlying the CF-LIBS analysis (in particular, quasi-repeatable excitation conditions across averaged shots and a consistent plasma state within a given acquisition gate) are only partially satisfied. Achieving quantitative repeatability would require acquiring spectra only once per thermal setpoint and then reconditioning the sample to the desired initial temperature before the next acquisition. This would be extremely time-consuming; therefore, the discussion is restricted to qualitative spectral trends.

For clarity, the spectra at the three initial-temperature conditions are shown as *overlays*: the Heated spectrum is plotted in the background, the Ambient spectrum in the middle, and the Cooled spectrum on top. In the overlay plots, the intensity is normalized to the Ambient spectrum, so that relative differences remain visible even when the overall signal changes substantially. Quantitative support is provided by peak heights (local baseline-subtracted), with emphasis on the reference lines adopted in the room-

temperature analysis: Si I at $\lambda = 390.5523$ nm and Al II at $\lambda = 281.6185$ nm.

Because the specimens differ in geometry and thermal mass, their approaches to thermal equilibrium in the chamber are not identical; therefore, differences between “cooled” and “heated” conditions should be interpreted as indicative of altered coupling at the beginning of the acquisition rather than as a controlled, steady-state temperature dependence.

4.10.1. SiO_2

In fig. 4.9 it is shown the overall emission of Quartz (crystalline SiO_2) and Infrasil (amorphous SiO_2) for the three initial-temperature conditions. In both materials, the Cooled case exhibits a pronounced reduction of the SiO_2 -related emission. The Heated and Ambient spectra are comparatively similar, suggesting that the dominant perturbation is associated with the cold start rather than with a moderate heating.

The $\text{H}\alpha$ region is shown in fig. 4.10. In Infrasil, $\text{H}\alpha$ is enhanced in the Cooled condition, whereas Quartz shows a smaller variation. A plausible interpretation is an increased contribution of hydrogen-bearing surface species (e.g. adsorbed water) on the colder surface. Such a thin surface layer can modify the effective absorbed fluence and the ablation efficiency, leading to a weaker emissive plume and reduced line emission in the early stages of the acquisition.

This reduction is also visible in the Si I line at 390.5523 nm (fig. 4.11). The Cooled condition suppresses this line by almost one order of magnitude for both Quartz and Infrasil (table 4.3), consistent with reduced ablation and/or reduced excitation/ionization efficiency.

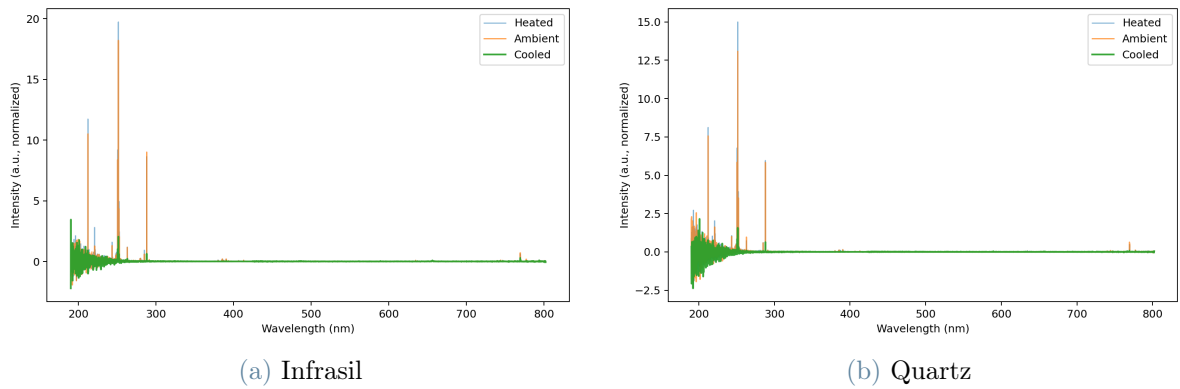


Figure 4.9: Normalized overlays of the overall spectra for Infrasil (amorphous SiO_2) and Quartz (crystalline SiO_2) at different initial sample temperatures.

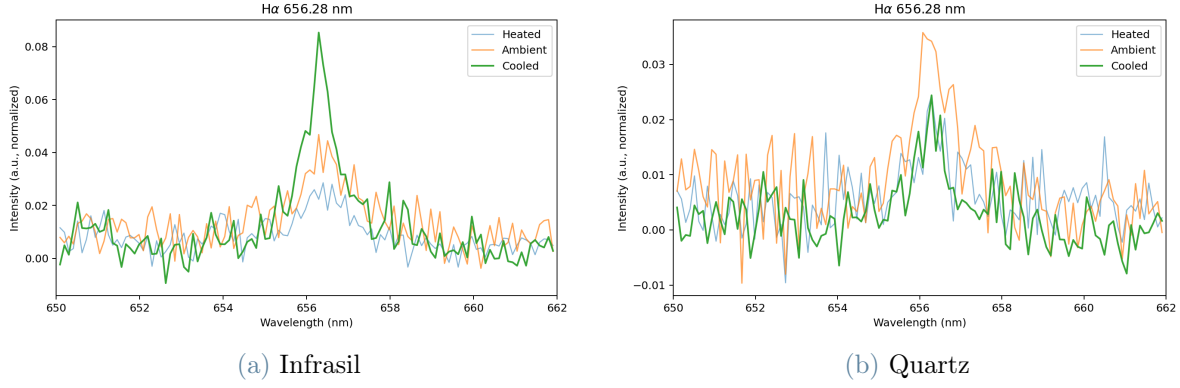


Figure 4.10: Zoom on $H\alpha$ $\lambda = 656.28$ nm for Infrasil and Quartz.

