Photoluminescent Ferroelectric LiNbO₃ Crystals Grown from MXenes

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MXenes have recently been used to grow highly textured potassium niobate ferroelectric crystals. Herein, the versatility of MXenes is further demonstrated by growing ferroelectric and luminescent lithium niobate (LiNbO₃) crystals from niobium carbide MXene (Nb₂CT_x). The formation of high-aspect-ratio LiNbO₃ rhombic crystals was confirmed by extensive structural analysis. The ferroelectricity of MXene-derived LiNbO₃ was verified, using standard ferroelectric, dielectric measurements. In addition, for the first time, we synthesized Pr³⁺-doped LiNbO₃ crystals with simultaneous visible photoluminescence (PL) from Nb₂CT_x MXene. Our work demonstrates that it is possible, by using the two-dimensional (2D) character of MXenes, to fabricate high aspect ratio and well-oriented photoluminescent ferroelectric crystals for advanced optoelectronic applications.

1. Introduction

MXenes constitute a new family of 2D- transition metal carbides, carbonitrides and nitrides with a general formula of $M_{n+1}X_nT_x$ ($n = 1-3$), where M represents an early transition metal (such as Ti, Zr, V, Nb, etc.), X is a carbon and/or nitrogen atom, and T_x is a combination of surface terminations (i.e., OH, O, and F)^[1]. MXenes have shown great potential for various applications including energy storage systems^[2-4], electromagnetic shielding^[5], reinforcement in nanocomposites^[6], water splitting^[7], plasmonics^[8,9], and gas-biosensors^[10]. However, their use for electronic and optical applications are mainly limited to the most mature MXenes (i.e., $Ti_3C_2T_x$). Recently, we used the 2D morphology of a lesser-known MXene, i.e., Nb_2CT_x , to synthesize nanoplates of potassium niobate ($KNbO_3$) ferroelectric crystals.^[11] In the present study, we further verify the feasibility and generality of our proposed method by successfully synthesizing Nb_2CT_x -derived plate-like $LiNbO_3$ crystals with robust ferroelectricity. In addition, we further expand the versatility of Nb_2CT_x MXenes by synthesizing well-oriented photoluminescent $LiNbO_3:Pr^{3+}$ crystals.

Over the past decades, $LiNbO_3$ has garnered significant interest from materials scientists because of its remarkable ferroelectricity, high Curie temperatures, excellent photorefractive and photovoltaic properties, and large electro-optic and acousto-optic coefficients. As a human-made material, it has a rather wide range of applications in actuators^[12-13], nonvolatile holographic storage^[14], acoustic tweezers^[15], waveguides^[16], and many more. The massive potential of $LiNbO_3$ has stimulated research on the synthesis of ceramics^[17], nanoparticles^[18], and films^[19]. However, the synthesis of plate-like $LiNbO_3$ ferroelectric crystals by hydrothermal method has not yet reported. Such method mostly gives irregularly-shaped crystals with little control over their

morphology. LiNbO_3 crystals are particularly interesting because they can be integrated with semiconductor electronics and optoelectronics devices. MXene-based well-orientated $\text{LiNbO}_3\text{:RE}^{3+}$ crystals would find many applications, such as waveguide lasers^[20], mechano-luminescence^[21-22], and upconversion light emission^[23].

In this study, we illustrate the preparation of plate-like textured LiNbO_3 crystals, using accordion-like Nb_2CT_x MXene as a precursor. The trigonal crystal structure (space group $R3C$) of the MXene-based LiNbO_3 (M-LN) was verified by both X-ray diffraction (XRD) analysis, and selected- area electron diffraction (SAED), in conjunction with high-resolution transmission electron microscopy (HRTEM). The robust ferroelectricity of M-LN was confirmed by the existence of a switching phase and a polarization. Furthermore, well-orientated photoluminescent MXene-based $\text{LiNbO}_3\text{:Pr}^{3+}$ (M-LN: Pr^{3+}) crystals were synthesized, following a unique chemical process.

2. Results and Discussion

Figure 1. a) Schematic illustration of the preparation of M-LN crystals using Nb₂AlC as precursor. b) Crystal structures of the Nb₂CT_x MXene, intermediate products Nb_xO_y, and the final product M-LN.

Figure 1a illustrates the synthesis process of Nb₂CT_x-based LiNbO₃ crystals. Ascribed to the weak Al-related binding energy in the Nb₂AlC MAX phase^[24], Al atoms were selectively etched using a specific acid (e.g. HF) to prepare Nb₂CT_x MXene, which was then used to fabricate the final product, i.e. LiNbO₃ crystals. Figure 1b shows the crystal structures of the reactant Nb₂CT_x MXene, intermediate products niobium oxides (Nb_xO_y), and the final product LiNbO₃, respectively. This was achieved by first oxidizing Nb₂CT_x MXene flakes in a LiOH aqueous

solution to form various types of niobium oxides, which we subsequently alkalinized to a Li^+ ions in the final M-LN crystals.

