Synthesis of large monolayer titania nanosheets through flux method

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ABSTRACT

Herein, we present the structural and electrical properties of layered titanate, the precursor of an ideal two-dimensional (2D) nanosheet. A K$_{0.8}$Ti$_{1.77}$Li$_{0.27}$O$_4$ (KTLO) sample was synthesized by the flux method to maximize the area of the, relative to that under conventional methods, and to assess the oriented growth direction of the synthesis process. The structure of the protonated layered titanate H$_{1.07}$Ti$_{1.77}$O$_4$ (HTO), obtained by replacing the intercalated K$^+$ cations with H$_3$O$^+$, was analyzed to observe the effect of variables in the acid exchange process. Notably, the electrical characteristics of both layered titanates in the bulk state have not been previously reported. Herein, we measured the dielectric permittivity of bulk layered titanates without thermal treatment, which was observed to be lower than that of the nanosheet form. Additionally, these titanates were successfully exfoliated into large single-layer nanosheets. Overall, these results provide insights to clarify the properties of layered materials prior to nanosheet exfoliation.

1. Introduction

Titanium dioxide (TiO$_2$) has been studied extensively owing to its noble properties [1] such as low cost [2], chemical stability [3], non-toxicity [4], photocatalytic properties [5,6], and electronics [7,8]. Layered titanates, composed of titanium oxide layers with a stable phase, can be used as a precursor for atomically thin titanium dioxide films. In this study, lepidocrocite-like K$_{0.8}$Ti$_{1.77}$Li$_{0.27}$O$_4$ (KTLO) and H$_{1.07}$Ti$_{1.77}$O$_4$ (HTO) were obtained using the flux method and acid exchange process [9,10]. The titania nanosheets obtained via exfoliation of these titanates exhibit very high dielectric constants and thinness owing to the different arrangements of rutile, anatase, and other structures [8]. Also, KTLO is known to be a promising material for a battery anode material because of its unique characteristics [11,12].

The study of nanosheets comprising a single layer of single-crystalline is considered to be a new field overcoming limitations on their size; this type of nanosheet has received considerable attention owing to its potential applications in electronics. Multilayer ceramic capacitors (MLCCs) for future electronics require higher dielectric permittivity under smaller sizes [13,14]. Heat stress during annealing processes involved in the fabrication of conventional materials is the main factor responsible for decreases in the dielectric constant. However, nanosheet technology not only solves this thermal problem but also enables materials with a thickness of less than a few nanometers to be obtained, allowing for the establishment of a suitable manufacturing environment for the fabrication of downsized devices. Well-known nanosheets, such as Sr$_2$Nb$_2$O$_{10}$ (SNO) [15] and Ca$_3$Nb$_2$O$_{10}$ (CNO) [15,16], have a lateral size of only a few hundred nanometers. The small nanosheet size limits the superior properties from their single crystallinity compared to conventional amorphous materials. In contrast, nanosheets are known to have a lateral size of a few tens of micrometers [17].

Thus, this study investigates the synthesis of large-area layered titanates and their properties, particularly focusing on the structural features of layered titanates under variables in the synthesis process. Specifically, the temperature and type of flux material were varied in KTLO synthesis process. The effects of acid species, reaction time, and humidity were also examined in HTO synthesis process. Subsequently, a structural analysis of the titane crystals being conducted from these experiments. Moreover, powder X-ray diffraction (XRD) patterns were used to identify the variables affecting the lattice constants of the layered titanates. The obtained relationship between each condition and the lattice constants allows for the analysis of the size and orientation of the layered titanate crystals. The dielectric properties of the two titanates were observed to be less significant than those of the nanosheet form, and the dielectric permittivity values of the lepidocrocite-like layered titanates decreased after protonation.

