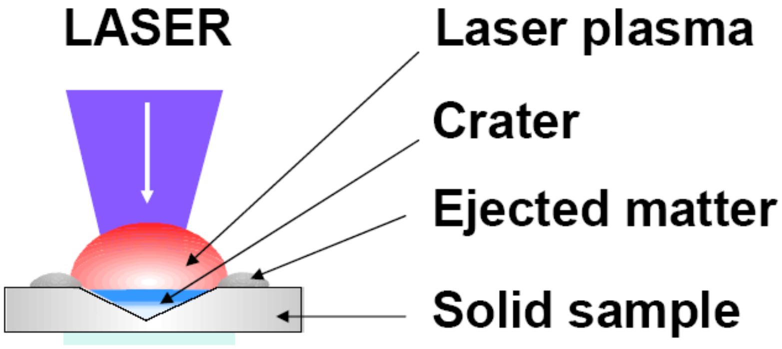
CHEM 517

Fundamentals And Applications of Laser Induced Breakdown Spectroscopy, LIBS

CHAPTER II

FUNDAMENTALS AND CHARACTERISTICS OF THE LASER PLASMA

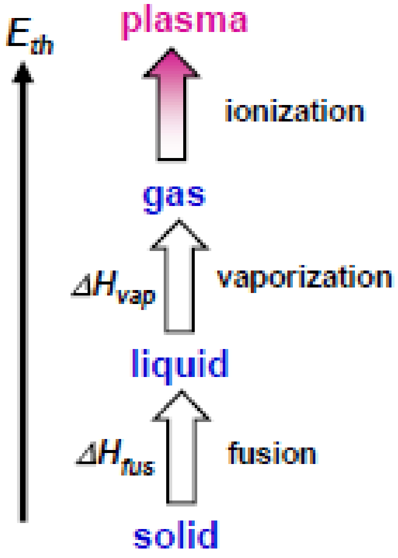


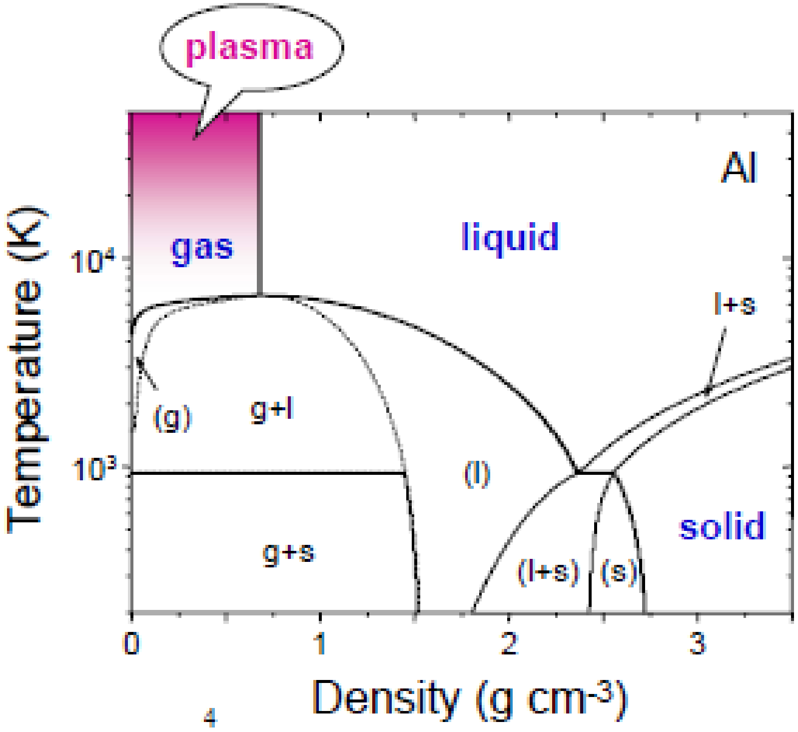
A brief description of laser induced plasmas:

- What is a plasma?
- Basic plasma parameters
- Local thermal equilibrium
- Properties of laser induced plasmas
- Plasma emission

∗What is a plasma?

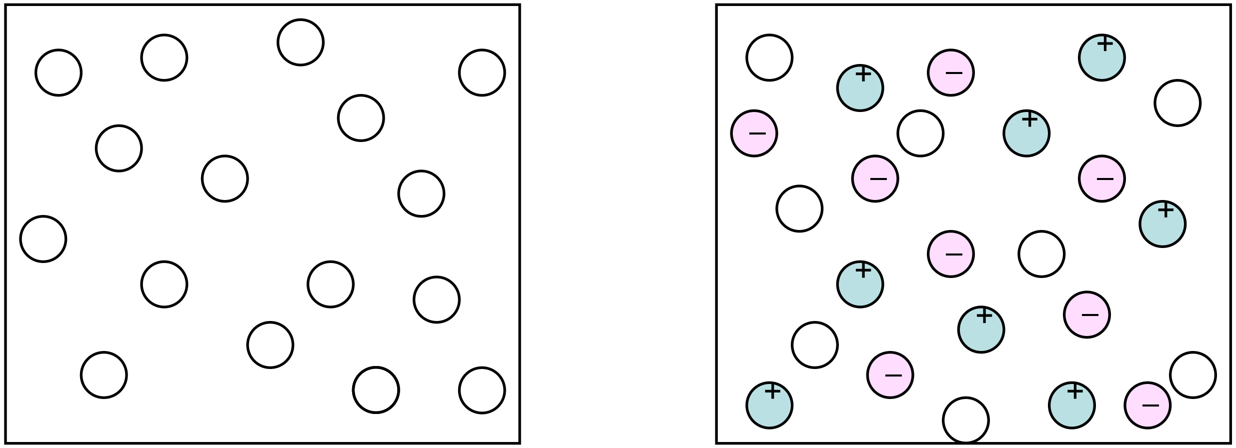
- ” 4th state of matter”
- local assembly of ions, electrons, neutrals





