Influence of Inorganic Bases on the Structure of Titanium Dioxide-Based Microsheets

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ABSTRACT: Laboratory synthesis of microsheets of titanium dioxide from titanyl sulfate involves the use of ammonia solution, whereas another inorganic base is most likely to be employed at the industrial level, as ammonia is a toxic agent and therefore should be avoided according to European Union (EU) regulations. Selected nontoxic bases such as sodium, potassium, and lithium hydroxides have been tested as an alternative to ammonia solution to obtain amorphous and crystalline TiO2-based microsheets. The final products obtained at each step of the procedure (samples lyophilized and annealed at 230 and 800 °C) were analyzed with electron and atomic force microscopy, X-ray powder diffraction, thermal analysis, and Fourier transform infrared (FTIR) and Raman spectroscopies to determine their morphology and phase composition. The differences in the morphology of the obtained products were described in detail as well as phase and structural composition throughout the process. It was found that, in the last step of the synthesis, microsheets annealed at 800 °C were built of small rods and oval or platy crystalline particles depending on the base used. The temperature of formation of anatase, rutile, and alkali-metal titanates in correlation with the ionic radius of the alkali metal present in the sample was discussed.

1. INTRODUCTION

Since Fujishima’s discovery of water photosplitting on titanium dioxide (TiO2) electrodes in the 1970s,1 TiO2 has aroused great interest in nanoscience and nanotechnology.2 TiO2 occurs in three crystalline phases—anatase, rutile, and brookite, with rutile being the most thermodynamically stable phase.3 The properties of TiO2 polymorphs are influenced by the morphology and crystalline structure of particles. Each polymorph of TiO2 displays different physical and chemical properties.4 It was found that higher photocatalytic activity exhibited nanoparticles of anatase,2,4 although mixtures of anatase and rutile5 also yielded satisfactory results. Pure bulk anatase is considered widely to begin to transform irreversibly to rutile in air at 600 °C; however, the reported transition temperatures vary in the range of 400–1200 °C.6,7 The generation of the phases of TiO2 depends significantly on the synthesis parameters, which in turn affect the product.7 The most common laboratory methods for TiO2 preparation by the solution route include precipitation, sol–gel method, solvo-thermal and hydrothermal methods, and combustion or electrochemical synthesis.8–10

In recent years, alkali titanates have attracted much attention due to their excellent ion-exchange/intercalation properties and high photocatalytic activity.11,12 To improve these functional properties, it is highly desirable to control the size and morphology of titanates.13

For a long time, mainly nanostructured TiO2 materials were developed.8 Nevertheless, due to the growing number of reported adverse effects of the nanosized TiO2,14 researchers focused more attention to microscale TiO2 particles, e.g., microsheets,15 microspheres,16 and microrods.17–19

In this work, an optimized synthetic method reported earlier20 was applied to prepare TiO2-based microsheets and detailed morphological, phase, and spectroscopic characterizations were performed. The need for ammonia substitution in the preparation of TiO2 microsheets for a less toxic agent for industrial use has initiated studies on the effects of inorganic base replacement. Sodium, potassium, and lithium hydroxides as alternatives to ammonia solution were tested to obtain amorphous and crystalline TiO2-based microsheets for potential use in photocatalysis,16,19,21 photovoltaics,15,16 ion exchangers,13 and lithium-ion batteries.22 The choice of these hydroxides was dictated by their nontoxic character, availability as well as purchase and waste disposal cost. The formation of titanates and TiO2 in different phase ratios (anatase/rutile) was observed. Further, the differences that may occur between the particles depending on the kind of base used were studied at each step of the synthetic process, i.e., in samples lyophilized and annealed at 230 and 800 °C.

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Table 1. Description of the Main Features of the Studied Samples

|        | LiOH | NaOH | KOH | NH₄OH |
|--------|------|------|-----|-------|
| LYO    | +++  | +++  | +++ | +++   |
| microsheets | ++ (Figure 1) | ++ (Figure 1) | +   | +     |
| microrods | ++   | +    | +   | +++ (Figure 2) |
| small particles | +++ | +   | +++ | +     |
| holes—size and shape | *1.5–6 μm—round, elongated | *0.5–3 μm—cracked/starlike | *0.6–2 μm—round | *2–3 μm—round |

