ACS Photonics

Open Access

This article is licensed under CC-BY 4.0

pubs.acs.org/journal/apchd5

Viewpoint

Optical Nonlinearity of Transparent Conducting Oxides: More Metallic than Realized

Cite This: ACS Photonics 2025, 12, 1718−1721

Read Online

ACCESS | Metrics & More | Article Recommendations

ABSTRACT: Transparent conducting oxides (TCOs) have recently been shown to have a remarkably strong nonlinear optical response. We show that the popular ascription of their nonlinearity to the temperature-dependence of the plasma frequency is only a partial description of their response to intense illumination. Specifically, we show that an increase in the electron collision rate upon illumination and consequent heating contributes to the permittivity in a manner that can be quantitatively comparable to the contribution of the temperature-dependent plasma frequency. This behavior makes the optical nonlinearity of TCOs more similar to that of noble metals than realized so far, and as far as the imaginary part of the permittivity is concerned, this behavior is qualitatively opposite compared to that assumed so far.

Downloaded via BEN GURION UNIV OF THE NEGEV on April 16, 2025 at 07:42:00 (UTC).
See https://pubs.acs.org/sharingguidelines for options on how to legitimately share published articles.

Transparent conducting oxides (TCOs) are highly doped semiconductors which are popular within the microelectronics industry due to their CMOS-compatibility and their use as transparent electrodes; frequently studied materials include indium tin oxide (ITO),[1] aluminum-doped zinc oxide,[2] cadmium oxide,[3] copper sulfide,[4] etc. From an optical point of view, they are frequently thought of as low electron density Drude (LEDD) metals,[5−9] i.e., their permittivity is given by

$$\epsilon(\omega) = 1 + \chi_{inter}(\omega) + \chi_{intra}(\omega),$$
$$\chi_{intra}(\omega) = -\frac{\omega_p^2}{\omega^2 + i\omega\eta}, \qquad \omega_p^2 = \frac{e^2 N_e}{m_e^* \epsilon_0} \tag{1}$$

where the plasma frequency ω_p is typically found within the visible spectral range, rather than in the soft UV, as for noble metals. This numeclature stems from the much lower conduction band electron density N_e (typically by 1−2 orders of magnitude) and the high frequency threshold for interband transitions in TCOs (e.g., ≈4.5 eV for ITO), which enables approximating $1 + \chi_{inter}(\omega)$ by the constant ϵ_∞ for near-infrared (IR) frequencies.

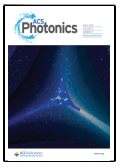
A key feature in the optical response of TCOs/LEDD metals is the convenient spectral position of their epsilon-near-zero (ENZ) spectral regime, i.e., the frequency range at which the material switches between being plasmonic to dielectric; this occurs indeed in the near-IR at $\omega_p/\sqrt{\epsilon_\infty} \approx \omega_p/2$. The ENZ spectral regime attracted ample attention due to associated unique opportunities to manipulate wave propagation, since phase distortions in this regime are minimal.[10−16]

More recently, TCOs/LEDD metals emerged as promising nonlinear optical materials.[7,17−29] Initially, the strong optical nonlinearity they exhibited in experiments was associated with operation in the near-IR ENZ frequency regime. This implies on a divergence of the *relative* permittivity change, which is the quantity that determines the strength of the nonlinear optical effects;[17,30−32] this explanation provided a *qualitative* match to the unprecedented observation of intensity-dependent permittivity changes of hundreds of percent.[17,18,20,22,26,28,29]

However, due to the electron collisions, represented by η, TCOs/LEDD metals are not truly transparent. Indeed, the imaginary part of their permittivity is small in the visible range, but in the ENZ spectral regime it does not vanish, with typical values not lower than $\epsilon'' \sim 0.3$.[33] Accordingly, the local field, hence nonlinear response, cannot diverge at the ENZ point, and instead, a resonance emerges, with moderate levels of local field enhancements.

