Ambient-condition growth of high-pressure phase centrosymmetric crystalline KDP microstructures for optical second harmonic generation

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Noncentrosymmetric potassium dihydrogen phosphate (KH₂PO₄ or KDP) in the tetragonal crystal phase is arguably the most extensively studied nonlinear optical crystal in history. It has prolific applications ranging from simple laser pointers to laser inertial confinement fusion systems. Recently, type IV high-pressure KDP crystal sheets with a monoclinic crystal phase having centrosymmetric properties have been observed. However, it was found that this new crystal phase is highly unstable under ambient conditions. We report ambient-condition growth of one-dimensional, self-assembled, single-crystalline KDP hexagonal hollow/solid-core microstructures that have a molecular structure and symmetry identical to the type IV KDP monoclinic crystal that was previously found to exist only at extremely high pressures (>1.6 GPa). Furthermore, we report highly efficient bulk optical second harmonic generation (SHG) from these ambient condition–grown single-crystalline microstructures, even though they have a highly centrosymmetric crystal phase. However, fundamental physics dictates that a bulk optical medium with a significant second-order nonlinear susceptibility supporting SHG must have noncentrosymmetric properties. Laue diffraction analysis reveals a weak symmetry-breaking twin-crystal lattice that, in conjunction with tight confinement of the light field by the tubular structure, is attributed to the significant SHG even with sample volumes <0.001 mm³. A robust polarization-preserving effect is also observed, raising the possibility of advanced optical technological applications.

INTRODUCTION

The potassium dihydrogen phosphate (KH₂PO₄ or KDP) crystal is one of the most investigated optoelectronic materials in modern optical technology. Its unique piezoelectric, ferroelectric, and electro-optic properties are of great importance in fast, high-power electro-optical applications, and its birefringence and nonlinear optical properties have made KDP the general reference standard for optical-field polarization manipulation and frequency conversion (1–5). Over the years, large, high-quality KDP crystals (6) have been developed for large-scale, high-power laser applications, such as frequency up-conversion processes at the National Ignition Facility (7). However, the nonlinear optical properties of low-dimensional, self-assembled KDP crystals, which may lead to new physics and important applications in photonics technologies, have been largely overlooked. Here, we report novel properties of one-dimensional, self-assembled, highly stable single-crystalline KDP hexagonal microstructures grown through a nonequilibrium process (8). The novel and yet unknown ambient-condition nucleation mechanism and crystal growth dynamics generate superb high-quality, large length-to-radius ratio column surfaces. Using these novel microstructures, we demonstrate a highly efficient optical second harmonic generation (SHG) process with a robust polarization-maintaining effect (9). These discoveries pose many intriguing challenges to crystallography, materials science, chemical physics, and other research disciplines and may lead to opportunities for both fundamental research and applications in advanced nonlinear microphotonics.

RESULTS

Here, a supersaturated KDP solution at 43°C is evaporatively cooled at room temperature and pressure on a specially treated glass substrate, resulting in crystallization of KDP that rapidly self-assembles and grows in one dimension. The crystallization process typically finishes in about 20 min, and bundles of single-crystalline KDP hollow-core and solid-core microstructures become readily observable with a simple optical microscope. The microstructures typically have diameters ranging from less than 1 μm to a few tens of micrometers, and their lengths can be as long as a few millimeters [length-to-diameter ratios of 500:1 to 1000:1 are common (Fig. 1A)]. Scanning electron microscopy (SEM) images show that the surface profile of these microstructures is generally scalene hexagonal in shape (Fig. 1B), although there are also other shapes and forms due to the non-equilibrium growth process. Depending on the timing of sample extraction and ambient conditions, various hollow-core and solid-core microstructures can be readily and reliably produced and extracted for analysis.

