Nonlinear optics in a high-index of refraction material

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Nonlinear response in a material increases with its index of refraction as \( n^4 \) [1, 2]. Commonly, \( n \sim 1 \) so that diffraction, dispersion, and chromatic walk-off limit nonlinear scattering [3]. Ferroelectric crystals with a periodic 3D polarization structure overcome some of these constraints through versatile Cherenkov and quasi-phase-matching mechanisms [4-9]. Three-dimensional self-structuring can also lead to a giant broadband refraction [10]. We here perform second-harmonic-generation experiments in KTN:Li with \( n > 26 \). Enhanced response causes wavelength conversion to occur in the form of bulk Cherenkov radiation without diffraction and chromatic walk-off, even in the presence of strong wave-vector mismatch and highly focused beams [11,18]. The process occurs with an arbitrarily wide spectral acceptance, more than 100 nm in the near infrared spectrum, an ultra-wide angular acceptance, up to \( \pm 40^\circ \), with no polarization selectivity, and can be tuned to allow bulk supercontinuum generation. Results pave the way to highly efficient versatile and adaptable nonlinear optical devices with the promise of single-photon-to-single-shot nonlinear optics [19].

Frequency conversion and parametric amplification are fundamental ingredients for a wide family of applications, including light sources, detection, optical processing, and quantum-state-generation [2, 3, 20, 21]. For quantum technology, a versatile and super-efficient nonlinear process is the key to photon-based quantum computing [22, 23]. Nonlinear scattering of optical waves can be described starting from the Taylor series expansion of the material polarization \( P \) in the propagating optical field \( E_{\text{opt}} \), i.e., \( P = \varepsilon_0 (\chi^{(1)} E_{\text{opt}} + \chi^{(2)} E_{\text{opt}}^2 + \ldots) \) [11,3]. The first term describes linear response through the first order susceptibility \( \chi^{(1)} = n^2 - 1 \), while higher-order terms describe nonlinear effects. The validity of the expansion implies \( \chi^{(m+1)}/\chi^{(m)} \sim 1/E_{\text{sat}} \), where \( E_{\text{sat}} \) is the scale of the atomic electric field of the substance. The intensity of an arbitrary allowed nonlinear scattering processes scales with \( (\chi^{(m)})^2 (E_{\text{opt}})^{2m} \sim (\chi^{(1)} E_{\text{opt}})^2 (E_{\text{opt}}/E_{\text{sat}})^{2m} \), and the intensity of any higher order scattering processes scales with \( n^4 \) [2]. Hence giant broadband refraction (GR), i.e., an index of refraction \( n \gg 1 \) across the visible and near infrared spectrum, emerges as a direct route to strongly enhanced nonlinear response.

In the paradigm nonlinear optical process, second-harmonic-generation (SHG), waves are generated at wavelength \( \lambda/2 \) (and angular frequency \( 2\omega \)) by the anharmonic response of dipoles driven by the pump at wavelength \( \lambda \) [24]. The process occurs most efficiently when the converted signal interferes constructively with the pump itself, a phase-matching condition (PM) that embodies momentum conservation for the interaction. For any given material, dispersion causes PM to occur naturally in the direction of the pump only for converted light (signal beam) whose wavevector \( k_{2\omega} \) forms a finite angle \( \theta_C \) relative to the pump itself \( k_\omega \). This leads to wavelength-dependent constraints on the process geometry while the wavevector mismatch \( \Delta k = k_{2\omega} - 2k_\omega \) is accompanied by chromatic walk-off [20] (see Fig.1A top panels). Collinear PM (\( \Delta k = 0 \)) can, in turn, be achieved using material birefringence, which introduces wavelength and polarization constraints [3], and quasi-phase-matching, that requires periodic material microstructuring and is also wavelength-selective [25,26]. With \( n \gg 1 \), the angle at which Cherenkov PM occurs is greatly reduced (\( \theta_C \approx 0 \)) so that chromatic walk-off does not intervene (see GR Cherenkov PM in Methods and bottom panels in Fig.1A).