In this context, a complementary explanation to the strong optical (near-IR, hence, intraband) nonlinearity ascribed it to the nonparabolicity of the conduction band.[1,6,34] This effect causes electrons excited to high momentum/energy states to experience a different band curvature, hence, a different effective mass, m_e^*. Under the assumption that the conduction band electron subsystem undergoes a particularly rapid thermalization, the nonlinear optical response associated with the nonparabolicity was described by an electron temperature -dependent plasma frequency, $\omega_p = \omega_p(T_e)$, where T_e is the electron temperature. More recently, this model was put in the general framework of a nonperturbative description of the nonlinearity,[35] where the optical response associated with the conduction band electrons was shown to gradually weaken upon illumination, i.e., to have a saturable-like response,[28,35] $\chi_{intra} \rightarrow \chi_{intra}/(1 + I/I_{sat})$. Remarkably, although this behavior emerges from a system at thermal equilibrium, it is similar to that of a true saturable absorber, a system which is as far as possible from thermal equilibrium due to a maximal inversion of its electron population.

Received: February 17, 2025
Published: April 16, 2025



ACS Publications

© 2025 The Authors. Published by American Chemical Society

https://doi.org/10.1021/acsphotonics.5c00384
ACS Photonics 2025, 12, 1718−1721

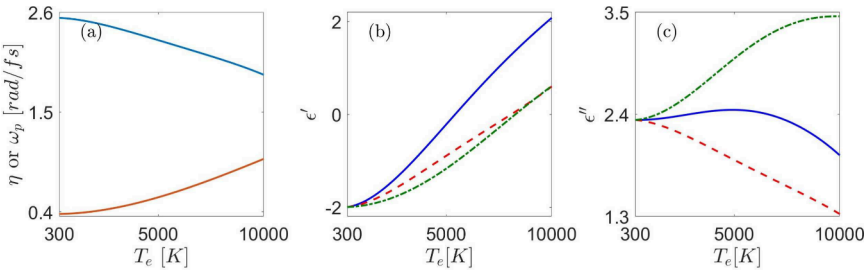


Figure 1. (a) Plasma frequency ω_p (blue) and damping rate η (red) as a function of the electron temperature. (b) Real and (c) imaginary parts of the permittivity as a function of T_e at $\hbar\omega \approx 0.75$ eV. The complete permittivity model (where $\omega_p = \omega_p(T_e)$ and $\eta = \eta(T_e)$; blue solid line) is compared to the more popular model[35,40] ($\omega_p = \omega_p(T_e)$ and constant η; dashed red line), as well as to a model where only the collision rate is temperature-dependent (dash-dotted green line). Parameters are taken from ref 1.

The rapid thermalization which is at the heart of this model must stem from frequent electron−electron ($e-e$) collisions. Indeed, in refs 8 and 9, a microscopic *nonthermal* rigorous model for the conduction electron dynamics showed that the conduction electron subsystem in LEDD metals (specifically, in ITO) thermalizes much faster than in noble metals. This fast electron collision rate is attributed to weaker screening effects arising from the low electron density and to the enhanced density of states resulting from the nonparabolic conduction band in LEDD metals.[8] Frequent collisions occur also with various phonons and impurities.[8,9] The sum of these collision rates (Matthiessen rule) can reach the level of a few femtoseconds (see Figure 1(a)).

The microscopic rigorous model also provided the distribution and dynamics of the conduction electrons, and demonstrated that a thermal model of the permittivity is justified even for pulses as short as a few 10s of femtoseconds. It also showed that the electron temperature can reach extremely high values, even exceeding the Fermi temperature (~10000 K). The predictions of the model of refs 8 and 9 were the first to reach qualitative and quantitative agreement with scattering measurements from an ITO layer.[17,26,28]

The goal of this Viewpoint is to highlight an implication of the success of the microscopic rigorous model which has been overlooked so far: since all the different electron collision rates naturally increase upon heating, the temperature-dependence of the total collision rate, $\eta = \eta(T_e)$, yields a large contribution to the optical nonlinearity of LEDD metals. This effect was accounted for in refs 28 and 36 using a qualitatively similar yet simpler *thermal* model; however, both works predicted a rather weak temperature dependence of η, whereas our quantitatively successful model implies that the strong sensitivity of η to the temperature, and the extremely high temperatures that can be reached gives rise to a nonlinearity which can become as important as that of the nonlinearity so far associated with the temperature-dependence of the plasma frequency $\omega_p = \omega_p(T_e)$.

