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# Beyond the perturbative description of the nonlinear optical response of low-index materials

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**We show that standard approximations in nonlinear optics are violated for situations involving a small value of the linear refractive index. Consequently, the conventional equation for the intensity-dependent refractive index, $n(I) = n_0 + n_2 I$, becomes inapplicable in epsilon-near-zero and low-index media, even in the presence of only third-order effects. For the particular case of indium tin oxide, we find that the $\chi^{(3)}$, $\chi^{(5)}$, and $\chi^{(7)}$ contributions to refraction eclipse the linear term; thus, the nonlinear response can no longer be interpreted as a perturbation in these materials. Although the response is non-perturbative, we find no evidence that the power series expansion of the material polarization diverges.** 

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Nonlinear optical effects are crucial to many applications in photonics, performing essential functions in lasing, frequency conversion, and entangled-photon generation, among others [1–4]. Due to the small intrinsic nonlinearities of common photonic materials, there has long been the desire to increase optical nonlinearities in order to increase conversion efficiencies, miniaturize device footprints, and reduce power requirements in optical devices. Much of the recent work has been towards enhancing nonlinearities by structuring materials, for example, using high-$Q$ micro-cavities [5–7] or photonic crystals with slow light propagation [7,8].

Recently, a class of low-index materials called epsilon-near-zero (ENZ) materials, whose real part of the electric permittivity $\epsilon'$ vanishes at a certain wavelength, has emerged as a promising platform to achieve unprecedented large nonlinear responses [9–11]. For example, in indium tin oxide (ITO), the nonlinear contribution to the index of refraction $\Delta n$ has achieved a value of 0.72 [9]. This value is considerably larger than what has been achieved in highly nonlinear chalcogenide glasses ($\Delta n \approx 10^{-6}$) [12–14], and could enable all-optical switching in a propagation length smaller than a single wavelength. With recent developments in the integration of zero-index metamaterials, whose zero-refractive-index wavelength can be arbitrarily selected to suit the application [15–19], it has become critical to conduct an in-depth investigation of the nonlinear optical response of low-index media.

The recently demonstrated magnitude of nonlinear responses of ENZ materials is paradigm-shifting, and questions certain established fundamental assumptions in the field of nonlinear optics. For example, in a recent publication on the nonlinearity of aluminum-doped zinc oxide (AZO), the authors claim that "the ENZ nonlinearity in AZO [is] in a regime where the approximation of expanding the material polarization in a power series breaks down" [10]. Here, we theoretically and experimentally explore the consequences of a vanishingly small permittivity on the nonlinear optical response.

We begin by deriving an expression for the intensity-dependent index of refraction caused solely by the third-order nonlinear susceptibility $\chi^{(3)}$. For simplicity, we assume a centrosymmetric material and neglect the tensor nature of the susceptibility, as well as material magnetic responses. This set of assumptions is reasonable for most nonlinear optical materials [4].

To the lowest nonlinear order, the polarization of a material illuminated by a monochromatic laser field is described as

$$P^{\mathrm{TOT}} = P + P^{\mathrm{NL}} = \epsilon_0 E[\chi^{(1)} + 3\chi^{(3)}|E|^2]. \tag{1}$$

Here, $E$ is the complex amplitude of the applied electric field and $\chi^{(1)} \equiv \epsilon^{(1)} - 1$ corresponds to the linear response of the material, with $\epsilon^{(1)}$ being the linear relative permittivity. Thus, the relative permittivity, including only the $\chi^{(3)}$ nonlinearity, is

$$\epsilon = \epsilon^{(1)} + 3\chi^{(3)}|E|^2. \tag{2}$$

Since all of these quantities may be complex, we define the complex relative permittivity as $\epsilon = \epsilon' + i\epsilon''$ and the complex refractive index as $n = n' + in''$, where a single prime denotes the real part, and the double prime denotes the imaginary part, respectively. These two quantities are related by [20]

$$n = \sqrt{\epsilon} = \sqrt{\epsilon^{(1)} + 3\chi^{(3)}|E|^2}. \tag{3}$$

Together, these equations can be used to obtain the complex, intensity-dependent index of refraction $n$ due to third-order contributions. We find that

$$n = \sqrt{n_0^2 + 2n_0 n_2 I}, \tag{4}$$

where we take $n_0 = \sqrt{\epsilon^{(1)}}$ to be the linear refractive index, $I$ to be the optical field intensity

