



# How Light Behaves When The Refractive Index Vanishes

## Physics and Applications of Epsilon-Near-Zero Materials

**Robert W. Boyd**

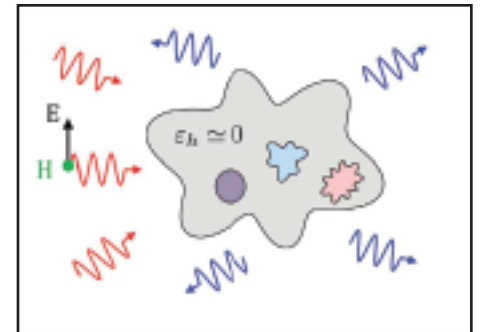
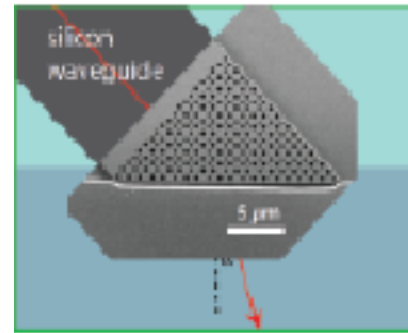
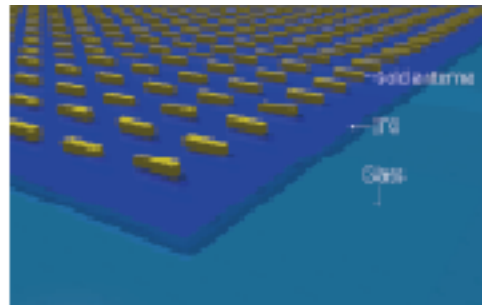
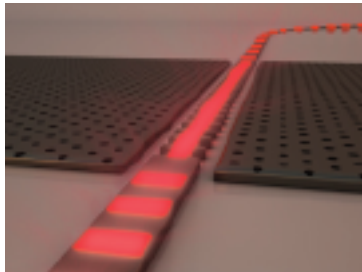
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University of Rochester



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# How Light Behaves when the Refractive Index Vanishes

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- Physics of Near-Zero Index (NZI) and Epsilon-Near Zero (ENZ) Materials
- Nonlinear Optical Properties of ENZ and NZI Materials
- Metamaterials for ENZ and NZI Studies
- Applications of ENZ and NZI Materials

# Spoiler Alert: Implications of ENZ Behavior for Nonlinear Optics

Here is the intuition for why the ENZ condition is of interest in NLO

Recall the standard relation between  $n_2$  and  $\chi^{(3)}$

$$n_2 = \frac{3\chi^{(3)}}{4\epsilon_0 c n_0 \operatorname{Re}(n_0)}$$

Note that under ENZ conditions the denominator becomes very small, leading to a very large value of  $n_2$

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Footnote:

Standard notation for perturbative NLO

$$\mathbf{P} = \chi^{(1)}\mathbf{E} + \chi^{(2)}\mathbf{E}^2 + \chi^{(3)}\mathbf{E}^3 + \dots$$

$\mathbf{P}$  is the induced dipole moment per unit volume and  $\mathbf{E}$  is the field amplitude.

Also, the refractive index changes according to

$$n = n_0 + n_2 I + n_4 I^2 + \dots$$

# Giant Nonlinear Response of ENZ Metastructures

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- Nonlinear Optics is important for a variety of reasons:

## Photonic Devices

All-optical switching, buffers and routers based on slow light

Used to create quantum states of light for

Quantum Computing/Communications/Imaging

Fundamental understanding of light-matter interactions

Not “just” Lorentz oscillator formalism

Understand rogue waves

Induce and control filamentation processes

- However, the nonlinear response is usually much weaker than the linear response
- Means to enhance the nonlinear response
  - Resonance interactions (atomic vapors)
  - Plasmonic systems
  - Electromagnetically induced transparency (EIT)
  - Metamaterials (composite materials)
- Our approach: Use epsilon-near-zero (ENZ) materials and metamaterials



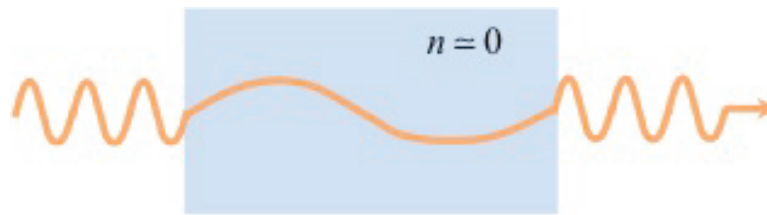
# Physics of Near-Zero-Index (NZI) and Epsilon-Near-Zero (ENZ) Materials

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- The wavelength of light is given by

$$\lambda = \lambda_{\text{vac}}/n$$

and is significantly lengthened in a NZI material. The wavelength approaches infinity as  $n$  approaches zero.



- The phase velocity of light is given by

$$v = c/n$$

and also approaches infinity as  $n$  approaches zero.

- For  $n$  approaching zero, the field oscillates in time but not in space; oscillations are in phase everywhere

Brown, Proc. IEE 100, 5 (1953).

Ziolkowski, Phys. Rev. E 70, 046608 (2004).

Silveirinha and Engheta, Phys. Rev. Lett. 97, 157403 (2006).

# Physics of Epsilon-Near-Zero (ENZ) Materials

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- Radiative processes are modified in ENZ materials \*

Einstein  $A$  coefficient (spontaneous emission lifetime =  $1/A$ )

$$A = n A_{\text{vac}}$$

We can control (inhibit!) spontaneous emission!

Einstein  $B$  coefficient

Stimulated emission rate =  $B$  times EM field energy density

$$B = B_{\text{vac}} / (n n_g)$$

Optical gain is very large!

Einstein, *Physikalische Zeitschrift* 18, 121 (1917).

Milonni, *Journal of Modern Optics* 42, 1991 (1995).

Equations are shown for nonmagnetic ( $\mu = 1$ ) materials

- Implications:
  - If we can inhibit spontaneous emission, we can build thresholdless lasers.
  - Expect superradiance effects to be pronounced in ENZ materials.

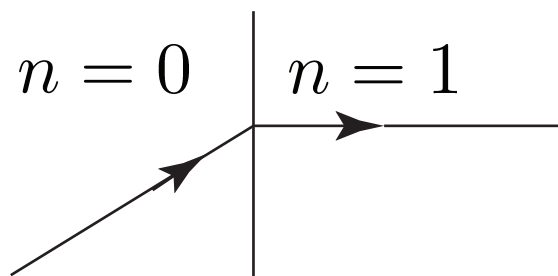
\* Lobet, Liberal, Knall, Alam, Reshef, Boyd, Engheta, and Mazur, *ACS Photonics* 7, 1965-1970 (2020).

# Optics of Zero-Index Materials

- Snell's law leads to intriguing predictions

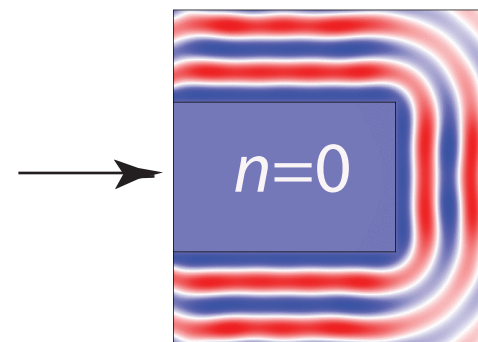
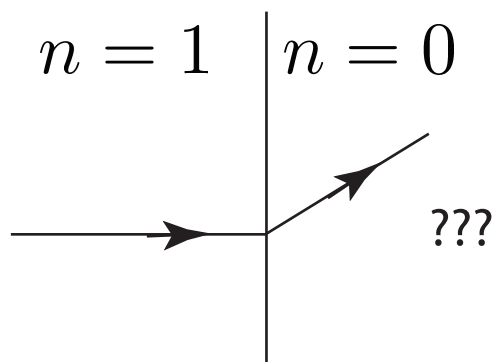
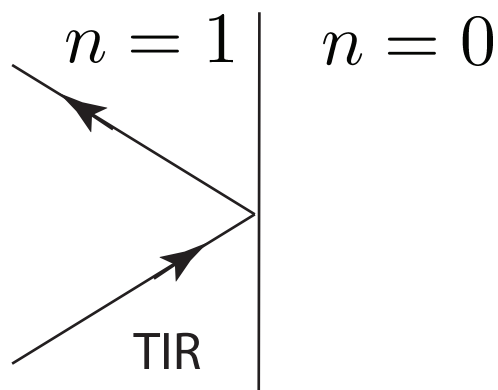
$$n_1 \sin \theta_1 = n_2 \sin \theta_2$$

- Light always leaves perpendicular to surface of ENZ material!



