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# EXPERIMENTAL INVESTIGATIONS OF A HYDROXYAPATITE LASER PLASMA

BY

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**Abstract.** Optical investigations in situ on the process of deposition of thin layers of hydroxyapatite are provided. In such conjecture ICCD camera measurements and optical emission spectroscopy resolved spatially and temporally are utilized. It results the separation of the plasma in components, a heterogeneity in the velocity distribution of the plasma component elements etc.

**Keywords:** hydroxyapatite; ICCD camera; optical emission spectroscopy.

## 1. Introduction

The purpose of this paper is to provide both in situ optical investigations on the process of deposition of thin layers of hydroxyapatite by laser ablation explained in the form of ICCD camera measurements and optical emission spectroscopy resolved spatially and temporally.

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## 2. Optical Investigations in situ on the Process of Deposition of thin Layers of Hydroxyapatite by Laser Ablation

In this section the experimental results on the dynamics of the transient plasmas produced by laser ablation on a hydroxyapatite target ($Ca_5(PO_4)_3(OH)$) are presented. The purpose of this study was to investigate, using optical methods, the dynamics of the particles ejected by laser ablation and their individual and global behavior.

The experiments were performed using the installation presented in detail (Irimiciuc *et al*., 2014). Plasma was generated by irradiation of the hydroxyapatite target with a pulse generated by an Nd:YAG (10 ns, 10 Hz, 532 nm) laser, with an energy per pulse of 80 mJ. The target used is disk-shaped (1 cm in diameter) and has been placed on an XYZ precision displacement system, being constantly shifted during irradiation to provide new surfaces for each irradiation. Other experimental details (investigations on the dynamics of the ablation plasma, emission spectra etc.) are specified in the same paper (Irimiciuc *et al*., 2014).

## 3. Fast Camera Measurements

To track the global evolutions of the transient plasmas produced by laser ablation on the hydroxyapatite target, the technique of rapid photography with the ICCD camera was used. The role of these investigations was to determine the structure and expansion velocities of the plasmas and to understand the effect of the target on the global dynamics of the plasma.

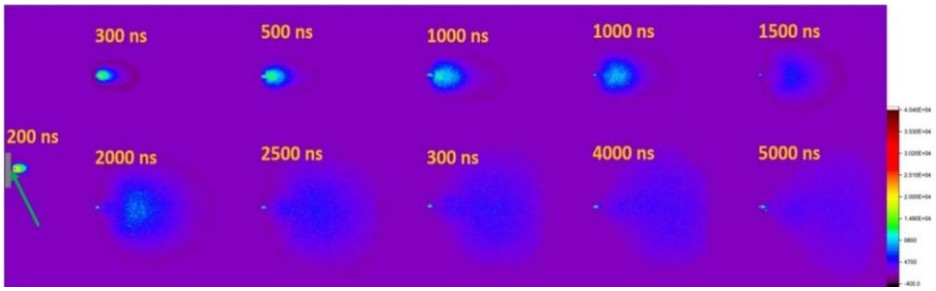



Fig. 1 – Temporal evolution of hidoxyapatite plasmas, determined with the ICCD camera.

Fig. 1 shows image sequences recorded during the expansion of a hydroxyapatite plasma. It can be observed that, during expansion, the plasma increases its volume and position of the center of mass (defined as the area with high emissivity) moving. Due to the fact that the experiments were performed at

low pressure, this displacement is described by a linear function, which highlights an expansion with a constant velocity. If the plasma pressure increases, the plasma dynamics undergoes significant changes: the ablation plasma, during evolution, is slowed down due to interactions with the waste gas molecules, its dynamics being described in this case by a "drag" type function (Aké *et al*., 2006). Also the global speeds of expansion can be determined by representing the movement of this "mass center" at different times of time.

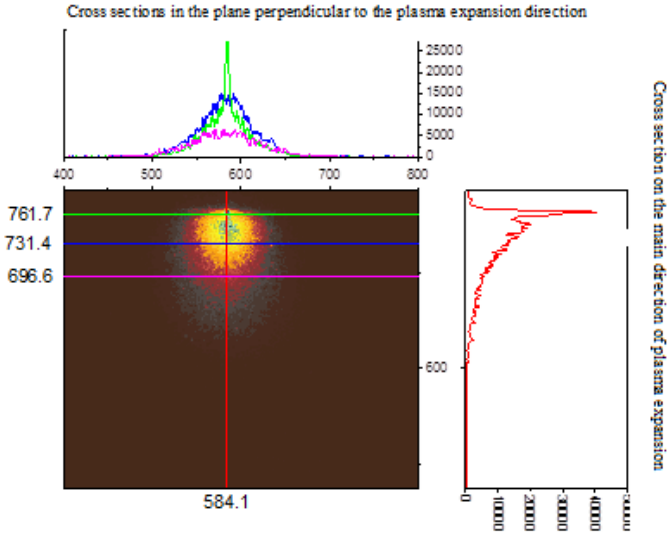



Fig. 2 – The image of a hydroxyapatite plasma recorded with the ultra-fast camera after 300 ns and the corresponding cross sections.

