Singularity-driven Second and Third Harmonic Generation in a ε-near-zero nanolayer

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Abstract

We show a new path to ε~0 materials without resorting to metal-based metamaterial composites. A medium that can be modeled using Lorentz oscillators usually displays ε=0 crossing points, e.g. ε=0 at λ~7μm and 20μm for SiO_2 and CaF_2, respectively. We show that a Lorentz medium yields a singularity-driven enhancement of the electric field followed by dramatic lowering of thresholds for a plethora of nonlinear optical phenomena. We illustrate the remarkable enhancement of second and third harmonic generation in a layer of ε~0 material 20nm thick, and discuss the role of nonlinear surface sources.

After the first demonstration of second harmonic generation (SHG) in 1961 [1], the enhancement of nonlinear processes has persisted as one of the main research activities in optics. A plethora of applications related to light generation at certain frequencies have been identified, and significant effort has been devoted to the study of harmonic generation from nanostructures having sizes that are not amenable to the use of phase-matching or quasi-phase-matching approaches. Several solutions have been proposed, all aiming at the enhancement of the electric field, that range from simple nanocavities [2, 3] to more complicated photonic crystals [4, 5]. The introduction of more sophisticated artificial structures and renewed interest in the excitation of surface waves [6] along the metal surface, and enhanced transmission [7], for example, have lead investigators to ask questions of a fundamental nature about the linear and nonlinear optical properties of metals and metal-based structures [8-11]. Surface plasmons are bounded waves at the surface between two media, and are usually accompanied by strong field enhancement in sub-wavelength regions [12, 13]. This observation has led to the exploration of nonlinear optical processes in structures that operate in the enhanced transmission regime: for example, studies of hole- and slit-arrays filled with a nonlinear medium have demonstrated that a boost in the linear response coincides with the enhancement of SHG and/or third harmonic generation (THG) [14, 15].

Centrosymmetric materials such as metals do not possess intrinsic, dipolar, quadratic nonlinear terms. Nevertheless, metals display an effective second order nonlinearity that arises from a combination of symmetry breaking at the surface, magnetic dipoles (Lorentz force), inner core electrons, and convective nonlinear sources and electron gas pressure [16]. They also possess a relatively large, third order nonlinearity that together with effective second order nonlinear sources introduce a non negligible contribution in the generated signals [15, 17, 18]. The detailed study and evaluation of these individual contributions has been made possible by the recent development of a dynamical model [16] for a nearly free electron gas where bound charges (or inner core electrons) also play a role in the determination of linear and nonlinear optical properties of metals [17, 18]. The model does not make any a priori assumptions about the relative weights of surface and volume sources, and has been shown to adequately predict SH and TH conversion efficiencies in semiconductor materials [19] where only bound electrons are present.

Quite recently epsilon-near-zero (ε~0) materials have been investigated for their peculiar linear [20, 21] and nonlinear optical properties [22-25]. In particular, studies in metal-dielectric composites having effective ε~0 have demonstrated that the extreme environment leads to significantly enhanced SH conversion efficiencies [23] and to peculiar memory and bistability features [24]. In fact, the longitudinal component of the (TM-polarized) electric field becomes singular anytime a material exhibits permittivity values close to zero due to the requirement that the longitudinal component of the displacement field be continuous [20-25].

In this letter we present results of a theoretical investigation of SHG and THG from a 20nm-thick layer of a new type of uniform material having ε~0 in the visible range that does not require the presence of metals. Harmonic generation is examined also by quantifying and comparing the role that surface and volume terms play with respect to intrinsic second and third order nonlinear susceptibilities. This evaluation becomes necessary because near the ε=0 condition the longitudinal electric field may be enhanced several hundreds to many thousands of times, resulting in strong nonlinear surface (quadrupole-like) and volume (magnetic dipole) sources beyond the contributions of the intrinsic nonlinearities. The nonlinear dynamics of bound electrons of ε~0 materials is thus modeled by including electric and magnetic forces as outlined in references [15, 16, 19]. Normalized conversion efficiencies of order of 10^{-5} and 10^{-7} are predicted for SHG and THG, respectively, when a uniform layer only 20nm thick having

$\chi^{(2)}$=20pm/V and $\chi^{(3)}$=10^{-20}(m/V)^2 is illuminated with TM-polarized light and peak intensity of 40MW/cm^2.