Y. Li, et al., Nat. Photonics 9, 738, 2015; D. I. Vulis, et al., Opt. Express 25, 12381, 2017.

- Thus light can enter an ENZ material only at normal incidence!



Light enters at normal incidence  
but leaves in all directions.

Y. Li, et al., Nat. Photonics 9, 738, 2015.

(wave-optics simulation - O. Reshef)

# Some Consequences of ENZ Behavior - 1

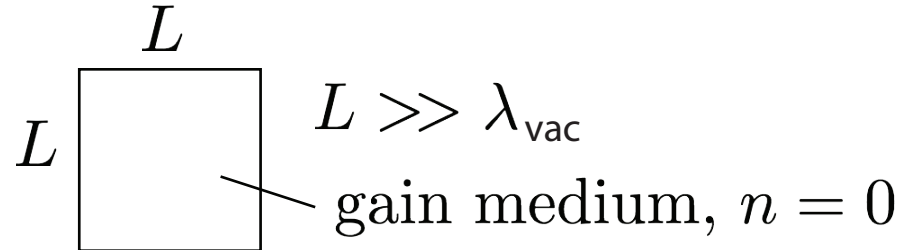
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- “Funny” lenses



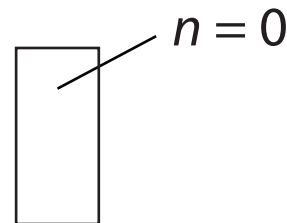
A. Alù et al., Phys. Rev. B 75, 155410, 2007; X.-T. He, ACS Photonics, 3, 2262, 2016.

- Large-area single-transverse-mode surface-emitting lasers



J. Bravo-Abad et al., Proc. Natl. Acad. Sci. USA 109, 976, 2012.

- No Fabry-Perot interference

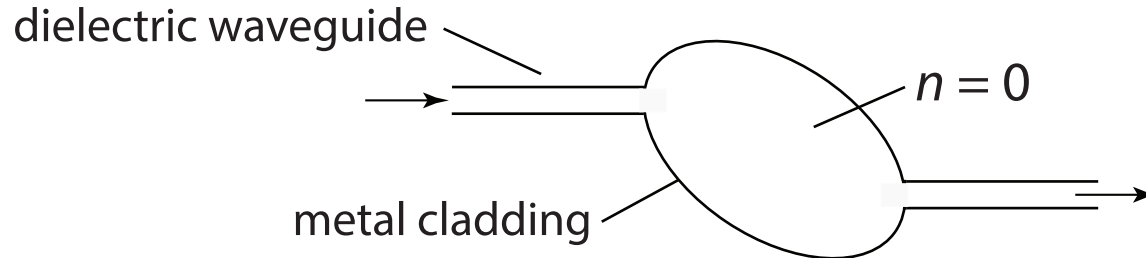


$$\Phi = \frac{n\omega L}{c}$$

O. Reshef et al., ACS Photonics 4, 2385, 2017.

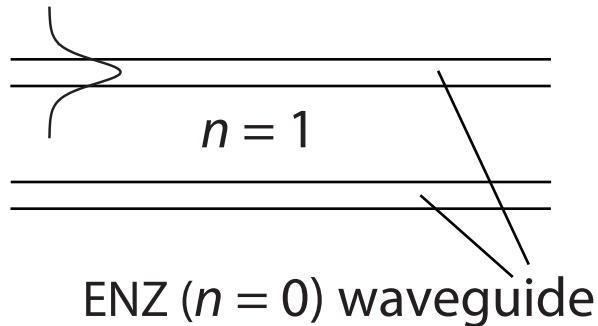
# Some Consequences of ENZ Behavior - 2

- Super-coupling (of waveguides)



M. G. Silveirinha and N. Engheta, Phys. Rev. B 76, 245109, 2007; B. Edwards et al., Phys. Rev. Lett. 100, 033903, 2008.

- Coupling between two distant waveguides



Mode of upper waveguide beams into the lower waveguide even for large separation

Recall that  $k = n \omega / c$  vanishes in an ENZ medium.

- Automatic phase matching of NLO processes

- Recall that we need  $\Delta k = 0$ , but when  $n=0$   $k = n\omega/c$  vanishes and so does  $\Delta k$ .

- We have observed this effect in a Dirac-cone, zero-index metamaterial.

- Usual four-wave mixing process



- With zero-index materials we can have

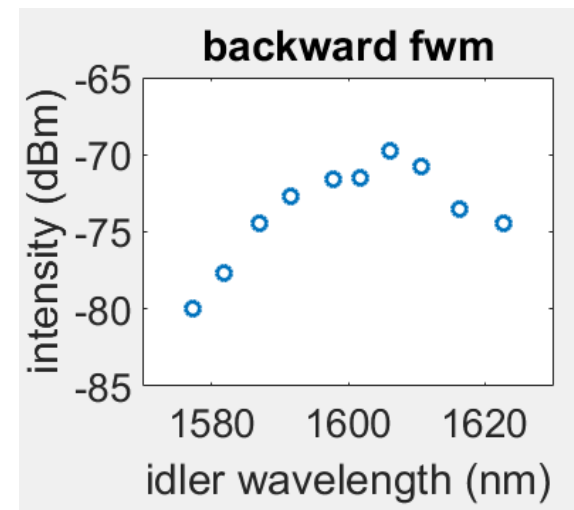
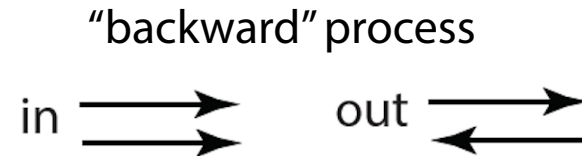
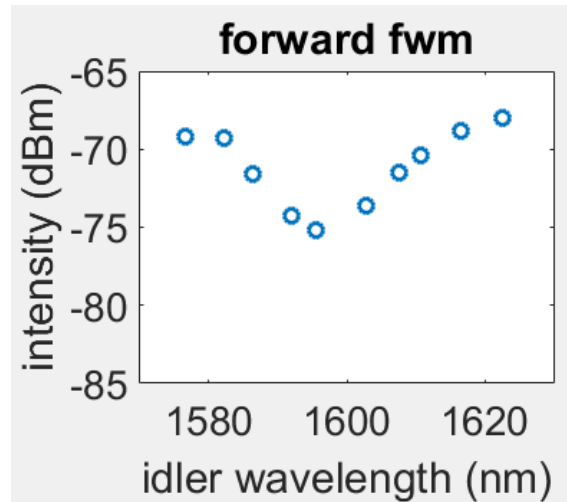
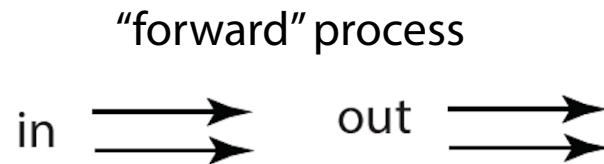
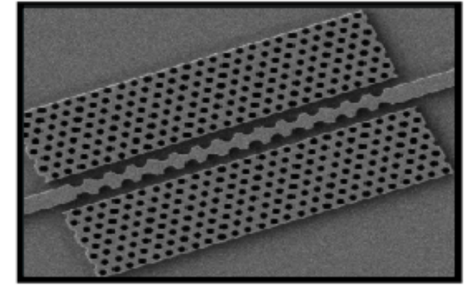


# Relaxed Phase-Matching Requirements in ENZ Media

- We study four-wave mixing in a zero-index waveguide

$$2\omega_p = \omega_s + \omega_i$$

- We find that an idler field is generated in both the forward and backward directions!
- Recall that we need  $\Delta k = 0$ , but when  $n = 0$ ,  $k = n \omega / c$  vanishes for each of the interacting waves and thus so does  $\Delta k$ .



- Significance: Nonlinear optical processes that were previously believed to be too weak to be useful can be excited through use of ENZ materials.

# Some Details from Electromagnetic Theory

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- The linear response of any material to electromagnetic radiation can be described by

- The dielectric permittivity (dielectric constant)  $\epsilon$  define through the relation

$$\mathbf{D} = \epsilon_0 \epsilon \mathbf{E}$$

where  $\mathbf{D}$ , known as the dielectric displacement, and  $\mathbf{E}$ , known as the electric field, are the two fields that describe the material response to an applied electric field

- The magnetic permeability  $\mu$  define through the relation

$$\mathbf{B} = \mu_0 \mu \mathbf{H}$$

where  $\mathbf{B}$ , known as the magnetic field, and  $\mathbf{H}$ , known as the magnetic intensity, are the two fields that describe the magnet response of a material to an applied field.

- It is straightforward to shown from the equations of electromagnetism that

$$n = \sqrt{\epsilon \mu}$$

- Thus,  $n=0$  when either  $\epsilon =0$  or  $\mu=0$  (or both  $\epsilon$  and  $\mu$  equal zero).