$$I = 2\mathrm{Re}(n_0)\epsilon_0 c|E|^2, \tag{5}$$

and we introduce the standard definition for the nonlinear index of refraction [4,20]

$$n_2 = \frac{3\chi^{(3)}}{4n_0\mathrm{Re}(n_0)\epsilon_0 c}. \tag{6}$$

In order to obtain a simpler relation for $n$, Eq. (4) is usually expanded in a power series under the assumption that $|2n_2 I/n_0| \ll 1$ [4], yielding

$$n = n_0\sqrt{1 + 2\frac{n_2 I}{n_0}} \approx n_0\left[1 + \frac{1}{2}\left(2\frac{n_2 I}{n_0}\right) + \ldots\right]. \tag{7}$$

In most materials, $|2n_2 I/n_0|$ is very small so that only the lowest order correction term is kept, resulting in the intensity-dependent refractive index being widely defined as

$$n = n_0 + n_2 I. \tag{8}$$

Hence, the change of the refractive index due to the nonlinearity is $\Delta n = n - n_0 \approx n_2 I$.

At this point, we pause to address a few concerns with this derivation when considering a vanishingly small index. First, in an ENZ material, $\Delta n/n_0$ can be larger than unity (e.g., in Al-doped ZnO, this ratio has been shown to equal 4.4 [10]). In this case, the assumption that permits the power series expansion of Eq. (7) and leads to Eq. (8) is violated. Therefore, this power series strictly *does not converge*, and Eq. (8) is not a valid approximation of the intensity-dependent index of refraction.

Second, Eq. (4) reveals an issue that is not immediately apparent from Eq. (8). As $|n_0| \to 0$, $n$ approaches zero as well, appearing to eliminate all refraction, including any nonlinearities. This conflict in fact also exists within Eq. (8)—as $|n_0| \to 0$, the optical field intensity vanishes while, simultaneously, $n_2 \to \infty$, leaving their product $(n_2 I)$ in Eq. (8) seemingly undefined. Note that $n_0$ is only introduced in the nonlinear contribution to Eq. (4) in order to obtain Eq. (8) in the appropriate limit, and it is this factor of $n_0$ that leads to the ostensible divergence of $n_2$ for low-index materials. No artificial effects of this kind appear when we phrase the nonlinear optical response purely in terms of the susceptibility and the electric field. $\chi^{(3)}|E|^2$ remains a robust measure of the nonlinear response, even when $n_2$ and $I$ take on exceptional values.

Thirdly, it is confounding to accurately interpret what it means to have an intensity that is identically zero when $\mathrm{Re}(n_0)$ vanishes in Eq. (5). When employing the optical field intensity instead of the complex field amplitude, we also need to address whether $n_0$ or $n$ should be used in its definition, which is typically not an important consideration when $\Delta n \ll 1$.

We must conclude that it does not seem beneficial to introduce $n_2$ or the nonlinear index of refraction, as defined in Eq. (8), in the context of low-index materials. In order to avoid these issues, we posit that it is preferable to use the intensity-dependent index of refraction, as defined in Eq. (3), with the square root, the nonlinear susceptibility, and the electric field amplitude directly. Though this equation is present in standard textbooks on nonlinear optics [4], it appears only as a step in the derivation for Eq. (8). Here, we have identified, to the best of our knowledge, the first case where its use becomes necessary to model the optical response.

We demonstrate the significance of these insights by considering experimental results. Except where explicitly stated, we focus our discussion on the single wavelength where the linear permittivity $\mathrm{Re}(\epsilon^{(1)}) = 0$, which typically corresponds to the wavelength where the index is at its lowest, and $\Delta n$ has been shown to attain its peak value [9]. In the experiment, originally reported in Ref. [9], the transmission and reflection are measured through a thin film as a function of intensity. Since the index change is so large, the Fresnel coefficients at the boundaries of the film change dramatically, which allows for the detection of measurable changes in these quantities as a function of intensity. We then extract both the real and imaginary parts of the refractive index from the measured transmission and reflection using a transfer-matrix method [21]. The measurements are performed on a 310 nm thick film of ITO using 150 fs pulses at an oblique angle of 30°. The linear permittivity of ITO has a zero-crossing at $\lambda = 1240$ nm and a correspondingly large nonlinearity at this wavelength [9]. However, it does not exhibit a true instantaneous Kerr nonlinearity, as the material exhibits a finite optical recovery time [22,23]. Additionally, extracting nonlinear coefficients using this method will be highly dependent on external factors other than the microscopic properties of the material. For these reasons, we denote the nonlinear orders of the susceptibility as *effective* susceptibilities and restrict our discussion to a fixed pulse width, wavelength, and angle of incidence.