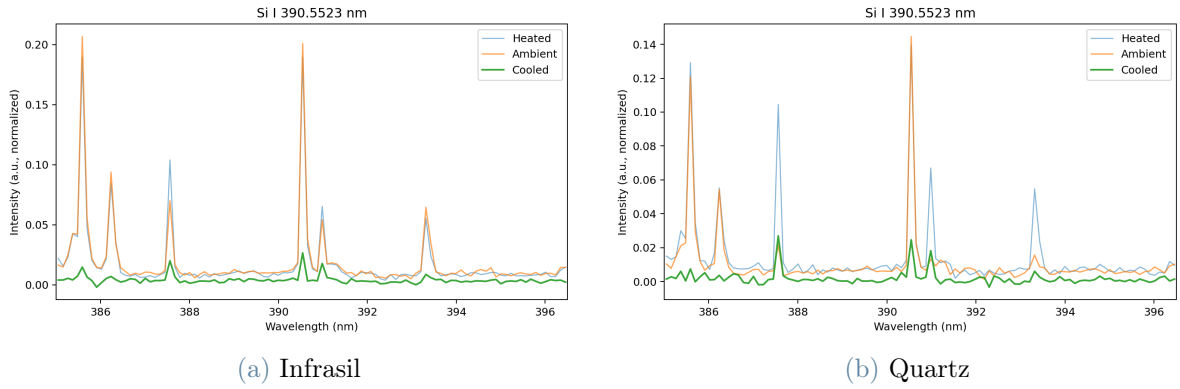


Figure 4.11: Zoom on Si I $\lambda = 390.5523$ nm for Infrasil and Quartz.

Line	Sample	Ambient	Cooled	Heated
Si I $\lambda = 390.5523$ nm	Infrasil	2578	220	2139
	Quartz	1683	256	1556
$H\alpha$ $\lambda = 656.28$ nm	Infrasil	311	631	212
	Quartz	276	208	235

Table 4.3: Peak heights (a.u., local baseline-subtracted) for selected features in the SiO_2 temperature analysis.

4.10.2. Al_2O_3

In fig. 4.12 it is shown the temperature overlays for Sapphire (single-crystal Al_2O_3) and Alumina (polycrystalline Al_2O_3). As for SiO_2 , the dominant change is observed for the Cooled condition; however, the magnitude of the effect depends on the material structure.

The $\text{H}\alpha$ region is shown in fig. 4.13. In Sapphire, $\text{H}\alpha$ decreases in the Cooled case, while Alumina shows a comparatively smaller variation (table 4.4). This indicates that the relative contribution of hydrogen-bearing surface species is not universal across the Al_2O_3 samples and may be influenced by differences in surface finish, roughness, and adsorption/desorption dynamics.

The ionic reference line used in the room-temperature analysis, Al II at 281.6185 nm, is shown in fig. 4.14. In Sapphire, the Cooled condition suppresses Al II by almost two orders of magnitude (table 4.4), suggesting a markedly lower ionization degree at the cold start. In Alumina, the decrease is less extreme (approximately by a factor three), consistent with a reduction of excitation/ionization efficiency that does not lead to a collapse of the ionic emission.

A likely contributor to the different responses is the different thermal equilibration during acquisition. The alumina specimen is smaller and can approach the chamber temperature more rapidly, so that the “cooled” and “heated” conditions may persist for a shorter fraction of the acquisition compared with sapphire. Conversely, the sapphire specimen retains the imposed initial temperature for longer, making the early-time coupling conditions (including possible effects of a cold-surface adsorbate layer) more influential on the recorded spectra.

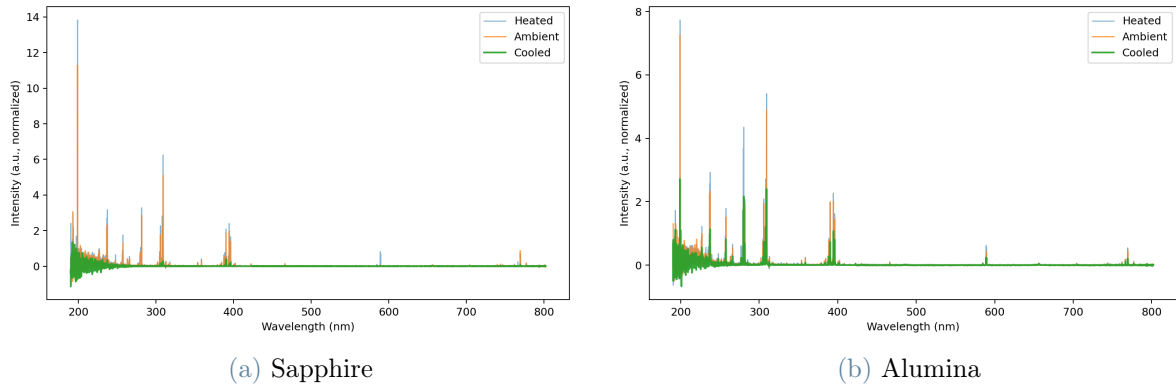


Figure 4.12: Normalized overlays of the overall spectra for Sapphire (single-crystal Al_2O_3) and Alumina (polycrystalline Al_2O_3) at different initial sample temperatures.