- Terminology:

ENZ: epsilon near zero

MNZ: mu near zero

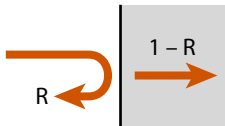
EMNZ: epsilon and mu near zero

# Surface Reflection

- There is a problem getting light into a zero-index material.
- There is always reflection from the boundary between two materials
- The impedance and surface reflectivity are given by

$$Z = \sqrt{\mu/\epsilon} \qquad R = \left| \frac{Z - 1}{Z + 1} \right|^2$$

- Thus the reflectivity will be 100% if  $\epsilon = 0$  unless  $\mu = 0$  as well.



- This is one reason for the interest in developing EMNZ materials (epsilon and mu near zero materials).



# How Light Behaves when the Refractive Index Vanishes

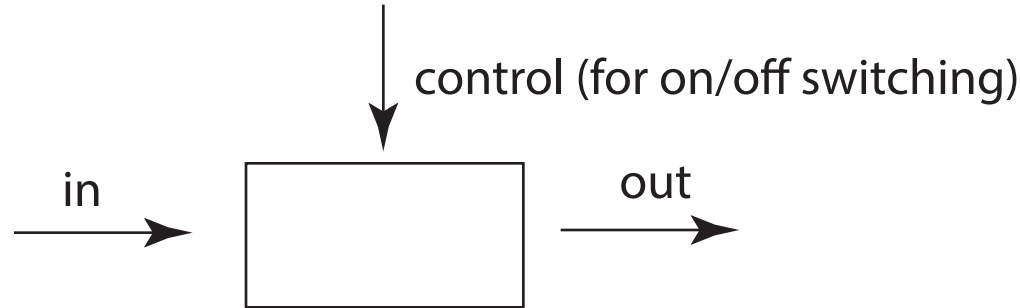
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- Physics of Near-Zero Index (NZI) Materials
- Nonlinear Optical Properties of NZI Materials
- Meta-materials for NZI Studies
- Applications of NZI Materials

# Nonlinear Optics and Optical Switching

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- An important application in photonic technologies is optical switching.



- One wants a switch with fast switching times and that operates with weak control fields.
- One needs a nonlinear interaction in order for one optical field to control another field.
- A strong nonlinear response is needed. How does one quantify the strength of a nonlinear response? Two standard methods:

$$n = n_0 + n_2 I$$

$$P^{\text{NL}} = 3\chi^{(3)} |E|^2 E$$

- The nonlinear coefficients are  $n_2$  and  $\chi^{(3)}$

# Implications of ENZ Behavior for Nonlinear Optics

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$\mathbf{P}$  is the induced dipole moment per unit volume and  $\mathbf{E}$  is the field amplitude.

Also, the refractive index changes according to

$$n = n_0 + n_2 I + n_4 I^2 + \dots$$

# How to Choose an Epsilon-Near-Zero Materials

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- Electrical conductors

All conductors display ENZ behavior at their (reduced) plasma frequency

Recall the Drude formula

$$\epsilon(\omega) = \epsilon_{\infty} - \frac{\omega_p^2}{\omega(\omega + i\gamma)}$$

Note that  $\text{Re } \epsilon = 0$  for  $\omega = \omega_p / \sqrt{\epsilon_{\infty}} \equiv \omega_0$ .

ENZ wavelength restricted to a limited range in the visible.

- Electrical insulators (dielectrics)

Dielectrics can show ENZ behavior at their (optical) phonon resonance.

ENZ wavelength restricted to a limited range in the mid-IR.

- Metamaterials

Can design the material so that the ENZ or EMNZ wavelengths are at any desired value.

- Challenge (for any material system). For low loss, we want  $\text{Im } \epsilon$  as small as possible at the wavelength where  $\text{Re } \epsilon = 0$ .

# Nonlinear Optics of Indium Tin Oxide (ITO)

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- We recently reported that, at its ENZ wavelength, ITO possesses a nonlinear coefficient  $n_2$  that is 100 times larger than those of previously reported materials [1].
- ITO is a degenerate semiconductor (so highly doped as to be metal-like).
- ITO has a large density of free electrons, and a bulk plasma frequency corresponding to a wavelength of approximately 1.24  $\mu\text{m}$ .
- Dielectric properties of ITO are well described by the Drude formula.

$$\epsilon(\omega) = \epsilon_{\infty} - \frac{\omega_p^2}{\omega(\omega + i\gamma)}$$

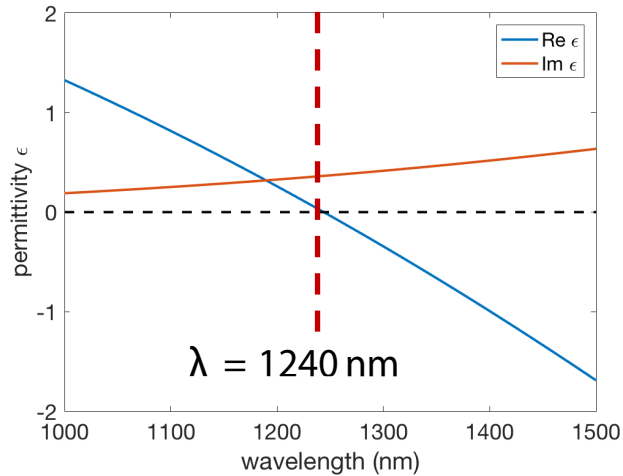
- Note that aluminum-doped zinc oxide (AZO), another transparent conducting oxide, also has strong nonlinear response at its ENZ wavelength [2].

1. Alam, De Leon and Boyd, Science 352, 795–797 (2016)

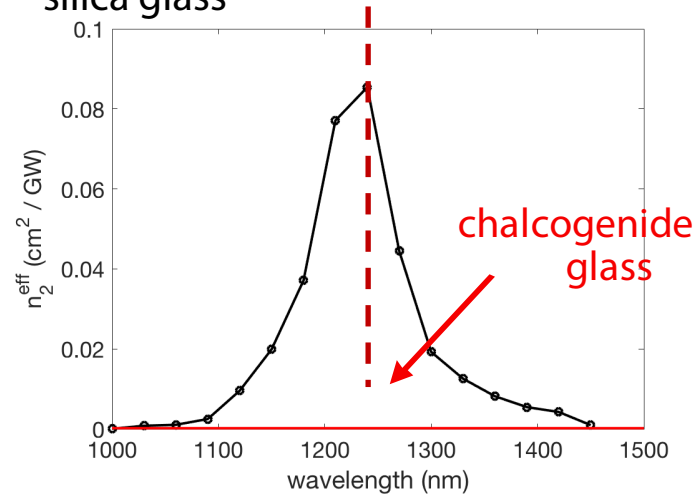
2. Caspani, Shalaev, Boltasseva, Faccio et al., Phys. Rev. Lett. 116, 233901 (2016).

# Huge, Fast NLO Response of Indium Tin Oxide at its ENZ Wavelength

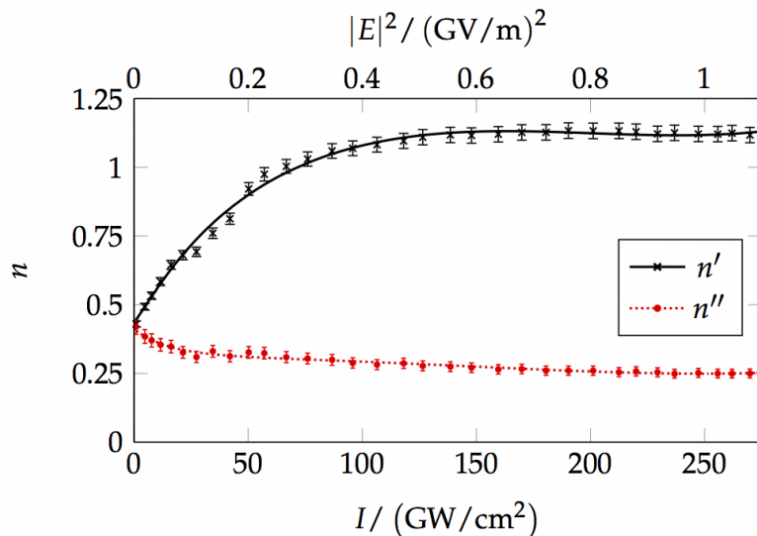
- ellipsometry



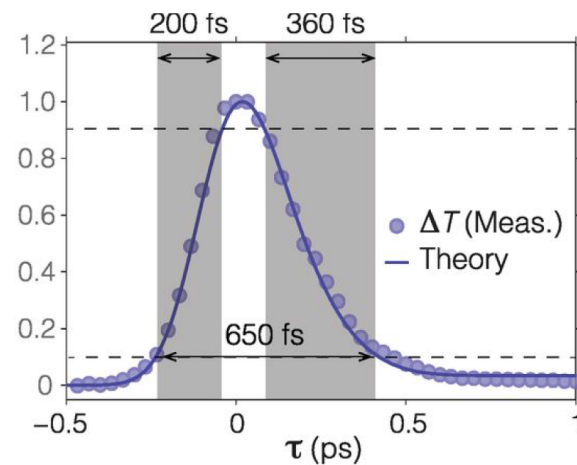
- $n_2$  can be  $3.4 \times 10^5$  times larger than that of silica glass



