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# Low-order harmonic generation in nanosecond laser ablation plasmas of carbon containing materials

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ABSTRACT

In this work we report on a systematic study of the spatiotemporal behaviour of low-order harmonics generated in nanosecond laser ablation plasmas of carbon containing materials. Plasmas were generated from targets of graphite and boron carbide ablated with a nanosecond Q-switched Nd:YAG laser at 1064 nm. Low-order harmonics (3rd and 5th) of the fundamental wavelength of a ns Nd:YAG driving laser, propagating perpendicularly to the ablation laser at variable time delays, were observed. The temporal study of the low-order harmonics generated under vacuum and atmospheres of Kr and Xe, revealed the presence of two populations that contribute to the harmonic generation (HG) at different times. It was found that under vacuum only small species contribute to the HG process, whereas under buffer gas, heavier species, such as clusters and nanoparticles, contribute to the HG at longer times. Optical emission spectroscopy, time of flight mass spectrometry and characterization of deposits collected on-line on a nearby substrate provided additional information that complemented the results of the spatiotemporal study of the generated harmonics. This approach to ablation plume analysis allows elucidating the identity of the nonlinear emitters in laser ablation plasmas and facilitates the investigation of efficient, nanoparticle-enhanced, coherent short wavelength generation processes.



## 1. Introduction

In recent years, the quest for coherent short wavelength radiation sources has motivated research on the conversion of intense laser radiation pulses to high-order harmonics, using as non-linear media atomic [1,2] and at a lesser extent molecular gas jets [3,4]. As an alternative, laser ablation plasmas emerge as attractive non-linear media for harmonic generation (HG) processes [5,6]. However, the conversion efficiency achieved following this strategy is still insufficient for many of the promising applications of extreme ultraviolet or X-ray coherent radiation.

The main advantage of laser ablation is that it opens the possibility of producing plasmas from a wide variety of materials, entraining in the gas phase different types of species like highly reactive fragments, multiple charged ions, as well as clusters and nanoparticles that could act as non-linear emitters [7–10]. Selection of the ablation parameters, such as laser wavelength, fluence, temporal regime or variation of the ablation atmosphere, enables control over plasma composition that can lead to an enhancement in the harmonics yield and to the extension of the harmonics cut-off [5,11,12].

In the case of low-order harmonic generation, two perspectives can be considered: on the one hand, it can be useful in the search for new efficient materials to act as a non-linear media in HG processes. On the other hand, it is appropriate as a diagnostic tool for the characterization of species present in the ablation plasma through the spatiotemporal study of the emitted harmonics signal [7–10]. Optical emission spectroscopy (OES), is a well suited technique to investigate the composition of laser-induced plasmas, however it usually provides information restricted to that derived from the emission of atoms and small molecules. Higher mass species, such as clusters and nanoparticles, could be also involved in the generation of harmonics, and therefore information regarding these plasma components can be obtained by the spatiotemporal analysis of harmonic signal. Moreover, this information is crucial to understand the HG process and increase the frequency up-conversion efficiency.

In this work, we have studied low-order HG in nanosecond laser ablation plasmas of two carbon containing materials, graphite and boron carbide ($B_4C$). Laser ablation plasmas of carbon containing materials have shown high harmonic conversion efficiency [13–18] and therefore knowledge upon the plasma species responsible for the frequency up-conversion is of great interest. To this purpose

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we carried out a systematic spatiotemporal study of the 3rd (TH λ = 355 nm) and 5th (FH λ = 213 nm) harmonics of a 1064 nm driving laser under different atmospheres. OES and time of flight mass spectrometry (TOF-MS) analysis of the plumes of these two carbon based materials, along with the analysis of deposits fabricated by on line pulsed laser deposition (PLD) gave further support to the conclusions obtained from the spatiotemporal study of HG. The results obtained have served to find a rich spatiotemporal distribution of non-linear emitters of different sizes, ranging from small molecules to nanoparticles, in the plasma plumes of graphite and boron carbide.