The specific geometrical structure of Cherenkov SHG combined with GR is illustrated in Fig.1B. The pump propagates inside the sample along the normal to its input facet irrespective of launch angle \( \theta_i \) (left panels) and the Cherenkov SHG copropagates with the pump inside the sample (\( \theta_C \approx 0 \), central panels). At the output facet the pump and signal separate at a now finite angle \( \theta_C \), as illustrated for the two cases of transverse electric (TE) and transverse magnetic (TM) polarizations (central and right panels, respectively). For the TE case, while the pump exits with an angle to the normal \( \theta_0 = \theta_i \), the Cherenkov SHG forms two beams angled with respect to the pump by \( \theta_0 \pm \theta_C \), with the same polarization as the
pump and on the incidence plane (the xz plane). In turn, for the TM case, the SHG Cherenkov radiation separates at the output in the orthogonal plane (the yz plane) (see GR Cherenkov SHG in Methods).

We perform experiments in two samples of nanodisordered oxide ferroelectric KTN:Li perovskites (see Materials Section in Methods). These manifest GR, with record-high broadband index of refraction \( n > 26 \) at visible wavelengths. The effect is associated to the emergence of an underlying super-crystal (SC) [4]. Each lattice site of the SC is the core of a periodic 3D vortex and anti-vortex structure, a mesh of spontaneous polarization that forms below the Curie point (see SC Preparation Section in Methods). Typical broadband GR for sample 1 is reported in Fig.1C (see GR Experiments Section in Methods). In Fig.1D we illustrate the scheme used to investigate SHG using 190 fs pulses from a mode-locked Ti:Sa source (see SHG Setup Section in Methods). In Fig.1E we report output SHG power versus pump input power. The observed scaling \( P_2 \propto (P_0)^2L_z^2 \), where \( L_z \) is the length of the sample in the z direction, is reminiscent of the undepleted pump regime of standard SHG [1-3]. The \( P_2/P_0 \) ratio is independent of input polarization, and output polarization is found to coincide with the input. In Fig.1F we report SHG conversion varying the pump wavelength in the available pump spectrum (see Acceptance Section in Methods). There is no wavelength selectivity and only a weak wavelength dependence. As reported in Fig.1G, SHG conversion is observed for all accessible input angles \( \theta_1 (= \theta_0) \), indicating that the conversion occurs also with no input angular acceptance (see Acceptance Section in Methods).

Wavelength conversion is mediated by the second-order nonlinear susceptibility response \( \chi^{(2)} \) of the KTN:Li perovskite in its noncentrosymmetric tetragonal 4mm state. In distinction to single-domain or to quasi-phase-matching schemes, the nonlinear process is mediated by a SC with its specific 3D geometry, GR, and underlying ferroelectric domain structure [15, 27]. Hence, while GR causes conversion efficiency to be essentially independent of polarization, input angle, and wavelength, the details of the SHG output strongly depend on input parameters and the SC structure. As illustrated in Fig.2A, the structure of the 3D SC is a volume lattice of 3D polarization vortices that emerge as the cubic symmetry is broken and polarization charge is screened [4, 10]. The prediction fits in well with the experimental data. The SC manifests localized peaks. A similar situation occurs also for light focused onto the bc facet, as reported in Fig.2D, where output SHG is emitted at all available angles (see Fig.2D inset photographs). The observed SHG follows the basic GR SHG Cherenkov mechanism illustrated in Fig.1B (see Cherenkov SHG Experiment Section in Methods).

