MXene-Derived Ferroelectric Crystals

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This study demonstrates the first synthesis of MXene-derived ferroelectric crystals. Specifically, high-aspect-ratio potassium niobate (KNbO₃) ferroelectric crystals is successfully synthesized using 2D Nb₂C, MXene, and potassium hydroxide (KOH) as the niobium and potassium source, respectively. Material analysis confirms that a KNbO₃ orthorhombic phase with *Amm2* symmetry is obtained. Additionally, ferroelectricity in KNbO₃ is confirmed using standard ferroelectric, dielectric, and piezoresponse force microscopy measurements. The KNbO₃ crystals exhibit a saturated polarization of $\approx 21 \mu\text{C cm}^{-2}$, a remnant polarization of $\approx 17 \mu\text{C cm}^{-2}$, and a coercive field of $\approx 50 \text{ kV cm}^{-1}$. This discovery illustrates that the 2D nature of MXenes can be exploited to grow ferroelectric crystals.

Transition metal carbides, carbonitrides, and nitrides (MXenes) have a general formula of $\text{M}_{n+1}\text{X}_n\text{T}_x$ ($n = 1-3$), where M represents an early transition metal (such as Sc, Ti, Zr, Hf, V, Nb, Ta, Cr, or Mo, among others), X is carbon and/or nitrogen and T_x represents surface terminations (for example, hydroxyl, oxygen, or fluorine).^[1] With wide chemical and structural variety, MXenes, including Ti_2CT_x , V_2CT_x , and Nb_2CT_x etc., have evidenced significant promise for energy storage applications.^[2-4] In addition, MXenes have immense potential in many applications, such as water purification,^[5] reinforcement in nanocomposites,^[6] gas- and biosensors,^[7,8] and photothermal therapy.^[9] However, researchers have not sufficiently explored the potential for MXenes in electronic applications. The present study reveals the excellent versatility of MXenes by demonstrating that their 2D character can be exploited to grow ferroelectric crystals.

To determine the feasibility of deriving ferroelectrics from MXenes, we chose to synthesize KNbO₃, which has several interesting properties and potential applications. Such applications include ferroelectric devices,^[10] optical waveguides,^[11] holographic storage systems,^[12] biocompatible transducer,^[13] and other electronic devices.^[14-17] At room temperature, KNbO₃ has an orthorhombic crystal structure that lacks a center of symmetry, hence exhibits ferroelectricity at ambient temperatures. Moreover, KNbO₃ is lead free, which makes it an environmentally friendly alternative to lead-based ferroelectrics.^[13] The

massive potential of KNbO₃ has stimulated research on the synthesis of powder, nanorods, nanowires, and films by solid-state reaction,^[18] a sol-gel process,^[19] hydrothermal treatment,^[20-22] and other means.^[23] However, no work explored the synthesis of ferroelectric KNbO₃ crystals with a large aspect ratio, which could significantly prompt the development of nano-electromechanical systems.^[21] Furthermore, KNbO₃ crystals that possess high aspect ratio structures could be suitable for utilization in integrated photonics, given that increasing the crystalline size is essential to maximize the electro-optic response.^[24] Compared to polycrystalline

perovskite materials, high aspect ratio crystalline perovskite thin films or crystals can dramatically reduce charge recombination, which would improve efficiency of perovskite oxides in some applications.^[25,26]

This work details the first use of 2D Nb₂C MXene and a hydrothermal method to synthesize KNbO₃ crystals that possess robust ferroelectric properties. Thin-layered KNbO₃ crystals were fabricated by selective etching of the Nb₂AlC MAX phase, followed by simultaneous oxidation and alkalization processes of the HF-etched Nb₂C MXene phase. The orthorhombic crystal structure of KNbO₃ was confirmed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). A ferroelectric tester was used to evaluate the existence of switching polarization in the KNbO₃ crystals, and well-defined piezoresponse force microscopy (PFM) amplitude butterfly loops and 180° phase switching further corroborated the robust ferroelectricity.