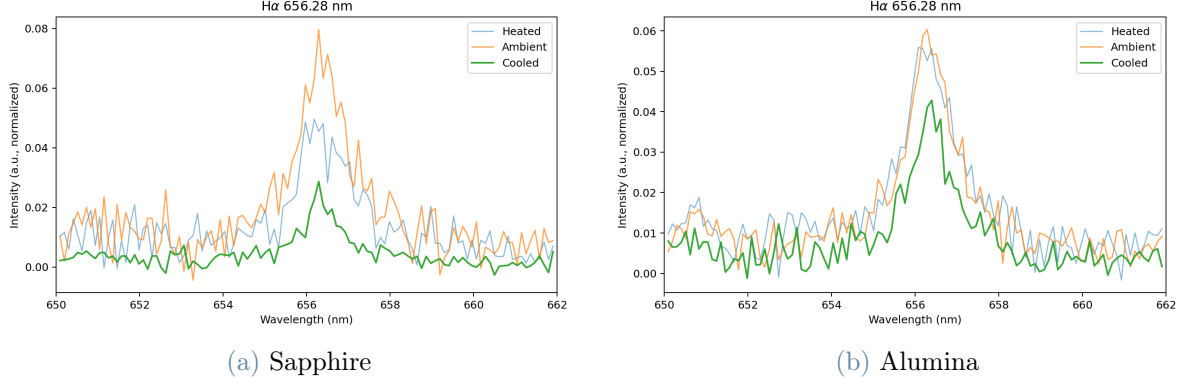


Figure 4.13: Zoom on $H\alpha$ $\lambda = 656.28$ nm for Sapphire and Alumina.

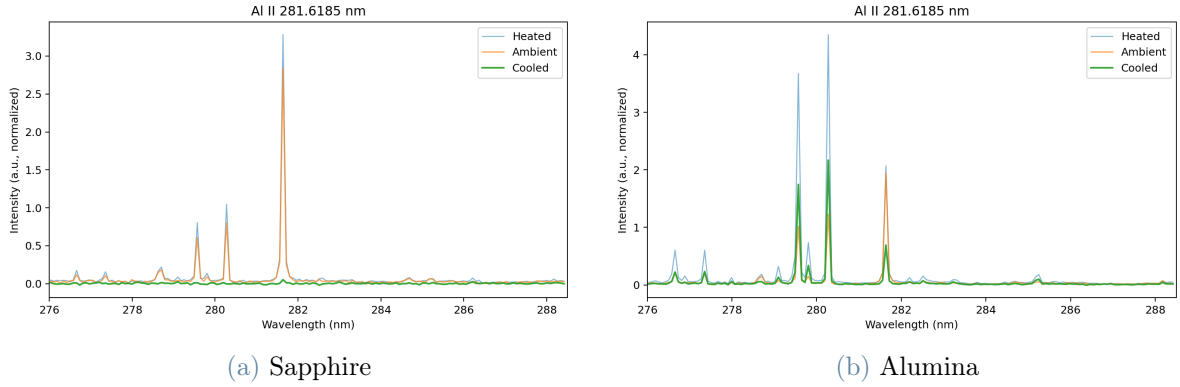


Figure 4.14: Zoom on $Al\ II$ $\lambda = 281.6185$ nm for Sapphire and Alumina.

Line	Sample	Ambient	Cooled	Heated
$Al\ II\ \lambda = 281.6185\ \text{nm}$	Sapphire	42545	867	50185
	Alumina	43413	15176	46362
$H\alpha\ \lambda = 656.28\ \text{nm}$	Sapphire	969	384	676
	Alumina	1048	908	1166

Table 4.4: Peak heights (a.u., local baseline-subtracted) for selected features in the Al_2O_3 temperature analysis.

5 | Conclusions

This thesis investigated and characterized matrix effects in Laser-Induced Breakdown Spectroscopy (LIBS) by comparing material pairs with identical empirical formula but different structural state and phase: crystalline quartz versus amorphous fused silica (Infrasil) for SiO_2 , and single-crystal sapphire versus polycrystalline alumina ceramic for Al_2O_3 . The central methodological choice was to use time-resolved acquisition and a Calibration-Free LIBS (CF-LIBS) workflow to reconstruct the temporal evolution of plasma temperature $T(t)$ and electron number density $n_e(t)$ under controlled instrumental conditions. This enabled a direct, physically interpretable comparison of how structural order, optical coupling, and thermophysical transport propagate into the plasma stage.

5.1. Main findings

Matrix effects are strongly time-dependent and are most visible at early delays. Across all samples, the plasma evolution can be interpreted in terms of two regimes. At early times, the plasma state retains a strong memory of the laser–material coupling and of the ablation efficiency, and therefore matrix effects are amplified. At later times, the evolution becomes progressively governed by plume expansion and cooling in the ambient gas, and material-dependent differences are reduced. This time dependence highlights the importance of the acquisition window in CF-LIBS.

The electron-density dynamics are broadly similar across matrices, while the temperature carries the most pronounced material signature. The reconstructed $n_e(t)$ decreases monotonically in time and is well described by an approximately exponential decay for all investigated materials. Within the experimental uncertainties, no clear systematic separation between crystalline and amorphous or polycrystalline structures emerges in $n_e(t)$. In contrast, $T(t)$ exhibits clearer, material-dependent trends, indicating that the dominant observable footprint of the matrix effect in the present conditions is encoded in the thermal/energetic state of the emitting plasma rather than in the overall free-electron population.