- overall change in refractive index of 0.8



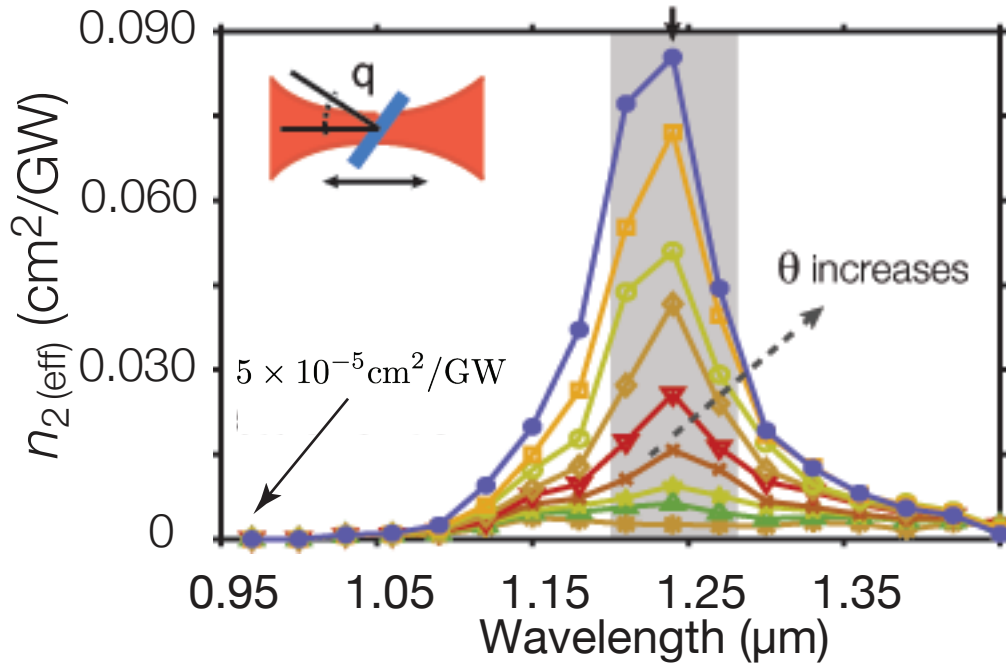
- sub picosecond reponse time



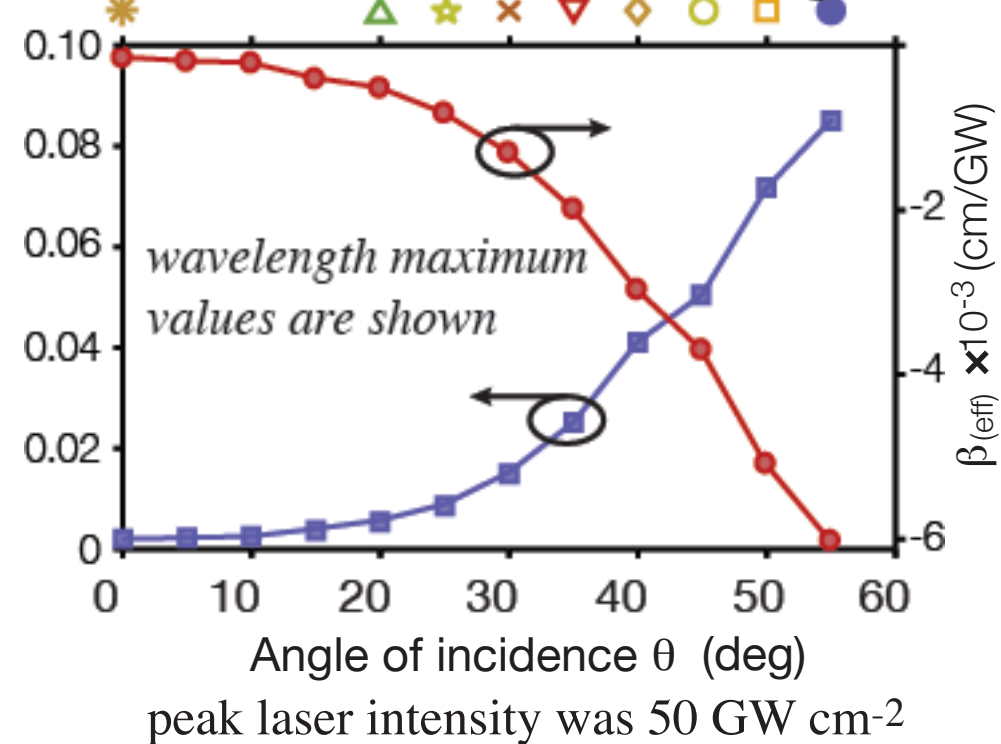
# Huge Nonlinear Optical Response of ITO

- Z-scan measurements for various angles of incidence

Wavelength dependence of  $n_2$



Variation with incidence angle



- Note that  $n_2$  is positive (self focusing) and  $\beta$  is negative (saturable absorption).
- Both  $n_2$  and nonlinear absorption increase with angle of incidence
- $n_2$  shows a maximum value of  $0.11 \text{ cm}^2/\text{GW} = 1.1 \times 10^{-10} \text{ cm}^2/\text{W}$  at  $1.25 \mu\text{m}$  and  $60 \text{ deg}$ . This value is 2000 times larger than that away from ENZ region.

# Why Does ENZ Lead to Large NLO Response?

1. From form of  $n_2$  
$$n_2 = \frac{3\chi^{(3)}}{4\epsilon_0 c n_0 \operatorname{Re}(n_0)}$$

2. From simple math:  $n = n_b + \Delta n$  and  $\epsilon = \epsilon_b + \Delta\epsilon$

$$n = \sqrt{\epsilon_b + \Delta\epsilon} \approx \sqrt{\epsilon_b} \left(1 + \frac{\Delta\epsilon}{2\epsilon_b}\right) = n_b + \frac{\Delta\epsilon}{2n_b} \text{ and thus } \Delta n = \frac{\Delta\epsilon}{2n_b}$$

3. Note behavior of wave equation for  $\epsilon = 0$

$$\nabla \times \nabla \times \mathbf{E} + \frac{\epsilon\mu}{c^2} \frac{\partial^2}{\partial t^2} \mathbf{E} = -\mu \frac{\partial^2 \mathbf{P}^{\text{NL}}}{\partial t^2}$$

4. From Maxwell's equations, it is easy to show that the nonlinear response scales as

$$\left. \frac{dH_x}{dz'} \right|_{\text{nl}} \frac{1}{|H_x|} \propto \sqrt{\frac{\mu_r}{\epsilon_r}}$$