KDP crystals are characterized by their polymorphisms, and to date, at least 13 polymorphs of KDP crystalline structures have been reported (1, 2). At room temperature, KDP crystals nucleate in supersaturated solutions predominantly in a tetragonal phase with a general morphology composed of a tetragonal prism ending with a tetragonal bipyramid (J). Here, x-ray diffraction (XRD) data of hexagonal-shaped KDP microstructures exhibit excellent single-crystalline characteristics, with a spectrum (Fig. 2, blue trace) and lattice parameters that are substantially different from the familiar XRD spectrum (Fig. 2, red trace) of the powder of the tetragonal phase of bulk KDP crystals. Structural analysis shows that these self-assembled quasi-one-dimensional hexagonal-shaped KDP microstructures belong to the monoclinic crystal family (monoclinic-prismatic) with centrosymmetric point symmetry
and space group $P2_1/c$. The crystal lattice parameters are $a = 14.598(5)$ Å, $b = 4.503(5)$ Å, and $c = 18.650(5)$ Å, with $\beta_{ab} = 90^\circ$, $\beta_{bc} = 90^\circ$, and $\beta_{ac} = 108.040(5)^\circ$. These are the exact molecular structure and packing parameters of the high-pressure (1.6 GPa) type IV KDP monoclinic crystal phase that was never known to crystallize under ambient conditions (10, 11). Note that the type IV KDP monoclinic crystals grown under extremely high pressures only form thin planar sheets, which are highly unstable and undergo phase transitions to the usual type I KDP phase (with a very different molecular structure and packing arrangement) when ambient pressure is restored (11, 12). However, the high-quality, one-dimensional, self-assembled single-crystalline KDP microstructures shown in Fig. 1B are very stable when exposed to dry air, suggesting very different and yet unknown nucleation and growth dynamics. Experimentally,
we found that these single-crystal KDP microstructures grow and self-assemble predominantly along their b axis (13). XRD data indicate with high accuracy that these KDP microstructures have centrosymmetric point symmetry. However, Laue diffraction also shows the presence of a very small fraction of an anisotropically distributed twin-crystal (TC) lattice [see the (hk0) plane of the reciprocal lattice in Fig. 3]. These self-assembled microstructures have hexagonal cross sections with high-quality side surfaces that extend more than a millimeter, indicating intriguing and yet unknown surface potential and chemical physics processes.

**DISCUSSION**

One of the motivations to develop microstructures with new molecular structures and packing arrangements, exotic shapes, and low dimensionality is to enhance our knowledge of nonlinear optics in these materials to facilitate novel device applications. Fundamental physics dictates that in a bulk optical medium, the molecular structure and packing arrangements must have noncentrosymmetric properties to give rise to a significant second-order nonlinear optical susceptibility (4, 5). Therefore, in dipole approximation, bulk nonlinear optical crystals with perfect centrosymmetry do not support SHG (4). Experimentally, however, we have observed highly efficient 532-nm SHG radiation by injecting continuous wave (CW) laser light (1 W) of a 1064-nm wavelength along the long axis of a microstructure. The SHG conversion efficiency observed in our system would surpass even the best results reported to date under identical pumping conditions when the length of the microstructures is scaled to that of the other systems reported (see Estimate of SHG efficiencies in Materials and Methods). This is quite remarkable for a material that has dominant centrosymmetric symmetry with a very small TC fraction (see discussion below).

Although SHG is strictly forbidden in materials with perfect centrosymmetric properties, SHG often arises from growth anomalies, even in very high-purity research-grade crystals where such anomalies and intra- or intermolecular charge transfer (14–16) can break the inversion symmetry, which results in a nonvanishing second-order susceptibility. Note that in low-dimensional structures, these anomalies become highly anisotropic. Here, we found that the highly efficient SHG can be attributed to the small fraction of an anisotropically distributed TC lattice, as exhibited in the (hk0) plane shown in Fig. 3. This growth anomaly weakly breaks the inversion symmetry, resulting in a small second-order susceptibility $\chi^{(2)}_{TC}$. Under the excitation of a pump field at frequency $\omega_1 = \omega_2 = \omega$, this leads to an effective nonlinear polarization (4) at the SHG frequency $2\omega = \omega_1 + \omega_2$ of

$$P(2\omega) = \chi^{(2)}_{TC} : E(\omega)E(\omega)$$

(1)

Although we believe that the TC lattice can satisfactorily explain our results, other weak symmetry-breaking mechanisms are also possible and will be investigated further. To measure SHG, we inject a CW pump light at 1064 nm through a microscope objective into the entrance of the microstructure. The SHG is collected at the exit of the microstructure using a microscope objective equipped with a 1064-nm filter and charge-coupled device (CCD) camera (see Materials and Methods). For the microstructures reported here, coherent propagation growth of the SHG is achieved by guided-wave mode enabled by total internal reflection (17), as in the case of step-index