SiO₂: quartz versus Infrasil shows a clear contrast in the early plasma temperature. For SiO₂, Infrasil yields a higher initial plasma temperature than crystalline quartz. This observation is consistent with a conduction-limited picture of laser energy deposition and removal: at the laser wavelength used in this work, Infrasil is characterized by a much stronger effective absorption and by a significantly lower thermal conductivity than quartz. These differences promote a more efficient and spatially confined energy deposition near the surface, which increases the effective energy per unit ablated mass and results in a steeper early-time temperature decay. At later times, the temperature decay becomes more similar for the two SiO₂ matrices, consistent with an evolution increasingly driven by plume expansion and recombination rather than by the details of the initial coupling.

Al₂O₃: sapphire versus alumina ceramic exhibits weaker contrasts, consistent with smaller thermophysical differences and competing microstructural effects. For Al₂O₃, the reconstructed temperature decays for sapphire and alumina are broadly comparable and show only modest differences within uncertainties. This weaker matrix contrast is consistent with the fact that the bulk thermophysical properties of sapphire and dense alumina are comparatively similar, so that large systematic shifts of the initial conditions are less expected than in the SiO₂ case. Any residual differences are plausibly associated with microstructure and surface-related effects (e.g. grain boundaries, scattering-driven coupling, porosity/roughness, and defect-mediated absorption in the ceramic), which can increase shot-to-shot variability and partially mask systematic trends. This also supports the practical advantage of averaging over many positions when the goal is to extract robust plasma-parameter trends rather than local microstructural signatures.

Spectral evolution supports the interpretation in terms of recombination and a transition from ionic to atomic emission. The progressive increase of the neutral-to-ionic spectral contribution with time provides an independent qualitative indicator of recombination during plasma cooling and expansion. In practical terms, this implies that early gates are more sensitive to ionic features and to matrix-driven differences in the initial ionization degree, while later gates tend to emphasize atomic emission under more homogeneous and less matrix-sensitive conditions.

5.2. Implications for CF-LIBS practice

A key implication of the present study is that “matrix effects” should not be treated as a single static correction, but rather as a time-dependent contribution that can be experimentally modulated. When the goal is robust quantitative analysis, later observation windows are generally advantageous because they reduce the impact of matrix-dependent initial conditions and mitigate strong continuum and gradients. However, late-time gating also reduces the intensity of ionic lines and may limit the use of ion-based diagnostics, so an optimal compromise window must be selected based on the required accuracy and signal-to-noise ratio. More broadly, these results support the view that time-resolved plasma diagnostics are not only a validation step for CF-LIBS assumptions, but also a direct tool to identify and minimize the dominant matrix-driven biases.

5.3. Outlook and future developments

5.3.1. Extending the material set to disentangle optical and thermophysical drivers

The approach adopted here, fixed instrumentation and comparison of materials with the same chemical formula, can be systematically expanded to build a more general and quantitative mapping between material parameters and plasma observables. A natural development is to enlarge the “same-stoichiometry” material set to include samples that span wider and more controlled ranges of optical and thermophysical properties, so that the dependence of plasma metrics on *specific* parameters can be isolated.

For SiO_2 , this can include additional polymorphs (or engineered silica glasses) with different refractive index, absorption at the laser wavelength, defect density, and thermal transport. For Al_2O_3 , complementary phases (e.g. γ -, θ -alumina) and ceramics with controlled grain size and porosity would allow probing microstructure-driven coupling and heat-flow effects while keeping stoichiometry fixed. More generally, one can design series where a single material property is intentionally tuned while others are kept as constant as possible (or, at minimum, independently measured), for example: (i) varying absorption via controlled defect/impurity content, (ii) varying thermal conductivity via porosity or grain-boundary engineering, (iii) varying surface roughness/finish to quantify threshold and coupling sensitivity, and (iv) exploiting anisotropy in single crystals by controlled orientation to separate direction-dependent k and optical constants.

Such an expanded dataset would enable regression or reduced-order modelling linking

early-time plasma observables (e.g. T_0 , early decay constants, ionic/neutral balance) to measured material parameters (μ , k , ρ , c_p , E_g , surface state), turning the qualitative notion of “matrix dependence” into quantitative sensitivities.

5.3.2. Improved initial-temperature experiments and explicit temperature-dependent material properties

The exploratory “initial temperature” study performed in this thesis indicates that changing the specimen starting temperature can strongly modify the recorded spectra, especially in the cold-start condition. However, the experiment also showed that a reliable quantitative CF-LIBS inversion is hindered when the sample temperature is not controlled during acquisition and drifts while averaging over many positions.

A clear next step is therefore to redesign the initial-temperature protocol with tighter experimental control, for example, by:

- using a temperature-controlled sample holder (Peltier/heated stage) with feedback control and sufficient thermal contact to enforce a steady-state surface temperature;
- measuring the surface temperature *in situ* (thermocouple close to the surface, IR pyrometry, or calibrated thermal imaging) to verify stability during acquisition;
- reducing or redesigning the averaging strategy (e.g. single-shot or few-shot acquisitions per temperature setpoint) so that each spectrum corresponds to a well-defined thermal state;
- defining the time required to reach thermal equilibrium and acquisition sequences that prevent uncontrolled relaxation toward the chamber temperature;
- controlling surface adsorption (notably water and hydrocarbons) by pre-baking, a controlled atmosphere, or standardized waiting times, since adsorbate layers can dominate cold-start differences.