5. Detailed numerical integration confirms this behavior.



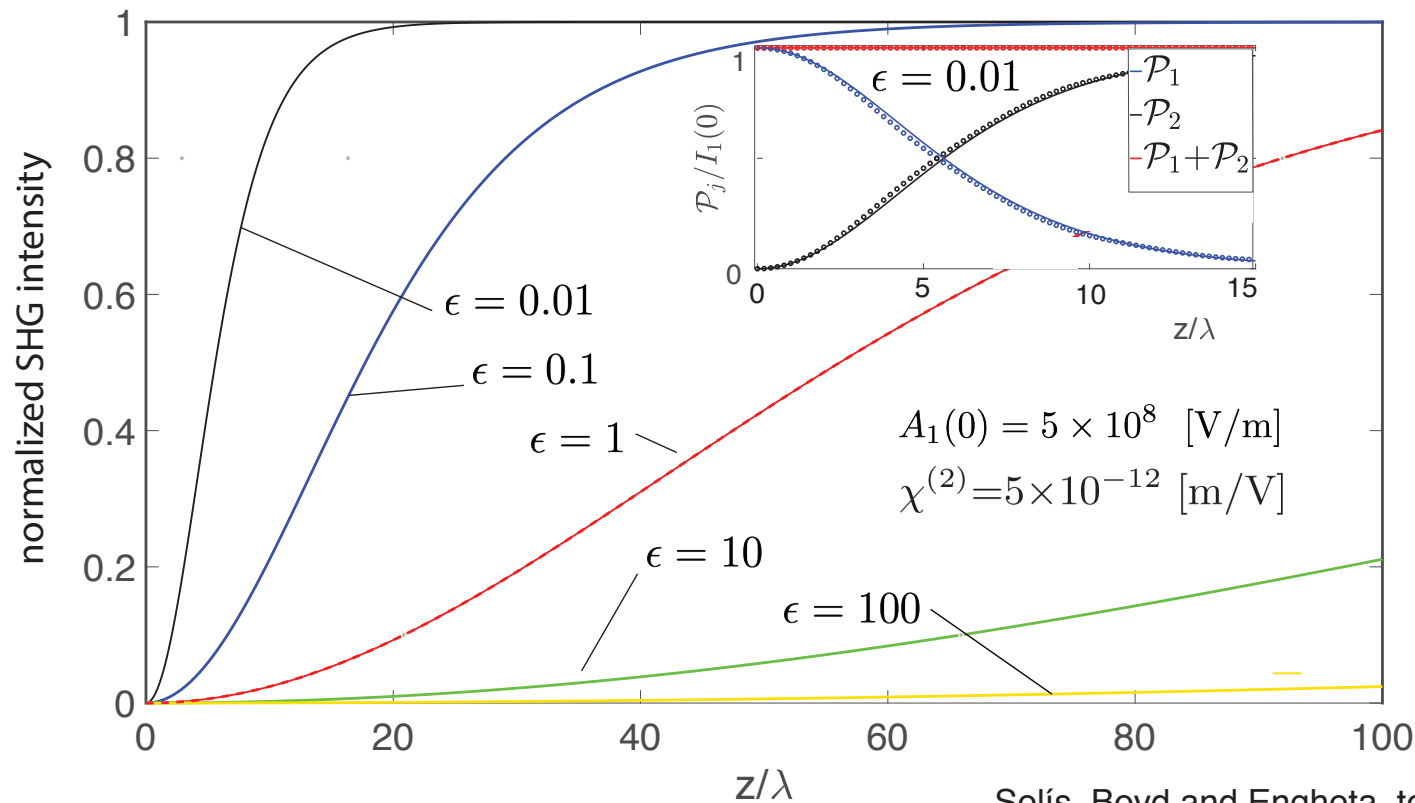
# Dependence of Second-Harmonic Generation on the Linear Dielectric Permittivity

- We solve the standard equations for second-harmonic generation

$$\frac{dA_1}{dz} = i \frac{\eta_1 \omega_1 \chi^{(2)}}{c} A_2(z) A_1^*(z) e^{-i\Delta k z},$$

$$\frac{dA_2}{dz} = i \frac{\eta_2 \omega_2 \chi^{(2)}}{2c} A_1^2(z) e^{i\Delta k z},$$

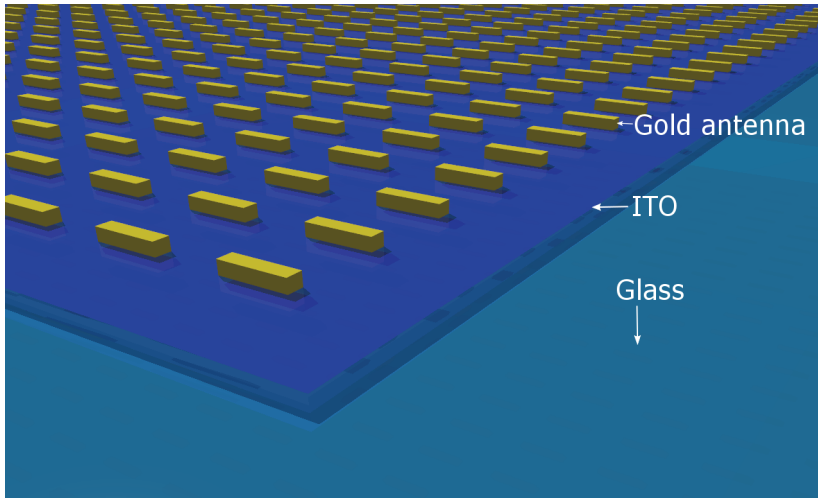
- We take  $\Delta k = 0$  and plot the solution for various values of the permittivity  $\epsilon$ .
- We find that the growth rate increases dramatically as the permittivity is decreased.



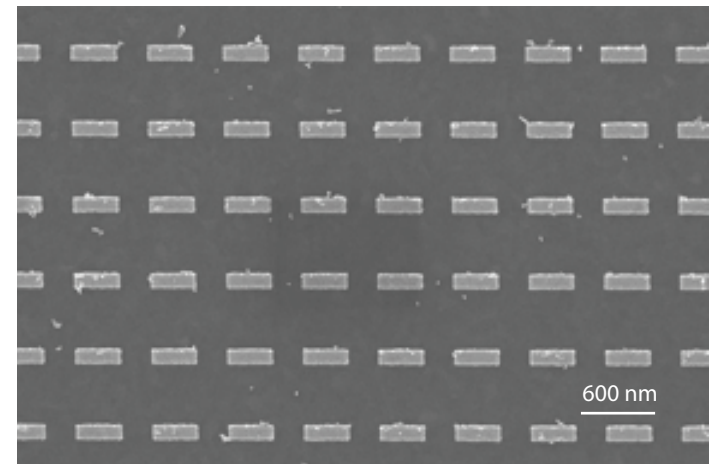
# An ENZ Metasurface

- We functionalize ITO by creating a photonic metasurface
- We obtain an even larger NLO response by placing a gold antenna array on top of ITO.
  - Lightning rod effect: antennas concentrate the field within the ITO
  - Coupled resonators: ENZ resonance and nano-antennas

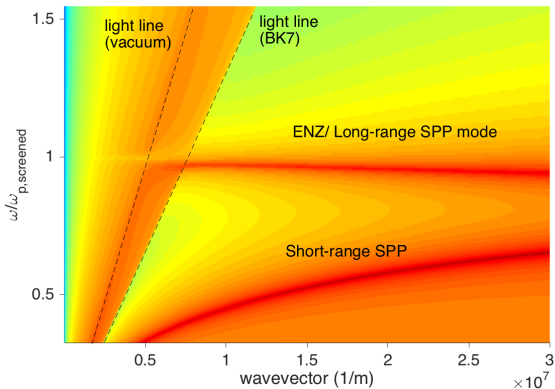
Concept:



SEM:



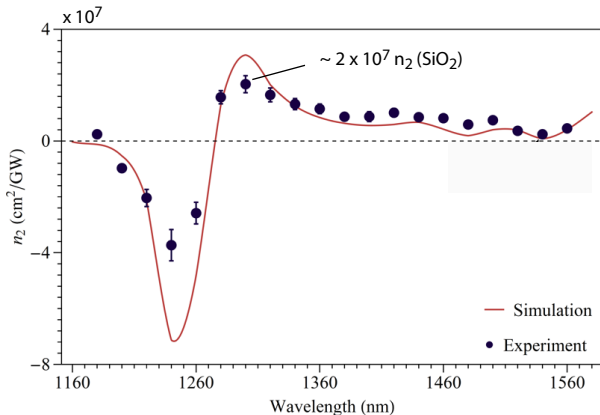
# A thin ENZ medium supports a bulk plasma mode.



A thin layer of ITO supports two modes

- the bulk plasma mode, also called the ENZ or long-range SPP mode
- the short range surface plasmon polariton (SPP) mode

# NLO response of the coupled antenna-ENZ system



The structure exhibits and extremely large  $n_2$  value over a broad spectral range. The on-resonance  $n_2$  value is **seven orders of magnitude** larger than that of silica glass.