Figure 2. a) A SEM micrograph of the Nb_2CT_x MXene. b) HRTEM image and c) selected area electron diffraction of NbO crystal taken along $\langle 001 \rangle$ zone axis. d) XRD patterns of Nb_2AlC MAX phase and Nb_2CT_x MXene. XRD patterns of final products after e) 24 hours, f) 96 hours chemical reaction.

Figure 2a shows the layered morphology of Nb_2C MXene obtained by etching out the Al layer from the Nb_2AlC MAX phase (Figure S2a). Compared with the XRD patterns of the Nb_2AlC MAX phase, the 2θ value of the characteristic (002) peak of Nb_2CT_x MXene shifts from 13° to 5° , indicating an increase of the d-spacing in the Nb_2CT_x MXene phase due to the removal of Al atoms (Figure 2d). The XRD analysis also shows the existence of NbC impurities in the obtained Nb_2CT_x MXene^[1], X-ray photoelectron spectroscopy (XPS) imaging of Nb_2CT_x (Figure S1a-c) confirms the existence of functional groups on the MXene surface (e.g. $-\text{O}$, $-\text{OH}$)^[25]. An analysis of the X-

ray diffraction patterns of the products under different lengths of reaction time (Figures 2e-f) is performed in order to investigate the process of hydrothermal chemical reaction. For the 24 h-reaction group, the characteristic peaks of NbC, NbO, Nb₂O₅ and LiNbO₃ were observed, which clearly conveyed that the Nb₂CT_x MXene was first oxidized to niobium oxides on the way to form LiNbO₃ crystals (Figure 2e). The existence of niobium oxides was further confirmed by electron microscopy characterization. Figure 2b shows a high resolution transmission electron microscopy (HRTEM) image of cubic NbO phase, and Figure 2c confirms its Pm-3m symmetry^[26] by selected area electron diffraction (SAED) pattern taken along the <001> zone axis. In addition, Figure S2b-c indicate the HRTEM image and SAED of a monoclinic Nb₂O₅ crystal (C 2/m)^[27]. For the 96 h-reaction group, only characteristic XRD peaks of LiNbO₃ crystals were detected in the final product (Figure 2f). It is worthy to note that both NbO and Nb₂O₅ inherit the two-dimensional character of Nb₂CT_x, which indicates that the oxidation initialed on the MXene flakes. Furthermore, we found out that both the two-dimensional character of Nb₂CT_x MXene and sodium dodecyl sulfate (SDS) surfactant played critical roles in the nucleation and growth of high aspect ratio LiNbO₃ crystals during the experimental process. Figure S2d-f present the final products obtained by using NLS (commercial NbC powder, LiOH, and SDS), ML (MXene and LiOH), and MLS (MXene, LiOH, and SDS) as reaction combinations, respectively. Figure S2d shows that only rhombic-like LiNbO₃ crystals were derived from the NLS reaction combination, while irregular products were obtained from the ML group (Figure S2e). Only in the case of MLS mixture, the final product presented to be symmetric shaped and large sized LiNbO₃ crystal.

Figure 3. a) A SEM image, b) XRD pattern, c) Raman spectrum, and d) HRTEM image of M-LiNbO₃ crystals. e) SAED pattern and f) Computed SAED pattern taken along the [100] direction of M-LiNbO₃ crystals.

Figure 3a displays a SEM image of typical Nb₂CT_x-derived LiNbO₃ (M-LiNbO₃) crystals obtained using MLS reactants and for a reaction time of 96 hours. Figure S3 shows the average size (25 μm * 40 μm) and thickness (150 nm) of M-LN crystals. LiNbO₃ crystals are expected to have a R3C symmetry at room temperature, which is verified by XRD analysis (Figure 3b^[28]). The microstructure of M-LN crystals was further investigated using electron microscopy. Figure 3d shows a high resolution TEM image of a [100] oriented M-LN crystal ($c = 13.86 \text{ \AA}$), and Figures e-f respectively represent the experimental and computed selected area electron diffraction pattern along the same [100] direction, which further confirms the rhombic crystal structure of the M-LN crystals^[28]. Figure 3c displays the Raman spectrum of M-LN crystals, the strong peaks at 149 cm⁻¹, 234 cm⁻¹, and 624 cm⁻¹ can be assigned to the E_{TO1} mode, E_{TO2} mode, and E_{TO9} mode, respectively. The additional peaks at 255 cm⁻¹, 271 cm⁻¹, 316 cm⁻¹, 333 cm⁻¹, 367 cm⁻¹, 432 cm⁻¹,

and 576 cm^{-1} respectively correspond to the modes of E_{TO3} , $A_{1(TO2)}$, E_{TO4} , $A_{1(TO3)}$, E_{TO5} , E_{TO7} , and E_{TO8} [29].