| 230    |       |      |     |       |
|--------|------|------|-----|-------|
| microsheets | +++  | +++  | +++ | +++   |
| microrods | ++   | +    | +   | +     |
| small particles | ++ | + | ++ | + |
| holes—size and shape | *7–15 μm—flowerlike | *4.7–6.7 μm starlike | *1.8–5.6 μm—round, cracked | *2.9–4.9 μm—round |
| shapes of the small particles forming the microsheets and microrods | *0.5–3 μm—irregular with lamellar divisions, sometimes hexagonal and angular holes | *0.15 μm—some hexagonal | *0.02–0.1 μm—nanorods | *polyhedrons smaller than in sample Na₈₀₀ (Figure 7) |
| holes—size and shape | *0.02–0.1 μm—netlike structure in microsheets with flowerlike holes (Figure S2b) | *0.02–0.1 μm—nanorods | *polyhedrons (Figure 6) | *oval particles resembling not fully developed polyhedrons (Figure 8) |

| 800    |       |      |     |       |
|--------|------|------|-----|-------|
| microsheets | ++  | ++   | +++ | ++    |
| microrods | ++   | +    | +   | +     |
| shapes of the small particles forming the microsheets and microrods | *0.5–3 μm—irregular with lamellar divisions, sometimes hexagonal and angular holes | *0.15 μm—some hexagonal | *0.02–0.1 μm—nanorods | *polyhedrons |
| holes—size and shape | *0.02–0.1 μm—octahedrons (Figure 5) | *0.02–0.1 μm—nanorods | *polyhedrons (Figure 6) | *oval particles resembling not fully developed polyhedrons (Figure 8) |

*a, Almost absent; ++, present; ++++, abundant.
2. RESULTS AND DISCUSSION

2.1. Morphology and Phase Composition. High-resolution scanning electron microscopy (HRSEM) was applied for the study of the morphology of the obtained products. All of the examined samples on different steps of the process, i.e., after lyophilization, annealing at 230 and 800 °C, showed inhomogeneous morphology. HRSEM observations helped to find some general features, which were useful for discriminating the samples, such as the presence of small particles, size and shape of the holes, and in the samples annealed at 800 °C, the shape of crystalline particles forming the microsheets and microrods. These features are summarized in Table 1. Detailed HRSEM micrographs can be found in the Supporting Information.

Figure 1. HRSEM micrographs of microrods in samples Li_LYO (a) and Na_LYO (b).

Figure 2. HRSEM micrographs of sample NH₄_LYO, with small particles growing on top of microsheets (a) and small particles at the edges of microsheets (b).

Figure 3. HRSEM micrographs of tiny holes in microsheets in sample K_LYO (a, b).

Figure 4. HRSEM micrographs of tiny particles on top of the microsheets (a,b), and a starlike hole (a) and angular holes (b) in sample Na_230.
The samples lyophilized and annealed at 230 °C were composed of large microsheets (Figures S1 and S2), microrods of variable size (Figure 1), and small (∼80 nm long) oval-shaped particles (Figure 2) in different proportions but usually with the predominance of microsheets (Table 1). Clear differences between the microsheets in the samples were already discernible after lyophilization. All of the microsheets had holes, created due to gaseous compounds evacuation, but the size and shape of the holes varied, depending on the type of base used (Figures S1–S3). Apart from large holes, up to 6 μm in diameter, smaller and more irregular holes in the range of several tens and hundreds of micrometers forming a netlike structure, especially in sample K_LYO (Figure 3), were detected (Table 1). Microsheets seemed to be the most
cracked in sample Na_LYO (Figure S1g,h) probably because of their thickness as proved by atomic force microscopy (AFM) results.

The features observed in the lyophilized samples were further developed during annealing. In samples Li_230 and NH4_230, a netlike structure, resembling the one detected in the K_LYO sample (Figure 3), was formed (Figure S2b,p). Some new characteristics appeared as well. In sample Na_230, the surface of the microsheets annealed at 230 °C has been covered with tiny particles spread around the microsheets (Figure 4) that were absent in the lyophilized sample (Na_LYO).

After annealing the samples at 800 °C, most of the microsheets disintegrated due to the growth of small crystalline particles of different shapes: platy, with not fully developed edges, and hexagonal (Li_800—Figure 5); octahedral and polyhedral (Na_800—Figure 6); bigger rods with a polyhedral cross-section (Na_800—Figure 6) and smaller rods (K_800—Figure 7); or oval particles sometimes resembling polyhedrons (NH4_800—Figure 8).