Results on Cherenkov SHG reported in Fig. 2 provide, through a direct measurement of \( \theta_C \), an estimate of the SC \( 2\Delta n_{2\omega} = \sin^2 \theta_C \) (see Cherenkov SHG Experiment Section in Methods). In the case of Fig.2B, \( 2\Delta n_{2\omega} \simeq 0.08 \). Snell refraction experiments in this direction provide \( n_{2\omega} > 26 \), so that we expect a \( \Delta n < 0.001 \), corresponding to an ultra-low approximate dispersion of \( dn/d\lambda < -0.002\mu m^{-1} \). The prediction fits in well with our understanding of the SC phase, for which chromatic dispersion is expected to be strongly reduced. To investigate this further we directly measured SC chromatic dispersion using group-velocity dispersion [28] for \( T > T_C \), where no SC forms, and \( T < T_C \), where the SC forms. Results are reported in Fig. 3A. As expected, the onset of the SC structure is accompanied by a sharp reduction in average values of dispersion, from \( dn/d\lambda \simeq -0.10\mu m^{-1} \) to \( dn/d\lambda \simeq -0.06\mu m^{-1} \). Strong SHG conversion does not allow a local vortex and anti-vortex dispersion measurement.

We compared SC SHG in the two samples to identify possible growth and composition related effects. We
found that sample 1 and 2 manifest the same geometrical behavior as regards to GR and Cherenkov SHG, while their net SHG conversion efficiency is considerably different, as reported in Fig.3B.

The angle at which Cherenkov phase-matching is achieved is wavelength-dependent ($\theta_C(\lambda)$). To characterize this we report in Fig.4A measurements of spectral acceptance for a detector able to collect light only from a limited cone at two fixed angles $\theta_1$ (yellow dots) and $\theta_2$ (magenta dots). The result is a spectral bandwidth whose peak follows $\theta_C(\lambda)$ and whose width is in agreement with the angular acceptance (see Angular versus Wavelength Acceptance Section in Methods). Since GR allows no diffraction or pump-signal walk-off, Cherenkov phase-matching will occur for all wavelengths. In turn, not all Cherenkov SHG can actually leave the output...
FIG. 2. SHG in a SC. (a) Illustration of a specific realization of a SC. The spontaneous polarization, the white arrows, determines the specific $\chi^{(2)}$ response of each composing tetrahedral (a color coding is implemented). The actual structure of a cube is illustrated through a sequential build-up adding groups of tetrahedral domains. The SC can have many different chiral realizations. The one illustrated here serves to explain the specific results found, relative to the crystal growth axis $a$. Indicated are the regions leading to strongest SHG, i.e., the core of polarization vortices in the $ab$ facet and the core of anti-vortices in the $ac$ and $bc$ facets. (b) SHG for a pump focused into a single polarization-vortex in the $ab$ facet. The only non-zero contributions to $\chi^{(2)}$ are illustrated for the TM (top left) and TE cases (bottom left). Output spatial distribution and polarization distribution for a pump polarized at 45 degrees (top image), TE (center), and TM (bottom). Left panel provides a panoramic of the experiments and the observed SHG. (c) SHG for a pump focused in an anti-vortex in the $ac$ facet. As illustrated in the right panel, the only finite contribution to SHG is mediated by $b$ polarized domains through the $d_{15}$ component for TM. (d) SHG for a pump focused in an anti-vortex in the $bc$ facet. Results are analogous to the $ac$ facet, while here a full angle Cherenkov emission is clearly visible ($\theta_C = \pi$). Note how, in distinction to random-phase-matching, no lateral emission is observed [29, 30], and all SHG is originating, as expected, solely from the output facet (see inset photographs).

facet of the sample, as total internal reflection occurs for wavevectors that have an internal incidence angle
\[ \theta_i > 1/n_{2\omega} \] with the output facet. Hence, for a \( \theta_i = 0 \), \( \theta_i = \theta_c = \arccos\left(\frac{n_{\omega}}{n_{2\omega}}\right), \) a zero emitted SHG will result for \( \arccos\left(\frac{n_{\omega}}{n_{2\omega}}\right) > 1/n_{2\omega} \). The effect can be appreciated recalling the full angle-integrated measurement reported in Fig.1F (blue circles). For a given pump wavelength, the same effect will occur as a function of \( \theta_i (\theta_c) \); assuming the previously evaluated \( \sqrt{2} \Delta n n_{2\omega} \approx 0.28 \), we expect to observe a total internal reflection for an input \( |\theta_i| > 46^\circ \) (see Total Internal Reflection Section in Methods).