As may easily be ascertained, any Lorentz-type material has readily accessible ε~0 regions. For example the permittivities of semiconductors like GaP, GaAs, and Si have high- and low-absorption ε=0 crossing points near 250nm and 100nm, respectively [26]. Fluorides, on the other hand, (LiF, CaF_2 or MgF_2) and oxides like SiO_2 have ε=0 crossing points in the 7-40μm range [26], where they display metallic behavior. Another peculiarity of typical Lorentz systems is that absorption tends to be somewhat abated at the short-wavelength crossing point, where for example CaF_2 and SiO_2 exhibit comparatively smaller absorption than semiconductors at their ε=0 crossing point, resulting in more favorable field enhancement conditions compared to semiconductors. For simplicity material X is modeled using a single species of resonant Lorentz oscillators as usual:

$$\varepsilon_x(\omega) = 1 - \frac{\omega_p^2}{\omega^2 - \omega_0^2 + i\gamma\omega} \tag{1}$$

where the plasma frequency $\omega_p=2\omega_r$, damping $\gamma=10^{-2}\omega_r$, the resonance frequency $\omega_0=0.5\omega_r$, and the reference frequency $\omega_r=2\pi c/1\mu m$. These parameters produce a strong resonance at 2μm (Fig.1 (b)) and a ε=0 crossing point at λ~485nm. In order to give our results a more realistic slant near the crossing point we have chosen γ so that the resulting peak dielectric and index values are similar to those displayed by CaF_2, with the exception that they are shifted toward the visible range. The main effect of choosing larger (smaller) γ is to reduce (increase) the maximum field amplitude in the material and, consequently, the strength of the nonlinear optical interaction.

The simple geometry of the structure under investigation is depicted in Fig.1 (a): a d=20nm thick layer of material X is illuminated with TM-polarized light. Incident wavelength and angle are varied to explore the linear properties of the slab and to evaluate the electric field enhancement inside the medium. As detailed elsewhere [20, 21], at the zero-crossing point linear transmission at normal incidence is nearly 100% (when absorption is neglected) and 0% for all other incident angles. If a material with non-zero damping is considered the transition between 100% and 0% transmission is more gradual, and the steepness of the transition depends also on material absorption.