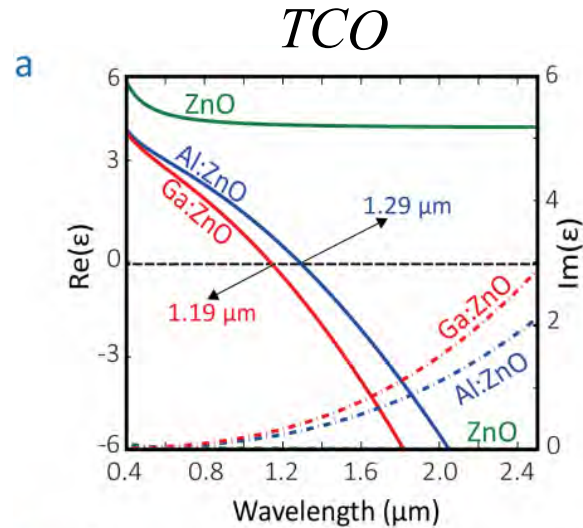
# Physics and Applications of Epsilon-Near-Zero Materials

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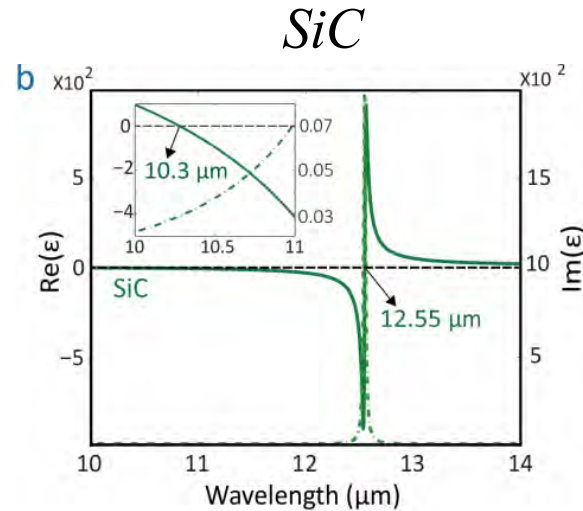
- Physics of ENZ Materials
- Huge NLO Response of ITO and ITO Metastructures
- Materials for ENZ
- Applications of ENZ Materials

# Epsilon-Near-Zero (ENZ) and Near Zero-Index (NZI) Materials

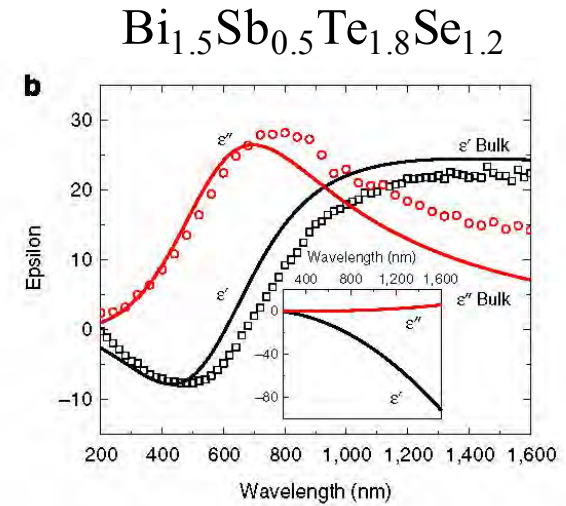
## Homogeneous materials



: A. Boltasseva (Purdue)  
Kim et al., *Optica* (2016)

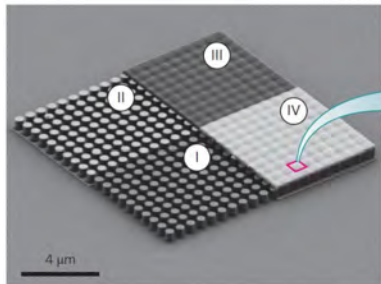


J. Caldwell (Vanderbilt)  
Kim et al., *Optica* (2016)

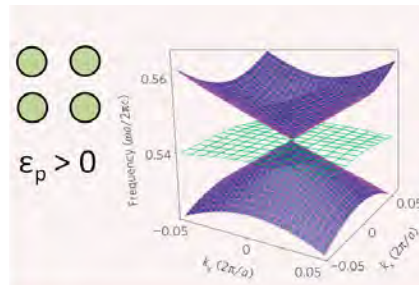


N. Zheludev (Southampton)  
Ou et al., *Nat. Commun.* (2014)

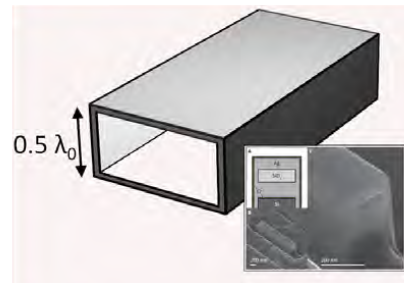
## Metamaterials



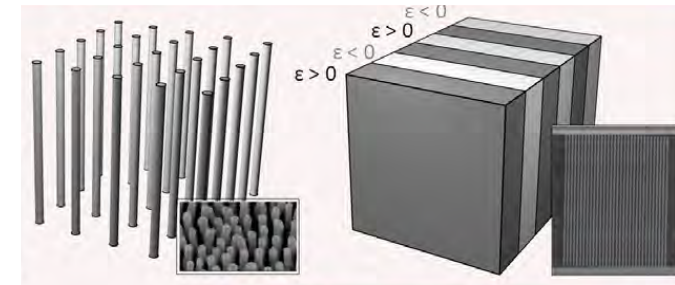
E. Mazur Li et al.,  
*Nat. Photon.* (2015)



Chan, Huang et al.,  
*Nat. Mater.* (2011)



SEM from: Polman's & Engheta's  
Vesseur et al., *PRL* (2013)



$$\text{Re}(\epsilon) \approx 0$$

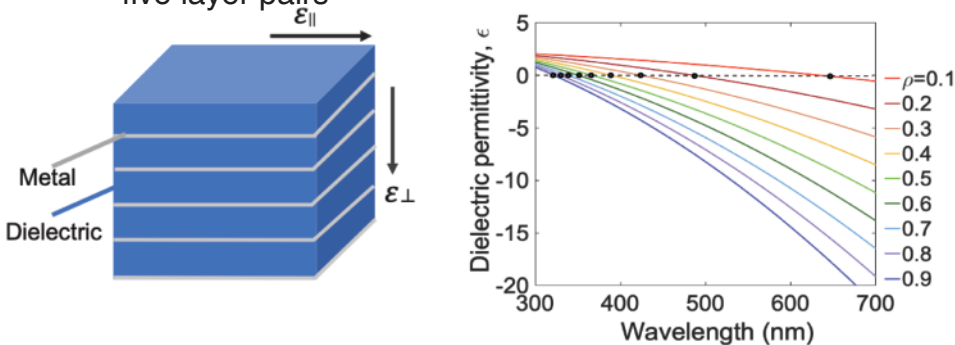
Wire SEM from: Zayatz & Podolskiy  
Pollard et al., *PRL* (2009)  
StackSEM from: Polman & Engheta  
Mass et al., *Nat. Photon.* (2013)

# Nonlinear Optical Properties of a Layered Metamaterial in its ENZ Region

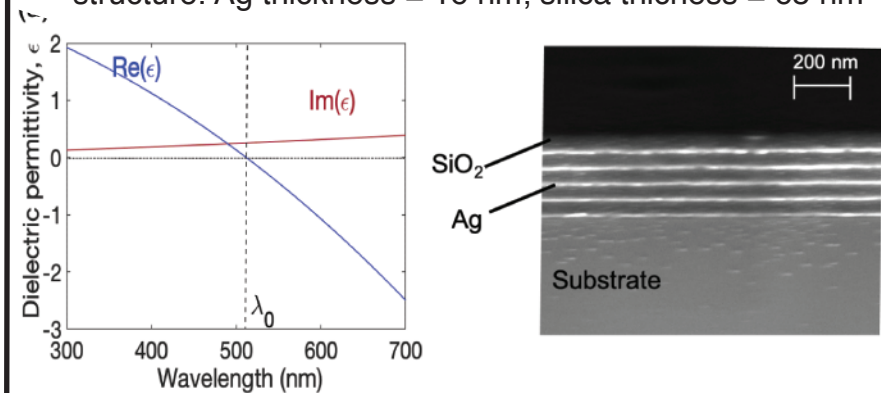
Do layered metamaterials also show enhanced NLO response at ENZ wavelength?

Can we use an effective-medium value of epsilon to determine the ENZ wavelength?

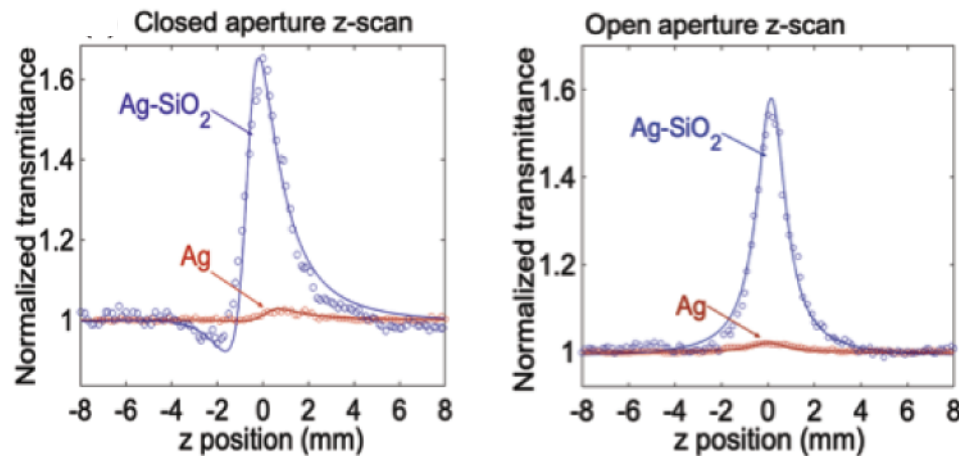
- By controlling the metallic fill fraction  $\rho$ , we can set the ENZ wavelength to be anywhere from 300 to 700 nm. We use  $\rho = 0.2$ , which corresponds to 500 nm. We deposit five layer pairs