With these improvements, an initial-temperature study becomes not only feasible but also highly informative, because material properties relevant to laser coupling and heat flow are generally temperature-dependent. In particular, thermal conductivity is more properly described as $k(T)$ along with refractive index, absorption coefficient, and even defect-mediated coupling channels that can vary with temperature. A controlled experiment could therefore be formulated as *time-resolved* mapping

$$T(t; T_s), \quad n_e(t; T_s), \quad \text{and selected line ratios/line intensities as a function of } T_s,$$

where T_s is the imposed sample temperature. By repeating the same delay/gate scan at different T_s , it would be possible to directly observe how changes in $k(T)$, $\mu(T)$, and related parameters shift the early plasma state and whether such shifts persist into the late-time expansion regime. This would connect matrix effects to a controllable external parameter (temperature) and provide an additional pathway to validate and refine laser-matter coupling models in the LIBS context.

5.3.3. Towards more predictive modelling and improved robustness

Finally, the combination of (i) expanded same-stoichiometry material sets and (ii) controlled initial-temperature studies provides a route toward predictive modelling of matrix effects. On the experimental side, adding complementary diagnostics (e.g., plume imaging for geometry, crater metrology for ablated mass, or independent measurements of optical absorption at the laser wavelength) would reduce the ambiguity in attributing observed spectral changes to either coupling, ablation yield, or plasma-stage effects such as optical thickness. On the analysis side, incorporating self-absorption-aware strategies (where required) and exploring simplified multi-zone descriptions would further improve the reliability of quantitative interpretation, especially for dielectric materials where deviations from ideal CF-LIBS assumptions are commonly the limiting factor.

In summary, this thesis shows that, for materials with identical chemical formula, the dominant and experimentally accessible signature of matrix effects under the investigated conditions is the early-time plasma temperature evolution, which reflects the material dependence of laser coupling and heat transport. Extending the approach to broader and more controlled material families, and performing carefully designed temperature-dependent experiments, offers a concrete path to transform matrix effects from a qualitative limitation into a quantitatively characterized and, to some extent, predictable contribution.

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A | Appendix A: Experimental apparatus

This appendix describes the experimental apparatus used for the LIBS measurements presented in this thesis. All experiments were carried out using a commercial CORALIS system (LTB Lasertechnik Berlin GmbH), which integrates Laser-Induced Breakdown Spectroscopy (LIBS) and Raman spectroscopy within a single enclosed platform.

The purpose of this appendix is to document the instrumental configuration and the operating conditions relevant to the LIBS measurements. General aspects related to LIBS principles and plasma physics are instead discussed in chapter 1.

A.1. CORALIS system overview

The CORALIS (COmbined RAman LIbs System) is a laboratory-grade spectroscopic instrument designed for combined elemental and molecular analysis. The system integrates multiple laser sources, an imaging module, a high-resolution Echelle spectrometer, and a fully enclosed laser-safe housing.

In the context of this thesis, only the LIBS functionality of the system was used. All measurements were performed on solid samples positioned inside the sealed measurement chamber.

Instrument control, laser triggering, detector synchronization, data acquisition, and spectral visualization are managed through the FusionRL software package provided by the manufacturer.

A.2. LIBS excitation source

Plasma generation for LIBS measurements is achieved using a Q-switched Nd:YAG laser operating at a wavelength of 1064 nm. The laser delivers nanosecond pulses with adjustable pulse energy ranging from approximately 0.04 mJ up to 24.7 mJ, at a fixed



Figure A.1: Overview of the CORALIS system.



Figure A.2: LIBS excitation laser integrated in the CORALIS system.

repetition rate of 40 Hz.

The laser beam is internally guided and focused onto the sample surface through a fixed optical path optimized for plasma ignition and emission collection. The system allows the user to define the number of laser pulses applied to each measurement position, including optional pre-cleaning shots used to remove superficial contamination prior to data acquisition.

The temporal delay between the laser pulse and the detection gate can be adjusted via the control software, enabling time-resolved acquisition of the plasma emission.