High-resolution transmission electron microscopy (HRTEM) analyses were performed to describe the morphology and to determine the phase composition of the prepared samples. The morphology of the samples was not homogeneous.

Sample Li_LYO (Figure 9a) consisted of both smaller and bigger microsheets. In the case of sample Na_LYO (Figure 9b), its morphology was similar to sample K_LYO (Figure 9c) and consisted of microsheets with microrods of various sizes. Sample NH4_LYO (Figure 9d) was composed of microsheets with clusters of nanoparticles. The results obtained by HRTEM of all of the above-described samples corresponded to the results obtained from HRSEM studies.

The results of HRTEM analyses of the samples annealed at 230 °C are shown in Figures 10–13. The morphology of the samples annealed at 230 °C was quite similar to the lyophilized ones but the forms seemed better constructed as the outlines of the individual particles building the microsheets and microrods were already discernable (Figure S4). High-resolution images were obtained for all of the annealed samples showing their emerging crystal structure; the fine fringe spacing d corresponded to the anatase structure (Figures 10b—13b). The size of the crystals varied from 2 to 10 nm. The anatase crystal structure was confirmed by the electron
diffraction patterns; see the characteristic results obtained from sample Li_{230} (Figure S6).

Studies of the samples annealed at 800 °C revealed a well-formed crystal structure (Figures 14−17 and S5). Their morphology has cardinaly changed under the influence of high temperature. Samples consisted of microsheets and microrods containing small crystals of various shapes. However, in between well-formed structures, not completely formed crystals of indistinct shape with not yet well-defined edges were found (e.g., Li_{800}).

Sample Na_{800} was well crystallized, but its morphology seemed not to be homogeneous; it consisted of separate 0.5−1.5 μm and nanosized rodlike crystals not forming anymore microsheets, as could be seen in HRSEM micrographs (Figure 6) and clusters of tiny crystals of various shapes (Figure 15a). Some microrods formed both by tiny crystals and rodlike particles were detected as well.

Sample K_{800} (Figure 16a) looked quite similar to sample Na_{800}, but the small rods were less frequent and smaller, and some other tiny particles of various shapes (rectangular, and sometimes polyhedral) were present. Microrods were built from crystals of similar shape and size as the ones in the microsheets. In some cases, it seemed that microrods were in fact rolled up microsheets.

Sample NH4_{800} (Figure 17) was more homogeneous than the others; it consisted of tiny crystals forming microsheets as well as microrods formed by crystals of similar size and shape to the ones in microsheets.

High-resolution micrographs were obtained for all samples annealed at 800 °C (Figures 14b−17b).

In contrast to the samples annealed at 230 °C, where the anatase phase was detected, in the samples annealed at 800 °C, both anatase (K_{800} and NH4_{800}) and titanate Na_{2}Ti_{6}O_{13} (Na_{800}) were identified; as for sample Li_{800}, it contained a mixture of titanate Li_{4}Ti_{5}O_{12}, anatase, and rutile. These results were confirmed by the electron diffraction patterns shown in Figures S7 and S8.

Figure 14. HRTEM micrographs of sample Li_{800} (a, b).

Figure 15. HRTEM micrographs of sample Na_{800} (a, b).

Figure 16. HRTEM micrographs of sample K_{800} (a, b).

Figure 17. HRTEM micrographs of sample NH4_{800} (a, b).

Atomic force microscopy (AFM) was used to study the thickness of the microsheets present in the samples. The AFM images of the lyophilized samples prepared by precipitation with various bases are shown in Figure 18. Previously, Zhang et al. presented AFM images of TiO_{2} nanosheets in the anatase form with thicknesses of around 2.3 and 3.1 nm. Generally, amorphous samples Li_{LYO}, K_{LYO}, and NH4_{LYO} were formed by microsheets with a thickness of around 30 nm, while the microsheets in sample Na_{LYO} were approximately twice as high (around 60 nm).

X-ray diffraction (XRD) measurements of the samples annealed at 230 and 800 °C were carried out to determine their phase composition. The obtained XRD patterns are shown in Figure 19. All samples annealed at 230 °C showed an amorphous character. The XRD patterns of the samples annealed at 800 °C differed in phase composition (Table 2). While only pure anatase phase was found in sample NH4_{800}, alkali-metal titanates were present in other three samples. The rutile phase was observed only in samples Li_{800} and Na_{800}, according to the Rietveld analysis, in both predominant (59 wt %) and negligible (4 wt %) quantities, respectively (Table 2). While a small amount of relatively large anatase crystals was preferably formed in sample Li_{800}, with increasing ionic radii in the order Li^{+} < Na^{+} < K^{+} < NH4^{+}, the content of anatase phase increased, but its size decreased (Table 2).

