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On the bounds of index tuning in transparent conducting oxides: opinion

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Abstract: For more than a decade, the linear and nonlinear optical responses of materials and composites exhibiting an epsilon-near-zero (ENZ) region have been of keen interest to the community. Among the variety of effects realized, achieving index modulation near unity on the picosecond (or less) timescale has generated the most significant impact. As a long-sought combination of strength and speed, ENZ nonlinearities have reignited interest in nonlinear processes that appear to go beyond the typical perturbative expansion (e.g., non-perturbative) as well as in time-varying nonlinear processes. Here, we aim to take a physical and intuitive look at the nonlinear index modulation in Drude-like ENZ films and highlight the physical limits of tuning. We will focus particularly on their connection (or lack thereof) with non-perturbative effects and time-varying processes and provide our opinions as to the strengths and weaknesses of ENZ films in these areas.

1. Introduction

From the turn of the millennium, investigating light-matter interactions in the extremes of permittivity and index in homogeneous and structured materials have been a major area of interest [1–3]. Within them, epsilon-near-zero (ENZ) effects have been a focus area with early studies using the impedance mismatch to manipulate radiation patterns [4–6], the generation of perfect absorption [7,8], and geometry invariant cavities among many others [9].

Demonstrated for both interband [10] and intraband effects [11,12] nearly 10 years ago, nonlinear modulation of the refractive index in epsilon-near-zero (ENZ) materials has garnered significant interest in the community that has long sought simultaneously large and fast control over index [13]. Because of this combination, ENZ materials have renewed interest in two effects, non-perturbative nonlinearities, and electromagnetic interactions in moving media. In light of these efforts, and the role in which ENZ materials are playing in this space, it is good to take a closer look at the physical origins of nonlinear index modulation in ENZ materials and ascertain the bounds of control. In the following we share our view of the nonlinearities in ENZ materials after nearly 10 years of study, focusing on a physical and intuitive description founded in the non-parabolicity of the conduction band, see our review for more information [14] . We hope that this discourse will serve as a useful tool to guide continued research and discussion in the area.

The ENZ condition, and resulting effects, have been shown in a wide variety of materials and structures [2]. Among them, transparent conducting oxides (TCOs) are the most popular platform due to their wide availability, ease of fabrication, ability to achieve high carrier densities with moderate mobility, fast relaxation for both inter- and intra-band excitation, and large detuning of interband absorption [13,14]. Hence, we will focus our attention on uniform TCOs thin films at near normal incidence. Generally speaking, TCOs exhibiting an ENZ condition belong to a broader class of heavily doped wide bandgap semiconductors or alloys whose permittivity near

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the ENZ region can be written as:

$$\varepsilon(\omega) = \varepsilon_\infty - \frac{Nq^2}{\varepsilon_o m_o m^*_{avg}} \frac{1}{\omega^2 + i\gamma\omega} = \varepsilon_\infty + \chi^{(1)}_{fc} \tag{1.1}$$

where m^*_{avg} is the effective mass of all electrons in the conduction band [15,16], and band edge absorption terms are neglected since we are far from resonance. When driven in the ENZ region, it has been widely shown that the nonlinear modulation of index arises from a free-carrier absorption process [15–17]. This generates a small fraction of extremely athermal (hot) electrons within the conduction band, which then relax and redistribute their energy over the rest of the electron population (thermalization), causing the population distribution to spread and occupy higher energy states. To explain why this results in a change in the index we consider a generalized conduction band dispersion such that $E(k) = (E_g/2)\left[\sqrt{1 + (k/k_o)^2} - 1\right]$ where $k_o^2 = m_e^* E_g/(2\hbar^2)$ is the nonparabolicity parameter and m_e^* is the effective mass at the band minimum [18]. We can find the velocity and optical (or sometimes called transport) effective mass as shown in [16]:

$$\begin{aligned} v(k) &= \frac{1}{\hbar}\frac{\partial E}{\partial k} = v_{sat}\frac{k/k_o}{\sqrt{1 + (k/k_o)^2}} \\ m^*(k)^{-1} &= (m_e^*)^{-1}\frac{2(k/k_o)^2 + 3}{3[1 + (k/k_o)^2]^{3/2}} \end{aligned}, \tag{1.2}$$