A.3. Sample chamber and positioning system

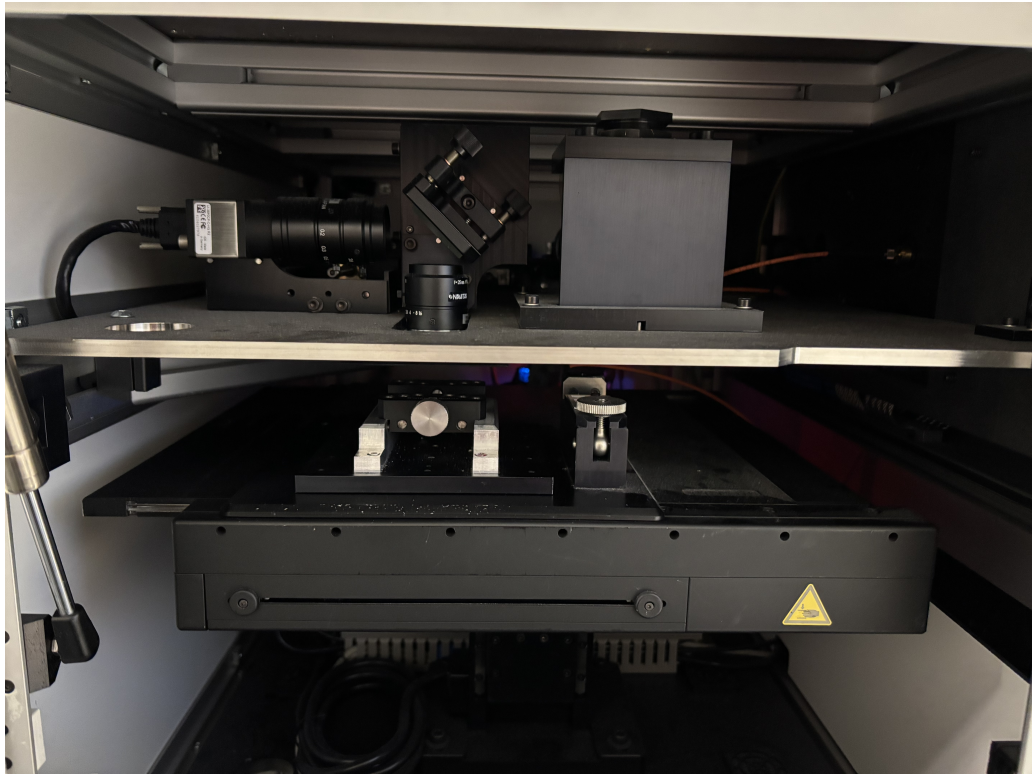


Figure A.3: Measurement chamber of the CORALIS system.

Samples are placed inside a fully enclosed measurement chamber classified as laser safety class 1 under normal operating conditions. The chamber door is interlocked by a magnetically activated safety circuit, which prevents laser emission when the chamber is open.

The sample is mounted on a motorized XYZ translation stage that allows precise positioning and focusing. Stage motion can be controlled either through the software interface or by means of a dedicated joystick. The Z-axis is used to ensure that the sample surface

is positioned at the focal plane of the excitation and collection optics.

A.4. Optical emission collection and spectrometer

The optical emission generated by the laser-induced plasma is collected through a dedicated optical path optimized for LIBS measurements and directed to an ARYELLE Butterfly Echelle spectrometer.

The spectrometer employs an Echelle grating combined with a prism for cross-dispersion, producing a two-dimensional spectral image on the detector. This configuration provides high spectral resolution over a broad wavelength range extending into the deep ultraviolet, which is essential for the detection of atomic and ionic emission lines relevant to LIBS analysis.

The ARYELLE Butterfly spectrometer integrates two optical channels on a single detector. One channel is dedicated to Raman spectroscopy, while the second channel is optimized for LIBS emission. In this work, only the LIBS optical channel was used.

A.5. Detection system and timing control

The dispersed LIBS emission is detected by a gated detector system synchronized with the laser pulse. Detector gain, gate delay, and gate width are controlled through the FusionRL software.

The use of adjustable temporal gating allows suppression of the intense early-time continuum emission and enables selective acquisition of atomic and ionic line radiation during the later stages of plasma evolution. This capability is essential for improving the signal-to-noise ratio and reducing spectral interference effects.

All spectra are recorded as intensity counts as a function of wavelength and are automatically stored in session-specific directories created by the control software.

A.6. Control software and data handling

All experimental operations are managed through the FusionRL software provided with the CORALIS system. The software allows the user to:

- acquire sample images and define regions of interest,
- control laser and detector parameters,

- perform LIBS measurements at individual points or across spatial grids,
- visualize and average acquired spectra,
- export spectral data in text format for offline processing.

In this work, raw LIBS spectra were exported and subsequently processed using calibration-free LIBS methods, as described in chapter 2. The built-in qualitative line identification and model-based analysis tools available in FusionRL were not used for the quantitative analysis presented in this thesis.

A.7. Operating conditions

All measurements were performed under ambient laboratory conditions, with the system operating within the environmental ranges specified by the manufacturer: room temperature between 15°C and 30°C and relative humidity between 15% and 80% (non-condensing).



Figure A.4: Cooling system of the CORALIS system.

The cooling system ensures thermal stabilization of the detector and associated electronics. This reduces dark current and thermal noise, while improving signal-to-noise ratio, spectral stability, and long-term measurement reproducibility.

List of Figures

1.1	Schematic representation of a typical LIBS experimental setup [10].	4
1.2	Schematic representation of the physical processes occurring during a LIBS measurement.	6
1.3	Schematic representation of the superposition of continuum emission and line radiation.	10
1.4	Temporal evolution of plasma emission features [7].	13
1.5	Schematic representation of an inhomogeneous plasma model [3].	14
1.6	Deconvolution process.	16
2.1	Line-centre spectral radiance (a,b) and line-integrated radiance (c,d) as functions of the Ge atomic number density and τ_0 (secondary x-axis) for weakly (a,c) and strongly (b,d) self-absorbed lines. The measurement was performed in argon on a Si/Ge thin film with a compositional gradient. The curves compare calculations for a uniform LTE plasma including (blue) and neglecting (green) self-absorption [16].	24
2.2	Example of a Boltzmann plot.	26
2.3	Algorithm of calibration-free LIBS analysis: (a) principal iteration loop with successive estimates of electron density, temperature, elemental fractions, and plasma diameter. Each estimate is obtained through the calculation loop (b) by varying the target parameter [16].	28
2.4	Measured spectrum and spectral radiance computed for different values of plasma size [16].	30
3.1	Photographs of the samples used in this work.	41
3.2	SEM images highlighting microstructural features: (a) Alumina (polycrystalline grains), (b) Infrasil (amorphous glassy morphology).	42
4.1	Cleaning analysis for the SiO ₂ samples. The Ca-line intensity decreases as successive shots remove surface contamination and progressively probe the bulk.	46