High-temperature XRD (HT-XRD) measurements were performed to understand the dynamics of phase transitions of the samples in the temperature range of 25−1000 °C depending on the base used for the synthesis. Figure 20 shows diffraction patterns of sample Li_{LYO}. Up to 350 °C, only the amorphous phase was present. Diffraction lines corresponding to anatase (PDF 21-1272) appeared from 400 up to 850 °C. At
a temperature above 700 °C, part of the anatase phase began to transform to rutile (PDF 21-1276) and diffraction lines corresponding to lithium titanate (Li$_4$Ti$_5$O$_{12}$, PDF 04-018-2223) appeared. Crystallization into another lithium titanate (Li$_2$Ti$_3$O$_7$, PDF 01-085-3966) was detected above 900 °C. A mixture of rutile and two titanates was found at a final temperature of 1000 °C.

Figure 21 represents diffraction patterns of sample Na_LYO with a similar trend to sample Li_LYO; however, all of the crystallizations were shifted to much higher temperatures. The amorphous phase started to crystallize at 450 °C, and the diffraction lines corresponding to anatase were found in the range of 500–950 °C. Sodium titanate (Na$_2$Ti$_6$O$_{13}$, PDF 04-009-3669) started to be formed (750 °C) and followed by the rutile phase (850 °C) even at higher temperatures.

HT-XRD patterns of sample K_LYO (Figure 22) confirmed the same trend; the individual phase transformations were shifted to even higher temperatures than in both previous cases (Li_LYO and Na_LYO). This behavior can be explained by the increasing ionic radii in the order Li$^+$ < Na$^+$ < K$^+$. In the sample containing K$^+$ ions with the largest ion diameter, their size prevented the crystallization and growth of anatase and rutile crystals at higher temperatures. Figure 22 displays a significant proportion of the amorphous phase up to 500 °C. The anatase phase first appeared at 500 °C and, unlike in the previous two cases, remained up to 1000 °C; in addition, the width of the anatase diffraction line and its crystallinity visibly

### Table 2. Phase Composition of the Samples Annealed at 800 °C

| sample | crystallite size (nm) | phase fraction (wt %) | crystallite size (nm) | phase fraction (wt %) | crystallite size (nm) | phase fraction (wt %) |
|--------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| Li_800 | 86                    | 17                    | 132                   | 59                    | 97                    | 24                    |
| Na_800 | 71                    | 22                    | 126                   | 4                     | 54                    | 74                    |
| K_800  | 59                    | 41                    | 71                    | 59                    | 71                    | 59                    |
| NH4_800| 48                    | 100                   |                       |                       |                       |                       |
narrowed and improved with increasing temperature. The diffraction lines corresponding to potassium titanate (K₂Ti₆O₁₃, PDF 40-403) appeared at 650 °C. The rutile phase was detected above 950 °C.

In the diffraction patterns of the sample precipitated with NH₄OH, only diffraction lines of anatase and rutile were found (Figure 23). The amorphous phase began to crystallize into anatase in the temperature range of 300–350 °C. The part of the anatase phase started to transform into the rutile phase at 650 °C; however, its significant increase is above 900 °C.

Thermal analysis of samples was measured to observe decompositions, crystallizations, and transitions to crystalline products and was accompanied with analysis of the evolved gases. The first degradation step occurred from 30 to 170–210 °C, and was smoothly followed by the second degradation step, which took place up to the temperature range of 300–390 °C (Figure 24a). These two steps were accompanied by a broad exothermic peak on the differential scanning calorimetry (DSC) curves (Figure 24b). During the first step, mainly residual water and CO₂ (m/z = 18 and 44, respectively) were released (Figure 25), which is in agreement with Yada et al.; in sample Li_LYO, evolution of oxygen (m/z = 16 and 32) also occurred. The exothermic process illustrated in Figure 24b can be explained as a disintegration of peroxide group. While signal for released oxygen (Figure 25) was detected in sample Li_LYO, oxygen caused oxidation of ammonia to NO and N₂O (m/z = 30 and 44, respectively) in sample NH₄_LYO. A higher intensity of fragment m/z = 44 was observed in all samples during the second step, suggesting that the evolved oxygen probably caused also decomposition of residual impurities (e.g., evolution of CO₂ from carbonates formed due to the hygroscopic properties of hydroxides or oxidation of organic impurities).