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2. Materials and methods

2.1. Synthesis and Preparation

In this study, potassium carbonate (K₂CO₃, ≥99.0 %, Sigma-Aldrich®), lithium carbonate (Li₂CO₃, ≥99 %, Sigma-Aldrich®), titanium(IV) oxide (anatase, TiO₂, 99.8 %, Sigma-Aldrich®), potassium molybdate (K₂MoO₄, 98 %, Aldrich®), molybdenum(VI) oxide (MoO₃, ≥99.5 %, Sigma-Aldrich®), nitric acid (HNO₃, 69.0–70.0 %, J.T. Baker®), hydrochloric acid (HCl, 36.5–38.0 %, J.T. Baker®), tetrabutylammonium hydroxide (TBAOH, ~40 wt.%, Sigma-Aldrich®) and polydiallyldimethylammonium chloride (PDDA ~35 wt.%, Sigma-Aldrich®) were used as reagents. Deionized water (DI water, ≥18 MΩ) was used throughout the experiments.

KTLO was synthesized via recrystallization from flux melt [9,12,18]. Stoichiometric mixture batches of powders were mixed using a zirconia mortar and pestle for 15 min each. Potassium molybdate flux (K₂MoO₄ or MoO₃) was mixed in the ratio of 7:3, as the molar ratio of flux by product. Additionally, Li₂CO₃ was added in excess of 10 % owing to its high volatility. The ground mixture was placed in an alumina crucible and maintained at a temperature of 900–1,200 °C for 10 h, slowly cooled to 900 °C for 50 h, and then cooled under ambient conditions in a furnace for 5 h. The reacted material was washed with DI water and using vacuum aspiration to remove the K₂MoO₄ flux. After three rounds of washing, the pure KTLO crystals were fully recovered. The as-synthesized KTLO powder was protonated to HTO via an acid exchange reaction. The KTLO powder (4 g) was then immersed and shaken in 200 mL of different acid solutions, varying across acid species, concentrations, and reaction times. Every 24 h, the acid was replaced with fresh solution. After the termination of the reaction, the powder was washed with copious amounts of DI water via decantation of the supernatant water into the remaining acid. The protonated titania HTO was kept in a humidity-controlled chamber with sedimented powder. Notably, 70 % relative humidity was maintained to conserve the HTO powder, and the powder was dried in ambient air before subsequent measurements and experiments. The synthesized KTLO and HTO powders were formed into pellets at a pressure of 3,500 psi. Subsequently, electrodes were printed using silver paste on both sides of the pellets to facilitate their use as capacitors. Finally, the pellets were dried in an oven at 100 °C for 2 h to strengthen the electrical contacts without humidity.

To exfoliate the layered titanate into single-layered titania nanosheets, a chemical exfoliation method was used. The nominal concentrations of the HTO powder and TBA solution were controlled at 50 g·L⁻¹ for exfoliation. The ion ratio of TBA⁺: H⁺ was maintained at 1:1 to avoid surplus ions from forming unwanted exfoliated HTO, an osmotic swelling phase [19], and restacking of the nanosheets [20]. This colloidal solution was shaken on a 30 rpm shaker for three weeks to prevent any external force from acting on the delaminated nanosheet during the process [9,21]. After exfoliation, the silk-textured suspension was collected after centrifugation for 10 min. The exfoliated titania nanosheet was deposited on a Si substrate to measure the AFM height profile using the previously described layer-by-layer method with a PDDA solution [22,23]. After the deposition sequence, the deposited substrate was exposed to UV light for 20 min to facilitate the decomposition of the interlayer organic ions, which would then form nanosheet layers in a polymer-free form [23].

2.2. Characterization

Powder XRD (X-ray diffractometer: Bruker D8 Advanced Lynxeye, USA) was used to refine the crystal structure. The increment was set at 0.02, and the scan speed was 4 °/min. The grain size, morphology, and microstructure of the titane powders were observed using field-emission scanning electron microscopy (FE-SEM microscope: FEI Inspect F50, USA) with a 10 kV electron beam, coated under 15 mA and 20 s of Pt sputtering to provide conductivity to the powders. The dielectric properties were measured with an impedance analyzer (Agilent Technology, HP 4294A, USA) in the range of 103–105 Hz. The thickness profile of the nanosheet was measured using a tapping mode atomic force microscope (AFM: Park Systems XE-70, Korea). The measurements were performed at ambient temperature and air pressure. The resonance frequency of the cantilever was 330 kHz, and the force constant was 42 N/m.