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**Fig. 3. Reciprocal lattice and Laue diffraction pattern of single-crystalline KDP.** (A) (0kl) plane of tetragonal KDP crystal and the corresponding Laue diffraction pattern (shown for [001]). (B) (0kl) plane of a monoclinic single-crystalline KDP microstructure and the corresponding Laue diffraction pattern (shown for [001]; data taken from single-crystal diffractometer). (C) (hk0) plane showing the presence of TC lattice (see below the image) in monoclinic single-crystalline KDP microstructures, which breaks the inversion symmetry of the system, resulting in the observed strong SHG.
optical fibers. This mechanism spreads out the propagation \( k \) vector for both the fundamental and SHG fields without changing frequencies (see Discussion of phase matching mechanism in Materials and Methods). Furthermore, the enhancement effect resulting from strong spatial confinement also significantly increases the efficiency of the nonlinear frequency conversion process. This automatic, “quasi-random” phase matching mechanism can be thought of as spatially confined and enhanced quasi-random phase-matched lasing.

Figure 4 (A and B) shows two SHG intensity distributions across the exit facet of a hollow-core (Fig. 4A) and a solid-core (Fig. 4B) microstructure, supporting the guided-wave SHG mechanism described above. Clearly, the coaxially focused pump injection geometry and the lack of high-intensity regions on the wall surfaces for the fundamental wave preclude any efficient surface symmetry-breaking-based SHG (18) or evanescent wave leakage mode. Indeed, the lack of any appreciable light outside the structure and the highly concentrated intensity distribution within the wall (hollow-core) and fully SHG-filled cross section (solid-core) clearly underscores the bulk effect-based SHG optical guided-mode propagation, as described above.

![Image](image_url)

**Fig. 4.** Guided-wave propagation in a single-crystalline KDP hexagonal microstructure. (A and B) SHG intensity distribution across the exit facet of (A) a hollow-core microtube (nominal diameter, 15 μm; wall thickness, 3 μm) and (B) a solid-core microrod (nominal diameter, 25 μm). Note that the SHG light fills the entire solid core, indicating a transversely confined bulk SHG effect. Typically, the yield of solid-core structures is a factor of three to five times higher SHG than that of the hollow-core structures. (C) Very weak 532-nm light is transversely focused on the left end of a microstructure. (D) CCD image captured above the sample showing no leakage light for a large segment of the microstructure (the small green spot in the middle is from the microstructure holder). At the right end, a bright light spot represents the light propagated through the microstructure by guided mode, vividly demonstrating efficient guided-wave propagation.

Guided-wave propagation for the microstructure presented in Fig. 4C is shown in Fig. 4D, where the surface light leakage/scattering image is captured by a transversely positioned CCD camera. Here, we focus a weak 532-nm laser (for better imaging) transversely on the left end of the microstructure. This lateral injection geometry, which results from focusing, allows only a small amount of the 532-nm light to be coupled into the microstructure from the side surface. Note that after the initial scattering phase, the 532-nm light settles in a guided-mode mode wherein there is no light leakage on the side of the microstructure. This lateral injection geometry, which results from focusing, allows only a small amount of the 532-nm light to be coupled into the microstructure from the side surface. Note that after the initial scattering phase, the 532-nm light settles in a guided-mode mode wherein there is no light leakage on the side of the microstructure. This proves that the microstructure supports guided-wave propagation of the coupled light at 532 nm.