In Fig.4B we report SHG output, for a strong Fresnel reflection at the input and output facets. In Rowe relationships, but no initial build-up is detected, (Fig.5C). Scattering from SHG along the propagation direction, and ultimately disappears altogether as the sample is heated above the Curie point. A detailed analysis indicates that the scattering is not enhanced SHG to have such an attenuated net efficiency nor does it relate to quasi-phase-matching. Cherenkov mechanism in action is not Bragg in nature but it must have a broad spectral and angular acceptance underline how the observed net output SHG efficiency leads to a limited typical output conversion ratio \( P_{2\omega}/P_{\omega} \sim 0.5\% \). The mechanism that causes what should be a strongly enhanced SHG to have such an attenuated net efficiency is analyzed in Fig. 5 for the conditions discussed in Fig.2C,D. The clue lies in the observation of the scattered SHG light from the body of the sample (see Fig.5A,B). A detailed analysis indicates that the scattering is not accompanied by an expected strong modulation along the propagation direction, and ultimately disappears altogether as the sample is heated above the Curie point \( T_C \) (Fig.5C). Scattering from SHG along the propagation direction should be qualitatively described by the Manley-Rowe relationships, but no initial build-up is detected, nor oscillations associated to out-of-phase-matching interaction, nor the characteristic exponential decay associated to a depleted pump in the presence of scattering [11, 33]. An explanation is that the \( n \gg 1 \) regime leading to SHG (as discussed in Fig. 2) is accompanied by strong Fresnel reflection at the input and output facets. This then allows cavitation inside the sample, leading to a propagation-independent scattering and a strongly reduced net conversion efficiency at the output. Congruently, the pump is no longer observed transmitted by the sample, and white light suffering linear GR launched in the sample focused in region leading to SHG leads to a similar propagation-independent scattering (see white-light scattering in Fig.5D). In turn, the existence of a strongly enhanced nonlinear interaction inside the sample is demonstrated by supercontinuum generation[32], reported in Fig.5G (see the Supercontinuum Generation Section in Methods). A basic challenge is then to identify and tailor a scheme or domain configuration able to harness this internal nonlinearity, for example using counterpropagating waves [34], or to combine GR with the ongoing drive to engineer innovative nonlinear periodic materials [34].

**METHODS**

**GR Cherenkov PM.** In a material with giant broadband refraction, \( n_{\omega}, n_{2\omega} \gg 1 \). At the sample input facet the plane-wave components of the pump refract according to the Snell law \( \theta_r = \arcsin\left(\frac{\sin \theta_i}{n_{\omega}}\right) \approx 0 \), where \( \theta_i, \theta_r \) are the incidence and refraction angle. Cherenkov PM occurs for GR wavevectors at an angle relative to the pump \( \theta_c = \arccos\left(\frac{n_{\omega}}{n_{2\omega}}\right) \sim 0 \), inasmuch that \( \Delta n = (n_{2\omega} - n_{\omega})/n_{\omega} \ll 1 \).