3. Results and discussion

KTLO has a lepidocrocite-like layered structure of a C-(1010)-base centered orthorhombic crystal, Cmcm (63) [11,18,24–26]. This layered structure is composed of titania octahedra (TiO₆) sheets, sharing corners and edges with Ti-O bonds. Potassium ions (K⁺) intercalate between titanium oxide sheets. However, primary research indicates that lithium ions (Li⁺) are positioned in the host framework, not in an intercalated gallery [24,26].

Figure 1 shows the effect of temperature variation on the phase of potassium lithium titanate. The XRD patterns, indicating that layered titanate KTLO was observed in notable amounts at the reaction temperatures of 900 °C, 1,000 °C, and 1,100 °C are shown in Figure 1(a–c), respectively. The (010) and (011) peaks were separated at low temperatures and gradually merged until the temperature reached 1,100 °C. The inset of Figure 1 shows the gap between the two basal reflections on the (020) peak, and the calculated lattice
constant data in Table 1 show gradual changes in the crystals at each temperature. The lattice constant is shown in Table 1, refined with the crystal structure of Cmcm (63) [11,18,24–26], which is typical of KTLO. The KTLO synthesized below 1100 °C was not in a single phase, but existed as the main phase at 900 °C and 1000 °C. In contrast, these phases were not observed under solid-state synthesis (600, 800, and 1000 °C) [27].

Figure 1. Powder XRD patterns of temperature-varied KTLO samples. (a) 900 °C, (b) 1,000 °C, (c) 1,100 °C, and (d) 1,200 °C. The insets show the separated (020) peak of KTLO.
Table 1. Lattice constants of HTO with relative humidity refined from XRD patterns. Calculated standard deviations are in parentheses.

| Temperature (°C) | a (nm) | b (nm) | c (nm) |
|------------------|--------|--------|--------|
| 900              | 0.3805 (2) | 1.5490 (9) | 0.2974 (2) |
| 1,000            | 0.3786 (2) | 1.5942 (8) | 0.2970 (2) |
| 1,100            | 0.3828 (1) | 1.5429 (3) | 0.2960 (1) |
|                  | 0.3825 (1) | 1.5512 (6) | 0.2963 (1) |
| 1,100            | 0.3817 (2) | 1.5516 (6) | 0.2967 (2) |

Notably, the b-axis distance was separated into two interlayer directions with broader spacing at lower temperatures. As the temperature increased, the wider b-axis narrowed, resulting in a unitary phase at 1,100 °C. This phenomenon has not been previously reported and predicted in KTLO; however, similar behavior and widening interlayer spacing have been reported for other types of layered titanate over cation uptake for hydrous processes [28]. The results suggest that the formation of lepidocrocite-like layered titanates may be affected by the synthesis temperature and cooling speed of the mixture.

The intensity ratio of the (0n0) peak at 1,100 °C was higher than that at 1,000 °C. This increase in the (0n0) intensity indicates that the crystal growth is oriented in a planar direction: the wide plate formed at 1,100 °C than that at 1,000 °C. This is also confirmed by the microstructural differences that can be seen in Figure 2(a,b), that is, by comparing the widths of the plate-like KTLO. The ICDD standard diffraction pattern (PDF #97-008-6641, QM = Calculated) matches well with both data, but the larger (0n0) direction is shown at 1,100 °C. In the context of larger nanosheets, this result leads to broader nanosheet production but requires a wider planar area of the precursor.

In addition, a sample at 1,200 °C does not show enough KTLO phase or the desired layered titanate structure. In Figure 1(d), the dominant peaks at 1,200 °C indicate priderite. This temperature setting was matched with previously reported priderite synthesis conditions [29]. The indexed priderite is composed of aluminum (Al), which requires the presence of Al in the reaction. The mixture has Li₂CO₃ with a low melting point, which leads to melting point depression during the high-temperature (≥1,200 °C) process. Thus, Al is eluted from the alumina (Al₂O₃) crucible and participates in the formation of priderite [29].