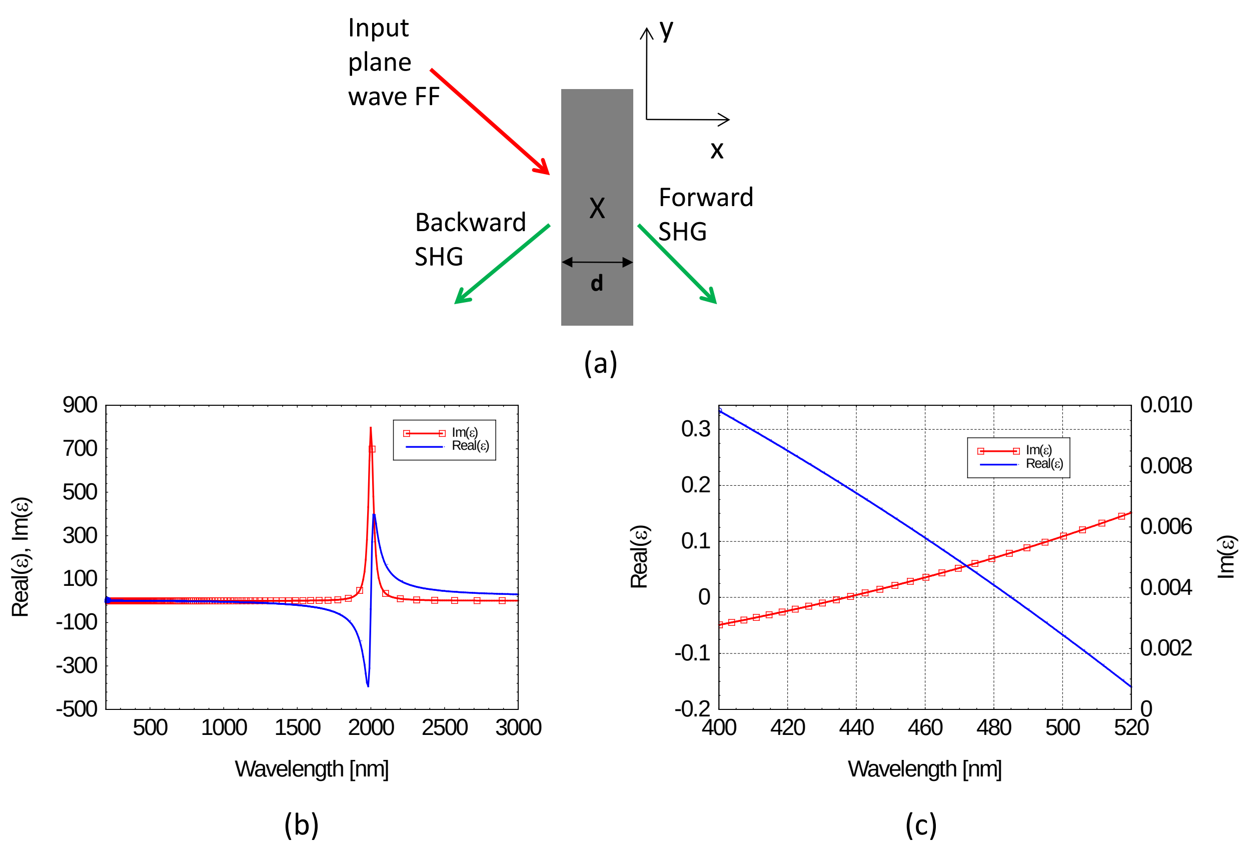

Fig.1: (a) A pump (FF) is incident on a 20nm-thick layer of uniform material composed of Lorentz oscillators resonant at 2μm. (b) Material dispersion and (c) detail of the ε=0 crossing region.

Let us now focus on the electric field enhancement of this structure in the vicinity of the zero-crossing point for different incident angles. Choosing a 20nm layer has the advantage of removing geometrical resonance phenomena that might otherwise complicate the analysis [22-25]. The linear optical properties of the structure were calculated using a standard transfer matrix method (TMM) [27]. As Fig.2 (a) shows, the longitudinal electric field intensity is amplified approximately 400 times relative to the incident field. As an example, we note that for $\gamma=10^{-4}$ the field is amplified approximately by a factor of 35000 compared to the incident field intensity, confirming the singularity-driven nature of the field near the crossing point. In the absence of other mechanisms (the thin layer is not resonant) the amplification of the field comes solely as a result of the fact that the longitudinal component of the displacement field must be continuous.