Figure 1a shows a schematic of the synthesis process used to derive KNbO₃ crystals from Nb₂C MXene. The methods section describes the solid-liquid reaction that was used to prepare the parent Nb₂AlC MAX phase. After this reaction, Nb₂C MXene phase was synthesized by selectively etching the Al layer from the pristine Nb₂AlC phase using HF acid according to previously established protocols.^[4,27] Finally, KNbO₃ crystals were fabricated via a hydrothermal method which consisted of oxidation and alkalization of Nb₂C MXene in a mixed solution of potassium hydroxide (KOH) solution and sodium dodecyl sulfate (SDS) surfactant (see the Experimental Section for details). **Figure 1b** schematically summarizes this Nb₂C to KNbO₃ phase transformation process.

Figure 2b depicts a scanning electron microscopy (SEM) of the accordion-like nanostructure, which indicates the successful synthesis of Nb₂C MXene from the densely packed Nb₂AlC MAX phase (**Figure 2a**), which was additionally confirmed by the XRD patterns in **Figure 2c**. The high-resolution X-ray photoelectron spectroscopy (XPS) analysis of Nb₂C MXene is shown in **Figure S1a-c** in the Supporting Information. **Figure S1b** in

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Figure 1. a) Crystal structures of the initial Nb₂AlC MAX phase, Nb₂C MXene after etching out Al, and MXene-derived KNbO₃ ferroelectric crystals (M-KNbO₃). b) Schematic illustrating the oxidation of Nb₂C MXene by OH⁻ to form various intermediate textured niobium oxides, alkalinization of Nb_xO_y by K⁺, and the final product (KNbO₃ orthorhombic crystals).

the Supporting Information illustrates that the Nb 3d peak can be fitted with six symmetric peaks at 203.8, 204.4, 206.5, 207.0, 207.8, and 209.8 eV, which correspond to Nb-C 3d_{5/2}, NbC_xO_y 3d_{5/2}, Nb-C 3d_{3/2}, Nb(V) 3d_{5/2}, NbC_xO_y 3d_{3/2}, and Nb(V) 3d_{3/2},^[28] respectively. The oxygen signal mainly originates from the intercalated water, surface oxidation, and surface functional groups.

To gain insight into the phase evolution process during the reaction, intermediate products obtained after different reaction times were collected and analyzed by XRD. Figure 2c–f depicts the XRD patterns of products obtained after hydrothermal reaction times ranging from 0 to 48 h. Figure 2c illustrates that the (002) peak of Nb₂C MXene is significantly shifted to the lower 2θ position, which signals expanded interlayer spacing. Previous work has also found the presence of niobium carbide

(NbC) impurity.^[4] After the hydrothermal treatment in the KOH aqueous solution, the Nb₂C MXene could be completely converted into KNbO₃ crystals. As Figure 2d displays, after 12 h of hydrothermal reaction time, the hydroxyl groups first oxidized the Nb₂C MXene to niobium oxides that include NbO, Nb₂O₃, NbO₂, and Nb₂O₅. Subsequently, in the alkalinization process, K⁺ reacted with the oxides, which initiated the formation of the KNbO₃ phase.^[29,30] Figure 2e shows that the product that was obtained after 24 h of reaction time consists of NbO and KNbO₃, which indicates that the oxidation and alkalinization reactions favor the formation of KNbO₃. Figure 2f illustrates that only pure KNbO₃ was observed after 48 h of hydrothermal reaction. For comparison, we synthesized KNbO₃ crystals using commercial, nonlayered NbC powder (Figure S2a, Supporting Information) and KOH as precursors, and SDS as surfactant.

Figure 2. a) A SEM image of the Nb₂AlC MAX phase. b) A SEM image of the Nb₂C MXene phase. c) XRD pattern of the Nb₂AlC MAX phase and the Nb₂C MXene. X-ray diffraction patterns obtained after different hydrothermal reaction times: d) 12, e) 24, and f) 48 h.

The SEM images reveal cube-like morphology of nonuniform size for the KNbO₃ products (Figure S2b, Supporting Information), which lack the highly textured morphology of MXene-derived KNbO₃. In addition, we have investigated the morphologies of intermediate products obtained during the hydrothermal synthesis of M-KNbO₃. Figure S2c in the Supporting Information shows an optical image of a single monoclinic Nb₂O₅ crystal (*P* 2/*m*) and hexagonal NbO₂ (*P*6₃/*mmc*) crystal, which both inherit the 2D character of the Nb₂C MXene flake. Thus, we believe that both oxidation and alkalization are initiated on the Nb₂C MXene substrates. In order to investigate the effect of SDS on the morphology of M-KNbO₃ crystals, we synthesized crystals under the same conditions without adding SDS surfactant. The final products turn out to be irregular crystals as shown in Figure S2d in the Supporting Information. Furthermore, only needle-like or rod-like KNbO₃ crystals have been hydrothermally synthesized by using Nb₂O₅, KOH as precursors,^[31] even when adding SDS as surfactant.^[20] These results indicate that the successful synthesis of symmetrically-shaped, large-sized, and *c*-axis oriented KNbO₃ crystals is possible thanks to the 2D character of MXene flakes and shape-determining effect of SDS. For the first time, we produce such large KNbO₃ crystals by hydrothermal synthesis with uniform shape, which makes them useful for practical electro-optic applications.