Figure 4. a) The ultraviolet -visible absorbance of M-LiNbO₃ crystals. Inset: Schematic illustration of M-LiNbO₃ photodetector. b) The UV light response of Pt/M-LiNbO₃/Pt device after the light illumination is switched on or off measured under 5 V. c) The P-V curve and J-V curve of the device measured under the applied external voltage from -5 V to 5V. d) The piezoresponse force microscopy of M-LiNbO₃ crystal.

Figure 4a presents the ultraviolet-visible absorption spectrum of M-LN crystals, which presents an only absorption at 340 nm within the 200 – 900 nm range. The bandgap of M-LN is evaluated and its measured value is $\sim 3.66\text{ eV}$, which is almost as same as that of ceramic LiNbO₃ ($\sim 3.7\text{ eV}$) [30]. In order to test the photo response of synthesized M-LN crystals, a Pt/M-LN/Pt UV light photodetector was fabricated using focus ion beam (FIB) microscope (Figure 4a inset). Figure 4b shows the photocurrent of Pt/M-LN/Pt device under 5 V, after it is switched on or off. The

device behaviors an obvious ON-OFF switching performance, which indicates that M-LN can be a good candidate as photodetector in spite of a relatively large bandgap. In addition, polarization versus voltage (P-V) curve, current density versus voltage (J-V) curve, and piezoresponse measurements were used to investigate the ferro/piezoelectric properties of R3C symmetric M-LN crystals. The P-V curve of Pt/M-LN/Pt was obtained with voltages ranging from -5 V to 5 V at 10 Hz, which presents a typical ferroelectric hysteresis loop (Figure 4c). The inserted J-V curve of the same device shows the switching current density at ± 3 V. Both P-V and J-V curves clearly show the robust ferroelectricity of M-LN crystals; the saturation polarization ($P_s \sim 76 \mu\text{C}/\text{cm}^2$), remnant polarization ($P_r \sim 68 \mu\text{C}/\text{cm}^2$), and coercive field ($E_c \sim 30 \text{ kV}/\text{cm}$) that we obtained were almost as good as the best ones reported in previous studies^[12]. In addition, Figure 4d shows the phase and amplitude responses under an applied electric field investigated using an atomic force microscope equipped with conductive metal-coated tips. We found that the phase of the [001] oriented M-LN crystal switched from 80° to 260° , at approximately $30 \text{ kV}/\text{cm}$, and switched back from 260° to 80° when the applied electric field swept to $\sim -30 \text{ kV}/\text{cm}$. The 180° phase variation confirmed the presence of ferroelectricity in M-LN crystals, with the butterfly-shaped amplitude loop characteristic of the piezoelectricity of M-LN crystals.

Figure 5. a) Schematic illustrating the synthesis process of Nb_2CT_x -based $\text{LiNbO}_3:\text{Pr}^{3+}$ crystals. b) Optical image of $\text{M-LN}:\text{Pr}^{3+}$ in alcohol under a 325 nm- UV light. c) Photoluminescence spectra of $\text{M-LN}:\text{Pr}^{3+}$ crystals at different excitation wavelengths. d) X-ray diffraction, e) SEM image, and f) PL lifetime spectra of $\text{M-LN}:\text{Pr}^{3+}$ crystals.

The doping of LiNbO_3 crystal with rare-earth ions have provided several novel optical properties, such as photoluminescence^[31] and mechanoluminescence^[22] to the LiNbO_3 crystals. However, to this day, and to the best of our knowledge, no synthesis of rare-earth-doped LiNbO_3 crystals using MXene as precursor using the hydrothermal method was ever reported. Figure 5a shows the designed process we used to synthesize $\text{LiNbO}_3:\text{Pr}^{3+}$ crystals with MXene-based trivalent rare-earth ions. Nb_2CT_x MXene and Li_2CO_3 were respectively selected as Nb and Li sources, and Pr^{3+} was selected as a dopant for M-LiNbO_3 crystals (see Experimental Section for details). Figure 5e shows well-oriented Pr^{3+} doped M-LiNbO_3 crystals with an average size of $\sim 1 \mu\text{m}^3$. In principle, Pr^{3+} ions may substitute for the niobium atoms, lithium atoms, lithium vacancies, and the available free sites^[32-33]. Compared to the XRD pattern of undoped LiNbO_3 crystals, the slight left shift of the XRD peaks of $\text{M-LN}:\text{Pr}^{3+}$ crystals (Figure 5d) confirms the lattice expansion