4.2	Irradiation study for single-shot acquisition: the SNR improves at moderate energies and degrades at higher energies due to the increasing continuum contribution.	47
4.3	Reference lines experimental (black) and computed (red) adopted for the SiO ₂ and Al ₂ O ₃ sample sets.	48
4.4	Fitted L_p values from reference curves.	49
4.5	$n_e(t)$ with the McWhirter criterion. LTE is preliminarily considered plausible when the measured n_e lies above the dashed line.	50
4.6	Plasma-parameter evolution after LTE screening with McWhirter criterion.	51
4.7	Exponential fits of the plasma-parameter evolution after LTE screening with the McWhirter criterion. Fits are performed only on the time points for which the LTE condition is simultaneously satisfied by both samples in each material pair.	52
4.8	Temporal evolution of the ratio between the number of identified neutral and singly-ionized lines (n_I/n_{II}). The increase of n_I/n_{II} indicates the progressive dominance of neutral emission due to recombination as the plasma cools and expands.	56
4.9	Normalized overlays of the overall spectra for Infrasil (amorphous SiO ₂) and Quartz (crystalline SiO ₂) at different initial sample temperatures.	57
4.10	Zoom on H α $\lambda = 656.28$ nm for Infrasil and Quartz.	58
4.11	Zoom on Si I $\lambda = 390.5523$ nm for Infrasil and Quartz.	58
4.12	Normalized overlays of the overall spectra for Sapphire (single-crystal Al ₂ O ₃) and Alumina (polycrystalline Al ₂ O ₃) at different initial sample temperatures.	59
4.13	Zoom on H α $\lambda = 656.28$ nm for Sapphire and Alumina.	60
4.14	Zoom on Al II $\lambda = 281.6185$ nm for Sapphire and Alumina.	60
A.1	Overview of the CORALIS system.	72
A.2	LIBS excitation laser integrated in the CORALIS system.	72
A.3	Measurement chamber of the CORALIS system.	73
A.4	Cooling system of the CORALIS system.	75

List of Tables

3.1	Selected properties relevant to matrix effects at room temperature.	42
3.2	XPS atomic concentrations (at.%) reported as mean $\pm$ standard deviation over 12 measured spots.	42
4.1	Spectroscopic parameters of the reference lines used for plasma diagnostics and normalization.	47
4.2	Exponential-fit parameters for $n_e(t)$ and $T(t)$. A_0 has the units of the fitted quantity (T in K, n_e in cm^{-3}); τ is in ns; χ_{red}^2 is the reduced chi-square of the weighted $\ln(y)$ fit.	53
4.3	Peak heights (a.u., local baseline-subtracted) for selected features in the SiO_2 temperature analysis.	58
4.4	Peak heights (a.u., local baseline-subtracted) for selected features in the Al_2O_3 temperature analysis.	60

List of Symbols

Laser and acquisition parameters

E_{laser} Laser pulse energy [J].

I_L Laser irradiance (average) [W m^{-2}].

Φ_p Pulse fluence [J m^{-2}].

τ_p Laser pulse duration [s].

R_s Surface reflectivity (Fresnel reflectance) [-].

μ Optical absorption coefficient in the solid target [m^{-1}].

δ Optical penetration depth, $\delta \sim \mu^{-1}$ [m].

t_{delay} ICCD gate delay time [s].

t_{gate} ICCD gate width [s].

N Number of spectra/shots averaged [-].

SNR Signal-to-noise ratio [-].

Plasma state and dynamics

T Plasma temperature (LTE temperature used in CF-LIBS) [K].

T_e Electron temperature [K].

n_e Electron number density [m^{-3}] (often reported in cm^{-3}).

n_i Ion number density [m^{-3}].

ρ Mass density [kg m^{-3}] (context-dependent: target, plume, or ambient).

v Expansion velocity [m s^{-1}].

P Pressure [Pa].

E_{int} Specific internal energy [J kg^{-1}].

ε_{abs} Volumetric absorbed power density [W m^{-3}].

ε_{rad} Volumetric radiative-loss power density [W m^{-3}].

$R(t)$ Shock-front radius [m].

E Energy released/deposited driving Sedov–Taylor expansion [J].

ρ_{ext} Ambient-gas mass density [kg m^{-3}].

ΔE Maximum energy-level separation used in the McWhirter LTE criterion [eV] (or J).

Laser–plasma interaction and characteristic frequencies

α_{IB} Inverse Bremsstrahlung absorption coefficient [m^{-1}].

ω Laser angular frequency [rad s^{-1}].

ω_p Plasma frequency [rad s^{-1}].

n_c Critical electron density [m^{-3}].

e Elementary charge [C].

m_e Electron mass [kg].

ε_0 Vacuum permittivity [F m^{-1}].

k_B Boltzmann constant [J K^{-1}].

h Planck constant [Js].

c Speed of light in vacuum [m s^{-1}].

Radiation transport and spectroscopy

λ Wavelength [m] (commonly expressed in nm).

λ_0 Central wavelength of a transition [m].

$I(\lambda, x)$ Spectral radiance/intensity along the line-of-sight (context-dependent units).

$\varepsilon(\lambda, x)$ Emission coefficient (emissivity) (context-dependent units).

$\alpha(\lambda, x)$ Absorption coefficient in the plasma [m^{-1}].

$B(\lambda)$ Planck spectral radiance.