The SEM image in Figure 3a displays the morphology and size of optimized MXene-derived KNbO₃ (M-KNbO₃) crystals (obtained using Nb₂C MXene, KOH as precursors, and SDS as surfactant at 48 h hydrothermal reaction time), which have an average width of 15 μm and average length of 30 μm. The atomic force microscopy (AFM) image in Figure 3b depicts the surface morphology of a 10 nm thick M-KNbO₃ crystals. The average thickness of M-KNbO₃ crystals is ≈200 nm (Figure S3,

Supporting Information). Furthermore, scanning transmission electron microscopy (STEM) elemental mapping reflects a homogeneous elemental distribution of K, Nb, and O in the M-KNbO₃ crystal (Figure 3c). In addition, the XRD shown in Figure 3d verifies the orthorhombic structure of the M-KNbO₃ phase. Figure 3e shows the Raman spectrum of M-KNbO₃ crystals, which exhibits strong peaks at 607 and 827 cm⁻¹ that can be assigned to the A₁-ω_{TO4} mode and A₁-ω_{LO4} mode, respectively. The additional peaks at 187, 190, 283, 290, and 511 cm⁻¹ can be respectively assigned to the vibrational modes B₁-ω_{TO1}, A₁-ω_{TO1}, A₂, A₁-ω_{TO2}, and B₂-ω_{TO3}.^[32] Figure 3f provides the UV-vis absorption spectrum of M-KNbO₃ crystals dispersed in ethanol. Strong absorption clearly occurs at a wavelength of about 305 nm, and there are no other obvious absorption bands in the whole wavelength range (200–800 nm). The bandgap of M-KNbO₃ crystals is estimated to be 4.06 eV from the onset of absorption, which is higher than that of KNbO₃ cubes (≈3.14 eV).^[33] The combined action of size and surface effect result in a blue shift of optical absorption that leads to larger energy gap. The inset in Figure 3f displays the photoluminescence (PL) spectrum of the M-KNbO₃ crystals, which exhibit a visible light emission peak at 545 nm (2.27 eV). Since the bandgap of M-KNbO₃ crystals is ≈4.06 eV, we can conclude that the light emissions that were observed from 500 to 600 nm are not caused by a direct electron transition between the valence and conduction bands. Researchers have found similar results in KNbO₃ nanowires and LiNbO₃ crystals.^[34,35] The luminescence of LiNbO₃ can reportedly be ascribed to the recombination of electrons captured by Nb⁵⁺ ions and holes captured by oxygen, and both site niobium (occupying the position of Nb) and antisite niobium (occupying the position of Li) are responsible for the main emission in LiNbO₃. It is well-known that thinner crystals correspond to higher surface-to-volume ratio

Figure 3. a) Scanning electron microscopy image and b) atomic force microscopy image of M-KNbO₃ crystal. c) Scanning transmission electron microscopy image of KNbO₃ crystal, which indicates the elemental distribution in the M-KNbO₃ crystal. d) XRD pattern and e) Raman spectrum of M-KNbO₃ crystals. f) The UV-vis absorbance of M-KNbO₃ crystals in alcohol. Inset: Photoluminescence spectrum of M-KNbO₃ crystals. g) High-resolution TEM image of M-KNbO₃ crystals. Inset i): Selected area electron diffraction pattern taken along the [001] direction of a crystal, which signifies the formation of the orthorhombic phase. h) A high-magnification HRTEM image of M-KNbO₃ crystal. i) Simulated image for calculating the defocus value based on (h). j) The contrast transfer function (CTF)-corrected HRTEM image of M-KNbO₃. Inset i): Atomic arrangement of K, Nb, and O.

and higher concentration of surface oxygen vacancies. Therefore, it is likely that the emission band centered at a wavelength around 545 nm of M-KNbO₃ crystals can be derived from oxygen vacancies, the site niobium, and antisite niobium.