**GR Cherenkov SHG.** SHG polarization is \( P_{2\omega} = d_{3jk} E_x^\omega E_y^\omega E_k^\omega \), where \( E^\omega \) is the pump field and \( d_{ijk} \) is the nonlinear optical susceptibility tensor, that has nonzero components \( d_{31}, d_{33}, \) and \( d_{15} \) for the tetragonal 4mm symmetry of KTN:Li [35]. Considering the TE case for a spontaneous polarization parallel to the optical polarization (along the y axis), \( P_{2\omega}^y = d_{33}(E_y^\omega)^2 \). The emitted Cherenkov radiation must then have a \( k_{2\omega} \) in a plane orthogonal to \( P_{2\omega} \), i.e., in the incidence plane (xz) (central panels in Fig.1B). Analogously for the TM case, in which, for a spontaneous polarization parallel to the optical polarization (along the x axis), the nonlinear polarization is dominated by the x component \( P_{2\omega}^x = d_{33}(E_x^\omega)^2 \), so that Cherenkov PM occurs in the yz plane (right panels in Fig.1B). In the TM case, a SHG contribution arises also for a domain with a spontaneous polarization along the z axis, i.e., \( P_{2\omega}^z = 2d_{15} E_z E_x^\omega E_y^\omega \) and \( P_{2\omega}^z = d_{31}(E_z^\omega)^2 \). The emitted Cherenkov SHG will then be TM polarized and have a \( K_{2\omega} \) orthogonal to \( P_{2\omega} \) in the incidence plane xy (i.e., along the y axis).

**Materials.** The two samples (sample 1 and sample 2) are zero-cut polished lithium-enriched solid-solutions of potassium-tantalate-niobate (KTN:Li). They have the same composition \( K_{0.997}Ta_{0.64}Nb_{0.36}O_3\)Li$_{0.003}$, while in the flux of sample 2 traces of Mo impurities are introduced. Sample 1 measures along its three axes 4.62(a) x 3.86(b) x 1.6(c) mm while sample 2 is 6.96(a) x 3.86(b) x 1.6(c) mm. The samples form perovskites with room-temperature cubic-to-tetragonal (m3m to 4mm) ferro-
electric phase-transition temperatures $T_{C,1} = 315$ K and $T_{C,2} = 333$ K. Both are grown through the top-seeded method that causes them to have a built-in spatially periodic oscillation in composition along the growth axis (the $a$ axis) that translates into an approximately periodic 50 μm striation grating that then determines the lattice constant of the underlying super-crystal [4].

**SC Preparation.** Each sample, initially equilibrated at $T = 298$K and unbiased, is heated to $\simeq 373$ K at a rate of 0.6 K/min and is DC-biased by an electric field that increases at a constant rate from 0 to 4 kV/cm. The sample is then cooled back down to $T = 298$K while the bias field remains constant at 4 kV/cm. The DC field is applied between the two parallel faces along the $a$ axis (growth axis). To minimize the temperature gradient, the sample is dipped into a Teflon holder that contains temperature resistant mineral oil. The SC can now be further modified having the sample undergo successive thermal cycles, composed of a first stage in which the unbiased sample is heated to $T_C + 10K$ at a rate of 0.35Ks$^{-1}$ immediately followed by a second cooling stage tp $T_C - 35$K at a rate of 0.1 Ks$^{-1}$. Once the thermal protocol in completed, each sample is used for optical experiments at a given temperature $T < T_C$.

**GR Experiments.** The sample is cooled using a current-controlled Peltier junction to $T_C - 35$K and rotated by a tunable angle $\theta_0$ with respect to the optical propagation axis $z'$ (see scheme illustrated in Fig.1C). Light is collected from a commercial projector (NEC-VE281X, XGA, 2800 lumens) polarized using a linear polarization filter and focused onto the input facet of the sample using a high-aperture long-working distance microscope objective (Edmund Optics, x100, 3mm working distance, achromatic, NA= 0.8) positioned $\simeq 30$cm from the output lens of the projector. The top-view image in Fig.1C is taken using an Apple iPhone7. Top-view scattered light from within the sample and from the metallic support indicates strong reflection from the input facet and a non-spreading propagation inside the sample normal to the input facet irrespective of wavelength, $\theta_0$, and launch polarization, and a regular diffraction of the beam exiting the sample, as expected for GR.