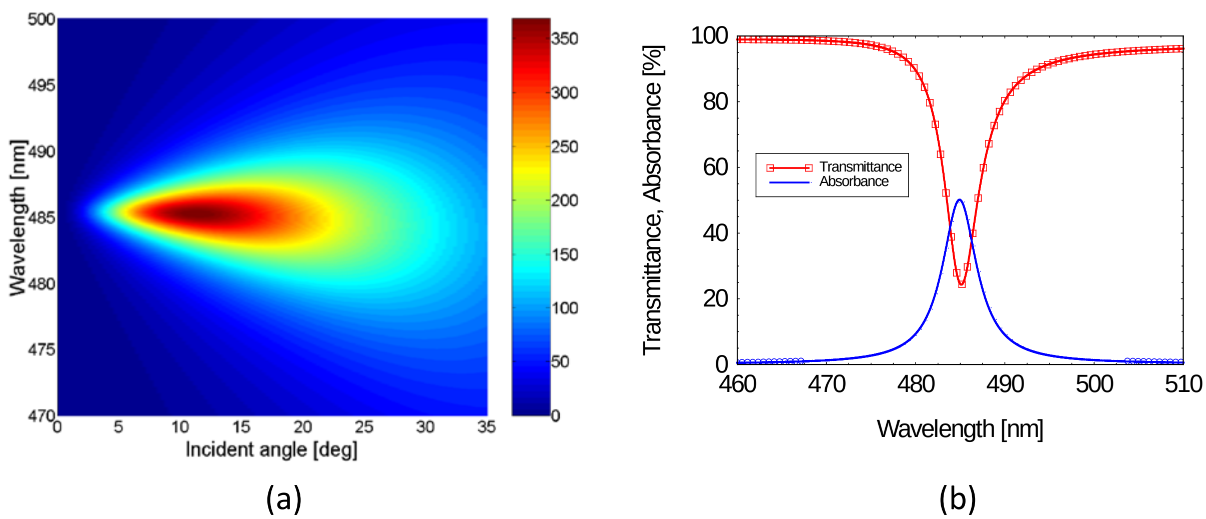

Fig.2: (a) Maximum intensity recorded inside the 20nm layer as a function of wavelength and incident angle, normalized with respect to the incident intensity. The intensity is distributed uniformly inside the layer with an amplification factor of ~400. (b) Transmission and absorption vs. wavelength when the field is incident at 12º. The peculiarity here is that maximum amplification occurs near the bottom of the transmission curve, (a rudimentary gap that forms when ε and μ have opposite signs) where absorption is also a maximum: nearly 50% of the incident light is absorbed.

The excitation of a large longitudinal electric field, highlighted in reference [23] in the context of SHG from metal-dielectric composites, is associated with a transversely moving wave, and may be interpreted simply as a guided mode resonance inside the slab, or a polariton, in a more common vernacular. The formation of this resonant mode is evident from the analysis of transmission and absorption properties of the structure, where nanometer-size resonant features appear at relatively small angles. In Fig.2 (b) we also show transmission and absorption for a wave incident at 12º. It is evident that in this system overall absorption is not negligible, in spite of the fact that Im(ε) is relatively small, because absorption is proportional to the product $\mathrm{Im}(\varepsilon)|\mathbf{E}|^2$. We reiterate that no geometrical resonances are excited, and that the enhancement of the field shown in Fig.2 (a) and (b) comes solely as a result of approaching the ε=0 conditions.

The nonlinear calculations were performed using three different methods: (i) finite difference time domain and (ii) fast Fourier transform spectral techniques, which were used to also study the effect of nonlinear surface sources, and (iii) Comsol Multiphysics [28] for the CW regime. In Figs.3 (a) and (b) we report conversion efficiencies for both SHG and THG vs. incident angle and wavelength. We remark that harmonic generation follows the electric field intensity enhancement profile of Fig. 2 (a), reaching efficiencies of order 10^{-5} for SHG and 10^{-7} for THG when $\gamma=10^{-2}$, which increase to 10^{-3} and 10^{-5} respectively, when $\gamma=10^{-4}$.