Figure 3g presents a high-resolution transmission electron microscopy (HRTEM) image that was captured along the [001] direction of the M-KNbO₃ crystal after an accurate calibration of sample motion. A high-magnification HRTEM image (Figure 3h) and its contrast transfer function (CTF)-calibrated image (Figure 3i) were compared to calculate the defocus value of the objective lens (−70 nm), which was used to calibrate the HRTEM image in Figure 3g. The HRTEM image of the crystal after defocus calibration (Figure 3j) shows the atomic

arrangement of an M-KNbO₃ crystal, which is indicative of the orthorhombic crystal structure of the M-KNbO₃ crystals. Notably, several areas on the same crystal were selected to perform electron diffraction, and all patterns contain one single orthorhombic reciprocal lattice, which evidences the formation of a single KNbO₃ crystal (Figure S4, Supporting Information).

The results of this study confirm that the crystal structure of M-KNbO₃ is orthorhombic, so M-KNbO₃ should be ferroelectric at room temperature. To perform ferroelectric measurements, Pt/M-KNbO₃/Pt two-terminal devices were fabricated by a focused ion beam (FIB) microscope. Figure 4a offers the current density versus electric field (*J*–*E*) curve of a Pt/M-KNbO₃/Pt device, which reflects a switching current density when

Figure 4. Ferroelectric measurement of M-KNbO₃ crystals. a) The J - E loop of a Pt/M-KNbO₃/Pt device measured with an electric field ranging from -50 to 50 kV cm⁻¹. b) The C - E loops of Pt/M-KNbO₃/Pt device measured with an electric field ranging from -50 to 50 kV cm⁻¹ and an AC voltage of 200 mV. c) The ferroelectric hysteresis loop of an M-KNbO₃ crystal measured over the same electric field. d) The corresponding PFM phase (dark cyan) and amplitude (orange) hysteresis loops during the switching process.

electric field is swept at ± 50 kV cm⁻¹. Figure 4b provides the capacitance versus electric field (C - E) curve of the Pt/M-KNbO₃/Pt device, which presents typical butterfly-type hysteresis over the same electric field range at the frequency of 10 Hz. Both J - E and C - E curves indicate switchable polarization in the M-KNbO₃ crystals. Furthermore, ferroelectric hysteresis loops were measured from the same device at 10 Hz as shown in Figure 4c.^[36,37] Evidently, M-KNbO₃ exhibits well-saturated ferroelectric hysteresis loops with a saturation polarization (P_s) of ≈ 21 $\mu\text{C cm}^{-2}$, a remnant polarization (P_r) of ≈ 17 $\mu\text{C cm}^{-2}$, and a coercive field (E_c) of ≈ 50 kV cm⁻¹. The remnant polarization of M-KNbO₃ crystal is close to the best result reported for ceramic KNbO₃ (≈ 18 $\mu\text{C cm}^{-2}$)^[18] (Table S1, Supporting Information). Piezoresponse force microscopy measurements were performed to further verify the existence of ferroelectricity in M-KNbO₃ crystals (Figure 4d). We conducted local switching tests by applying a bias between the conductive PFM tip and the platinum-coated silicon substrate. The well-defined butterfly loops of the PFM amplitude signals and the distinct 180° switching of the phase signals further corroborate the presence of ferroelectricity in M-KNbO₃ crystals. Compared to randomly oriented polycrystalline materials, layer structured ferroelectrics are preferred for ferroelectric and piezoelectric applications due to their lower anisotropy and larger number of permissible orientations for the spontaneous polarization.^[38,39] Templated grain growth is one of the promising routes for fabricating textured ferroelectric ceramics with improved functional properties.^[40] The platelet-like MXene-derived KNbO₃ crystals

reported here can be used to fabricate textured KNbO₃ ceramics with advanced ferroelectric, piezoelectric, and dielectric properties due to their high aspect ratio and robust ferroelectricity.