**SHG Setup.** SHG experiments (see scheme and photo of apparatus in Fig. 1D) are carried out in the 790-880 nm range using a Tsunami Spectra Physics Ti:Sa CW mode-locked laser (maximum output power of 0.6W at $\lambda = 810 \pm 7$ nm), with a repetition rate of 80 MHz and a pulsewidth of 190 fs. Laser beam linear polarization, TM or TE, or a superposition of the two, is set using a $\lambda/2$ waveplate. The beam is focused onto the input facet of the $\theta_0$-rotated sample using a 50-mm-focal-length lens. The pump beam is focused to an input FWHM $\simeq 15 \mu m$. The SHG pattern is detected on a white screen placed at $d= 7.0$ cm from the output facet of the sample using a Canon EOS 50d.

**Acceptance.** Spectral acceptance is reported for $\theta_0 = 0$
in arbitrary power units $P_{2\omega}$ normalized to the peak spectral value. Since each measurement at different wavelengths is carried out with different pump power, the output signal is rescaled appropriately, i.e., divided by the input power squared. Angular acceptance is evaluated for a 810 nm pump and for all accessible launch angles. In both spectral and angular acceptance experiments, output SHG is collected by a lens and focused onto a power meter.

**Cherenkov SHG Experiment.**

$$\cos(\theta_C') = \frac{(2k_\omega/k_{2\omega}) n_\omega}{n_{2\omega}} n_{2\omega} = n_{2\omega} - \Delta n,$$

so that $\theta_C' \ll 1$, $\theta_C' \simeq \sqrt{2\Delta n/n_{2\omega}}$. Outside the sample, $\sin(\theta_C') = n_{2\omega} \sin \theta_C' \simeq n_{2\omega} \theta_C'$. Measuring $\theta_C'$ leads to an estimate of $\Delta n = (\sin(\theta_C'))^2/(2n_{2\omega})$. For a pump focused on the ab facet in Fig.2B, for both the TE and TM cases, the two SH beams emerge in the x-z (i.e., ac) and y-z (i.e., bc) planes at an angle $\theta_C' \simeq 0.28$ rad with respect to the pump (for all accessible values of $\theta_C$). According to the Cherenkov model, this implies that $\sqrt{2\Delta n n_{2\omega}} \simeq 0.28$. For light focused on the ac facet in Fig.2C and bc facet in Fig.2D, SHG is generated from tetrahedral domains oriented along the $b$ and $a$ axis, respectively, i.e., with a spontaneous polarization orthogonal to the input facet. Involving both $d_{31}, d_{33}, d_{15}$, the result is a TM SHG in the $bc$ and $ac$ plane, respectively. The observed $\theta_C' \simeq \pi/2$ (see detailed photos in the inset of Fig.2D), corresponding to a $\sqrt{2\Delta n n_{2\omega}} \simeq 1$.

**Angular versus Wavelength Acceptance.** To test this we maximized SHG efficiency, i.e., Cherenkov phase-matching is established for the specific pump wavelength $\lambda$, and the SHG signal detector is placed so as to capture a single output diffraction-limited mode. As reported in Fig.4A, changing the pump wavelength without altering the crystal and detector geometry leads to a relative spectral acceptance $\Delta \lambda/\lambda \simeq 0.047$ that is in agreement with the input pump numerical aperture $2\lambda/\pi w_0 \simeq 0.05$.

**Total internal reflection.** Total internal reflection of the SHG signal occurs at the output facet when approximately $\theta_C' + \theta_r > 1/n$, where $\theta_r = \sin(\theta_0)/n$. Assuming $\theta_C' = \sqrt{2\Delta n/n_{2\omega}}$, we have that total internal reflection occurs for $|\sin(\theta_0)| > 1 - \sqrt{2\Delta n n_{2\omega}}$. Taking the value of $\sqrt{2\Delta n n_{2\omega}} \simeq 0.28$ gives $|\theta_0| > 46^\circ$.

**Supercontinuum generation.** Experiments are carried out replacing the 50 mm lens with a 25 mm one. The pump is now focused in proximity of the input facet of sample 1 (Fig.5E) and a characteristic white plume is detected.