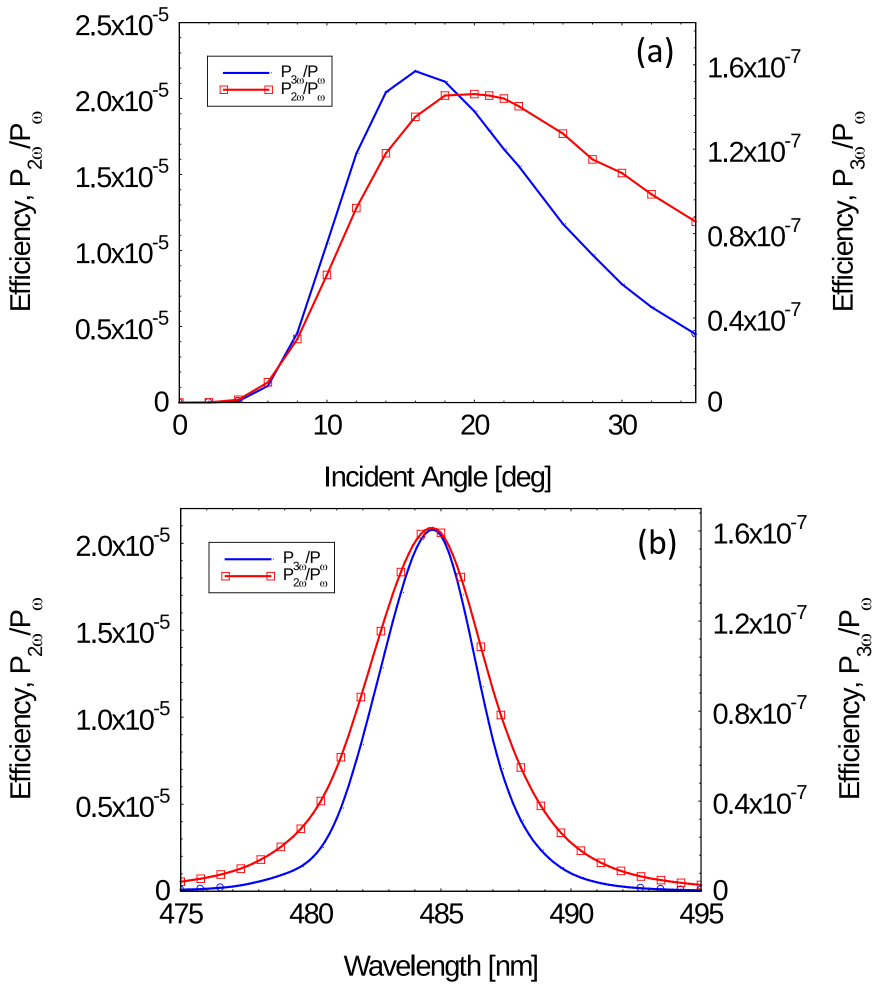

Fig.3: (a) SH and TH conversion efficiencies vs. incident angle for the 20nm layer of Fig.1 (a). (b) Emitted spectra for SH and TH fields centered at 242nm and 161nm at 18°.

In order to provide context for these conversion efficiencies we compared these results with the predictions of SHG and THG made in reference [15] for a resonant metal grating 100nm thick, filled with GaAs. In that case, using intensities of order $2GW/cm^2$ $\chi^{(2)}$=100pm/V in GaAs sections of the grating, and $\chi^{(3)}=10^{-15}(m/V)^2$ in the bulk metal [17] the best conversion efficiencies attainable were 10^{-6} and 10^{-3} for SHG and THG, respectively.

The kind of field enhancement and related discontinuities that we are discussing naturally raise the possibility that harmonic generation from nonlinear surface and magnetic dipole sources may come into play in media with low $\chi^{(2)}$ and $\chi^{(3)}$. In modeling the medium care must thus be taken to include and assess these effects. For this reason we use the model outlined in references [15, 16, 19], where it was used in the context of harmonic generation from metal surfaces [16], metal nanocavities containing semiconductor materials [15], and for the study of harmonic generation from a GaP substrate [19]. Our findings indeed suggest that in materials like glasses and fluorides that display relatively low nonlinear coefficients [29], for example, $\chi^{(2)}$=1pm/V and $\chi^{(3)}=10^{-21}(m/V)^2$ and also depending on the magnitude of the damping coefficient, nonlinear surface sources should be included because conversion efficiencies are sensitive to the choice of the bound electron's effective mass, i.e. a distinctive feature that determine nonlinear harmonic gain [19]. So while it is apparent that another interesting chapter waits to be written on the subject, we leave that task for another time.

The question that one now may ask is how to best achieve conditions for an experimental verification of enhanced harmonic generation near the $\varepsilon=0$ point in simple Lorentz systems. Although semiconductors like Si and GaP display relatively low absorption at $\lambda\sim100$nm, fluorides and glasses may be directly addressed using appropriate IR sources. However, it is likely that for improved performance some engineering may be required, and it may be easier to approach the problem in the visible or IR ranges using glasses or liquids doped with dyes [30]. Typical visible and near-IR dyes that are commercially available have near-Lorentzian absorption profiles that may be engineered almost at will, thus making it likely that a dye-based solution may provide a good test-bed.