4^{th} Euro-Mediterranean Symposium on Laser-Induced Breakdown Spectroscopy
Paris, 10 sept. 2007

Principle difference to non-ionized gas:



✷ Non-ionized gas

-insulator

✷plasma

- large electrical conductivity

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∗ Basic plasma parameters:

- Degree of ionization
- Temperature, T_e, T_i
- electron density, n_e

Degree of ionization:

degree of ionization

$$\alpha = \frac{n_i}{n_i + n_n}$$

plasma is globally neutral

$$n_e = \langle z \rangle \, n_i$$

n_i=density of ions

z= charge number

n_e= electron number density

LIBS plasmas WEAKLY IONIZED PLASMAS

Evaluation of plasma parameters:

1. Determination of plasma temperature, T

$$\boxed{I_{ki} \propto N_k . A_{ki} . h\upsilon_{ki}} \quad (1)$$

N_k=density of excited neutral atoms

A_{ik}=transition probability

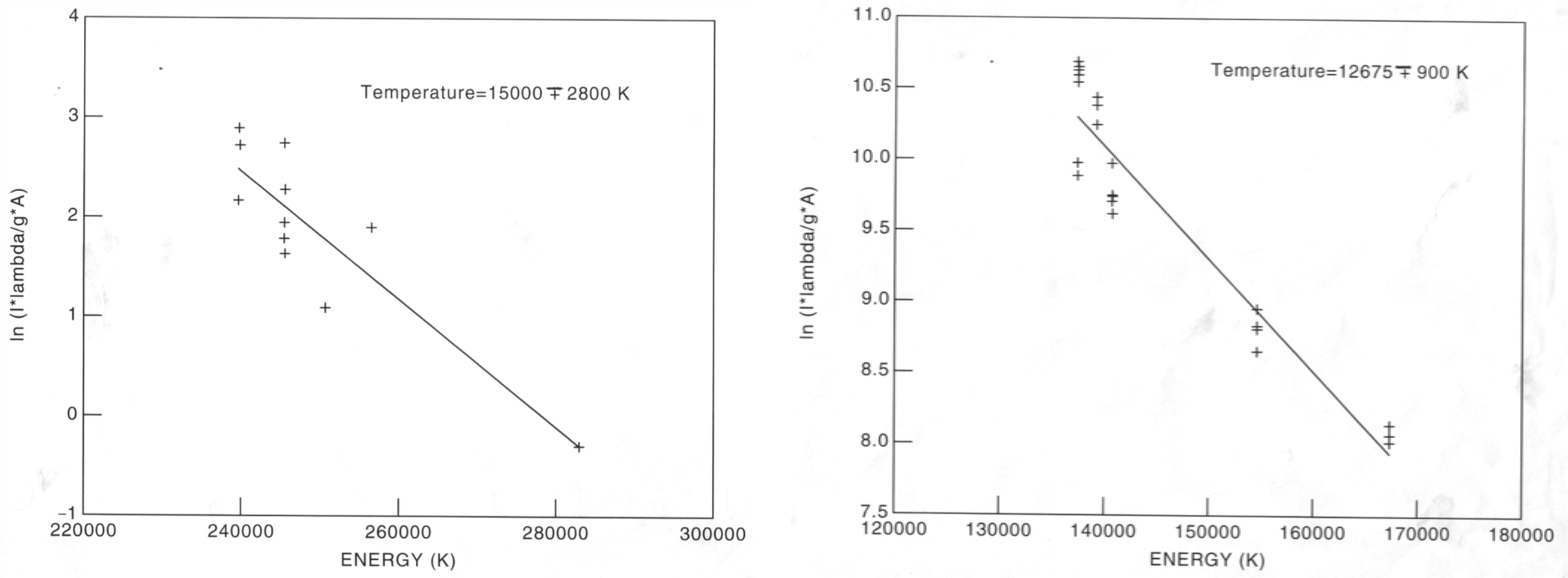
V_{ki}=frequency of the transition

Boltzmann equation

$$\boxed{N_k = N_i \left(\frac{g_k}{g_i}\right) \exp\left(\frac{-E_k}{kT}\right)} \quad (2)$$

$$\boxed{\ln \frac{I_1}{I_2} = \ln \frac{g_1 A_1 \lambda_2}{g_2 A_2 \lambda_2} - (E_2 - E_1)/kT} \quad (3)$$

Boltzmann plot: Same element, same ionization stage



Nd:YAG, 532 nm, 10 ns, T_d=1.2 μsec.