A_{ul} Einstein spontaneous-emission coefficient of transition $u \rightarrow l$ [s^{-1}].

g_u, g_l Statistical weights (degeneracies) of upper/lower levels [–].

n_u, n_l Upper/lower level population number densities [m^{-3}].

- E_u, E_l Upper/lower level energies (often in cm^{-1} or eV, as specified) [energy].
- $U(T)$ Partition function [-].
- $L(\lambda, x)$ Normalized line-shape function (profile) [-].
- $\Delta\lambda_{\text{FWHM}}$ Full width at half maximum (generic) [m].
- $\Delta\lambda_G$ Gaussian FWHM (Doppler + instrumental) [m].
- $\Delta\lambda_L$ Lorentzian FWHM (mainly Stark) [m].
- $\Delta\lambda_{\text{inst}}$ Instrumental FWHM [m].
- $\Delta\lambda_D$ Doppler FWHM [m].
- $\Delta\lambda_{1/2}$ Stark FWHM used for n_e diagnostics [m].
- $w(T)$ Stark broadening parameter for a given line [m].
- L_p Effective plasma path length / characteristic emitting thickness [m].
- τ_0 Line-centre optical thickness [-].
- $G_{ff}(\lambda, T_e)$ Free-free Gaunt factor [-].
- $\xi(\lambda, T_e)$ Biberman factor [-].

CF-LIBS: plasma composition and equilibrium

- n_A Total number density associated with element A [m^{-3}].
- n_A^z Number density of element A in charge state z [m^{-3}].
- $n_{A_2}^z$ Number density of homonuclear diatomic species A_2 in charge state z [m^{-3}].
- n_{AB}^z Number density of heteronuclear diatomic species AB in charge state z [m^{-3}].
- z_{max} Maximum charge state included in the model [-].
- N_0 Total number density of the emitting species (used in Boltzmann relations) [m^{-3}].
- N_0^I Number density of neutral species (Saha-Eggert) [m^{-3}].
- N_0^{II} Number density of singly ionized species (Saha-Eggert) [m^{-3}].
- C_A Atomic fraction of element A , $C_A = n_A/n_{\text{tot}}$ [-].
- n_{tot} Total atomic number density, $n_{\text{tot}} = \sum_A n_A$ [m^{-3}].
- M Number of elements included in the plasma model [-].
- Q_A^0 Partition function of neutral atom A [-].
- Q_{AB}^0 Partition function of neutral diatomic molecule AB [-].

D_0 Ground-state dissociation energy of molecule AB [J] (or eV).

μ_{AB} Reduced mass of the A – B pair, $\mu_{AB} = m_A m_B / (m_A + m_B)$ [kg].

E_{ion} Ionization energy [J] (or eV).

C Grouped constant (instrumental and physical constants) in Boltzmann/Saha plots [–].

Spectral processing, fitting, and mismatch metric

S_{ul} Line-integrated signal (area under the line after baseline subtraction) [a.u. $\times$ nm].

F Instrumental factor / optical-chain response (as used in the line-integral definition) [–].

$I_{\text{raw}}(\lambda)$ Raw measured spectrum [counts].

$I_{\text{dark}}(\lambda)$ Dark signal/background [counts].

$R(\lambda)$ Apparatus response function [–].

$I_{\text{corr}}(\lambda)$ Response-corrected spectrum [a.u.].

$I_{\text{base}}(\lambda)$ Estimated baseline/continuum [a.u.].

χ^2 Spectral mismatch metric used in CF-LIBS iterations [–].

$I_{\text{meas}}(\lambda_i)$ Measured intensity at sampled wavelength λ_i [a.u.].

$I_{\text{comp}}(\lambda_i)$ Computed/synthetic intensity at sampled wavelength λ_i [a.u.].

Uncertainty and statistics

X_i Generic measurement (e.g. T or n_e) at index i .

$\overline{X}$ Sample mean, $\overline{X} = \frac{1}{n_{\text{meas}}} \sum_{i=1}^{n_{\text{meas}}} X_i$.

n_{meas} Number of measurements used for averaging [–].

σ_i Uncertainty (standard deviation) associated with X_i .

$\sigma_{\overline{X}}$ Uncertainty of the mean.

$\text{Cov}(X_i, X_j)$ Covariance between X_i and X_j .

ρ_{ij} Correlation coefficient between X_i and X_j .

A_0 Amplitude (prefactor) of the exponential fit [units of the fitted quantity].

τ Characteristic decay time constant of the exponential fit [s].

N_{fit} Number of fitted data points [–].

z_i Measured data point used in the fit (generic dependent variable) [units of z].

z_i^{fit} Fitted/model value corresponding to z_i [units of z].

σ_{z_i} Uncertainty associated with z_i [units of z].

ν Number of fitting parameters [-].

χ_{red}^2 Reduced chi-square goodness-of-fit metric, $\chi_{\text{red}}^2 = \frac{1}{N_{\text{fit}} - \nu} \sum_{i=1}^{N_{\text{fit}}} \left(\frac{z_i - z_i^{\text{fit}}}{\sigma_{z_i}} \right)^2$ [-].

Material properties (matrix-effects chapter)

n Refractive index [-].

n_{ord} Ordinary refractive index [-].

n_{extra} Extraordinary refractive index (birefringent crystals) [-].

k Thermal conductivity [$\text{W m}^{-1} \text{K}^{-1}$].

c_p Specific heat capacity at constant pressure [$\text{J kg}^{-1} \text{K}^{-1}$].

E_g Band-gap energy [eV].

ϵ_r Relative permittivity [-].