In summary we have presented a new type of $\varepsilon \sim 0$ materials whose topology does not require a metal-dielectric metamaterial infrastructure. Using this simple approach we are able to extract a unique type of phenomenology that lowers the threshold for a wealth of nonlinear optical phenomena, from harmonic generation to optical bistability and switching, and from quantum optical interaction like stimulated Raman scattering to soliton formation and high field ionization, to name a few. We have investigated harmonic generation in media with relatively small $\chi^{(2)}$ and $\chi^{(3)}$ (20pm/V and 10^{-20} m^2/V, respectively), dielectric-like materials with a $\varepsilon=0$ crossing in the visible range, and predicted SHG and THG conversion efficiencies as high as 10^{-5} and 10^{-7} in a 20nm thick layer of realistic material, with only a few MW/cm^2 of input power in the presence of realistic absorption. Strong electric field enhancement inside the nanolayer is due to the continuity of the longitudinal component of the displacement field which in $\varepsilon \sim 0$ materials causes the relative component of the electric field to approach singular behavior. Our calculations also suggest that symmetry breaking and nonlinear volume sources arising from magnetic dipoles have to be included in the model if the intrinsic nonlinear coefficients are small, as might be the case for glasses and liquids. Finally, it is clear that while some molecular and material engineering may be required for experimental verification, it should also be apparent that an equally clear and relatively straightforward path now exists to the development of exotic and extreme nonlinear optical phenomena in the KW/cm^2 range.

References

[1] P. Franken, A. Hill, C. Peters, and G. Weinreich, "Generation of Optical Harmonics," *Physical Review Letters* **7,** 118 (1961).

[2] H. Cao, D. B. Hall, J. M. Torkelson, and C.-Q. Cao, “Large enhancement of second harmonic generation in polymer films by microcavities”, *Appl. Phys. Lett.* **76**, 538 (2000).

[3] J. Trull, R. Vilaseca, Jordi Martorell, and R. Corbalán, “Second-harmonic generation in local modes of a truncated periodic structure”, Opt. Lett **20**, 1746 (1995).

[4] Jordi Martorell, R. Vilaseca, and R. Corbalán, “Second harmonic generation in a photonic crystal”, Appl. Phys. Lett. **70**, 702 (1997).

[5] M. Scalora, M. J. Bloemer, A. S. Manka, J. P. Dowling, C. M. Bowden, R. Viswanathan, and J. W. Haus , “Pulsed second-harmonic generation in nonlinear, one-dimensional, periodic structures”, Phys. Rev. A **56**, 3166 (1997).

[6] William L. Barnes, Alain Dereux, and Thomas W. Ebbesen, “Surface plasmon subwavelength optics”, *Nature* **424**, 824 (2003).

[7] T. W. Ebbesen, H. J. Lezec, H. F. Ghaemi, T. Thio & P. A. Wolff, “Extraordinary optical transmission through sub-wavelength hole arrays,” *Nature* **391**, 667-669 (1998).

[8] D. T. Owens, C. Fuentes-Hernandez, J. M. Hales, J. W. Perry, and B. Kippelen, “A comprehensive analysis of the contributions to the nonlinear optical properties of thin Ag films,” J. Appl. Phys. **107**, 123114 (2010).

[9] D. Krause, C. W. Teplin, and C. T. Rogers, “Optical surface second harmonic measurements of isotropic thin-film metals: Gold, silver, copper, aluminum, and tantalum,” J. Appl. Phys. **96**, 3626 (2004).

[10] A. Nahata, R. A. Linke, T. Ishi, and K. Ohashi, “Enhanced nonlinear optical conversion from a periodically nanostructured metal film,” Opt. Lett. **28**, 423 (2003).