**FIG. 5.** Strong SHG conversion versus limited net conversion efficiency. (a), (b) Top view of pump and SHG signal scattered light. (c) Analysis of the scattered light versus propagation distance in the sample for different temperatures indicates a characteristic absence of propagation dynamics for the ferroelectric case ($T = T_C - 35K$, magenta full circles), for the Curie temperature on heating from the ferroelectric phase ($T_C^+$) and on cooling from the paraelectric phase ($T_C^-)$). (d) White-light linear scattering indicating GR behavior accompanied by propagation-direction-independent scattering from the body of the sample. (h) Evidence of supercontinuum generation (see Supercontinuum Generation Section in Methods).
[1] Armstrong, J. A., Bloembergen, N., Ducuing, J., & Pershan, P. S., “Interactions between Light Waves in a Nonlinear Dielectric,” Phys. Rev. 127, 1918 (1962).

[2] Loudon, R., The Quantum Theory of Light, 3rd ed., (Oxford Science Publications, 2010).

[3] Boyd, R.W., Nonlinear Optics, 3rd ed., (Academic Press, 2008).

[4] Pierangeli, D., Ferraro, M., Di Mei, F., Di Domenico, G., de Oliveira, C.E.M., Agranat, A.J., & DelRe, E. “Super-crystals in composite ferroelectrics,” Nat. Commun. 7, 10674 (2016).

[5] Wei, D., Wang, C., Wang, H., Hu, X., Wei, D., Fang, X., Zhang, Y., Wu, D., Hu, Y., Li, J., Zhu, S., & Xiao, M., “Experimental demonstration of a three-dimensional lithium niobate nonlinear photonic crystal,” Nat. Photon. 12, 596-600 (2018).

[6] Xu, T., Switkowski, K., Chen, X., Liu, S., Koykov, K., Yu, H., Zhang, H., Wang, J., Sheng, Y., & Krolkowski, W., “Three-dimensional nonlinear photonic crystal in ferroelectric barium calcium titanate,” Nat. Photon. 12, 591-595 (2018).

[7] Zhang, X., Yang, Q.X., Liu, H.L., Wang, X.P., Xu, T., Switkowski, K., Chen, X., Liu, S., Koynov, K., “Nonlinear Cherenkov difference-frequency generation exploiting birefringence of KTP,” Appl. Phys. Lett. 108, 031104 (2016).

[8] Chang, D. E., Vuleti, V. & Lukin, M. D. “Quantum nonlinear optics - photon by photon,” Nat. Photon. 8, 685-694 (2014).

[9] Shen, Y. R., The Principles of Nonlinear Optics (Wiley-Interscience, New York, 1984).

[10] Brown, E., McKee, T., d’Tomaso, E., Pluen, A., Seed, B., Boucher, Y., & Jain, R. K., “Dynamic imaging of collagen and its modulation in tumors in vivo using second-harmonic generation,” Nat. Med. 9, 796-800 (2003).

[11] Jelley, J.V., Cerenkov Radiation (Pergamon Press, 1958).

[12] Mathieu, E., “Conditions for quasi Cerenkov radiation, generated by optical second harmonic polarisation in a nonlinear crystal,” Journal of Applied Mathematics and Physics(ZAMP) 20, 433439 (1969).

[13] Tien, P. K., Ulrich, R., & Martin, J. “Optical second harmonic generation in form of coherent Cerenkov radiation from a thin-film waveguide,” Appl. Phys. Lett. 17, 447 (1970).

[14] Zhang, Y., Gao, Z. D., Qi, Z., Zhu, S. N., & Ming, N. B. “Nonlinear erenkov Radiation in Nonlinear Photonic Crystal Waveguides,” Phys. Rev. Lett. 100, 163904 (2008).

[15] Sheng, Y., Best, A., Butt, H.-J., Krolkowski, W., Arie, A., & Koykov, K. “Three-dimensional ferroelectric domain visualization by Cerenkov-type second harmonic generation,” Opt. Exp. 18, 16539 (2010).

