







How Light Behaves When The Refractive Index Vanishes Physics and Applications of Epsilon-Near-Zero Materials

Robert W. Boyd

Department of Physics and Max-Planck Centre for Extreme and Quantum Photonics University of Ottawa

Institute of Optics and Department of Physics and Astronomy University of Rochester



The visuals of this talk are posted at boydnlo.ca/presentations

Presented at CLEO / Europe, as a virtual conference, June 21, 2021.

How Light Behaves when the Refractive Index Vanishes

- 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

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

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

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

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

Footnote:

Standard notation for perturbative NLO

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

P is the induced dipole moment per unit volume and 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

• 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

• The wavelength of light is given by

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

and is significantly lenthened 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

- Radiative processes are modified in ENZ materials *

Einstein A coefficient (spontaneous emission lifetime = 1/A) $A = n A_{vac}$ We can control (inhibit!) spontaneous emission!

Einstein B coefficient

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

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

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).

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!



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

(wave-optics simulation - O. Reshef)

• "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

$$L \longrightarrow L \gg \lambda_{\rm vac}$$
gain medium, $n = 0$

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

• No Fabry-Perot interference



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

Some Consequences of ENZ Behavior - 2



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

- Usual four-wave mixing process



- With zero-index materials we can have



Some Details from Electromagnetic Theory

- The linear response of any material to electromagnetic radation can be described by
 - The dielectric permittivity (dielectric constant) $\boldsymbol{\epsilon}$ define through the relation

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

where **D**, known as the dielectric displacement, and **E**, known as the electric field, are the two fields that describe the material response to an electric field.

- The magnetic permeability $\boldsymbol{\mu}$ define through the relation

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

where **B**, known as the magnetic field, and **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 ε =0 or μ =0 (or both ε and μ 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

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

• Thus the reflectivity will be 100% if ϵ = 0 unless μ = 0 as well.

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

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 Δk .



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

How Light Behaves when the Refractive Index Vanishes

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

• 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:

$$n = n_0 + n_2 I$$

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

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

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 $\chi^{(3)}$

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

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

Footnote:

Standard notation for perturbative NLO

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

P is the induced dipole moment per unit volume and 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

• 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 $\operatorname{Re} \epsilon = 0$ 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 Im ϵ as small as possible at the wavelength where Re ϵ =0.

Nonlinear Optics of Indium Tin Oxide (ITO)

- We recently reported that, at its ENZ wavelength, ITO possesses a nonlinear coefficient n₂ 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 $1.24 \mu m$.
- 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



The NLO Response Is Larger For Oblique Incidence

We observe that the reflected wave is very weak.

Standard boundary conditions show that:



 $D_{\mathrm{in},\perp} = D_{\mathrm{out},\perp} \implies E_{\mathrm{in},\perp} = E_{\mathrm{out},\perp}/\epsilon = E_{\mathrm{out}}\cos\theta/\epsilon$

Thus the total field inside of the medium is given by

$$E_{\rm in} = E_{\rm out} \sqrt{\cos^2 \theta + \frac{\sin^2 \theta}{\epsilon}}$$

Note that, for $\epsilon < 1, E_{\text{in}}$ exceeds E_{out} for $\theta \neq 0$. Note also that, for $\epsilon < 1, E_{\rm in}$ increases as θ increases.

Huge Nonlinear Optical Response of ITO



- Note that n_2 is positive (self focusing) and β is negative (saturable absorption).
- Both n_2 and nonlinear absorption increase with angle of incidence
- n_2 shows a maximum value of 0.11 cm²/GW = 1.1 × 10⁻¹⁰ cm²/W at 1.25 µm and 60 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 $\epsilon = \epsilon_b + \Delta \epsilon$ $n = \sqrt{\epsilon_b + \Delta \epsilon} \approx \sqrt{\epsilon_b} \left(1 + \frac{\Delta \epsilon}{2\epsilon_b} \right) = n_b + \frac{\Delta \epsilon}{2n_b}$ and thus $\Delta n = \frac{\Delta \epsilon}{2n_b}$

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

$$abla imes
abla imes \mathbf{E} + rac{\epsilon \mu}{c^2} rac{\partial^2}{\partial t^2} \mathbf{E} = -\mu rac{\partial^2 \mathbf{P}^{\mathrm{NL}}}{\partial t^2}$$

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

$$\left. rac{dH_x}{dz'}
ight|_{\mathrm{nl}} \propto \sqrt{rac{\mu_r}{\epsilon_r}}$$

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

$$\begin{aligned} \frac{dA_1}{dz} &= i \frac{\eta_1 \omega_1 \chi^{(2)}}{c} A_2(z) A_1^*(z) e^{-i\Delta kz} \\ \frac{dA_2}{dz} &= i \frac{\eta_2 \omega_2 \chi^{(2)}}{2c} A_1^2(z) e^{i\Delta kz}, \end{aligned}$$

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

,



See also Solís, CLEO Poster JW2D.15

- 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









Alam, Schulz, Upham, De Leon and Boyd, Nature Photonics 12, 79-83 (2018).