[11] M. Airola, Y. Liu, and S. Blair, “Second-harmonic generation from an array of sub-wavelength metal apertures,” J. Opt. A, Pure Appl. Opt. **7**, S118 (2005).

[12] H. Raether, *Surface Polaritons on Smooth and Rough Surfaces and on Gratings*, Springer-Verlag, Berlin (1988).

[13] S. Meier, *Plasmonics: Fundamentals and applications*, Springer – New York (2007).

[14] W. Fan, S. Zhang, N. C. Panoiu, A. Abdenour, S. Krishna, R. M. Osgood, K. J. Malloy, and S. R. J. Brueck, “Second Harmonic generation from a nanopatterned isotropic nonlinear material,” Nano Lett. **6**, 1027 (2006).

[15] M. A. Vincenti, D. de Ceglia, V. Roppo, and M. Scalora, "Harmonic generation in metallic, GaAs-filled nanocavities in the enhanced transmission regime at visible and UV wavelengths”, Opt. Express **19**, 2064 (2011).

[16] M. Scalora, M. A. Vincenti, D. de Ceglia, V. Roppo, M. Centini, N. Akozbek, and M. J. Bloemer, “Second and Third Harmonic Generation in Metal-Based Structures,” Phys. Rev. A **82**, 043828 (2010).

[17] N. N. Lepeshkin, A. Schweinsberg, G. Piredda, R. S. Bennink, and R. W. Boyd, “Enhanced nonlinear optical response of one-dimensional metal-dielectric photonic crystals,” Phys. Rev. Lett. **93**, 123902 (2004).

[18] D. T. Owens, C. Fuentes-Hernandez, J. M. Hales, J. W. Perry, and B. Kippelen, “A comprehensive analysis of the contributions to the nonlinear optical properties of thin Ag films,” J. Appl. Phys. **107**, 123114 (2010).

[19] V. Roppo, J. Foreman, N. Akozbek, M.A. Vincenti, and M. Scalora, “Third Harmonic Generation at 223nm in the Metallic Regime of GaP”, Applied Physics Letters **98**, 111105 (2011).

[20] M. Silveirinha and N. Engheta, “Tunneling of Electromagnetic Energy through Subwavelength Channels and Bends using *ε*-Near-Zero Materials”, Phys. Rev. Lett. **97**, 157403 (2006) .

[21] A. Alù, M. G. Silveirinha, A. Salandrino, and N. Engheta, “Epsilon-near-zero metamaterials and electromagnetic sources: Tailoring the radiation phase pattern”, Phys. Rev. B **75**, 155410 (2007)

[22] A. Ciattoni, C. Rizza, and E. Palange, “Extreme nonlinear electrodynamics in metamaterials with very small linear dielectric permittivity”, Phys. Rev. A **81**, 043839 (2010).

[23] A. Ciattoni, “Highly efficient second-harmonic generation from indefinite epsilon-near-zero slabs of subwavelength thickness”, http://arxiv.org/abs/1103.2864 (2011).

[24] A. Ciattoni, C. Rizza, and E. Palange, “Transmissivity directional hysteresis of a nonlinear metamaterial slab with very small linear permittivity,” Opt. Lett. **35**, 2130 (2010).

[25] A. Ciattoni, C. Rizza, and E. Palange, “All-optical active plasmonic devices with memory and power-switching functionalities based on *ε*-near-zero nonlinear metamaterials,” Phys. Rev. A **83**, 043813 (2011)

[26] E. D. Palik, *Handbook of Optical Constants of Solids* (Academic Press, London-New York (1985).

[27] Grant R. Fowles, *Introduction to Modern Optics* (Courier Dover Publications, 1989).

[28] Comsol Multiphysics, http://www.comsol.com/

[29] V. M. Gordienko, N. G. Khodakovskij, P. M. Mikheev, F. V. Potemkin, and K. Ju. Zubov, “THG in dielectrics using low-energy tightly-focused femtosecond laser: third order nonlinearity measurements and the evolution of laser induced plasma,” Journal of Russian Laser Research **30**, 599 (2009).

[30] http://www.qcrsolutions.com