which remains finite even in the linear region of the conduction band. Plotting the normalized values for the band energy, velocity, and effective mass, we can identify the parameter k_o as the 'nonparabolicity threshold' - the approximate location where the band shifts from being predominantly parabolic to being predominantly linear (see Fig. 1(a)). For most TCOs with ENZ region in the near infrared, the Fermi level is degenerate by ~1 eV such that $k_F \sim k_o$ and we are in the quasi-linear regime. Thus, the increase in average energy of the electron gas effectively transfers a fixed fraction f of the carrier density N from below k_F and moves them to higher momentum states which exhibit a higher effective mass. We can linearize this as m^*_{avg}=$m^*_{avg,0}(1 + \mathrm{M}\Delta k)$ where M is the slope of m^* versus k which in the linear region is proportional to ${k_o}^{-1}$ and Δk represents the change in momentum of the electron gas due to the absorption of light and subsequent rise in temperature. Combining this with our general permittivity description we see $\varepsilon(\omega) = \varepsilon_\infty + \chi^{(1)}_{fc,0}(1 + \mathrm{M}\Delta k)^{-1}$. This simple assumption is valid for the case when $\mathrm{M}\Delta k<1$ which is quite common even for irradiance values exceeding several 100's GW/cm^2 where the shift of the plasma frequency remains within a few hundred nanometers of its original value and serves our purpose here. We then see that for a large change in permittivity (index) one is required to modulate the momentum on the scale of k_o, or as we see from the definition of k_o, comparably modify the average energy of the electron gas on the scale of E_g. For a more extensive description see [19].

If we take a few values of $\mathrm{M}\Delta k$ for a prototypical TCO with zero-crossing permittivity at ~1500 nm ($\varepsilon_\infty = 4$, $N = 6\times10^{20}$ cm^{-3}, $m^* = 0.3$, $\gamma = 6$ fs) we can observe the key result, that the permittivity (and index) modulation naturally tends to saturate, see Fig. 1(b),(c). This occurs for two reasons. First, because the modulation of the effective mass is in the denominator of the plasma frequency, even a continued linear shift of m^* with irradiance results in diminishing returns on permittivity modulation at a fixed frequency. Secondly, because of the inherent dispersion in $\chi^{(1)}_{fc}$ whose slope reduces at higher energies leading to a reduced change in permittivity for a fixed shift of the plasma frequency. Lastly, we note that since Δk is proportional to the absorbed energy and $\mathrm{M} \propto k_o^{-1}$ which defines the intrinsic nonparabolic threshold of the material, without loss of generality, we can rewrite the previous expression with the form $\varepsilon(\omega) = \varepsilon_\infty + \chi^{(1)}_{fc,0}(1 + I/I_{sat})^{-1}$, making the role of saturation readily clear [19].

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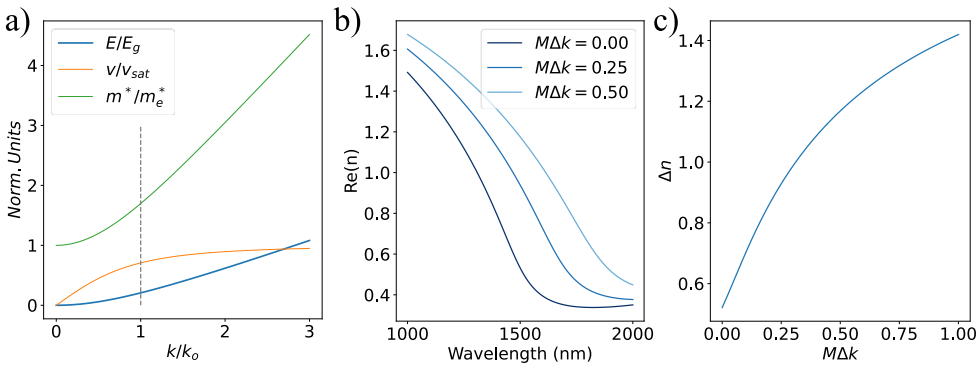

Fig. 1. (a) Relationship between nonparabolic conduction band (blue), velocity (orange), and effective mass (green) versus crystal momentum. (b) Refractive index of the ENZ film for various values of shifted momentum. (c) The change in index at the zero-crossing permittivity versus the change added momentum to the electron sea.

This result is important for two reasons. First, recent efforts in time varying optics benefit from large index modulation [20–23]. This saturation style effect illustrates the fundamental bounds on modulation, essentially that one cannot modify the permittivity more than the complete detuning of the plasma frequency from the region of operation. This is equivalent to making electrons practically immobile due to a very large effective mass, thus driving $\chi_{fc}^{(1)} \rightarrow 0$. In this case, one would expect the index to return to its undoped condition. As shown for typical values of ENZ materials in the NIR, the best index tuning one would expect is ~1.7. Of course, this value is not miniscule and could be useable, although it would require extreme irradiance levels (> TW/cm^2) to achieve. Thus, it is not typical for one to *completely* detune the plasma frequency and in practice most changes in the index are limited to approximately 0.7, which represents a shift in the plasma frequency of almost 100 - 200 nm, usually achieved with irradiance values of ~1TW/cm^2 and below [12,24]. However, the loss associated with ENZ materials is a key concern. This is not typically discussed as ultrafast experiments are generally conducted with low duty cycle excitation (kHz repetition rates) which allow the system to cool between pulses. Thus, single time varying interfaces can be realized but repetitive index modulations will require significant effort to extract heat to avoid detrimental buildup of thermal nonlinearities and eventual damage.