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 n2 value over a broad spectral range. The on-resonance n2 value is seven orders of magnitude larger than that of silica glass.

Alam, Schulz, Upham, De Leon and Boyd, Nature Photonics 12, 79-83 (2018).

- 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



Metamaterials





E. Mazur Liet al., Nat. Photon. (2015)

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



SEM from: Polman's & Engheta's

Vesseur et al., PRL (2013)



 $\operatorname{Re}(\varepsilon) \cong 0$ Wire SEM from: Zayat & 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?



Wavelength (nm)

Suresh, Reshef, Alam, Upham, Karimi and Boyd

- Physics of ENZ Materials
- 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)



Alam, Fickler, Reshef, Giese, Upham, and Boyd



Spatial and temporal refraction

Spatial (ordinary) refraction.

Refractive index changes at some spatial coordinate.

Frequency remains unchanged, but the wavelength changes according to



Time refraction.

Refractive index changes at some moment in time

Wavelength remains unchanged, but the frequency changes according to



Salem, Foster, and Gaeta, Advances in Optics and Photonics 5, pp. 274-317 (2013).

Adiabatic Wavelength Conversion through Time Refraction

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

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



• Time refraction (analog of Snell's law)

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



index vs. time

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:

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

Previous work on adiabatic wavelength conversion



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 Δn

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



15 -72 Max wavelength shift (nm) Max frequency shift (THz) 1240 nm С 10 -49 Blueshift 5 -25 0 0 -5 26 0 0 0 0 0 -10 53 0 0 Redshift -15 81 200 0 400 600 Intensity (GW/cm²)

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

Zhou, Alam, Karimi, Upham, Reshef, Liu, Willner and Boyd, Nature Commun. 11:2180 (2020)

Ultra-strong coupling of surface plasmon polariton (SPP) and ENZ modes in gold-ITO bi-films

- Integrate ENZ materials with waveguide structures, such as plasmonic waveguides
 - Thin metal film + thin TCO film Could this work as a highly nonlinear switching device?
- We first characterize the linear properties of the device
 - Modes supported
 - Propagation lengths
 - Mode confinement







Fig. 2: Reflectivity map of a bi-film (50 nm gold, 23 nm ITO) obtained from the transfer matrix method (TMM).

Some Results



Fig. 1: Reflectivity maps of a bi-film (50 nm gold, 23 nm ITO) (a) measured experimentally using attenuated total reflection spectroscopy, and (b) obtained from TMM simulations.



- Very close agreement between experiment and TMM simulations for the upper polariton branch.
- We are now measuring the lower polariton branch with the help of a newly acquired spectrometer capable of measuring signals in the wavelength range of 1.6 to 3.0 microns.
- The data points that lie above the dashed-black line satisfy the ultra-strong coupling criteria - T_{ITO} lies between 35 nm and 60 nm.

Ultra-strong coupling in NIR!

Fig. 2: Variation of the coupling strength Γ_R with the thickness of the ITO in the bi-film obtained by curve fitting the dispersion curves with a Hopfield-Bogoliubov model.

Comments

- Hybrid polariton modes supported by gold-ITO bi-films have
 - Lower losses than the bare ENZ mode
 - Propagation lengths of several microns
 - Stronger mode confinement than the bare SPP mode
- These bi-films could be useful for exploring ultrafast nonlinearities due to the huge sub-ps nonlinearity of the ITO near the ENZ wavelength, such as wave-mixing, soliton formation, and adiabatic frequency conversion.
- Being very easy to fabricate, they offer a very useful platform for ENZ related nanophotonic applications in the NIR regime.



Dynamic nanocavity for applications in AWC and switching

Current status:

- Designed and fabricated nanocavities made of 310-nm-thick ITO, SiO₂ spacer layers, and TiN back reflectors.
- A nonlinear change in the ITO layer changes the effective cavity length leading to a change in the resonance wavelength.
- ITO layer acts both as a mirror and a spacer layer.
- Potentially allow AWC over a few hundred nm of bandwidth (an order of magnitude improvement) .
- Numerical study shows a trade off between linewidth and absolute tunability





Reflectance as a function of plasma frequency. d is the thickness of the glass spacer layer

Ultrafast induced dichroism in a symmetric metasurface

Status Report:

- Fabricated Greek-cross-antenna metasurface on ITO.
- The device is polarization insensitive in its linear response.
- Under illumination with a sufficiently strong pump the device can become birefringent
- A nonlinear change in the ITO layer changes resonance condition along the polarization direction of the pump.



SEM image of the metasurface



Linear measurements exhibits no polarization sensitivity

Ultrafast dichroism in a symmetric metasurface





- Figure shows the change in transmittance for parallel (TE) and perpendicular (TM) components of the probes. The pump is always TE polarized.
- TE resonance is seven times more sensitive to the pump than the TM resonance.
- Very large ultrafast induced dichroism (two orders of magnitude better than previous reports in metasurfaces).

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

Special thanks to:

- Nader Engheta, Eric Mazur and Alan Willner for close collaboration throughout this project.
- DARPA, ARO, and NSERC for financial support.
- And especially to my students and postdocs

Rochester Group



Ottawa Group