resulting from the site occupancy by Pr^{3+} dopants. Figure 5b displays the red-emitting photoluminescence (PL) of $\text{M-LiNbO}_3\text{:Pr}^{3+}$ crystals under UV light at a wavelength of 325 nm. Excitation sources with 365 nm, 353 nm, and 274 nm wavelengths were applied to investigate the photoluminescent properties of M-LN:Pr^{3+} . All the PL spectra of M-LN:Pr^{3+} crystals obtained under different excitation conditions (Figure 5c) consistently exhibited strong peaks at 618 nm and 635 nm. For comparison, PL spectra of undoped LiNbO_3 crystals were also investigated, indicating no emission peak, for wavelengths ranging from 300 nm to 700 nm (Figure S4). By combining the PL spectra with the energy levels diagram of trivalent praseodymium ion (Figure S5), we can conclude that the two luminescence peaks (618 nm and 635 nm) of M-LN:Pr^{3+} crystals originate from the dominant $\text{D}_2 \rightarrow {}^3\text{H}_4$ and ${}^3\text{P}_0 \rightarrow {}^3\text{H}_6$ transition of Pr^{3+} , respectively^[34]. Figure 5f presents the PL lifetime spectra of M-LN:Pr^{3+} crystals (excitation: 254 nm, emission: 618 nm), which can be well- fitted using a double exponential equation.

$$L = L_0 + a_1 e^{-t/\tau_1} + a_2 e^{-t/\tau_2} \quad (1)$$

where L and L_0 represent the luminescence intensities at times t and 0, a_1 and a_2 are fitting constants, and τ_1 and τ_2 correspond to different lifetime constants, respectively. We also applied the fitting and lifetime constants to calculate the effective lifetime constant (τ_e) of M-LN , as shown in Equation 2:

$$\tau_e = \frac{a_1 \tau_1^2 + a_2 \tau_2^2}{a_1 \tau_1 + a_2 \tau_2} \quad (2)$$

The fitting results showed that lifetime τ_1 , τ_2 , and τ_e were approximately 1.6 μs , 20.9 μs , and 1.9 μs , respectively (see Table S1 for details). The double- exponential decay is likely due to the cross-relaxation process of ${}^3\text{P}_0 + {}^3\text{H}_4 \rightarrow {}^1\text{D}_2 + {}^3\text{H}_6$ ^[35]. We found that the effective PL lifetime of the ${}^1\text{D}_2$ level was approximately 33 μs for 0.04 mol % Pr -doped LiNbO_3 ^[36]. The doping concentration of

our M-LN:Pr³⁺ crystals was approximately 1.0 mol %, and thus it is reasonable to attribute the shorter luminescent decay of the M-LN:Pr³⁺ crystals due to the well-known concentration quenching effect^[36]. Li/Nb ratio plays a predominant role in the photoluminescent (PL) and mechanoluminescent (ML) properties of Pr³⁺-doped LiNbO₃ crystal. For nonstoichiometric Li_xNbO₃:Pr³⁺, PL intensity increases with increasing x value, until reaching maximum intensity at x = 1.00, and the slightly Li-rich samples have the best ML performance^[22]. We have investigated the Li/Nb ratio of M-Li_xNbO₃:Pr³⁺ samples using inductively coupled plasma optical emission spectrometry (ICP-OES), and the highest Li/Nb ratio turns out to be x = 0.97 (Table S2). The deficiency of Li in our sample is the main reason that M-Li_xNbO₃:Pr³⁺ is photoluminescent, instead of mechanoluminescent.

Conclusions

This study presented a methodology to exploit the 2D character of Nb₂CT_x MXenes to fabricate plate-like LiNbO₃ crystals with a rhombic crystal structure and a robust ferroelectricity. The saturation polarization, remnant polarization, and the coercive field of M-LN are almost equal to those reported in previous studies. For the first time, we doped trivalent rare-earth ions in the M-LN crystals using a different synthesizing process, and successfully provided the doped LiNbO₃ crystals with photoluminescent properties in. Our discovery not only expands the feasibility of deriving oriented ferroelectric crystals using the two-dimensional character of MXenes, but it also offers a new approach for synthesizing MXene-based materials with advanced optoelectronic applications.

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Conflict of Interest

The authors declare no conflict of interest.

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MXene-derived high aspect- ratio lithium niobate (LiNbO_3) single crystals are successfully synthesized using two-dimensional Nb_2C MXene and LiOH as the lithium and niobium sources, respectively. In addition, for the first time, trivalent rare-earth ions in the M-LN crystals are doped using a different synthesizing process, and provide photoluminescent properties to those doped LiNbO_3 crystals.