Fig. 2 shows an image of the ablation plasma after 350 ns from the interaction of the laser pulse radiation with the target and two cross sections on the main expansion axis (where the separation of structures is highlighted) and on a series of three axes parallel to the target surface (where the symmetry of the plasma with respect to the transverse axis is highlighted). The important feature highlighted by these images is the presence of a plasma separation process in two structures: the first structure (fast structure) and the second structure (slow structure). This phenomenon was also observed for Cu (Irimiciuc *et al*., 2017), Al (Focșa *et al*., 2017) or graphite (Harilal *et al*., 2003) plasmas and was found numerically in a hydrodynamic fractal model (Gurlui *et al*., 2008). The observed structures move at constant speeds of the order of 104 m/s for the first structure and 103 m/s for the second structure. The experimental results highlighted the good agreement between the values obtained and other values reported in the literature (Harilal *et al*., 2003; Gurlui *et al*., 2008; Ojeda *et al*., 2017; Cănulescu *et al*., 2009). The generated plasma is characterized by

a global expansion speed of 4.5 km/s for the slow structure and 17 km/s for the fast structure.

It is important to mention that the values of expansion speeds depend on the structure and nature of the target material. Thus, in the literature there are situations in which plasmas produced on materials with high atomic mass can move at low speeds (Ojeda *et al*., 2017; Cănulescu *et al*., 2009), and in the case of a complex target, there was a heterogeneity in the velocity distribution of the plasma component elements, which leads to a separation of the expansion velocities by the mass of the species present in the plasma (Ojeda *et al*., 2017; Cănulescu *et al.*, 2009). Recent results have confirmed the above statements (Irimiciuc *et al*., 2017).

This separation of the plasma into two or more components is presented in the literature as an effect of the interactions between the plasma particles and those of the waste gas (Harilal *et al*., 2003). However, given the high vacuum conditions in which our experiments were performed, the plasma separation process may be related to the different ejection mechanisms that are manifested. Thus, the fast structure is due to the presence of electrostatic mechanisms, such as the Coulomb explosion (Bulgakova *et al.*, 2005), while the slow structure is due to the presence of thermal mechanisms (phase explossion (Kelly and Miotello, 1997)). The results also show the presence of a third component of the plasma (identified in Fig. 2 through zone 1). This is present in the vicinity of the target and has expansion speeds of 520 m/s. Fig. 2 shows that the structure has a small angular distribution, compared to the classical structures, and is defined by a strong emission. These properties are characteristic, according to the results of the specific literature (Bindhu *et al*., 2003), the dynamics of nanoparticle clusters or molecules that can be found in plasma in the Knudsen layer region.

## 4. Optical Emission Spectroscopy Solved Spatially and Temporally

The recording of the global emission by fast photography only gives a preliminary image on the dynamics of the plasma, which is not able to highlight the individual contributions of each species present in the plasma. For the purpose of separating these contributions, a temporal and spatial resolved spectral study was performed using the optical emission spectroscopy technique. In order to have an overview of the species present in the plasma, a global spectrum was recorded (using a high integration time ~ 1 μs). The results are shown in Fig. 3. From the recorded spectra, the nature of the species present in the plasma can be identified using the authorized databases (Kramida *et al*., 2014). In the spectra we have identified characteristic lines for the atoms, ions and ions twice ionized. The abundance of these lines differs from one target to another, but is present in all investigated plasmas. This result is to be expected

given the differences in energy levels for each species (Ralchenko, 2005). This type of experiment manages to highlight very well the complex nature of hydroxyapatite, as shown in Fig. 3. In this figure it can be observed that the global emission spectrum has predominantly characteristic lines Ca, for which we have found correspondences for both atoms and ions.