In Fig. 5 (top panel), we plotted SHG power measurements for two single-crystalline KDP microstructures with different nominal diameters as a function of pump power. The solid blue curve in Fig. 5A is the fit that uses \( P(k) = C_2 \cdot P(n_0) \), where \( P(k_0) \) and \( P(n_0) \) are the power of the SHG field and the pump field, respectively, with fitting parameter \( C_2 \approx \frac{1}{2} \). For the microstructure shown in Fig. 5A, we estimate a normalized conversion efficiency, \( \eta = \frac{P(k_0)}{P(n_0)} \approx 10^{-4} \) W\(^{-1}\) (see Materials and Methods). Similar efficiency is also obtained for the microstructure used in Fig. 5B. This is a markedly efficient frequency conversion process, given such a small interaction volume. This conversion efficiency is already on the same level as that of a bulk potassium titanyl phosphate (KTP) crystal (19) (which is more efficient than bulk KDP crystals), under the same CW excitation conditions (see Materials and Methods). In Fig. 5 (bottom panel), we display polarization measurements of the input (Fig. 5A, purple), the residual 1064-nm pump (Fig. 5B, red), and the 532-nm SHG (green, Fig. 5C, green) light at the exit facet of a microstructure. The orthogonal polarizations of the 1064-nm light and 532-nm light at the exit clearly indicate that coherent SHG light is generated through a type I phase-matched guided-mode propagation process (20). The polarization of the residual pump at the exit is always identical to that of the 1064-nm pump at the entrance, regardless of the length of the microstructure, indicating that there is no polarization rotation of the 1064-nm light by the microstructure. This polarization-maintaining effect arises from the fact that the hexagonal cross section is stretched along one diagonal direction (ratio of three distances between opposite planes parallel to the growth axis is approximately 1:1:0.8). This polarization-maintaining effect has not been observed with microstructures with the usual tetragonal crystal phase of KDP crystal because of their perfectly square cross section. This robust polarization-preserving effect is an important feature of this new single-crystalline KDP microstructure, which can be exploited for advanced optical communication technological applications.

To conclude, we have developed one-dimensional, self-assembled, single-crystalline KDP microstructures under ambient conditions having centrosymmetry, with the lattice constants identical to those of the previously known unstable high-pressure type IV KDP crystal phase. Our KDP microstructures have also been shown to support a highly efficient optical SHG process. Our work opens many intriguing and challenging questions about unit-cell nucleation and the physics of its growth dynamics. The understanding of the nonequilibrium growth mechanism may affect a broad spectrum of research fields, such as material science, chemical physics, crystallography, and nonlinear optics. With further technological refinements, these exotic single-crystalline KDP microstructures and other structures that use different single-crystalline materials may be directly grown on a silicon surface of a light-emitting
device, presenting application possibilities such as direct on-chip surface generation of entangled-photon pairs. These microstructures can also be coated with metallic/graphene layers and contact-bundled to form unique engineered super optical materials from which novel, robust, environmentally insensitive, highly efficient frequency up-conversion devices with excellent heat exchange capabilities can be fabricated for extremely high-power laser applications. It is also possible to embed atoms and even ions inside the hollow core of the microstructures, thereby creating a novel platform that may lead to a host of new phenomena that have a great deal of application potential in advanced nonlinear microphotonic technologies.

**MATERIALS AND METHODS**

**Material preparation and characterization**

We created single-crystal KDP microtubes and microrods using a supersaturated KDP solution at 43°C with a typical concentration of 35.97 g of KDP in 100 g of H₂O. The solution was taken from an ultrahigh-purity KDP solution tank used for growing high-quality products for extremely high power laser applications. The solution underwent constant and stringent impurity monitoring using multiple highly sensitive optical and mass spectroscopic analyses. The glass substrates were pretreated to remove surface dust and greasy residuals, and a supersaturated solution was placed onto the substrates and evaporated at room temperature and pressure (21). The initial nucleation is very rapid and has the characteristics of dendritic growth.

The new single-crystal structure has a monoclinic crystal phase and is characterized by its short b axis and long a and c axes, and it grows rapidly along its b axis. As a comparison, the commonly used bulk KDP crystals belong to the tetragonal crystal family with noncentrosymmetric point symmetry (4/2m) and space group I 4 2d (a = b = 7.45280 Å, c = 6.97170 Å; β_ab = β_ac = β_bc = 90°), and the growth is predominantly along the crystal's c axis. The new crystal crystallizes into a monoclinic structure from the edge of the droplet toward the center, where the abundance of materials, temperature gradient, thickness of the liquid drop, and other ambient conditions all play important roles in the diffusion-limited growth process. In the crystal growth phase, slight contact forces can easily break the monoclinic microstructures into small fragments. XRD confirms that these fragments have a single tetragonal phase as do normal bulk KDP crystals. This explains why the commonly used fast bulk KDP production protocols (6), where vigorous solution stirring is required, do not produce crystals with the molecular structure and crystalline phase reported in this work. The single-crystal KDP microstructures are stable when exposed to dry air, and the crystal growth process can be directly imaged and recorded in real time using a microscope equipped with a camera.