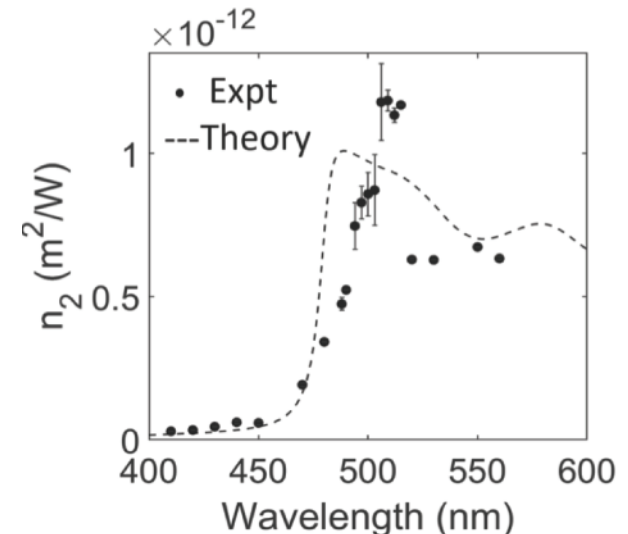
- Note that the real part of epsilon vanishes at 508 nm, close to the design wavelength. The SEM shows our structure. Ag thickness = 16 nm; silica thickness = 65 nm



- We perform Z-scan measurements on the sample. Note the enhanced response of the composite as compared to a single layer of silver.



- Note the pronounced peak in the value of  $n_2$  around the ENZ wavelength. We find a good but not perfect agreement with a simple effective medium theory.



# Physics and Applications of Epsilon-Near-Zero Materials

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- Huge NLO Response of ITO and ITO Metastructures
- Materials for ENZ
- Applications of ENZ Materials

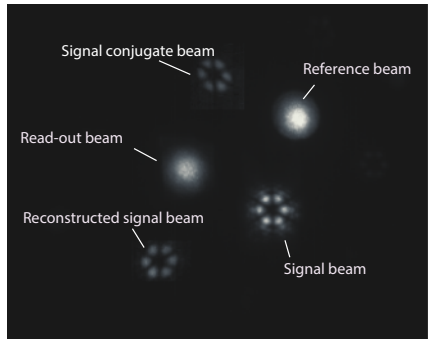
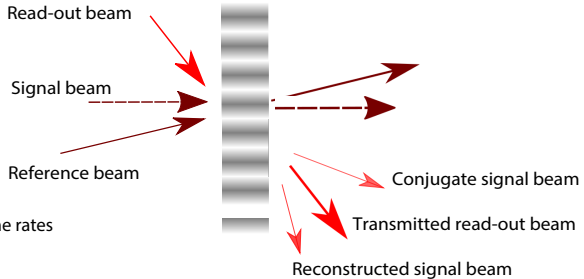


# Real-Time Holography with THz Refresh Rates

- Goal: Real-time holography with video or much faster refresh rates.
- The ultrafast response of ITO permits THz refresh rates
- Important applications involve image processing and signal processing
- Current real-time holographic materials cannot even support video frame rates



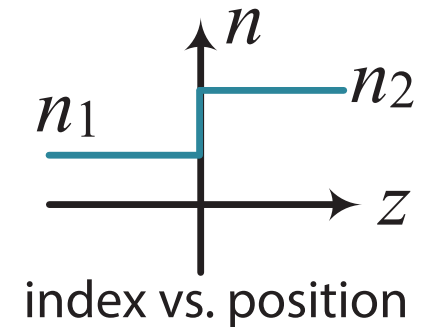
- Demonstration of image processing (edge enhancement)



# Adiabatic Wavelength Conversion through Time Refraction

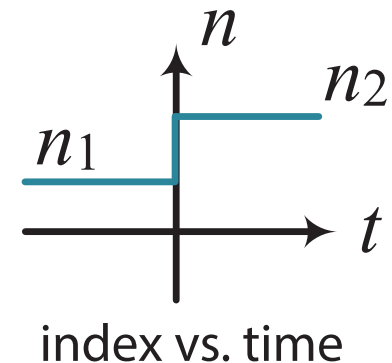
- Space refraction (e.g., Snell's law)

$$\frac{c}{f} = n \cdot \lambda \longrightarrow n_1 \lambda_1 = n_2 \lambda_2$$



- Time refraction (analog of Snell's law)

$$\frac{c}{f} = n \cdot \lambda \longrightarrow n_1 f_1 = n_2 f_2$$

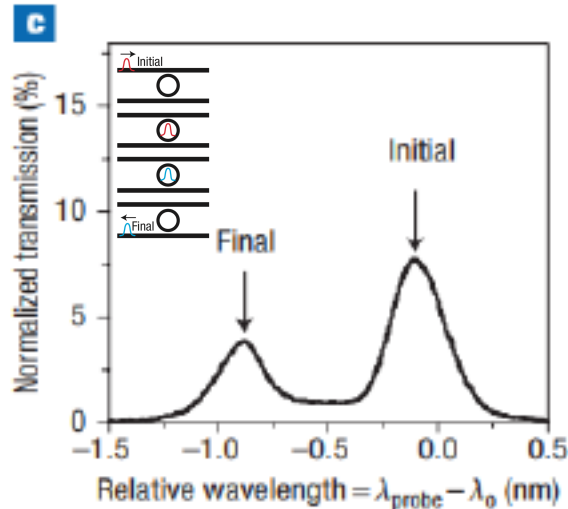


Photon frequency (energy) is changed because of the temporal change in index, but the wavelength (inverse of momentum) is conserved in the absence of any spatial asymmetry

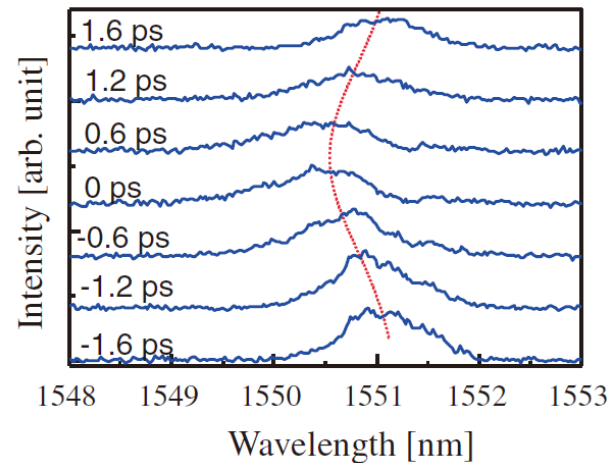
- Time refraction is an alternative way of understanding frequency broadening and shifting by self-phase modulation:

$$\delta\omega(t) = \frac{d}{dt}\phi_{\text{NL}} = \frac{d}{dt}[n_2 I(t)\omega/c]$$

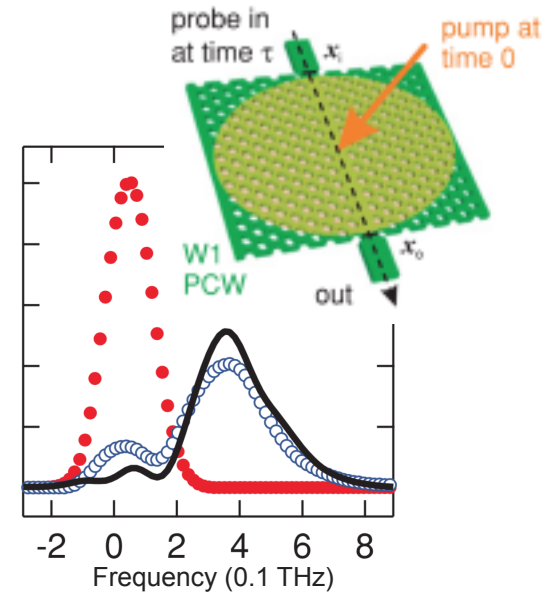
# Previous work on adiabatic wavelength conversion



Nat. Photonics, 2007, 1(5): 293



Appl. Phys. Ex., 2010, 3(6): 062001.