## 2. Experimental

The experimental set-up has been described previously elsewhere [10], hence only a brief account is given here. The targets of graphite (purity 99.99%) and boron carbide (purity 99.9%), both from Tech Supplies LTD, were mounted on a rotating holder to avoid cratering of the surface and placed inside a vacuum chamber. Laser ablation plasmas were produced by the fundamental 1064 nm output of a Q-switched Nd:YAG laser (Spectra Physics, Quanta Ray Indi-HG, 7 ns full width at half maximum, 10 Hz) at normal incidence with respect to the target surface. The radiation was focussed onto the target with a 17 cm focal length lens resulting in a spot size of 800 μm diameter. A fluence of 3 J/cm$^2$ was used for all experiments. A second Q-switched Nd:YAG laser (Lotis TII LS-2147, 17 ns full width at half maximum, 10 Hz) propagating parallel to the target surface and fired at a given temporal delay, was used as harmonic driving radiation. This radiation was focussed in the plasma plume using a 30 cm focal length lens. The intensity in the focal area was ~0.5 GW/cm$^2$. In this arrangement the directions of propagation of ablation laser and driving laser beams define the *x* and *z* axes respectively. The system is disposed in such a way that the displacement of the target allowed the spatial scanning of the plume along the *x* axis (*x*-scan). In the same way, displacement of the driving laser focus position across the plasma plume allowed the spatial scanning along the *z* axis (*z*-scan). After the interaction of the driving pulse with the plasma, the TH radiation was guided to the entrance slit of a spectrograph (Bentham, TMc300, 300 lines per millimetre grating) and separated from the driving laser radiation with the help of two highly IR transmissive, UV reflective mirrors. The detection was performed with a time-gated ICCD camera (Andor Technologies, 2151) with an integration time of 100 ns and by accumulation of the signal of 250 laser shots, corresponding to one target revolution. In all measurements, the main experimental error source is the pulse to pulse laser energy fluctuation, estimated at 10%. A second detection system was used for the detection of the generated FH. This system consisted of a photomultiplier (Hamamatsu, PMT R928, rise time 2.2 ns) coupled to a spectrograph (CVI, CM110, 1/8 Metre monochromator). In OES experiments, the two dichroic mirrors used in HG measurements were replaced by an 8 cm focal length lens in order to form the image of the plume on the entrance slit of the detection system described for TH detection. Spectral acquisition was carried out at zero delay and by accumulation of the signal of the same number of laser shots. Experiments were carried out under vacuum conditions better than $2 \times 10^{-2}$ mbar. Additionally, a background pressure of 1 mbar of He, Kr and Xe was used in the experiments performed under non-reactive gas atmosphere in order to assess the effect of aggregation of plasma species. TOF-MS analysis of the plume was carried out using the same experimental set-up as described in [6].

Material ejected in the ablation plume of the studied targets was collected on substrates, simultaneously with the HG measurements using a typical PLD arrangement [19]. The ablated material was collected under vacuum conditions on monocrystalline silicon (1 0 0) wafers, placed parallel to the target surface at a distance of 4 cm. Time deposition was fixed to 1 h at a repetition rate of 10 Hz. Characterization of the deposits was performed by environmental scanning electron microscopy (ESEM) (Phillips XL30).

## 3. Results and discussion

A systematic study of the spatiotemporal behaviour of the TH and FH generated in plasmas of graphite and boron carbide was performed by exploring the plasma plumes at controlled positions (*x* and *z*-scans) and for a range of temporal delays between the ablation event and the arrival of the driving laser pulse. As mentioned, the interest of studying carbon containing materials resides in their high harmonic conversion efficiency. In particular, graphite is a pure carbon compound that serves as a simple model in the study of harmonic generation processes. Boron carbide is an extremely hard chemical material used in tank armour, bullet-proof vests, and numerous industrial applications. With a hardness of 9.3 on the Moh's scale, it is one of the hardest materials known, behind cubic boron nitride and diamond. The use of such a sample is profitable from the point of view of stability of plasma formation (compared with milder graphite). It is especially important in the case of ablation with high pulse repetition rate lasers. On the other hand, in $B_4C$, boron atoms can contribute to the nonlinear process and differences in carbon content could affect the harmonics yield. The TH of the 1064 nm driving laser radiation at 355 nm was observed in both graphite and boron carbide. The non-linear conversion efficiency was estimated for both materials following the procedure described in [10]. Boron carbide showed a three times higher TH conversion efficiency in comparison with the graphite plasma. The FH at 213 nm was also observed in case of $B_4C$ plasma. The FH conversion efficiency was estimated to be one order of magnitude lower with respect to that of the TH in the case of boron carbide. In graphite, the detection of the weak FH signal was hindered by the overlapping intense atomic carbon emission lines in the region of 213 nm.

In order to confirm the energy dependence of the harmonic generation process in both materials, the evolution of the harmonics signal with the driving laser energy was studied. Fig. 1 shows examples of those measurements for graphite and boron carbide. Values of the slopes in log–log plots are in agreement with the expected cubic dependence for the TH. The FH signal from the boron carbide plasma (not shown) displays a fifth power dependence as expected.

The temporal evolution of the observed TH signal was analysed by varying the delay between the ablation and the driving laser pulses. Fig. 2 shows measurements in plasmas of graphite and boron carbide with the driving laser interacting with the plume

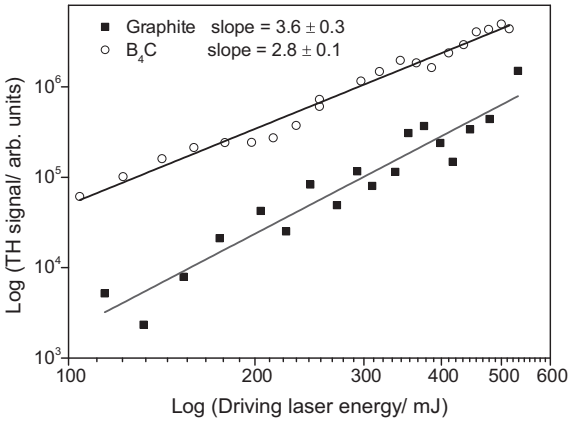


**Fig. 1.** Log–log plot of the TH signal as a function of the driving laser energy in graphite (solid squares) and boron carbide (open circles).