[16] Sheng, Y., Kong , Q. , Roppo, V. , Kalinowski , K., Wang, Q., Cojocaru, C., & Krolkowski, W. “Theoretical study of eренkov-type second-harmonic generation in periodically poled ferroelectric crystals,” J. Opt. Soc. Am. B 29, 312-318 (2012).

[17] Roppo, V., Kalinowski, K., Sheng, Y., Krolkowski, W., Cojocaru, C., & Trull, J. “Unified approach to Cerenkov second harmonic generation,” Opt. Express 21, 25715-25726 (2013).

[18] Ni, R., Du, L., Wu, Y., Hu, X. P., Zou, J., Sheng, Y., Arie, A., Zhang, Y., Zhu, S. N., “Nonlinear Cherenkov interference-frequency generation exploiting birefringence of KTP,” Opt. Express 19, 10674 (2011).

[19] Reiserer, A., Kel, N., Rempe, G., & Ritter, S. “Quantum gate between a flying optical photon and a single trapped atom,” Nature 508, 241 (2014).

[20] Reiserer, A., Kel, N., Rempe, G., & Ritter, S. “Quantum gate between a flying optical photon and a single trapped atom,” Nature 508, 237 (2014).

[21] Kleinman, D. A., “Theory of Second Harmonic Generation of Light,” Phys. Rev. 128, 1761 (1962).

[22] Fejer, M. M., Magel, G. A., Jundt, D. H., & Byer, R. L., “Quasi-phase-matched second harmonic generation: tuning and tolerances,” J. Quant. Electron. 28, 2631-2654 (1992).

[23] Saltiel, S. M., Neshev, D. N., Krolkowski, W., Arie, A., Bang, O., & Kivshar, Y. S., “Multiorder nonlinear diffraction in frequency doubling processes,” Opt. Lett. 34, 848-850 (2009).

[24] Wang, J., Jin, K., Gu, J., Wan, Q., Yao, H., & Yang, G., “Direct evidence of correlation between the second harmonic generation anisotropy patterns and the polarization orientation of perovskite ferroelectric,” Sci. Rep. 7, 9051 (2017).

[25] Bor, Z., & Rcz, B., “Dispersion of optical materials used for picosecond spectroscopy,” Appl. Opt. 24, 3440-3441 (1985).

[26] Ayyoub, M., Imbrock, J., & Denz, C., “Second harmonic generation in multi-domain $\chi^2$ media: from disorder to order,” Opt. Express 19, 11340-11354 (2011).

[27] Roppo, V., Wang, W., Kalinowski, K., Kong, Y., Cojocaru, C., Trull, J., Vilaseca, R., Scalora, M., Krolkowski, W. & Kivshar, Y., “The role of ferroelectric domain structure in second harmonic generation in random quadratic media,” Opt. Express 18, 4012-4022 (2010).

[28] Suchowski, H., O’Brien, K., Wong, Z. J., Salamdrino, A., Yen, X., & Zhang, X. “Phase MismatchFree Nonlinear Propagation in Optical Zero-Index Materials,” Science 342, 1223-1226 (2013).

[29] Jankowski, M., Langock, C., Desiatov, B., Marandi, A., Wang, C., Zhang, M., Phillips, C. R., Lonar, M., & Fejer, M. M., “Ultrafast nonlinear optics in nanophotonic periodically poled lithium niobate waveguides,” Optica 7, 40-46 (2020).
[33] Canalias, C., & Pasiskevicius, V., “Mirrorless optical parametric oscillator,” Nat. Photon. 1, 459-462 (2007).
[34] Segal, N., Keren-Zur, S., Hendler, N., & Ellenbogen T., “Controlling light with metamaterial-based nonlinear photonic crystals,” Nat. Photon. 9, 180-184 (2015).
[35] Yariv, A., & Yeh P., Optical Waves in Crystals: Propagation and Control of Laser Radiation, (Wiley, 2002).

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**Competing Interests.** The authors declare that they have no competing financial interests.

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