To demonstrate this point, we show an example in which in addition to the rapid $e-e$ collisions, there is also a high density of impurities (or equivalently, surface roughness). Figure 1(b) shows that the contribution to the real part of the permittivity (ϵ') by the temperature-dependent collision rate is qualitatively and quantitatively comparable to that of the strong temperature dependence of the plasma frequency. This happens because the relatively fast collision rate in ITO is only 1 order of magnitude smaller than the typical operating near-IR frequencies at room temperature, and because at elevated electron temperatures, it may even be comparable to it (see Figure 1(a)). This contrasts the situation in noble metals where the collision rate is 2 orders of magnitude smaller than the operating frequency. The meaning of these results is that it is easy to confuse the contributions of ω_p and η to the nonlinearity in experimental data.

In addition, the plasma frequency and the (total) electron collision rate have opposing effects on the imaginary part of the permittivity, ϵ'', see Figure 1(c). In particular, the strong increase in η can be the dominant effect at electron temperatures of up to a few thousands K, giving rise to a net increase of ϵ''. From the physics point of view, this behavior makes the intensity-dependence of the imaginary part of the permittivity of TCOs/LEDD metals similar to that of the intraband thermal nonlinearity of noble metals.[32,37−39] This also means that under these conditions, the change of ϵ'' upon heating is the opposite to that predicted by the "saturation"-like model of Khurgin and Kinsey.[35,40] Nevertheless, for even higher temperatures, the decreasing plasma frequency may become the dominant effect on the change of ϵ'', which thus decreases upon further heating. Under these conditions, the permittivity follows qualitatively the "saturation" model of Khurgin and Kinsey.[34,35] Unfortunately, since the relative changes to the imaginary part of the permittivity are smaller than those of the real part, it is challenging to observe this behavior in experimental data. Thus, our finding should motivate experimental efforts to isolate the absorption and its temperature-dependence (as in ref 18) toward a resolution of the magnitude of the two contributions to the thermal nonlinearity.

The observation highlighted in this Viewpoint is generic to TCOs/LEDD metals, yet, it is quantitatively sensitive to the exact values of the material parameters and to the details of the various collision mechanisms, which may vary significantly from one sample to another, as well as from one TCO to another. For example, for a stochiometric alloy, the effects of the impurities will be reduced, and the analysis of refs 34 and 35 will provide a better match to observations. Conversely, lattice heating (not accounted for here) would make the η growth stronger; a proper account for it requires a specification of a structure and a self-consistent solution of the electric field, permittivity and electron distribution, as in ref 9. Further complexity is expected with variations in the nonparabolicity, effective mass, etc.

Our analysis means that the quantitative claims on $\omega_p(T_e)$ obtained in previous work might need to be rescaled. It also serves as a basis for future quantitative modeling of TCO intensity-dependent nonlinearities and even for distorted scaling of harmonic generation induced by massive heating-induced permittivity changes.[23,41,42] Our analysis further

https://doi.org/10.1021/acsphotonics.5c00384
ACS Photonics 2025, 12, 1718−1721

emphasizes the importance of absorption to the ultrafast optical nonlinearity of TCOs/LEDD metals, as well as its thermal nature; it is not a Kerr nor a saturable nonlinearity that are proportional to the instantaneous value of the electric field, but rather a delayed nonlinear response that is accumulated upon absorption (and also decays at a rate slower than that of the electric field), as pointed out already in ref 6. In that sense, the similarity to the intraband optical nonlinearity of noble metals[32,37−39] is further emphasized.

Finally, we note that the nonlinear optical response of TCOs to even shorter pulses, down to single cycle durations, may exhibit further complexity, which is the subject of ongoing investigations.[43,44] Resolution of these requires more detailed modeling of the interband contribution and is the key to understanding the ability of TCOs/LEDD metals to withstand the high fluences associated with illumination levels required for realization of photonic time crystals.[45,46]

Ieng-Wai Un orcid.org/0000-0002-7156-0019
Naama Harcavi orcid.org/0009-0003-3286-1585
Yonatan Sivan orcid.org/0000-0003-4361-4179

AUTHOR INFORMATION

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsphotonics.5c00384

Author Contributions

#These authors contributed equally to this work (I.-W.U. and N.H.).

Funding

I.W.U. was funded by the Guangdong Natural Science Foundation (Grant No. 2024A1515011457). N.H. and Y.S. were partially funded by a Lower-Saxony - Israel collaboration, Grant No. 76251-99-7/20 (ZN 3637), as well as an Israel Science Foundation (ISF) Grant (340/2020).

Notes

Views expressed in this Viewpoint are those of the author and not necessarily the views of the ACS.
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank M. Scalora, N. Kinsey, and J. Khurgin for their careful reading and many useful comments.