Crystallization of amorphous materials to anatase was associated with the third degradation step (with the exception of sample K_LYO) and evolution of the same gaseous products as during the second degradation step. An increase in the ionic radii of alkali metal increased the crystallization temperature of anatase: Li_LYO < Na_LYO < K_LYO, as can be seen in Table 3. The crystallization of anatase found by DSC was slightly higher compared to the results achieved by HT-XRD (differences can be caused by different temperature programs and atmosphere), but the order of crystallization was the same. Similar exothermal transformation to anatase at approximately 425 °C was recorded in lithium titanates in the works by Selvamurugan et al. and Motlochová et al.

Over 700 °C, a broad exothermic peak emerged on DSC curves connected with gradual crystallization to rutile, in agreement with Ryu et al. The transformation temperatures to rutile or titanates according to DCS are shown in Table 3. Transformation temperatures of sodium and potassium

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**Figure 20.** HT-XRD analysis of the sample precipitated with LiOH: A = anatase, R = rutile, X = Li₂Ti₃O₇, Y = Li₄Ti₅O₁₂.

**Figure 21.** HT-XRD analysis of the sample precipitated with NaOH: A = anatase, R = rutile, X = Na₂Ti₆O₁₃.

**Figure 22.** HT-XRD analysis of the sample precipitated with KOH: A = anatase, R = rutile, X = K₂Ti₆O₁₃.

**Figure 23.** HT-XRD analysis of the sample precipitated with NH₄OH: A = anatase, R = rutile.
titanates and rutile in samples K_LYO, Na_LYO, and NH₄_LYO detected by HT-XRD were in good agreement with the results of DSC.

2.2. Structural Characterization. The Fourier transform infrared (FTIR) and Raman spectra of samples lyophilized and annealed at 230 and 800 °C are shown in Figures 26–28. The FTIR spectra of all samples contained O–H stretching vibration of water (surface-adsorbed or coordinated to TiO₂) at ~3440 cm⁻¹. The second band corresponding to the bending mode of water Ti–OH was present at ~1638 cm⁻¹, and the band related to Ti–O modes was present at ~1384 cm⁻¹. All of these band intensities decreased in the case of samples annealed at 800 °C. The region 450–750 cm⁻¹ exhibited strong absorption bands due to Ti–O–Ti and/or Ti–O bonding. The band of O–Ti–O vibration arrangement was present in lyophilized samples (Li_LYO, Na_LYO, K_LYO) at ~906 cm⁻¹ and shifted for sample NH₄_LYO to 937 cm⁻¹ (Figure 26a). The Raman spectra of all lyophilized samples (Figure 26b) contained typical broad bands for such type of amorphous samples. The binding vibration of

| sample      | anatase | rutile | titanates |
|-------------|---------|--------|-----------|
| Li_LYO      | 390–480 °C | broad exothermic peak |
| Na_LYO      | 490–540 °C | 790–910 °C | 730–760 °C |
| K_LYO       | 510–570 °C | max. at 980 °C | 630–680 °C |
| NH₄_LYO     | 370–440 °C | max. at 930 °C |

Figure 24. Thermal behavior of Li_LYO, Na_LYO, K_LYO, and NH₄_LYO: (a) thermogravimetry (TG) curves and (b) DSC curves.

Figure 25. Analysis of evolved gases of samples Li_LYO (a), Na_LYO (b), K_LYO (c), and NH₄_LYO (d).
O−Ti−O appeared at 277 cm$^{-1}$, and stretching vibration appeared at 388, 523, and 676 cm$^{-1}$. The synthetic pathway could explain the band at 903 cm$^{-1}$, where the peroxo bond was formed for Ti−O−O−Ti. The broadening of the band at ~523 cm$^{-1}$ was not observable in the Raman spectra of samples NH$_4$ LYO and Li LYO as in the case of samples Na LYO and K LYO, which proved the presence of Ti−O− Ti vibration of TiO$_6$ in the region of titanates. The most evident broadening was seen for the symmetrical Ti−O−Ti vibration at 482 cm$^{-1}$ in sample K LYO.