S. Yalcin, D.R. Crosley, G.P. Smith, G.W. Faris, *Hazardous Waste & Hazardous Materials*, 13(1), 51-61, 1996.

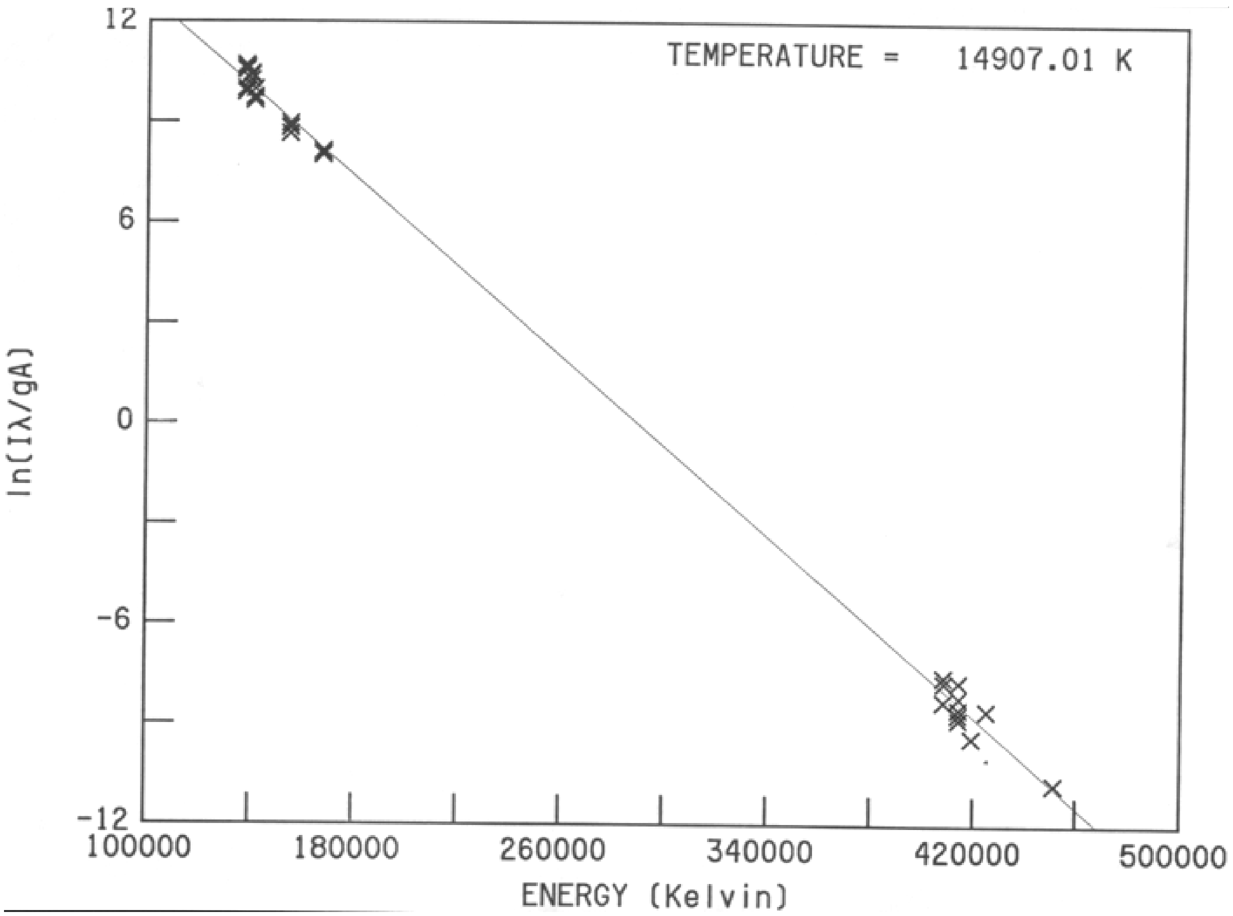
Saha equation: successive ionization stages

$$\boxed{\frac{N_z}{N_{z-1}} = \frac{2g_z\left(2\pi mkT\right)^{3/2}}{g_{z-1}h^3 n_e}\exp\left(-\frac{E_\infty^{z-1}-\Delta E_\infty^{z-1}}{kT}\right)} \qquad (4)$$

-Saha-Boltzmann equation

$$\boxed{\frac{I_1}{I_2} = 2\frac{g_1 A_1 \lambda_2}{g_2 A_2 \lambda_1}\frac{(2\pi mk)^{3/2}}{h^3}\frac{1}{n_e}T^{3/2}\exp\left[-\frac{\left(E_1+E_\infty-E_2-\Delta E_\infty\right)}{kT}\right]} \qquad (5)$$

Saha-Boltzmann plot:



Nd:YAG,

532 nm, 10 ns

T_d=1.2 μsec.

S. Yalcin, D.R. Crosley, G.P. Smith, G.W. Faris, *Hazardous Waste & Hazardous Materials*, 13(1), 51-61, 1996.

Evaluation of plasma parameters:

2. Determination of the electron number density, N_e

Stark broadening of Hα linewidth

A brief description of laser induced plasmas:

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• Local Thermodynamic Equilibrium, LTE

A gaseous system in complete or at least local thermodynamic equilibrium is characterized by the following conditions:

i) The velocity distributions of all kinds of free particles (molecules,ions,atoms and electrons) in all energy levels satisfies Maxwell's equation;

ii) For each seperate kind of particle the relative population of energy levels conforms to Boltzmann's distribution law;

iii) Ionization of atoms, molecules and radicals is described by Saha's equation.