Figure 2(a,b) shows a significant plate-like KTLO with a noticeable size difference between the 1,000 °C and 1,100 °C synthesis temperatures. The 1,100 °C case had a much larger (~1 mm) KTLO. The 1,000 °C case exhibits a size of a few tens of micrometers. This comparative size difference supports the oriented growth of KTLO synthesis conditions. Moreover, the step-like patterned microstructure shown in Figure 2(d) is a known feature observed in priderite crystals [29].

Figure 2. FE-SEM image of temperature-varied KTLO samples. (a) 1,000 °C, (b) 1,100 °C, (c) and (d) 1,200 °C with enlarged microstructure.
The XRD pattern of the KTLO sample that started with MoO$_3$ flux formed a potassium hexatitanate (K$_2$Ti$_6$O$_{13}$) second phase, as shown in Figure 3(a) and previous studies [9]. In addition, the case involving the direct use of K$_2$MoO$_4$, as shown in Figure 3(b), is a feasible choice for removing the unwanted second phase. This difference indicates that an excessive K$_2$CO$_3$ supply was used not only to make the K$_2$MoO$_4$ flux but also to form K$_2$Ti$_6$O$_{13}$.

Figure 3. Powder XRD patterns about synthesized KTLO with different flux species. (a) K$_2$MoO$_4$, and (b) MoO$_3$.

Figure 4. Powder XRD patterns of different acid types and durations for HTO samples. (a) HNO$_3$ and (b) HCl.
Another study showed that K2Ti6O13 synthesized by a similar flux method differed in the potassium carbonate ratio [30].

The protonation of KTLO to HTO is only affected by the reaction time, regardless of the acid species. According to the XRD patterns, HNO3 (Figure 4(a)) and HCl (Figure 4(b)) show the same product for protonation to HTO. As described later, XRD measurements of HTO were performed in a wholly dried environment to reduce the effect of humidity. During the reaction, the crystal structure did not change, and the data showed almost the same XRD patterns, although the whole reflection intensities were weakened as the acid exchange duration increased. This result indicates the crystal structure of HTO. In particular, the intensity of the (0n0) peaks decreased with longer reaction times, while other peak intensities remained. This decrease in the (0n0) intensities shows that the reaction time affects the planar size of the HTO, which is not desirable for large nanosheets. Hence, optimization of the duration is required to minimize the size shrinkage of the final nanosheet.

Intercalated ion species are involved in the humidity relevance of HTO. As the intercalated ions are not protons (H+) and hydronium ions (H3O or H2O2) are more sensitive to environmental conditions such as humidity and temperature. In this research, decreasing the relative humidity reduced the layer distance. The primary cause of this phenomenon is the evaporation of intercalated water molecules [10]. The (0n0) peaks in Figure 5 shift dramatically to a lower angle, conjugated with the relative humidity values. In Table 2, the lattice constants refined from the XRD patterns show that the interlayer distance (b-axis) decreases with decreasing humidity, while the interplanar lengths (a, c-axes) did not change. The refinement worked with the same crystal structure as HTO (body-centered orthorhombic, Immm) [31]. This result indicates that the crystal structure does not change when the layers shrink owing to humidity. Based on this interpretation, the temperature is the principal variable for the crystallinity of HTO. Thermal stimulation can cause the decomposition of HTO into the conventional anatase form, as reported in previous studies [10,32]. In addition, the intensity of the (0n0) peaks decreases with increasing humidity. As the HTO was immersed in the reaction, the interlayer distance could be affected by humidity control. Along with the decrease in length during the drying process, it can also be enlarged through excess humidity lead layer fracture, derived from the re-intercalation of water molecules. This result suggests that adequate humidity can ensure the maximum planar size in a given environment.