The binding vibrations of O−Ti−O of the samples annealed at 230 °C were shifted from 906 to 895 cm$^{-1}$ in the FTIR spectra (Figure 27a) and slightly shifted with a higher intensity to 280, 381, 511, and 684 cm$^{-1}$ in the Raman spectra (Figure 27b) in comparison to the lyophilized samples. The optimized annealing process should achieve the amorphous sample free from peroxo bond, which failed for samples Li$_{230}$ and Na$_{230}$, where the Ti−O−O−Ti vibration was still present at 900 cm$^{-1}$ in the Raman spectra. The band of symmetrical Ti−O−Ti vibration of TiO$_6$ in positions not typical for anatase was expanded and shifted from 482 cm$^{-1}$ (sample K LYO) to ~454 cm$^{-1}$ for sample K$_{230}$ in the Raman spectrum. The FTIR spectra of the samples annealed at 800 °C (Figure 28a) showed O−Ti−O vibration at 892 cm$^{-1}$ for Li$_800$, significantly shifted for Na$_800$ and K$_800$ to 965 cm$^{-1}$ and for NH$_4$$_800$ to 941 cm$^{-1}$. These large differences confirmed...
the presence of discrepancies in the octahedral arrangement around Ti. The Raman spectra of the samples annealed at 800 °C (Figure 28b) exhibited significant differences. The synthesis using LiOH resulted in the formation of rutile phase in sample Li_800. The typical rutile contains a broad band at ~231 cm\(^{-1}\) (two-photon scattering) and a band for B\(_{1g}\) mode at 141 cm\(^{-1}\), which was expected to be weaker in rutile phase compared to anatase. The further rutile vibration of sample Li_800 showed E\(_g\), A\(_{1g}\) modes at 446, 607 cm\(^{-1}\), while B\(_{2g}\) mode was not present (usually at ~825 cm\(^{-1}\)). Samples Na_800, K_800, and NH\(_4\)_Lyo contained typical anatase vibration corresponding to E\(_g\), E\(_{1g}\), A\(_{1g}\)/B\(_{1g}\) and E\(_g\) modes at 137, 193, 390, 511, and 634 cm\(^{-1}\).3,35 The spectra of samples Na_800 and K_800 proved the presence of sodium or potassium titanates (respectively)—their spectra contained many specific vibration bands. The typical vibrations of Na\(_2\)Ti\(_6\)O\(_{13}\) (the presence of which was confirmed in sample Na_800 by HT-XRD) described in the literature are as follows: the Ti−O−Ti stretching vibration in corner-shared TiO\(_6\) at 740 cm\(^{-1}\); in edge-shared TiO\(_6\) at 670 cm\(^{-1}\); the Ti−O−Ti bonding vibration at 863 cm\(^{-1}\); and vibrations between sodium and oxygen bonds ~274 and 304 cm\(^{-1}\).3,35,36 The Raman spectra confirmed the presence of all of these vibrations in samples Na_800 and K_800. Beyond the anatase bands, the symmetrical and asymmetrical Ti−O−Ti vibrations for titanates at 473 and 862 cm\(^{-1}\) for samples Na_800, and 453 and 851 cm\(^{-1}\) for sample K_800 and Ti−O−Ti stretching vibration in edge-shared TiO\(_6\) at 670 cm\(^{-1}\) for sample Na_800 appeared. Additionally, the vibration of titanates was also confirmed by the presence of Na−O−Ti vibration at 272 cm\(^{-1}\) and K−O vibration at 274 cm\(^{-1}\).

### 2.3. Elemental Composition

Since each analytical technique has its own detection limits, several methods had to be applied to obtain the information about elemental composition of the synthesized microsheets. Energy-dispersive spectrometry (EDS) was used to measure the quantities of sodium, potassium, and titanium in samples Na_Lyo and K_Lyo. Elemental analysis (CHNS) was used to determine the quantity of nitrogen in sample NH\(_4\)_Lyo. Finally, laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was used to measure lithium and electron probe microanalyzer to determine the quantity of titanium in sample Li_Lyo. All of the measurements were performed on lyophilized nonannealed samples. The results are shown in Table 4.

| Sample | Method          | Selected Elements | Expression (%) | Element/Ti Ratio |
|--------|-----------------|-------------------|----------------|------------------|
| Li_Lyo | LA-ICP-MS       | Li                 | 2.79           | Li/Ti 17.2       |
| Na_Lyo | EDS             | Na                 | 5.4            | Na/Ti 8.2        |
| K_Lyo  | EDS             | K                  | 7.6            | K/Ti 5.9         |
| NH\(_4\)_Lyo | Elemental analysis | N          | 2.91           |                  |