velocities :	$f(v) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}$	*Maxwell*
population densities :	$n_i = n\frac{g_i}{Q} e^{-E_i/kT}$	*Boltzmann*
chemical composition :	$\frac{n_A n_B}{n_{AB}} = \frac{(2\pi \mu kT)^{3/2}}{h^3} \frac{Q_A Q_B}{Q_{AB}} e^{-E_{AB}/kT}$	*Saha*

Main Events in the LIBS process :

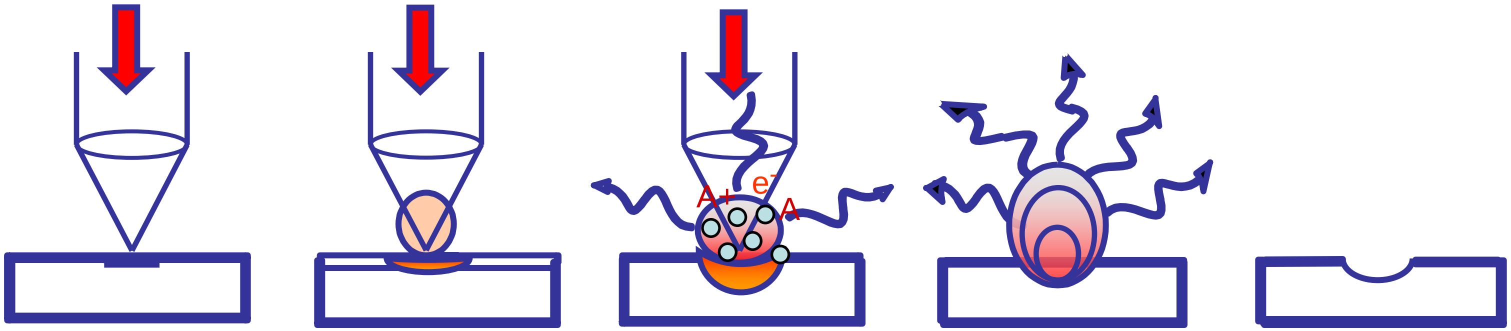
Laser Absorption

Heating Melting Evaporation & Breakdown

Atomization Ionization Plasma formation

Expansion Shock Waves & Plazma emission

Crater



Laser power density > (Ablation Threshold) **10^2 mJ/cm^2**

(Breakdown Threshold) **~1J/ cm^2** (metal)

GW/cm^2 ⇒nanosecond lasers

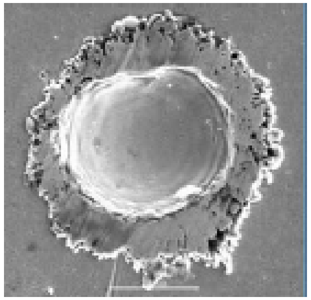
TW/cm^2 ⇒femtosecond lasers

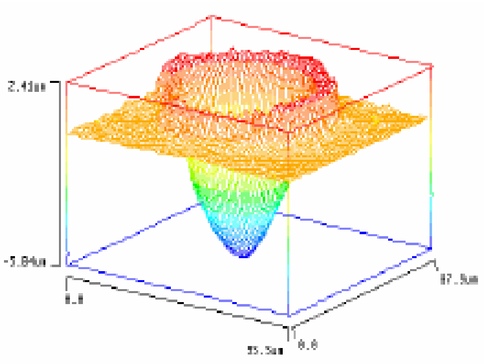
Plazma:

T~ 20.000 K $N_e \sim 1x10^{18}$

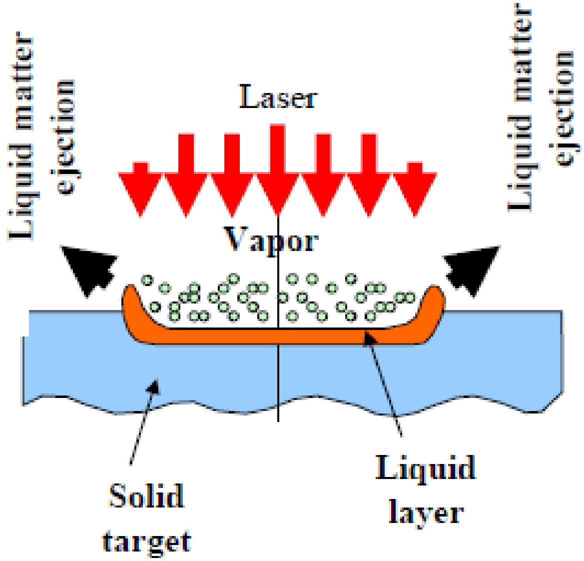
Effect of laser wavelength on ablation :

Crater (pure Cu, 6 ns laser)