REFERENCES

(1) Liu, X.; Park, J.; Kang, J.-H.; Yuan, H.; Cui, Y.; Hwang, H. Y.; Brongersma, M. L. Quantification and impact of nonparabolicity of the conduction band of indium tin oxide on its plasmonic properties. *Appl. Phys. Lett.* **2014**, *105*, 181117.
(2) Naik, G. V.; Liu, J.; Kildishev, A. V.; Shalaev, V. M.; Boltasseva, A. Demonstration of Al:ZnO as a plasmonic component for near-infrared metamaterials. *Proc. Nat. Acad. Sci. U.S.A* **2012**, *109*, 8834−8838.
(3) Yang, Y.; Kelley, K.; Sachet, E.; Campione, S.; Luk, T. S.; Maria, J.-P.; Sinclair, M. B.; Brener, I. Femtosecond optical polarization switching using a cadmium oxide-based perfect absorber. *Nat. Photonics* **2017**, *11*, 390−395.
(4) Cordova-Castro, R. M.; Casavola, M.; van Schilfgaarde, M.; Krasavin, A. V.; Green, M. A.; Richards, D.; Zayats, A. V. Anisotropic plasmonic CuS nanocrystals as a natural electronic material with hyperbolic optical dispersion. *ACS Nano* **2019**, *13*, 6550−6560.
(5) Kinsey, N.; Khurgin, J. Nonlinear epsilon-near-zero materials explained: opinion. *Opt. Mater. Express* **2019**, *9*, 2793.
(6) Khurgin, J. B.; Clerici, M.; Kinsey, N. Fast and Slow Nonlinearities in Epsilon-Near-Zero Materials. *Laser Photon. Rev.* **2021**, *15*, 2000291.
(7) Wang, H.; Du, K.; Jiang, C.; Yang, Z.; Ren, L.; Zhang, W.; Chua, S. J.; Mei, T. Extended Drude Model for Intraband-Transition-Induced Optical Nonlinearity. *Phys. Rev. Applied* **2019**, *11*, 064062.
(8) Sarkar, S.; Un, I. W.; Sivan, Y. The electronic and thermal response of low electron density Drude materials to ultrafast optical illumination. *Phys. Rev. Applied* **2023**, *19*, 014005.
(9) Un, I. W.; Sarkar, S.; Sivan, Y. An electronic-based model of the optical nonlinearity of low electron density Drude materials. *Phys. Rev. Applied* **2023**, *19*, 044043.
(10) Alu, A.; Silveirinha, M. G.; Salandrino, A.; Engheta, N. Epsilon-near-zero metamaterials and electromagnetic sources: Tailoring the radiation phase pattern. *Phys. Rev. B* **2007**, *75*, 155410.
(11) Liu, R.; Cheng, Q.; Hand, T.; Mock, J. J.; Cui, T. J.; Cummer, S. A.; Smith, D. R. Experimental Demonstration of Electromagnetic Tunneling Through an Epsilon-Near-Zero Metamaterial at Microwave Frequencies. *Phys. Rev. Lett.* **2008**, *100*, 023903.
(12) Silveirinha, M.; Engheta, N. Tunneling of Electromagnetic Energy through Subwavelength Channels and Bends using permittivity-Near-Zero Materials. *Phys. Rev. Lett.* **2006**, *97*, 157403.
(13) Capretti, A.; Wang, Y.; Engheta, N.; Dal Negro, L. Enhanced third-harmonic generation in Si-compatible epsilon-near-zero indium tin oxide nanolayers. *Opt. Lett.* **2015**, *40*, 1500−1503.