We begin by examining input intensities up to 50 GW/cm$^2$, above which higher-order nonlinearities begin to make significant contributions to refraction. We present the outcome of this measurement in Fig. 1 as a function of the free-space incident pulse intensity $I_0$. We also plot Eq. (8) for comparison, using values extracted from independent ellipsometry and $Z$-scan measurements ($\mathrm{Re}(n_0) = 0.44$ and $\mathrm{Re}(n_2) = 0.016$ cm$^2$/GW) [9,24]. This equation provides an adequate estimate of the index at low intensities, but quickly fails to describe the refractive index as the intensity increases.

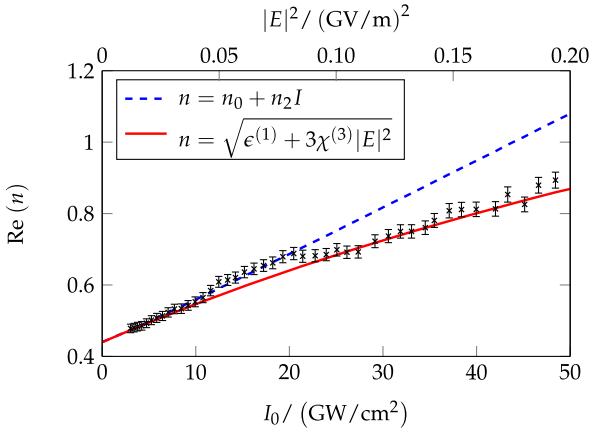


**Fig. 1.** Intensity-dependent index of the refraction of ITO at $\lambda = 1240$ nm, where the real part of the linear permittivity $\epsilon^{(1)}$ vanishes. Equation (8) performs poorly at describing the refractive index at most intensities (dashed blue line). Using Eq. (3), we obtain much-improved agreement with the measurement without additional fit parameters (red line). $I_0$ and $E$ refer to the free-space intensity and the corresponding field magnitude for a plane wave inside the material, respectively.

In comparison, we plot Eq. (3) using these same material values. The resulting curve follows the measured refractive index much more accurately. We stress that the form of this curve is due solely to the square-root nature of Eq. (3); it is not caused by any absorption-based saturation effects or higher-order contributions to the nonlinear susceptibility. Recall that this form of the equation has been derived assuming only third-order contributions to the nonlinear polarization. Our treatment is different from a polynomial fit to the refractive index, since it preserves the original definition of $n_2$ and describes some of the nonlinear behavior, even in lowest order. At higher input intensities, the curve begins to deviate significantly from the measured values, due to the emergence of higher-order nonlinear effects. We discuss the contribution of these nonlinearities to refraction in the following.

The nonlinear polarization $P^{\mathrm{NL}}(E)$ can be defined to be a complex function of the electric field amplitude. Its explicit form may depend highly on the experimental realization and the microscopic model that describes the material. Therefore, its analytical form might not be accessible at all. In the present context, we are content with expanding the nonlinear polarization in a power series and describing the interaction by its macroscopic properties. Thus, our method can be applied even if there exists no good microscopic model for the material response.

For a single-beam input, we represent the material polarization with the following power series:

$$P^{\mathrm{TOT}}(E) = \epsilon_0 E \sum_{j\,\mathrm{odd}}^{\infty} c_j \chi^{(j)} |E|^{j-1}, \tag{9}$$

where $c_j$ is a degeneracy factor [4]. We have included only odd orders of $\chi^{(j)}$ because only those contribute to refraction.

We extract $\epsilon$ from Eq. (9) and fit to the real and imaginary parts of the intensity-dependent refractive index of ITO for intensities up 275 GW/cm$^2$. The resulting curve correctly describes both $n'$ and $n''$ at all intensities (Fig. 2). The extracted $\chi^{(j)}$ values are listed in Table 1. The real part of $n_2$ calculated using $\chi^{(3)}$ extracted in this process is $\mathrm{Re}(n_2) = 0.016$ cm$^2$/GW, in agreement with the previous measurement.