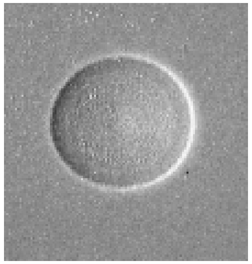


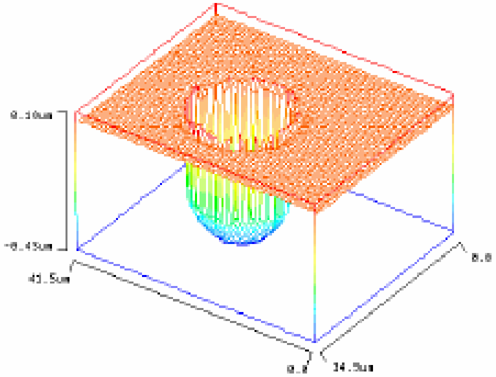


532 nm, 30 laser shots, TEM_{00}
25 µm, 10 mJ, 20 J/cm²



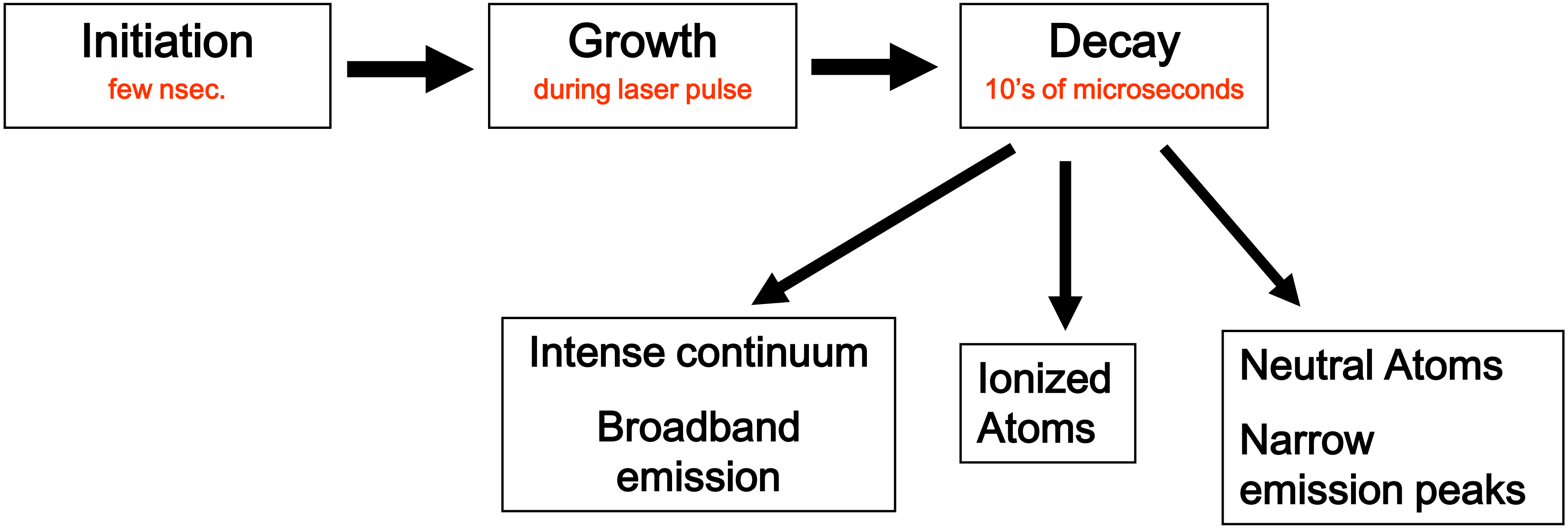
Al_2O_3, 1 shot, 800 nm, 60 fs
100 µJ





STAGES OF THE BREAKDOWN PLASMA :

1. INITIATION
2. GROWTH
3. DECAY



Initiation
few nsec.

Growth
during laser pulse

Decay
10’s of microseconds

Intense continuum

Broadband emission

Ionized Atoms

Neutral Atoms

Narrow emission peaks

1. Breakdown Initiation

Laser power density > (AblationThreshold) **10^2 mJ/cm^2**

(Breakdown Threshold) **~1J/ cm^2** (metal)

GW/cm^2 ⇒nanosecond lasers

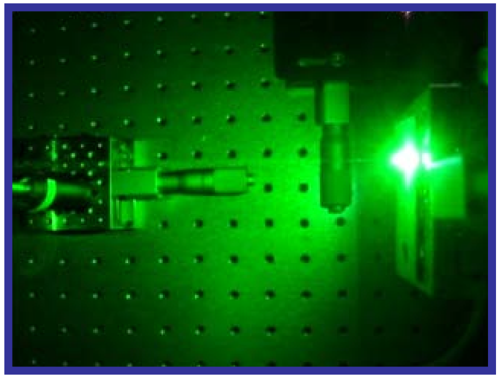
TW/cm^2 ⇒femtosecond lasers

Ablation Threshold; Fluence required to observe a visible damage on the target

Breakdown Threshold; Fluence required to create a luminescent plasma

Plazma:

T~ 20.000 K $N_e \sim 1 \times 10^{18}$



Two steps leading to breakdown of a gas due to optical excitation

A. Multiphoton Ionization,(MPI):

- involves the simultaneous absorption of a sufficient number of photons by an atom or molecule to cause its ionization

$$M + nh\upsilon \longrightarrow M^+ + e-$$

- The energy of a single photon from lasers used to generate the spark is usually much less than the energy needed to ionize an atom. e.g.The energy from Nd:YAG lasers are 1.17 eV, Ruby: 1.79 eV, respectively, whereas,the IP of inert gases is 12 eV or greater. However, because of high power density (MW/cm^2) and large photon flux (photons/cm^2) of the focused laser pulses, there is a high probability that ionization will occur by the absorption of many laser photons during the laser pulse.

- This mechanism may also supply the initial electrons . Any impurity with a low-ionization potential, such as organic vapors or even dust particles contributes significantly to the generation of initial electrons by MPI.

- MPI is important only at short wavelengths (< 1 μm), and at low gas pressures.