Secondly, saturation is relevant for discussions around non-perturbative effects which can arise when observations of a strong change in index are found. Such terminology typically originates from the introduction of the nonlinear polarization of the bound electron clouds wherein it is assumed that $P_{NL} = \chi^{(2)}E^2 + \chi^{(3)}E^3 + \ldots << P_L = \chi^{(1)}E$. The order of magnitude of the nonlinear susceptibility is roughly $\chi^{(n)} < \chi^{(1)}/E_{ia}^{n-1}$ where E_{ia} is the intrinsic or inter-atomic field that is typically on the scale of 10^{10} V/m. Because the external fields are much smaller, this series expansion is almost always a good assumption when far from resonance – which most nonlinear optics falls under. This assumption breaks down when operating near resonances and real transitions with finite lifetimes begin to contribute to the effect – most readily seen through descriptions of nonlinearities in two-level systems [25]. In this case, we speak of saturation due to the increased population of an excited state rather than considering that the linear process continues undisrupted, and a second effect competes to cause the reduced change in permittivity. ENZ processes fall under this category, that of slow nonlinear processes involving real state transitions (transfer between states in the conduction band) [16,26]. Unlike the typical picture whose atomic displacement can literally be described as a power series versus applied field, there is no clear physical analogy for the introduction of the power series expansion on the state

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population. Instead, the peak change of refractive index is dictated by the competition between the rate of energy absorption and the rate of relaxation of the excited carriers. Thus, while the same 'language' can be used for ENZ effects and coefficients such as $\chi^{(3)}$, $\chi^{(5)}$, etc. introduced, they are not connected to physical processes within the material and thus cannot provide much guidance beyond a numerical fit. Moreover, because their description is not rooted in properties of the material, they are inherently sensitive to material properties and excitation conditions which dictate the value of Δk introduced for a given incident irradiance. Thus, one must be very careful when using quoted coefficient values and efforts taken to operate within similar material and excitation conditions.

To conclude this discourse, we emphasize that it is important to understand, at least at a high level, the physical processes at play when evaluating nonlinear effects in materials to guide the selection of models and explanation of results. A rigorous predictive model is not usually needed (although it is always a nice gut-check if available). Rather, phenomenological models which match underlying processes can be sufficient to fit data and draw conclusions. For TCOs excited near the ENZ region, this is almost always a free carrier absorption process which modulates the effective mass of electrons within the nonparabolic conduction band. While a true fast nonlinear process does also exist, it is several orders of magnitude smaller and thus is not usually a contributor to index modulation [16,19,27]. We note that descriptions of the free-carrier process (including ours here) generally consider that any change in the scattering rate γ is negligible, although in certain cases this may not be a good assumption [28,29]. From this, we see that a saturation-style description is a direct outcome of the process. The result is a clear understanding on the limits of permittivity and index modulation for a given wavelength as well as the effect of dispersion, optical loss, dependence with irradiance, and more – all of which greatly expand the generality. Thus, we can see that in light of recent developments, ENZ materials *do not* fit into the picture of non-perturbative nonlinear effects but are likely to play a role in time-varying interactions due to the ability to achieve such strong index modulation. Yet, repeated modulation will be a significant challenge due to the absorptive nature of the nonlinearity and subsequent heating.