Single-crystal XRD and Laue diffraction analysis were carried out on a commercial diffractometer using graphite-monochromated MoKα radiation (λ = 0.71073 Å). The microstructure data were collected at room temperature (296 K). Data integrations, together with semiglobal unit-cell refinements, were performed using commercial software. The molecular structures and packing arrangements were

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**Fig. 5. Global quasi-type I phase-matched guided-wave SHG in single-crystalline KDP hexagonal microstructures with a robust polarization-maintaining effect.**

(A and B) SHG power P(2ω) as a function of the pump power P(ω) from microstructures of (A) d = 15 μm and L = 1 mm, and (B) d = 25 μm and L = 1.1 mm. The blue curve in (A) is the fit using P(2ω) = Cω2P(ω). (C) Linear polarization of the pump laser. (D) Polarization measurement of the residual 1064-nm pump at the exit of the microstructure. (E) Polarization measurement of the SHG at the exit of the microstructure. The orthogonal polarizations between the pump and SHG light at the exit indicate this as a type I phase-matched SHG generation process with guided-mode propagation of the SHG light.
obtained by direct computational methods and then refined using a full-matrix least-squares technique. For the purpose of comparison, XRD of fine-ground KDP bulk crystal and a group of monoclinic KDP single-crystal microstructures was performed using a different commercial powder x-ray diffractometer equipped with a diffracted beam monochromator set for CuKR radiation ($\lambda = 1.54056$ Å) in the 2θ range from 10° to 90°, with a step size of 0.0216048° and scan speed of 10°/min.

**Estimate of SHG efficiencies**

All microstructures used for SHG measurements have nominal diameters $\geq$10 μm. We measured SHG as follows:

(i) For the injection and collection efficiencies, we measured the 1064-nm pump power before and after the pump injection assembly to obtain its transmission loss. The collection efficiency was determined using the 532-nm light produced by a KTP crystal by measuring the 532-nm light intensity before and after the collection assembly to obtain the transmission loss of the collection assembly.

(ii) To estimate the microstructure’s entrance and exit loss, we injected a weak 1064-nm pump (below the SHG threshold) into a sample microstructure. The alignment of the injected light was optimized to maximize the exiting 1064-nm power, and from that, the microstructure injection efficiency was deduced. This step is important because the facets of the microstructure are neither cleaved nor polished. All filters were precalibrated at both 1064- and 532-nm wavelengths. In addition, the 532-nm output from the KTP crystal was measured with both a power meter and a CCD camera to calibrate these two light detection devices.

All optical measurements were carried out with a 1-W CW Nd: YVO$_3$ 1064-nm laser that was linearly polarized and had a beam diameter of 2 mm. A 100× microscope objective launched the pump field through the entrance facet of the microstructure. The entrance and exit facets of the microstructures were not cleaved, and this resulted in less than 20% coupling efficiency at each facet (a rough estimate). At the exit of the microstructure, laser-grade 1064-nm filters blocked the residual pump light, and the SHG light was collected and focused onto a CCD camera and a high-resolution power meter by a microscope objective (10× or 40×).

Using the data given in Fig. 5, we estimated the normalized conversion efficiency to be $\eta = P(2\omega)/P(\omega)^2 \approx 10^{-4}$ W$^{-1}$. Neglecting confinement and shape effects and assuming bulk crystal propagation (see below) with a nondoped pump (4), we also estimated $|\chi^{(2)}_{\text{TC}}| \approx 10^{-11}$ (electrostatic unit). This is about two orders of magnitude smaller than the corresponding second-order susceptibility of the commonly used noncentrosymmetric bulk KDP crystal (22) but is consistent with the assumption that the observed SHG effect arises from weak symmetry-breaking mechanisms, such as a TC in a predominantly centrosymmetric medium. As a comparison, under the same 1-W excitation condition, a periodically poled KTP crystal waveguide with $L = 19$ mm and an effective pump beam diameter, $d = 37$ μm, inside the waveguide has achieved an efficiency of $\eta \approx 8.3 \times 10^{-3}$ W$^{-1}$ (23).