B. Avalanche Ionization / Cascade Ionization:

- Dominates at long wavelengths and at moderate to high pressures

- involves absorption of laser radiation by electrons when they collide with neutrals (inverse Bremsstrahlung). If the electrons gain sufficient energy they can impact ionize the gas or solid through the reaction

$$e^- + M \longrightarrow 2e^- + M^+$$

This produces other free electrons that gain energy from the electric fields and causes further ionization. This process of electron multiplication continues throughout the laser pulse and results in significant ionization of the gas and breakdown.

- Since the cascade ionization theory requires the pre-existance of initial electrons as a necessary condition, it is assumed that these are provided by MPI

Atomic Processes in Plasmas

- Collisional excitation
- Collisional Ionization
- Photo excitation
- Photoionization
- Bremsstrahlung-inverse Bremsstrahlung

Bremsstrahlung-Inverse Bremstrahlung

- *Bremsstrahlung* (German for "braking radiation") is a type of electromagnetic radiation emitted by high-temperature plasmas -- where atoms are ionized -- when free electrons interact with the electric field surrounding atomic nuclei. Bremsstrahlung is also known as *free-free emission* because the electrons merely pass by the atomic nuclei, and are not locked into the electron orbitals.
- *Bremsstrahlung* occurs when a free electron collides with another particle (e.g.ion)and makes a transition to another free state of lower energy, with the emission of a photon. The spectrum is a continuum.
- *Inverse Bremsstrahlung:* A reverse process, in which an electron absorbs a photon as it moves from one free state to a more energetic one in the field of an ion. Electrons in a laser field will gain energy to ionize and increase in number through electron-neutral inverse bremsstrahlung (IB)
- IB is of basic importance as a mechanism for plasma heating by laser light of all wavelengths.

2. Plasma Development(Growth)

- With the onset of breakdown a rapid plasma development stage results in the formation of a highly ionized plasma in which further absorption and photoionization occur
- Plasma shielding
  - Occurs at high power densities
  - thick plasma shields the laser beam, therefore, inefficient ablation occurs
  - the intensity of the analytical emission lines reduced

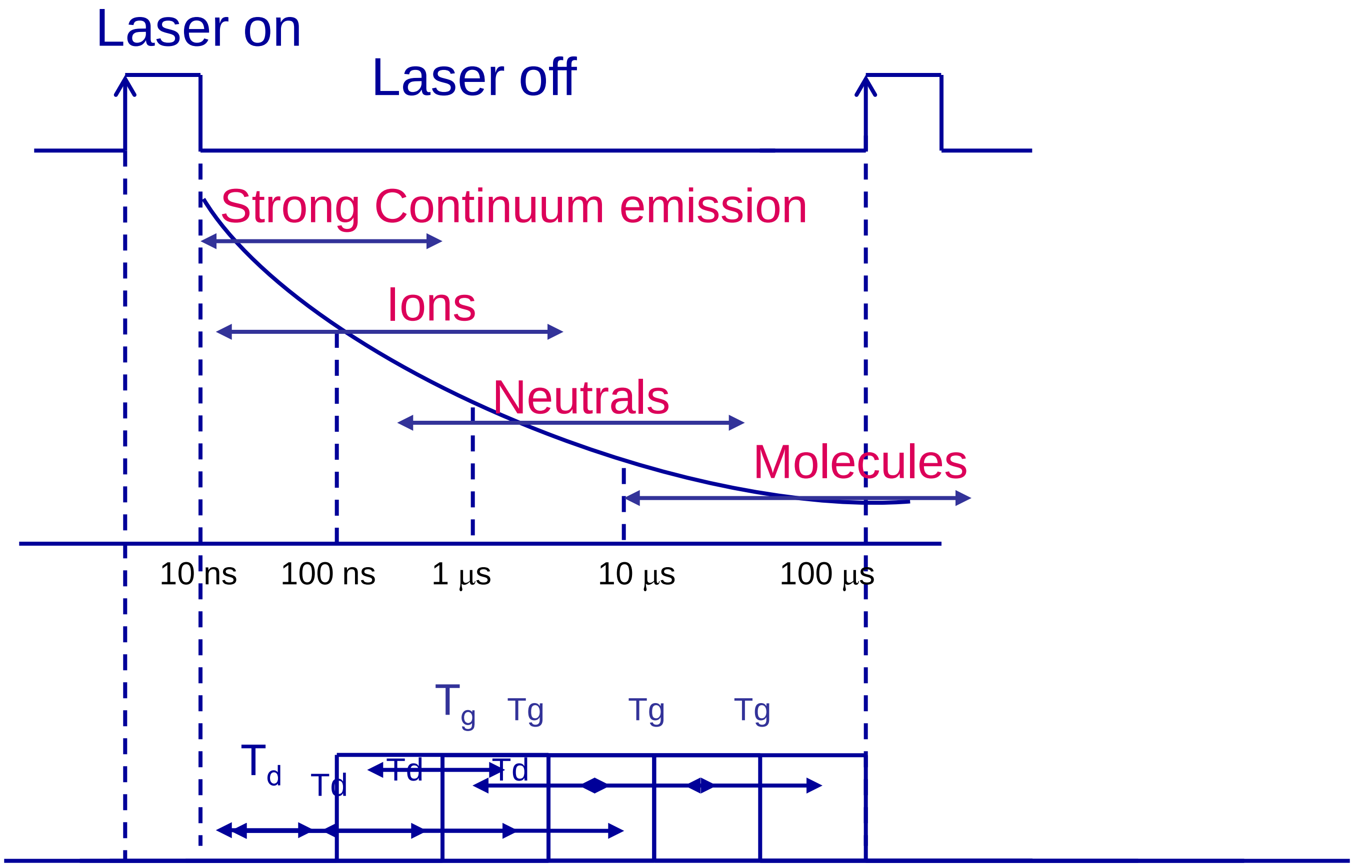
3. Plasma Decay

- With the end of the laser pulse, the plasma gradually dies away as a result of

  - -radiation and conduction of thermal energy,
  - -diffusion,
  - -attachment, and recombination of ions and electrons

until local thermodynamic equilibrium with the surrounding gas is restored.