(14) Vassant, S.; Archambault, A.; Marquier, F.; Pardo, F.; Gennser, U.; Cavanna, A.; Pelouard, J. L.; Greffet, J. J. Epsilon-Near-Zero Mode for Active Optoelectronic Devices. *Phys. Rev. Lett.* **2012**, *109*, 237401.
(15) Liberal, I.; Mahmoud, A. M.; Engheta, N. Geometry-invariant resonant cavities. *Nat. Commun.* **2016**, *7*, 10989.
(16) Wu, J.; Xie, Z. T.; Sha, Y.; Fu, H. Y.; Li, Q. Epsilon-near-zero photonics: infinite potentials. *Photonics Research* **2021**, *9*, 1616−1644.
(17) Alam, M. Z.; De Leon, I.; Boyd, R. W. Large optical nonlinearity of indium tin oxide in its epsilon-near-zero region. *Science* **2016**, *352*, 795−797.
(18) Caspani, L.; Kaipurath, R. P. M.; Clerici, M.; Ferrera, M.; Roger, T.; Kim, J.; Kinsey, N.; Pietrzyk, M.; Di Falco, A.; Shalaev, V. M.; Boltasseva, A.; Faccio, D. Enhanced Nonlinear Refractive Index in ϵ-Near-Zero Materials. *Phys. Rev. Lett.* **2016**, *116*, 233901.
(19) Guo, P.; Schaller, R. D.; Ketterson, J. B.; Chang, R. P. H. Ultrafast switching of tunable infrared plasmons in indium tin oxide nanorod arrays with large absolute amplitude. *Nat. Photonics* **2016**, *10*, 267−273.
(20) Clerici, M.; Kinsey, N.; DeVault, C.; Kim, J.; Carnemolla, E. G.; Caspani, L.; Shaltout, A.; Faccio, D.; Shalaev, V.; Boltasseva, A.; Ferrera, M. Controlling hybrid nonlinearities in transparent conducting oxides via two-colour excitation. *Nat. Commun.* **2017**, *8*, 1−7.
(21) Passler, N. C.; Razdolski, I.; Katzer, D. S.; Storm, D. F.; Caldwell, J. D.; Wolf, M.; Paarmann, A. Second Harmonic Generation from Phononic Epsilon-Near-Zero Berreman Modes in Ultrathin Polar Crystal Films. *ACS Photonics* **2019**, *6*, 1365−1371.
(22) Bohn, J.; Luk, T. S.; Tollerton, C.; Hutchings, S.; Brener, I.; Horsley, S.; Barnes, W. L.; Hendry, E. All-Optical Switching of an Epsilon-Near-Zero Plasmon Resonance in Indium Tin Oxide. *Nat. Commun.* **2021**, *12*, 1017.
(23) Yang, Y.; Lu, J.; Manjavacas, A.; Luk, T. S.; Liu, H.; Kelley, K.; Maria, J.-P.; Runnerstrom, E. L.; Sinclair, M. B.; Ghimire, S.; Brener, I. High-harmonic generation from an epsilon-near-zero material. *Nat. Phys.* **2019**, *15*, 1022−1026.
(24) Bruno, V.; et al. Negative Refraction in Time-Varying Strongly Coupled Plasmonic-Antenna-Epsilon-Near-Zero Systems. *Phys. Rev. Lett.* **2020**, *124*, 043902.
(25) Scalora, M.; Trull, J.; de Ceglia, D.; Vincenti, M. A.; Akozbek, N.; Coppens, Z.; Rodríguez-Sune, L.; Cojocaru, C. Electrodynamics of conductive oxides: Intensity-dependent anisotropy, reconstruction of the effective dielectric constant, and harmonic generation. *Phys. Rev. A* **2020**, *101*, 053828.