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References

1. I. Liberal and N. Engheta, "Near-zero refractive index photonics," Nat. Photonics **11**(3), 149–158 (2017).
2. N. Kinsey, C. DeVault, A. Boltasseva, *et al.*, "Near-zero-index materials for photonics," Nat. Rev. Mater. **4**(12), 742–760 (2019).
3. I. Liberal and N. Engheta, "The rise of near-zero-index technologies," Science **358**(6370), 1540–1541 (2017).
4. R. W. Ziolkowski and E. Heyman, "Wave propagation in media having negative permittivity and permeability," Phys. Rev. E **64**(5), 056625 (2001).
5. S. Enoch, G. Tayeb, P. Sabouroux, *et al.*, "A Metamaterial for Directive Emission," Phys. Rev. Lett. **89**(21), 213902 (2002).
6. J. Kim, A. Dutta, G. V. Naik, *et al.*, "Role of epsilon-near-zero substrates in the optical response of plasmonic antennas," Optica **3**(3), 339 (2016).
7. Y. Yang, K. Kelley, E. Sachet, *et al.*, "Femtosecond optical polarization switching using a cadmium oxide-based perfect absorber," Nat. Photonics **11**(6), 390–395 (2017).
8. T. S. Luk, S. Campione, I. Kim, *et al.*, "Directional perfect absorption using deep subwavelength low-permittivity films," Phys. Rev. B **90**(8), 085411 (2014).
9. I. Liberal, A. M. Mahmoud, and N. Engheta, "Geometry-invariant resonant cavities," Nat. Commun. **7**(1), 10989 (2016).
10. N. Kinsey, C. DeVault, J. Kim, *et al.*, "Epsilon-near-zero Al-doped ZnO for ultrafast switching at telecom wavelengths," Optica **2**(7), 616–622 (2015).
11. M. Z. Alam, I. De Leon, and R. W. Boyd, "Large optical nonlinearity of indium tin oxide in its epsilon-near-zero region," Science **352**(6287), 795–797 (2016).
12. L. Caspani, R. P. M. Kaipurath, M. Clerici, *et al.*, "Enhanced nonlinear refractive index in epsilon-near-zero materials," Phys. Rev. Lett. **116**(23), 233901 (2016).

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13. O. Reshef, I. De Leon, M. Z. Alam, *et al.*, "Nonlinear optical effects in epsilon-near-zero media," Nat. Rev. Mater. **4**(8), 535–551 (2019).
14. D. Fomra, A. Ball, S. Saha, *et al.*, "Nonlinear optics at epsilon near zero: From origins to new materials," Appl. Phys. Rev. **11**(1), 011317 (2024).
15. R. Secondo, J. Khurgin, and N. Kinsey, "Absorptive loss and band non-parabolicity as a physical origin of large nonlinearity in epsilon-near-zero materials," Opt. Mater. Express **10**(7), 1545 (2020).
16. J. B. Khurgin, M. Clerici, and N. Kinsey, "Fast and Slow Nonlinearities in Epsilon-Near-Zero Materials," Laser Photonics Rev. **15**(2), 2000291 (2021).
17. H. Wang, K. Du, C. Jiang, *et al.*, "Extended Drude Model for Intraband-Transition-Induced Optical Nonlinearity," Phys. Rev. Appl. **11**(6), 064062 (2019).
18. E. O. Kane, "Band structure of indium antimonide," J. Phys. Chem. Solids **1**(4), 249–261 (1957).
19. J. B. Khurgin and N. Kinsey, ""Nonperturbative Nonlinearities": Perhaps Less than Meets the Eye," ACS Photonics **11**(8), 2874–2887 (2024).
20. E. Galiffi, R. Tirole, S. Yin, *et al.*, "Photonics of time-varying media," Adv. Photonics **4**(01), 014002 (2022).
21. C. Caloz and Z. L. Deck-Leger, "Spacetime Metamaterials-Part II: Theory and Applications," IEEE Trans. Antennas Propagat. **68**(3), 1583–1598 (2020).
22. C. Caloz and Z. L. Deck-Leger, "Spacetime Metamaterials-Part I: General Concepts," IEEE Trans. Antennas Propagat. **68**(3), 1569–1582 (2020).
23. A. Shaltout, M. Clerici, N. Kinsey, *et al.*, "Doppler-Shift Emulation Using Highly Time-Refracting TCO Layer," in *Conference on Lasers and Electro-Optics* (OSA, 2016), p. FF2D.6.
24. J. B. Khurgin, M. Clerici, V. Bruno, *et al.*, "Adiabatic frequency shifting in epsilon-near-zero materials: the role of group velocity," Optica **7**(3), 226 (2020).
25. Y. R. Shen, *The Principles of Nonlinear Optics*, 1st ed. (John Wiley & Sons, 2002).
26. R. W. Boyd, "Slow and fast light: fundamentals and applications," J. Mod. Opt. **56**(18-19), 1908–1915 (2009).
27. D. De Ceglia, S. Campione, M. A. Vincenti, *et al.*, "Low-damping epsilon-near-zero slabs: Nonlinear and nonlocal optical properties," Phys. Rev. B **87**(15), 155140 (2013).
28. I. W. Un, S. Sarkar, and Y. Sivan, "Electronic-Based Model of the Optical Nonlinearity of Low-Electron-Density Drude Materials," Phys. Rev. Appl. **19**(4), 044043 (2023).
29. I.-W. Un, N. Harcavi, and Y. Sivan, "Optical Nonlinearity of Transparent Conducting Oxides: More Metallic than Realized," ACS Photonics **12**, 1718–1721 (2025).