Time resolution:



Laser on

Laser off

Strong Continuum emission

Ions

Neutrals

Molecules

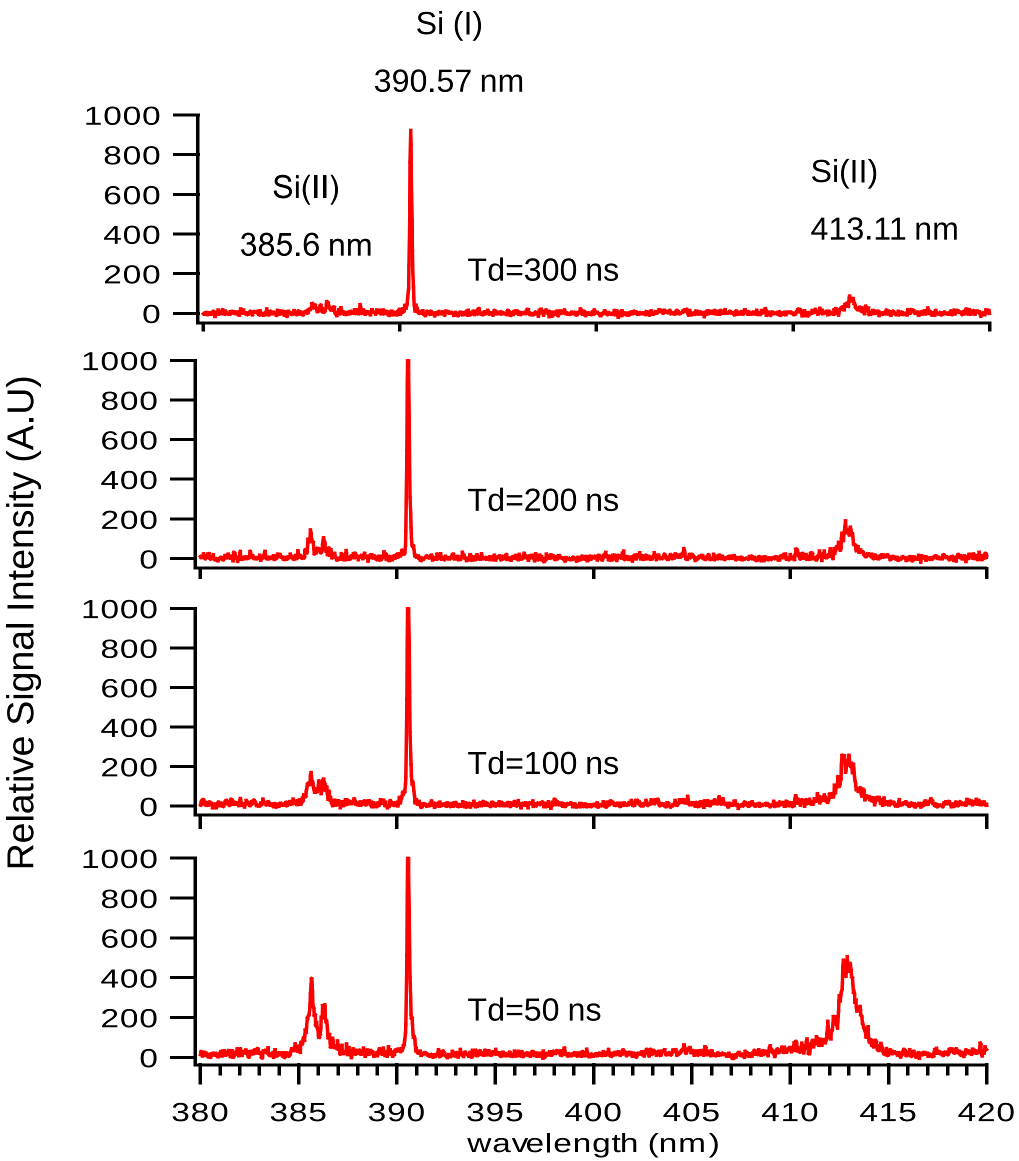
10 ns 100 ns 1 µs 10 µs 100 µs

T_g Tg Tg Tg

T_d Td Td Td

Td: delay time wrt laser pulse

Tg: gate time


Si (I)
390.57 nm
Si(II)
385.6 nm
Si(II)
413.11 nm
Td=300 ns
Td=200 ns
Td=100 ns
Td=50 ns
Relative Signal Intensity (A.U)
0
200
400
600
800
1000
380
385
390
395
400
405
410
415
420
wavelength (nm)