(26) Tirole, R.; Galiffi, E.; Dranczewski, J.; Attavar, T.; Tilmann, B.; Wang, Y.-T.; Huidobro, P. A.; Alú, A.; Pendry, J. B.; Maier, S. A.; Vezzoli, S.; Sapienza, R. Saturable time-varying mirror based on an epsilon-near-zero material. *Phys. Rev. Applied* **2022**, *18*, 054067.
(27) Minerbi, E.; Sideris, S.; Khurgin, J. B.; Ellenbogen, T. The Role of Epsilon Near Zero and Hot Electrons in Enhanced Dynamic THz Emission from Nonlinear Metasurfaces. *Nano Lett.* **2022**, *22*, 6194−6199.
(28) Baxter, J.; Perez-Casanova, A.; Cortes-Herrera, L.; Cala Lesina, A.; De Leon, I.; Ramunno, L. Dynamic Nanophotonics in Epsilon-Near-Zero Conductive Oxide Films and Metasurfaces: A Quantitative, Nonlinear, Computational Model. *Adv. Photonics Res.* **2023**, *4*, 2200280.
(29) Anopchenko, A.; Gurung, S.; Bej, S.; Lee, H. W. H. Field enhancement of epsilon-near-zero modes in realistic ultrathin absorbing films. *Nanophotonics* **2023**, *12*, 2913−2920.
(30) Reshef, O.; Giese, E.; Zahirul Alam, M.; De Leon, I.; Upham, J.; Boyd, R. W. Beyond the perturbative description of the nonlinear optical response of low-index materials. *Opt. Lett.* **2017**, *42*, 3225−3228.
(31) Alam, M. Z.; Schulz, S. A.; Upham, J.; De Leon, I.; Boyd, R. W. Large optical nonlinearity of nanoantennas coupled to an epsilon-near-zero material. *Nat. Photonics* **2018**, *12*, 79−83.
(32) Gurwich, I.; Sivan, Y. A Metal Nanosphere under Intense Continuous Wave Illumination - a Unique Case of Non-Perturbative Nonlinear Nanophotonics. *Phys. Rev. E* **2017**, *96*, 012212.
(33) Kinsey, N.; DeVault, C.; Boltasseva, A.; Shalaev, V. M. Near-zero-index materials for photonics. *Nat. Rev. Mater.* **2019**, *4*, 742−760.
(34) Secondo, R.; Khurgin, J.; Kinsey, N. Absorptive loss and band non-parabolicity as a physical origin of large nonlinearity in epsilon-near-zero materials. *Opt. Mater. Express* **2020**, *10*, 1545−1560.
(35) Khurgin, J. B.; Kinsey, N. "Nonperturbative Nonlinearities": Perhaps Less than Meets the Eye. *ACS Photonics* **2024**, *11*, 2874.
(36) Wang, H.; Du, K.; Liu, R.; Dai, X.; Zhang, W.; Chua, S. J.; Mei, T. Role of hot electron scattering in epsilon-near-zero optical nonlinearity. *Nanophotonics* **2020**, *9*, 4287−4293.
(37) Stoll, T.; Maioli, P.; Crut, A.; Del Fatti, N.; Vallee, F. Advances in femto-nano-optics: ultrafast nonlinearity of metal nanoparticles. *Eur. Phys. J. B* **2014**, *87*, 260.
(38) Sivan, Y.; Chu, S.-W. Nonlinear Plasmonics at High Temperatures. *Nanophotonics* **2017**, *6*, 317−328.
(39) Un, I. W.; Sivan, Y. The Thermo-Optic Nonlinearity of Single Metal Nanoparticles under Intense Continuous-Wave Illumination. *Phys. Rev. Mater.* **2020**, *4*, 105201.
(40) Secondo, R.; Fomra, D.; Izyumskaya, N.; Avrutin, V.; Hilfiker, J. N.; Martin, A.; Özgür, U.; Kinsey, N. Reliable modeling of ultrathin alternative plasmonic materials using spectroscopic ellipsometry. *Opt. Mater. Express* **2019**, *9*, 760−770.
(41) Minerbi, E.; Keren-Zur, S.; Ellenbogen, T. Nonlinear Metasurface Fresnel Zone Plates for Terahertz Generation and Manipulation. *Nano Lett.* **2019**, *19*, 6072−6077.
(42) Tian, W.; Liang, F.; Lu, D.; Yu, H.; Zhang, H. Highly efficient ultraviolet high-harmonic generation from epsilon-near-zero indium tin oxide films. *Photon. Res.* **2021**, *9*, 317−323.
(43) Lustig, E.; Segal, O.; Saha, S.; Bordo, E.; Chowdhury, S. N.; Sharabi, Y.; Fleischer, A.; Boltasseva, A.; Cohen, O.; Shalaev, V. M.; Segev, M. Time-refraction optics with single cycle modulation. *Nanophotonics* **2023**, *12*, 2221−2230.
(44) Narimanov, E. Ultrafast Optical Modulation by Virtual Interband Transitions. *ACS Photonics* **2025**, *12*, 402−408.
(45) Lustig, E.; Segal, O.; Saha, S.; Fruhling, C.; Shalaev, V.; Boltasseva, A.; Segev, M. Photonic time-crystals - fundamental concepts. *Opt. Express* **2023**, *31*, 9165.
(46) Hayran, Z.; Khurgin, J. B.; Monticone, F. $\hbar\omega$ versus $\hbar k$: dispersion and energy constraints on time-varying photonic materials and time crystals. *Optical Materials Express* **2022**, *12*, 3904.

https://doi.org/10.1021/acsphotonics.5c00384
ACS Photonics 2025, 12, 1718−1721