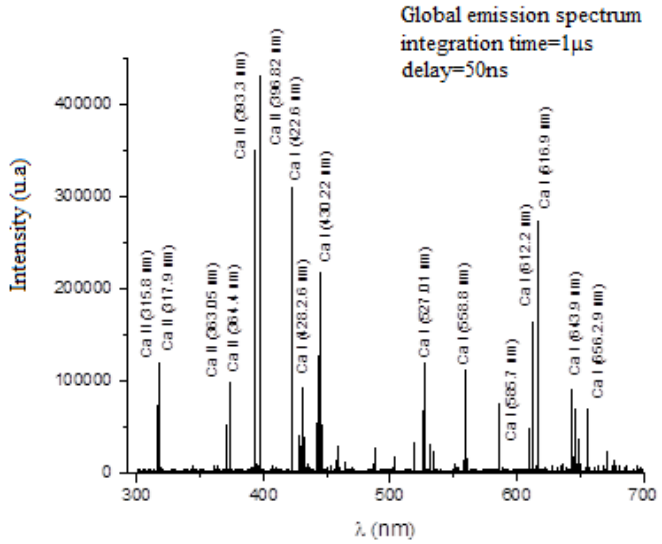



Fig. 3 – Global emission spectrum, acquired with an integration time of 1 μs at 50 ns.

We will use the Boltzmann method to determine the excitation temperature of the species present in the plasma (Cremers and Radziemski, 2006). This is a method applicable to thermodynamically balanced systems (local or global). In Fig. 4 it can be seen that the representations for atoms and ions are described by linear decreases, over a wide range of energies attributed to the energetic levels excited in the plasma. The presence of this type of dependence specifies the existence of a local thermodynamic equilibrium.

The analysis of the spectra determined the excitation temperatures for Ca I (~ 0.3 eV), Ca II (~ 1.58 eV). Recent studies have shown an inverse proportionality relationship between the global values of the excitation temperatures and the atomic mass of the elements. Of course, one can comment on the validity of the global value of the excitation temperature in the context of the fast variation of plasma parameters. In literature (Amoruso *et al*., 2002; Delserieys, 2008) it is known that for small times and distances, temperature increase is observed followed by a decrease of the excitation temperatures specific to atoms and ions, an evolution that faithfully follows the global emission distribution of plasmas.

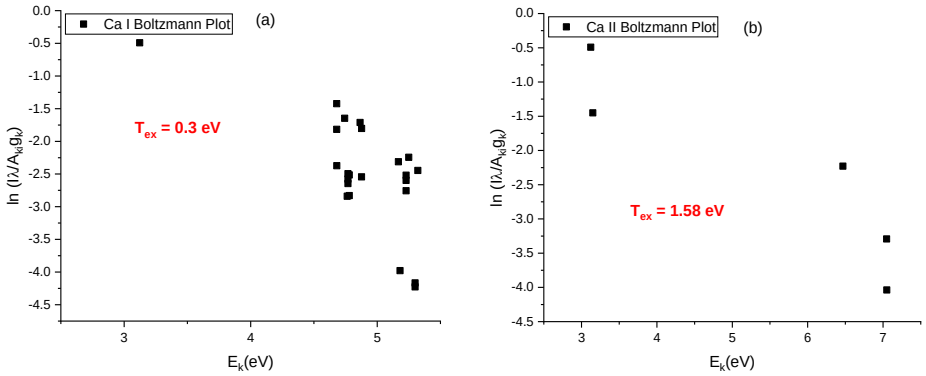



Fig. 4 – Boltzmann representation for excited states corresponding to Ca atoms (*a*) and ions (*b*) in plasma.

An important aspect highlighted by our study is the differences found between the excitation temperatures of the atoms and ions in the same plasma. This result can be regarded as an effect of the heating differentiated by the laser pulse.

In order to be able to differentiate between the individual contributions of each species, the space-time evolution of the emission lines characteristic to the plasma atoms and ions was followed. The results of these studies are shown in Fig. 5, where the characteristic signals are shown for Ca I (396.15 nm) and Ca II (546 nm) calcium ions. Thus we observe that the first emission spectral lines detected after the laser pulse are those of the atoms (sign of a slow expansion rate). These are followed by the lines corresponding to the ions. Such an analysis allows the investigation and separation of the dynamics of the ejected particles after their speed of expansion.