Figure 6(b,c) show the bulged microstructure of the bulk HTO compared to the smooth surface morphology of KTLO in Figure 6(a). A comparison of KTLO and HTO, such as the accordion-like swelled layered structure of HTO, is shown in Figure 6(a, b), respectively. The magnified layered structure of the HTO shows fractures in several sections, as shown in Figure 6(c). Bulging of the layer is a natural phenomenon reported from the protonation of other layered materials [14,33]. In addition, the fractures appear to have no favored direction but are limited to be orthogonal to other fractured lines. These fracture patterns indicate that each single plate-like HTO particle is a genuine single-crystal obtained from KTLO [10,33], based on both lepidocrocite-like layered titanate with an orthorhombic crystal structure ($a = \beta = y = 90^\circ$). Moreover, this fracture unavoidably affects the size reduction of the nanosheets.

The dielectric properties of both layered titanates were measured from 103 Hz to 105 Hz, as shown in Figure 7, including the relative dielectric permittivity constant ($\varepsilon_r$) and loss factor (tan $\delta$). The $\varepsilon_r$ value decreased entirely on HTO compared to KTLO; a similar trend was also observed for the loss factor. As described above, the layered titanates KTLO and HTO are structurally vulnerable at high temperatures, so the phase transition into priderite and anatase [10,32] occurs during annealing. Therefore, we applied a higher pressure to reduce the number of pores. This resulted in the following dielectric permittivity values: $\varepsilon_r$ of KTLO (~40) and HTO (~37.5) lower than the nanosheet form (~125), in the 100 Hz region, and high loss (> 2 in the low-frequency region) were observed [8]. Besides, larger grain size can lead to higher dielectric permittivity values, as reported previously [34].

Figure 8 shows successfully delaminated single-layered titania nanosheets of a few-μm in the planar direction. The height of single layers (0.8 nm) is consistent with previous research [8,9]. Owing to technical difficulties, the dielectric properties of the nanosheets were not measured. The nanosheet size was reduced from the original precursor sizes of KTLO and HTO. This size reduction is inevitable in soft-chemical exfoliation [9]. The nanosheets were scaled down by several variables: the shaking speed and shaking method [9]. Therefore, increasing the size and orientation of the precursor grains allows the formation of broader nanosheet grains.
in terms of the final product. Hence, further research on single-layer nature requires the further utilization of nanosheet technology.

4. Conclusions

This study shows that the structural and dielectric properties of layered titanates can be exfoliated
Table 2. Lattice constants of HTO with relative humidity refined from XRD patterns. Calculated standard deviations are in parentheses.

| Relative humidity | a (nm)  | b (nm)  | c (nm)  |
|-------------------|---------|---------|---------|
| 0 %               | 0.3800 (1) | 1.4392 (7) | 0.2982 (2) |
| 70 %              | 0.3777 (1) | 1.8001 (2) | 0.2990 (1) |
| 80 %              | 0.3762 (2) | 1.8303 (9) | 0.2968 (2) |
| 90 %              | 0.3772 (1) | 1.8486 (5) | 0.2980 (1) |

into single-layered titania nanosheets. The layered titanate KTLO was synthesized by the flux method to form oriented crystal growth, to maximize the planar width at 1,100 °C. In addition, the synthesis temperature shows a sub-phase of KTLO from 900 °C, which is thoroughly merged at 1,100 °C. The protonated layered titanate HTO, obtained by acid treatment to replace K⁺ with H₃O⁺, shows humidity dependence for the reduction of interlayer distance concerning to the evaporation of intercalated water molecules. Both layered titanates in the bulk state have dielectric permittivity values εᵣ of approximately 40 and 37.5, which are relatively lower than the values of the nanosheet form. The layered

Figure 6. FE-SEM microstructure images of (a) KTLO with smooth side face (b) and (c) after acid-treated HTO with significantly inflated nature.

Figure 7. εᵣ and tan δ values measured from the KTLO and HTO pellets at various frequencies.
Titanate was successfully exfoliated into a large-scale single-layer titania nanosheet with a thickness of 0.8 nm and a few µm in the planar direction, as confirmed by AFM measurements. Hence, nanosheet technology requires a more versatile methodology for future research.

Disclosure statement
No potential conflict of interest was reported by the author(s).

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Figure 8. AFM topography and height profile of titania nanosheet exfoliated from layered titanates KTLO.
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