The conversion efficiency of our system, when extrapolated to the length of 19 mm, would surpass even the best results available in literature. However, note that optical crystals with a monoclinic crystal phase are biaxial crystals, and the calculations of nonlinear optical properties are much more complex than the simple estimate that uses the bulk formula described above. Experimentally, however, it is almost impossible to accurately measure the dielectric tensor elements for samples that are tens of micrometers in diameter or size, even with the most advanced ellipsometric techniques or equipment. Indeed, state-of-the-art ellipsometric techniques require samples with at least a 1-mm$^2$ surface size because of diffraction resolution, diffraction efficiency, and signal discrimination considerations. This is the primary reason why no study of nonlinear optical crystals of micro or nano dimensions reports measurements (or attempted measurements) of dielectric tensor elements, which are required for any sensible numerical guided-wave simulation. Therefore, for microcrystals of lower symmetry such as ours, it is not possible to obtain elements of the dielectric tensor from SHG measurements, and therefore, a numerical simulation that requires accurate dielectric tensor elements is not attainable. Experimental observations of no-leakage light and measurements of input-output light intensity conversion provide, in the current ellipsometric measurement technology, sufficient criteria for validating the presence of highly efficient guided-wave SHG processes in these microstructures.

**Discussion of phase matching mechanism**

The polarization measurements shown in Fig. 5 clearly indicate that overall quasi–type I phase matching is the underlying mechanism for coherent SHG generation. Here, both the pump and SHG fields propagate in guided modes (24), just as in multimode fibers and waveguides (see Fig. 4D). The focused-injection fundamental wave launch geometry necessarily spreads the pump field $k$ vector that corresponds to the SHG field within the numerical aperture, resulting in an angularly distributed pump that guarantees that there will always be a certain portion of the pump that satisfies the type I phase matching condition. Because of this spread of $k$, only about 2% of the pump light effectively has the right $k$ for efficient phase matching inside the microstructure, which, on average, results in an “effective quasi–phase matching.” This further shows the unusual SHG conversion efficiency demonstrated in our work and the great application potential of the low-dimensional KDP microstructures. Note that this spread in $k$ and effective quasi–phase matching indicate that frequency doubling at other wavelengths using the same KDP microstructure without a specific entrance-surface angle cut is possible.

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**Acknowledgments:** We thank W.-T. Yu of the State Key Laboratory of Crystal Materials of Shandong University for discussions and B. Wang for providing high-purity KDP solution. L.D. also thanks W. R. Ganett of the University of Tennessee for discussions on random phase matching. **Funding:** Y.R. was financially supported by the Natural Science Foundation of Shandong Province (ZR2015EM001) and the Foundation of State Key Laboratory of Crystal Materials of China. **Author contributions:** L.D. and E.W.H. conceptualized the idea and proposed the research. L.D. designed and supervised experiments. Y.R. performed all experimental measurements. X.Z. carried out part of the calculations. Y.R., X.Z., L.D., and E.W.H. discussed the results. L.D. and E.W.H. wrote the manuscript, and all authors contributed to the revision. **Competing interests:** The authors declare that they have no competing interests. **Data and materials availability:** All data needed to evaluate the conclusions in the paper are presented in the paper. The crystallographic information file of KDP microstructures has been deposited in the FIZ Karlsruhe Inorganic Crystal Structure Database (ICSD) with CSD number 427178 (http://fiz-karlsruhe.de/icsd.html). Additional data related to this paper may be requested from Y.R. (ry@sdu.edu.cn).

Submitted 9 March 2016
Accepted 29 July 2016
Published 26 August 2016
10.1126/sciadv.1600404

**Citation:** Y. Ren, X. Zhao, E. W. Hagley, L. Deng, Ambient-condition growth of high-pressure phase centrosymmetric crystalline KDP microstructures for optical second harmonic generation. Sci. Adv. **2**, e1600404 (2016).