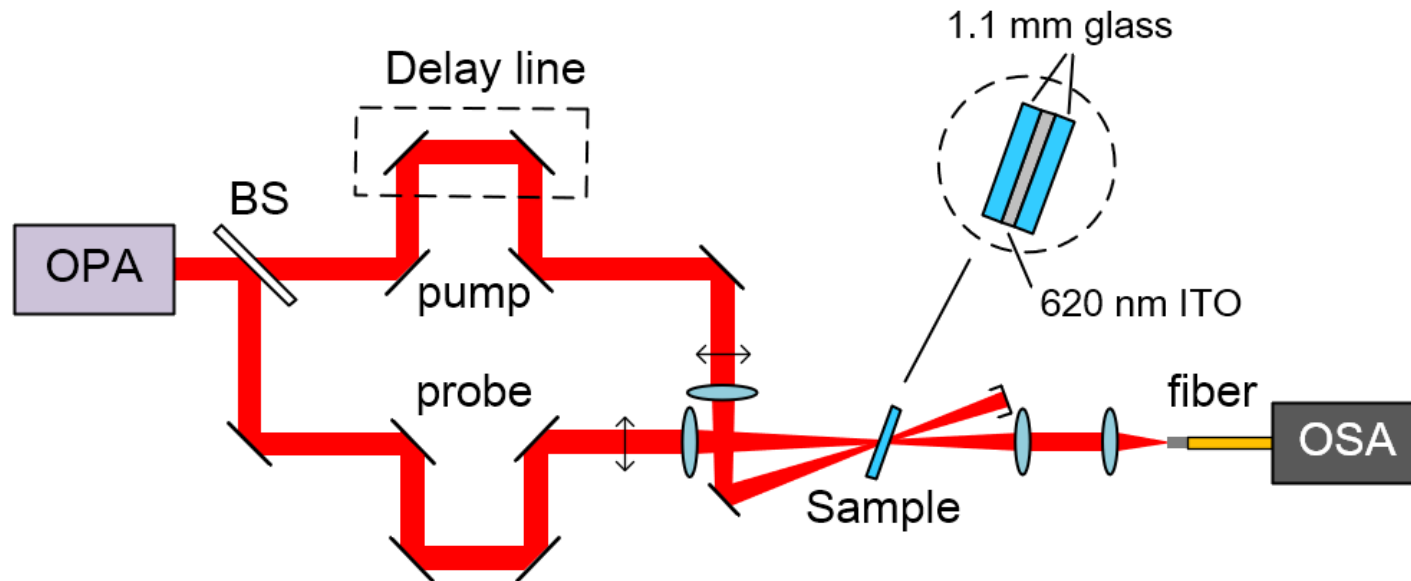
Phys. Rev. A., 2010, 81: 043837.

For small change in index  $\Delta n \sim 10^{-4}$ , one gets a small change in frequency (e.g., 0.06%)

But with ENZ materials we can obtain a much larger  $\Delta n$

# Laboratory Study of Wavelength Conversion by Time Refraction

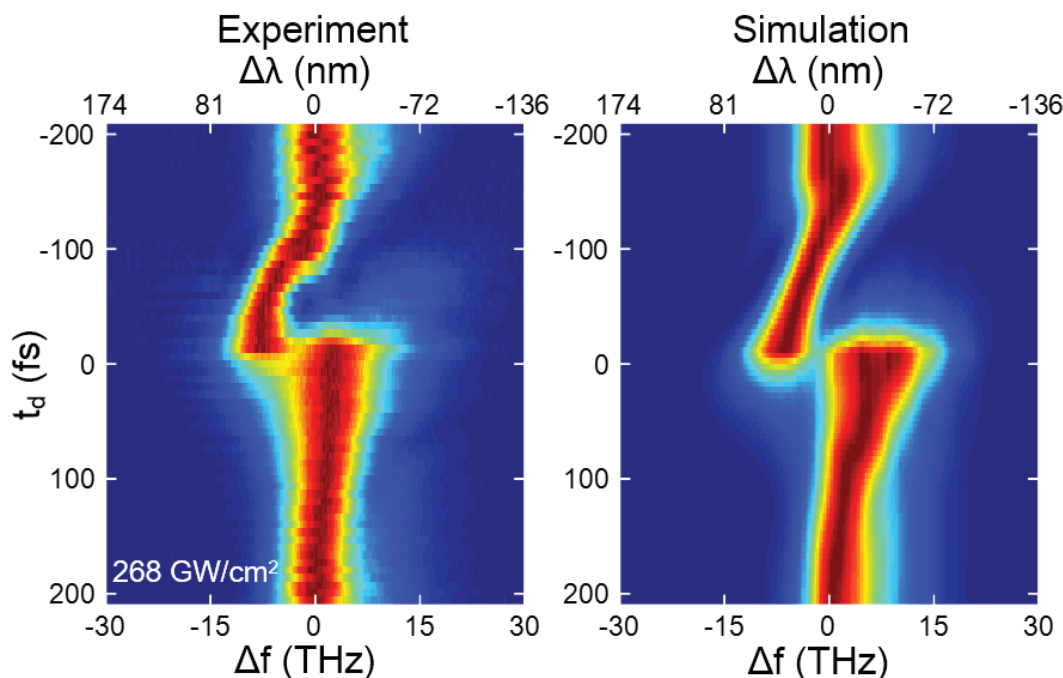
- Pump beam creates a time-varying refractive index in ITO sample
- Frequency of probe beam is thereby modified.



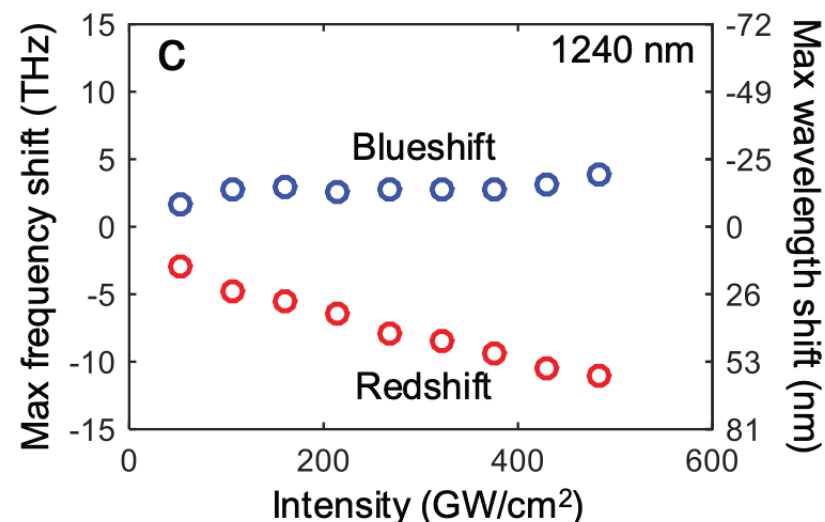
OPA = optical parametric amplifier  
wavelength = 1240 nm  
pulse duration = 120 fs  
OSA = optical spectrum analyzer

# Results: Adiabatic Wavelength Conversion by Time Refraction

Experimental results at 1240 nm



Probe phase and amplitude are measured by frequency-resolved optical gating (FROG)



The wavelength shift can be controlled by the pump intensity and the sign of the time delay.

- The observed effect is 100 times larger with almost 100 times smaller propagation distance than previous reports of AWC.
- Application: wavelength-division multiplexing for telecom

# Summary: Physics and Applications of ENZ Materials

- Extremely interesting physical processes occur in ENZ materials
- ENZ materials, metamaterials, and metastructures display extremely large NLO response
- The huge, ultrafast NLO response of ENZ materials lend themselves to many important applications

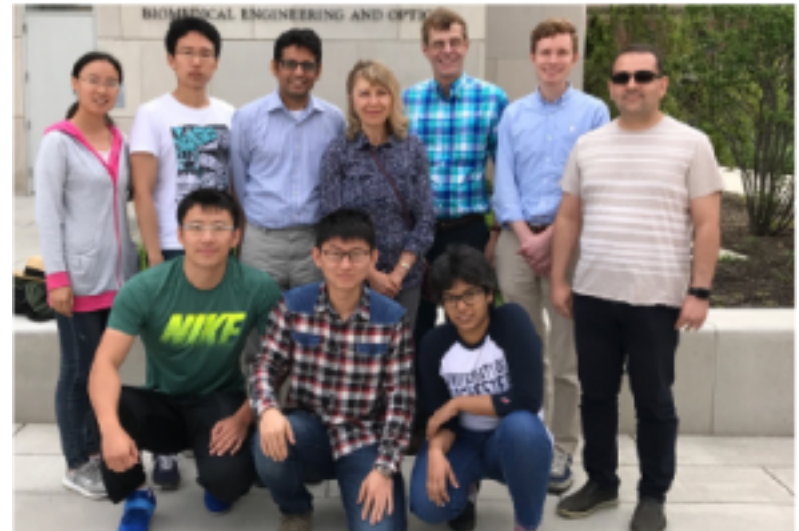
The visuals of this talk are posted at [boydnlo.ca/presentations](http://boydnlo.ca/presentations)

# Special thanks to:

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- Nader Engheta, Eric Mazur and Alan Willner for close collaboration throughout this project.
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Rochester Group



Ottawa Group