We use Pearson's statistical chi-squared value to determine the most appropriate fit for this dataset [25]. Fits with fewer nonlinear orders than $\chi^{(7)}$ yield a significantly larger statistical error (i.e., larger chi-squared). Including orders beyond $\chi^{(7)}$ only improves the statistical error marginally, indicative of overfitting. We thus attribute the nonlinear refraction of ITO to $\chi^{(3)}$, $\chi^{(5)}$, and $\chi^{(7)}$ nonlinearities at the investigated intensities.

**Table 1. Values Extracted from the Fit to Eq. (9) with a Third-, Fifth-, and Seventh-Order Nonlinearity**

| $j$ | $\mathrm{Re}(\chi)^{(j)}/(10^{-9}\mathrm{m/V})^{j-1}$ | $\mathrm{Im}(\chi)^{(j)}/(10^{-9}\mathrm{m/V})^{j-1}$ |
|---|---|---|
| 1 | $-0.980 \pm 0.008$ | $0.36 \pm 0.01$ |
| 3 | $1.60 \pm 0.03$ | $0.50 \pm 0.05$ |
| 5 | $-0.63 \pm 0.02$ | $-0.25 \pm 0.04$ |
| 7 | $(7.7 \pm 0.3) \times 10^{-2}$ | $(3.5 \pm 0.8) \times 10^{-2}$ |

To examine the contributions of different orders to the refractive index, we plot them as functions of intensity in Fig. 3. At the highest input intensities, the linear refractive index makes only the fourth largest contribution to the total refractive index, providing further evidence that nonlinear optical effects cannot be treated solely as perturbations to linear optics. In fact, for an accessible range of operating intensities, nonlinear effects dominate the optical response of this material.

At the maximum utilized pump intensity, $I_{\mathrm{max}} = 275$ GW/cm$^2$, the $\chi^{(5)}$ term makes the largest contribution to the total refractive index; this term contributes more than the $\chi^{(3)}$ term, which is typically considered to be the dominant mechanism for $n_2$ and $\Delta n$. Additionally, the $\chi^{(7)}$ term is also significant, accounting for 20% of the total susceptibility.

Next, we use these extracted values to directly address whether the large nonlinearities that have been observed in ENZ materials violate traditional formulations of nonlinear optics that are based on the power series expansion of the nonlinear polarization.

The convergence of the power series in Eq. (9) can be determined using the ratio test

$$\lim_{j\to\infty} \left| \frac{c_{j+2}\chi^{(j+2)}|E|^{j+1}}{c_j \chi^{(j)}|E|^{j-1}} \right| < 1. \tag{10}$$

When this inequality is satisfied, the series converges. Thus, we see that $\Delta n/n$ and $n_2$ are not the relevant quantities for a discussion on convergence of the nonlinear polarization, even

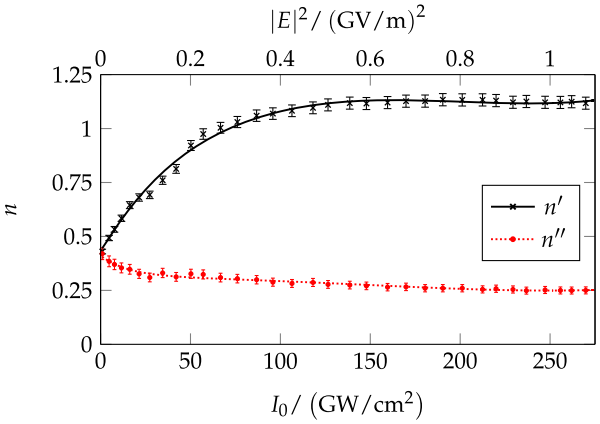


**Fig. 2.** Despite the saturation behavior at high intensities, we can correctly fit both the real and imaginary parts of the index of refraction of ITO for intensities up to 275 GW/cm$^2$ with the addition of appropriate $\chi^{(5)}$ and $\chi^{(7)}$ terms.