To summarize, we have demonstrated that 2D MXenes can be utilized as precursors to synthesize ferroelectric single crystals for the first time. As an example, we synthesized orthorhombic KNbO₃ ferroelectrics from Nb₂C MXene. Materials and electrical characterization confirm the crystal structure and ferroelectricity of KNbO₃. The MXene-derived KNbO₃ crystals exhibit a saturation polarization, a remnant polarization, and a coercive field of ≈ 21 $\mu\text{C cm}^{-2}$, ≈ 17 $\mu\text{C cm}^{-2}$, and ≈ 50 kV cm⁻¹, respectively. Our discovery illustrates that the 2D character of MXene can be exploited to grow ferroelectric crystals with specific orientations.

Experimental Section

Synthesis of Nb₂AlC: Nb₂AlC powders were synthesized by mixing powders of niobium (Alfa Aesar, 325 mesh, 99.8%), aluminum (Sigma Aldrich, 325 mesh, 99.5%), and graphite (Sigma Aldrich, 300 mesh, 99.99%) in a molar ratio of 2.0:1.1:1.0, respectively. The powders were further ball-milled at 100 rpm for 18 h. The mixture was pressed into a cube and then heated in a tube furnace to 1600 $^\circ\text{C}$ at a heating rate of 5 $^\circ\text{C min}^{-1}$ under a flow of Ar. The powder was then soaked at that temperature for 4 h. After cooling the furnace to room temperature, lightly sintered blocks were obtained. The powders were then sieved, and only ≤ 45 μm powders were used for further experiments.

Synthesis of Nb₂C MXene: 1 g of the obtained Nb₂AlC MAX powders was immersed in 10 mL of 48% concentrated HF solution and stirred

for 48 h at 55 °C. After the HF treatment, the resulting suspension was washed with deionized water and centrifuged (4,500 rpm for 3 min) to separate the settled powders from the supernatant. The washing process was repeated until the pH of the supernatant increased to ≈6. The settled powders were then removed from vials with ethanol and dried at 80 °C in the vacuum oven.

Synthesis of MXene-Derived KNbO₃ Crystals: For typical synthesis of orthorhombic M-KNbO₃ crystals, 420 mg of Nb₂C MXene powder was added into a 30 mL aqueous solution of 18 g of KOH (Sigma Aldrich, >85%). After vigorous stirring for 30 min at 50 °C, 4.33 g of SDS (Fisher Scientific, 99%) surfactant was added, then the reaction mixture was subsequently sealed in a 45 mL Teflon-lined stainless-steel autoclave (4744 General Purpose Autoclave, Parr Instrument Company, Illinois, USA) and heated at 190 °C under the autogenerated pressure for 0 to 48 h. After cooling to room temperature, the products were washed several times with distilled water and ethanol and then dried at 80 °C for 12 h in the vacuum oven. In comparison, 440 mg of commercial NbC (Alfa Aesar, 99%) powder was selected to conduct the same hydrothermal process as Nb₂C MXene to synthesize KNbO₃ crystals.

Equipment and Characterization: The morphology and structure of Nb₂C MXene were studied through SEM (Zeiss Merlin), XRD (Bruker D8 Advance and Bruker D8 Venture), and XPS (Amicus), respectively. The crystal structure of MXene-derived KNbO₃ crystals was investigated with XRD and HRTEM. HRTEM images were obtained by merging 80 frames exposed in 2 s (40 frames s⁻¹) after accurate sample motion calibration. A high-magnification HRTEM image and its CTF-calibrated image was compared to calculate the defocus value of objective lens (−70 nm), which was used to calibrate and obtain the HRTEM image with atomic resolution. Raman spectroscopy was performed on a Horiba LabRAM HR Raman Microscope with 660 nm laser excitation, while the morphology of MXene-derived KNbO₃ crystals was investigated with SEM (Zeiss Merlin) and AFM (Asylum research, MFP-3D model). The capacitance versus voltage (C–V) curves were measured with an Agilent LCR meter (4980A), whereas the current versus voltage (I–V) switching current loops were measured with an Agilent B1500A system. The hysteresis loops were measured with a commercial ferroelectric tester (Radiant Technologies, Inc. Precision Premier 200V ferroelectric test system). PFM measurements were carried out on the M-KNbO₃ crystals by applying a bias between the conductive PFM tip and the platinum-coated silicon substrate (Asylum research, MFP-3D model). The switching spectroscopic loops were recorded under resonance-enhanced PFM mode by applying an alternating current (AC) electric field superimposed on a direct current (DC) triangle saw-tooth waveform.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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