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Frequency mixing in boron carbide laser ablation plasmas

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ABSTRACT

Nonlinear frequency mixing induced by a bichromatic field (1064 nm + 532 nm obtained from a Q-switched Nd:YAG laser) in a boron carbide (B_4C) plasma generated through laser ablation under vacuum is explored. A UV beam at the frequency of the fourth harmonic of the fundamental frequency (266 nm) was generated. The dependence of the efficiency of the process as function of the intensities of the driving lasers differs from the expected behavior for four-wave mixing, and point toward a six-wave mixing process. The frequency mixing process was strongly favored for parallel polarizations of the two driving beams. Through spatiotemporal mapping, the conditions for maximum efficiency were found for a significant delay from the ablation event (200 ns), when the medium is expected to be a low-ionized plasma. No late components of the harmonic signal were detected, indicating a largely atomized medium.

1. Introduction

Boron carbide (B_4C) is a material with outstanding properties, and applications in high-technology industries: one of the hardest materials known, it displays very high resistance to chemical agents, high melting point, low density and a high neutron absorption cross section [1]. Deposition of boron carbide thin films with controlled properties is intensely sought for, and several techniques like chemical vapor deposition (CVD) [2], laser-assisted CVD [3] or magnetron sputtering [4] have been attempted, but both the stoichiometry and crystallinity of the deposits are very sensitive to variations in the deposition conditions. Pulsed laser deposition (PLD) of boron carbide has been explored only to a limited extent [5–8], and may be of high value since laser ablation easily overcomes the difficulties associated with the high melting point of B_4C and allows for a broad range of deposition conditions through the control of the laser properties, together with the atmosphere, geometry and temperature. In this context, the *in-situ* study of laser ablation plasmas of B_4C is of interest as a guide for controlled thin film synthesis through PLD.

Nonlinear optical processes in laser-produced plasmas were first observed in the 1970s [9], and the idea that nonlinear optical processes can be used as a diagnostic of complex media like plasmas or gas flows was proposed in the pioneering works of Zheltikov et al. [10–12]. These studies are based on the use of tight focusing geometries where the driving fields are employed as probes of local density in these media that act as 3D microscopes. In some of these works [11], resonances have been used for enhanced sensitivity to particular species. In less stringent conditions, recent work by our group has shown that low-order harmonic generation is sensitive to the presence of atoms, molecules, clusters and nanoparticles in a laser ablation plasma [13–15], and can, in some cases, be used as a probe of their density.

A significant body of work has been constructed over the last years on high-order harmonic generation in laser ablation plasmas ([16,17] and references therein), most of which have concentrated on high-order harmonic generation of intense ultrashort laser pulses. Harmonic generation in plasmas using bichromatic driving fields has also been studied in references [18–20].

Generation of odd low-order harmonics of an IR driving laser beam in B_4C plasmas was explored by our group in previous work [15]. Symmetry prevents the emission of even harmonics in center-symmetric systems if a single-color driving beam is employed. This restriction is lifted if bichromatic driving fields are employed, which have the additional advantage that they permit the exploitation of a broader range of resonances in the nonlinear species. This work explores the generation of a frequency-mixed beam at the frequency of the fourth harmonic of the fundamental, resulting from a parametric process in a NIR ns laser-produced plasma of the B_4C material. For that purpose, a bichromatic field composed of a NIR fundamental at 1064 nm and a visible second harmonic at 532 nm

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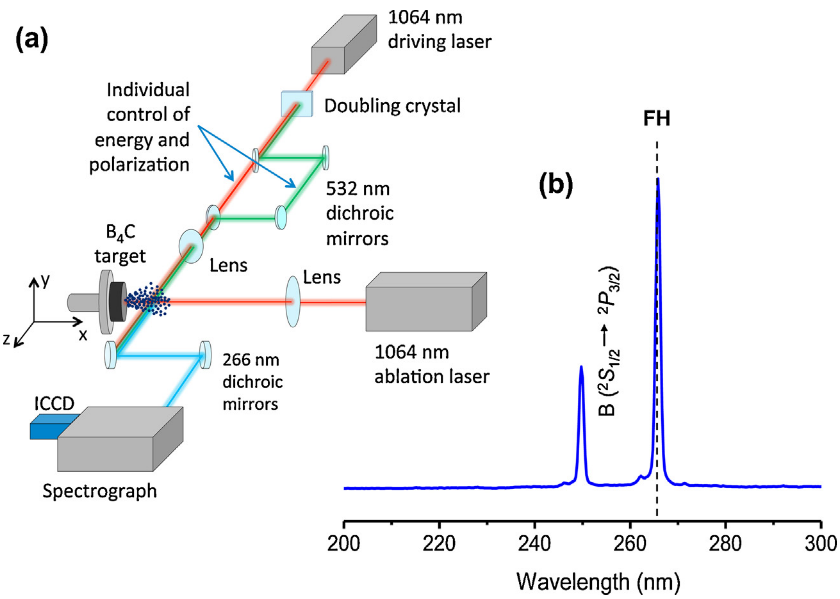