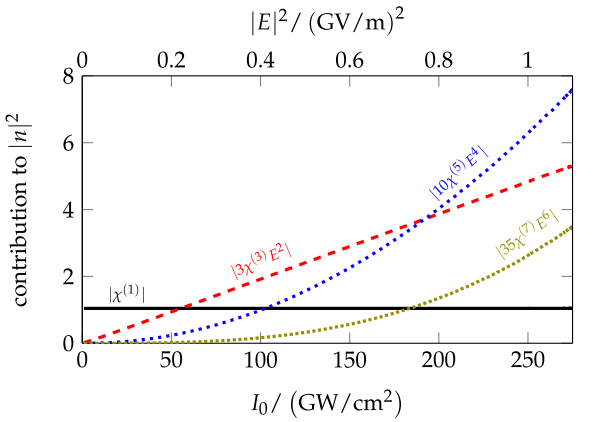


**Fig. 3.** Absolute contribution of the various orders of the nonlinear susceptibility to the refractive index of ITO at the wavelength where $\mathrm{Re}(\epsilon^{(1)}) = 0$. These contributions are estimated using the values for $\chi^{(j)}$ in Table 1.

though their magnitude is critical to the convergence of Eq. (7). Instead, the various nonlinear orders of the susceptibility $\chi^{(j)}$ determine its convergence. We note from Fig. 3 that the first few terms in the series violate the inequality since, at the maximum intensity investigated, the fifth-order contribution to refraction ($7.6 \pm 0.3$) is larger than the third order-contribution ($5.30 \pm 0.09$) which, in turn, is larger than the linear contribution ($1.043 \pm 0.004$). However, the corresponding ratio between the $\chi^{(7)}$ and $\chi^{(5)}$ terms obeys the criterion in Eq. (10).

Though we have no access to the coefficients in the limit of $j \to \infty$, we remark that they must be negligible at the investigated intensities, since we can accurately fit to the refraction without them. For example, $\chi^{(9)}$ was not found to be statistically different from zero; therefore, its contribution to the refractive index is insignificant, even at the maximum intensity investigated and, in particular, must be smaller than the seventh-order term, obeying the convergence criterion. Thus, we conclude that the large nonlinear index of refraction that is observed in ENZ materials is nonetheless consistent with a power series description of the nonlinear polarization.

The above treatment and discussion prominently demonstrate that there is indeed a need to reinterpret established quantities related to the optical response in materials with small indices of refraction. We conclude that, in this unique scenario, it is no longer appropriate to use the approximation of the intensity-dependent index of refraction that only depends linearly on the intensity, even when only accounting for $\chi^{(3)}$ nonlinearities. Instead, we have introduced a more general equation with a square-root dependence. The linear slope with which the community is familiar is merely a special case of Eq. (3) for when the linear index is large. Because it is based on so few assumptions, our method will continue to work in cases that are not explicitly considered in this Letter, such as if $|n_0| \gg 0$ or $|\Delta n/n| \sim 1$. The generalized equation developed here has the benefit of preserving the standard historical definition of $n_2$ as a function of $\chi^{(3)}$ [Eq. (6)], as well as the physical definition of $n_2$ as the *initial* slope for the refractive index with respect to the applied optical intensity, i.e., $n_2 \equiv \lim_{I\to 0} \partial n/\partial I$. However, since the definition of $n_2$ is problematic in the context of low-index materials, $\chi^{(3)}$ or $\Delta n$ should be used to characterize materials, instead.

We have demonstrated how to extend our generalized equation to incorporate higher-order nonlinear terms and absorption. Besides the assumption that the nonlinear susceptibility can be expanded in a power series, this treatment tracks the measured refraction for intensities up 275 GW/cm$^2$ without the need for a detailed microscopic model or empirical saturation equations [26,27]. Though our treatment cannot make predictions for even higher intensities, it enables quantitative statements regarding the convergence of the material polarization. It may also be used to systematically estimate the magnitude of higher-order contributions. Incidentally, we have shown that the nonlinear properties of ITO are even more striking than previously realized. At the highest probed intensities, the index of refraction is dominated by a fifth-order nonlinearity whose contribution grows roughly with $I^2$. We have also detected significant contributions to refraction caused by seventh-order nonlinearities. The nonlinear contributions from $\chi^{(3)}$, $\chi^{(5)}$, and $\chi^{(7)}$ terms each exceed the linear refraction term, making ENZ materials, to the best of our knowledge, the first solid-state platform to possess this property.

Finally, we have quantitatively shown that there is no evidence that the power series expansion for the nonlinear polarization in ENZ materials diverges at the wavelength where the linear permittivity vanishes. However, the dominant higher-order nonlinear contributions that have been observed reveal that ENZ materials operate in a regime where nonlinear optical effects can no longer be treated as a perturbation to linear optics.

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