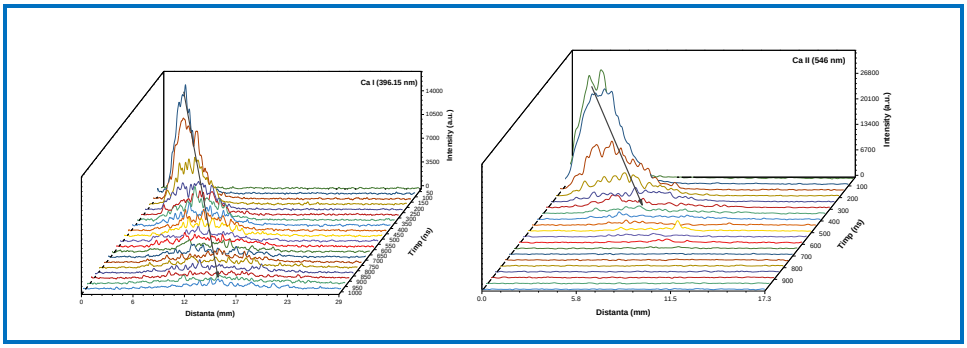
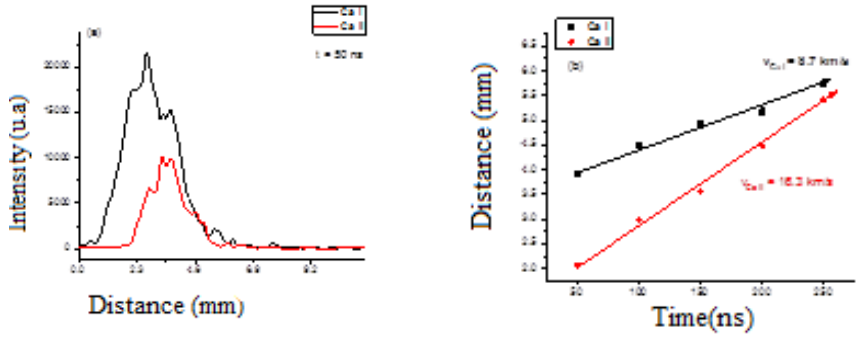



Fig. 5 – The comparative spatio-temporal evolution of the emission lines corresponding to Ca I atoms (396.15 nm) and Ca II ions (546 nm).

At the same time, we can see that the spatial profiles are structured in two main groups: a fast one, represented by the spectral lines of the ions, and a slower one, due mainly to the contribution of the neutrals. Such behavior may be related to the temporal evolution of the plasma recorded by fast photography with the ICCD camera. The velocity analysis of these groups confirms that the first structure observed by fast photography consists mainly of ionic species, while the second structure consists of neutral atoms.

In order to determine the expansion velocity of the individual species and then to compare with the global speeds presented above, the spatial evolutions of the intensities of the respective species were represented at different time points (Fig. 6). It is observed that the emission maximum undergoes a displacement to greater distances with the evolution of the plasma. By representing this spatio-temporal variation and fitting with a linear function (Fig. 6*b*), the expansion velocities of atoms (Ca I - 8.7 km/s) and ions (Ca II - 16.3 km/s) were determined. The evolution of plasma species velocities highlights a link between the degree of ionization and the rate of expansion. This dependence specifies the influence of the fundamental particle ejection mechanisms. In general, atomic species are removed by thermal mechanisms that impose an inverse proportional time link between velocity and the atomic mass radical. Plasma ions do not have the same type of dependence, most of them being removed by electrostatic mechanisms, which explains the speed differences between the two species.




*a* *b*

Fig. 6 – The comparative spatial distribution of Ca atoms and ions recorded after 50 ns (*a*) and the dependence of the maximum emission in space-time for the two species followed (*b*).

## 5. Conclusions

In the present paper optical investigations in situ on the process of deposition of thin layers of hydroxyapatite are presented. In such conjecture

ICCD camera measurements and optical emission spectroscopy resolved spatially and temporally are utilized. It results the separation of the plasma in two components, a heterogeneity in the velocity distribution of the plasma component elements, an inverse proportionality relationship between the global values of the excitation temperatures and the atomic mass of the elements etc.

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## INVESTIGAŢII EXPERIMENTALE ALE UNEI PLASME LASER DE HIDROXIAPATITĂ

(Rezumat)

Au fost făcute investigaţii optice in situ ale procesului de depunere de straturi subţiri de hidroxiapatită. Într-o asemenea conjunctură, măsurătorile efectuate atât cu camera ultrarapidă cât şi cu spectroscopia de emisie (rezolvată spaţial şi temporal), au specificat o separare a plasmei de ablaţie în mai multe componente, o neomogenitate în distribuţia de viteze etc.