Typical LIBS plasma

- strong ionization $\alpha \approx 0.1 \ldots 1$

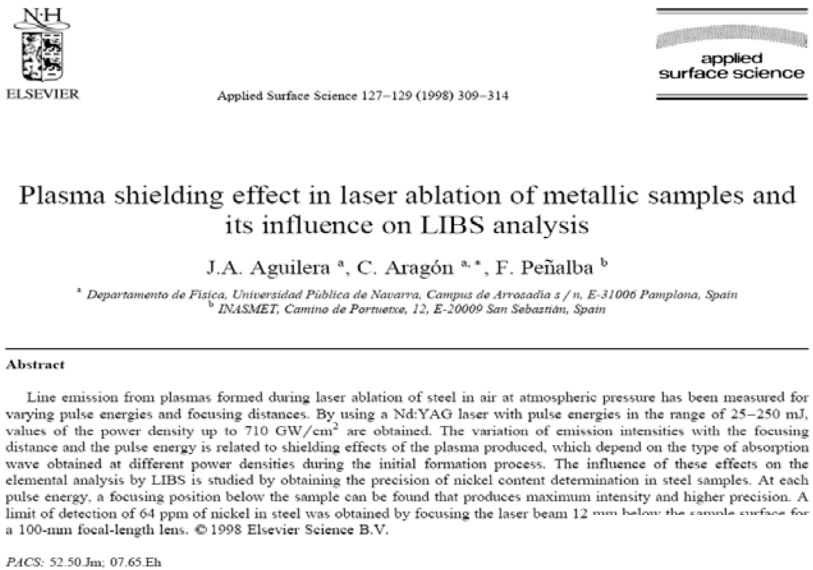
- large electron density $n_e \approx 10^{16} \ldots 10^{18}$

– LTE is valid

- self-absorption significant

    - not only for major elements

    - not only for ground state transitions



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Plasma shielding effect in laser ablation of metallic samples and its influence on LIBS analysis

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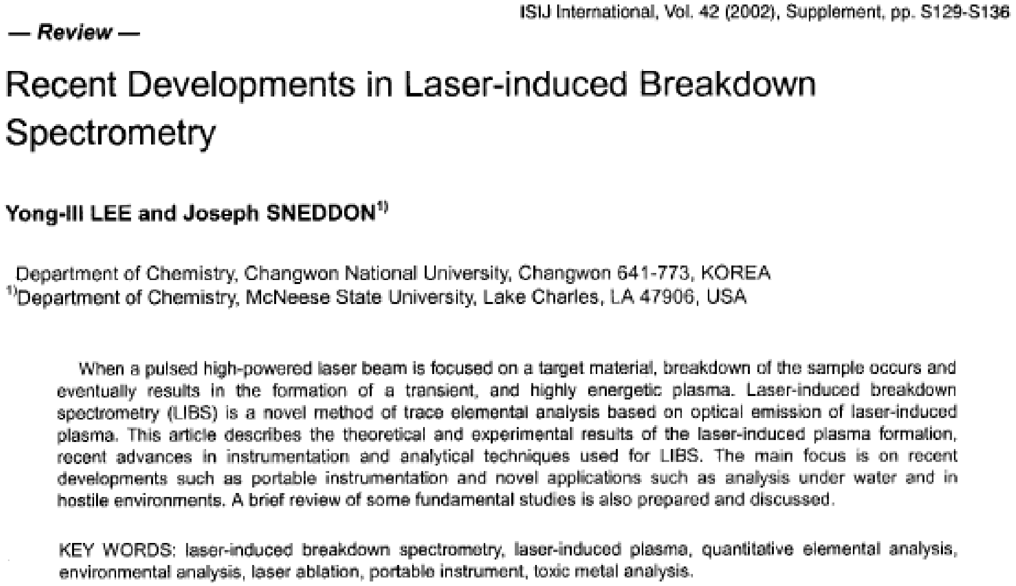
Abstract

Line emission from plasmas formed during laser ablation of steel in air at atmospheric pressure has been measured for varying pulse energies and focusing distances. By using a Nd:YAG laser with pulse energies in the range of 25–250 mJ, values of the power density up to 710 GW/cm^2 are obtained. The variation of emission intensities with the focusing distance and the pulse energy is related to shielding effects of the plasma produced, which depend on the type of absorption wave obtained at different power densities during the initial formation process. The influence of these effects on the elemental analysis by LIBS is studied by obtaining the precision of nickel content determination in steel samples. At each pulse energy, a focusing position below the sample can be found that produces maximum intensity and higher precision. A limit of detection of 64 ppm of nickel in steel was obtained by focusing the laser beam 12 mm below the sample surface for a 100-mm focal-length lens. © 1998 Elsevier Science B.V.

PACS: 52.50.Jm; 07.65.Eh

Keywords: Laser ablation; Laser-produced plasmas; LIBS



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— Review —

Recent Developments in Laser-induced Breakdown Spectrometry

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When a pulsed high-powered laser beam is focused on a target material, breakdown of the sample occurs and eventually results in the formation of a transient, and highly energetic plasma. Laser-induced breakdown spectrometry (LIBS) is a novel method of trace elemental analysis based on optical emission of laser-induced plasma. This article describes the theoretical and experimental results of the laser-induced plasma formation, recent advances in instrumentation and analytical techniques used for LIBS. The main focus is on recent developments such as portable instrumentation and novel applications such as analysis under water and in hostile environments. A brief review of some fundamental studies is also prepared and discussed.

KEY WORDS: laser-induced breakdown spectrometry, laser-induced plasma, quantitative elemental analysis, environmental analysis, laser ablation, portable instrument, toxic metal analysis.