Fig. 1. Scheme of the experimental setup employed for frequency mixing experiments in a B_4C plasma (a), and typical result (b). The ablation laser interacts with the B_4C target at normal incidence and generates an ablation plasma that expands away from the surface. The driving laser is first frequency-doubled and later split in two arms in order to generate a bichromatic (1064 nm + 532 nm) driving beam. This beam interacts with the plasma after an electronically controlled delay, and generates a range of harmonics and frequency-mixed beams that copropagate with the driving beam. A set of dichroic mirrors discards the fundamental beams and drives the beam of interest toward the spectrometer, at the exit of which sits an ICCD device. The typical result is the spectrum shown in part (b), where the FH 266 nm beam can be detected, together with dominant spontaneous emission in this range, corresponding to the excited B atom.

was employed as the driving beam, and in these conditions a UV beam at 266 nm, which will be called FH for “fourth harmonic”, was generated collinearly. The spatiotemporal characterization of this FH beam provided a map of the presence of nonlinear optical species in the plasma, and the behavior as a function of the intensities of both driving beams provided clues as to the nature of the nonlinear frequency mixing process responsible for FH generation [21].

2. Material and methods

The setup employed was a variation of a system that had been reported previously [13]. It is schematically depicted in Fig. 1(a). The B_4C target (from Tech Supplies LTD, purity 99.9%) was mounted on a rotating holder to minimize cratering, inside a vacuum chamber (<10^{-5} mbar). A plasma was generated near the surface of the target by laser ablation with the fundamental radiation of a Q-switched Nd:YAG laser (Spectra Physics, Quanta Ray Indi-HG, 1064 nm, 7 ns full width at half maximum (FWHM), 10 Hz) that typically delivered on-target fluences in the region of 3 J cm^{-2} at normal incidence. After an electronically controllable delay, a second Q-switched Nd:YAG laser system (Lotis TII LS-2147, 15 ns FWHM, 10 Hz) was fired as the driving source for harmonic generation and frequency mixing in the B_4C plasma. Its fundamental output at 1064 nm was first frequency doubled in a type I KDP crystal, yielding a 532 nm beam with 4% efficiency, and later split in two arms with dichroic mirrors. Separate energy and polarization control in each arm was possible with variable attenuators and wave retarders for each wavelength. The NIR (1064 nm) and visible (532 nm) beams were later recombined with another dichroic element so that they copropagated parallel to the surface of the target and toward the plasma. No additional elements for phase control were introduced, because the optical path difference of the NIR and visible driving beams was significantly longer than the coherence length of the Nd:YAG laser, so no fixed phase relation can be expected. The beams were focused inside the plasma with a 20 cm focal length lens, attaining intensities in the region of 0.2 TW cm^{-2} and 3 GW cm^{-2} for the NIR and the visible beam, respectively. Some degree of chromatic focal mismatch ($\Delta f_{vis-NIR} \sim 5$ mm) was present but it was measured to be within the Rayleigh range ($b_{vis} \sim 9$ mm, $b_{NIR} \sim 4$ mm). The distance from the focal spot to the B_4C surface could be varied along the x-axis, but for most experiments it was fixed at 0.6 mm. Also, the position of the focus with respect to the plasma along the z axis (the driving laser propagation coordinate) could be scanned.

In these conditions, a beam at 266 nm (FH), resulting from frequency mixing, was generated in copropagation with the driving beams, and was separated from them with two dichroic mirrors that drove it to the entrance of a spectrograph (Bentham, TMc300, 300 lines per millimeter grating), at the exit of which sat a time-gated ICCD camera (Andor Technologies, 2151). The gate was typically set at 100 ns width, synchronous with the driving laser. Spectra resulting from the accumulation over 125 laser shots were acquired in the spectral region of the vicinity of the FH wavelength, with the result that is shown in Fig. 1(b). It is important to note that the FH was detected only in the presence of both driving beams at 1064 nm and 532 nm. Together with the FH signal, the strong spontaneous emission of excited boron atoms in the plasma in the $^2S_{1/2} \rightarrow {}^2P_{3/2}$ transition [22] was visible at 249.8 nm.

Additional experiments were carried out to obtain a separate diagnostic of the B_4C-ablated medium, which consisted of the detection of spontaneous emissions from electronically excited species formed in the ablation plasma. For these experiments, the driving laser was blocked, and an imaging lens was placed in the detection arm so that the image of the plasma was formed on the entrance slit plane of the spectrometer. This allowed us to obtain either 2D projections of the emissions, by using the diffraction grating of the spectrometer as a mirror (*i.e.* at zero order), or 1D spatially-resolved spectra. Temporal resolution was achieved by adequately gating the ICCD device.