Although the precipitates were thoroughly washed during the synthesis process, some residual quantities of alkali metals remained in the lyophilized products. The present results showed that the highest weight percentage of alkali metal was left in sample K_Lyo, and the lowest in Li_Lyo. The quantity of the alkali metal in the final product decreased in accordance with the atomic weight of the element K > Na > Li and its ionic radius K\(^+\) > Na\(^+\) > Li\(^+\). For the samples prepared with LiOH and NaOH, this agrees with the results presented above (XRD)—the more alkali metal was left, the higher the quantity of titanates found in the samples annealed at 800 °C and above this temperature (see results of HT-XRD and thermal analysis). Yet, this rule does not apply to the sample prepared with KOH, although the quantity of titanates detected in it with XRD and Raman spectroscopy is equally important. In the sample prepared with NH\(_4\)OH, due to nitrogen oxidation to NO\(_x\) species during the annealing process (see thermal analysis results), crystallization of titanates was not observed.

### 3. Conclusions

The main goal of this experimental study was reached—a synthetic procedure allowing the preparation of the amorphous and crystalline TiO\(_2\)-based microsheets with the use of three different bases (LiOH, NaOH, KOH) replacing the ammonia solution was elaborated. The influence of different bases on the morphology, phase composition, and crystal structure in three different steps of the preparation process, i.e., after lyophilization, and annealing at 230 and 800 °C, was studied.

In all of the examined samples, microsheets were predominant; other forms such as microrods and small particles of various shapes were present. Significant differences were found already after the lyophilization, especially regarding the thickness of the microsheets and their surface. After annealing the samples at 230 °C, no substantial changes in the morphology were observed, but some features already present in the lyophilized samples were developed. The most notable changes in the morphology of the samples took place after annealing at 800 °C with the growth of individual crystals from which microsheets and microrods were constructed (oval particles—NH\(_4\)_800; smaller and bigger rods—Na_800 and K_800; polyhedrons—K_800, Na_800, Li_800; platy particles—Na_800, Li_800).

The choice of the annealing temperatures should lead to the formation of amorphous, peroxide-free (at 230 °C), and well-crystallized samples (at 800 °C). According to HT-XRD and thermal analyses, the first crystallites should have appeared above 350 °C, and the decomposition of peroxide group should occur at around 230 °C (see DSC curves). The results of XRD and Raman analyses confirmed that all samples lyophilized and annealed at 230 °C were amorphous. In contrast, HRTEM studies indicated the growth of anatase in all of the samples annealed at 230 °C. Nevertheless, the amount and size (2−10 nm) of crystallites were probably not sufficient for XRD detection. Moreover, in the Raman spectra of the samples Li_230 and Na_230, the peroxo bonds Ti−O−O−Ti were still observable.

The phase composition of all of the samples annealed at 800 °C (XRD) indicated the presence of anatase; its formation began at the lowest temperature in sample NH\(_4\)_800 and subsequently increased with increasing ionic radii (Li\(^+\) < Na\(^+\) < K\(^+\)). Furthermore, it was found that with increasing ionic radii (Li\(^+\) < Na\(^+\) < K\(^+\) < NH\(_4\)\(^+\)), the size of the anatase crystals decreased and their content increased. Moreover, a large proportion of the rutile phase was found in sample Li_800 and a small portion was found in sample Na_800. Rutile was not detected in XRD measurements of sample K_800, but it appeared in HT-XRD and thermal analyses at higher temperatures (950 and 980 °C, respectively).
With increasing atomic weight of cations (Li⁺ < Na⁺ < K⁺), more alkali metal remained in the lyophilized samples, which facilitated the crystallization of titanates, as seen in XRD patterns of the samples Li_800 (Li₄Ti₅O₁₂), Na_800 (Na₂Ti₆O₁₃), and K_800 (K₂Ti₆O₁₃). In the Raman spectra, the presence of the Ti—O—Ti vibration of TiO₂ in the region of titanates was found already for samples K_LYO and K_230 and all characteristic titanates vibrations were found in samples Na_800 and K_800.

Generally, the synthetic procedure elaborated initially for acquiring anatase microsheets with the use of ammonia solution could be replaced by a similar procedure with the use of other bases. However, this study showed a certain number of discrepancies between the final products of the synthesis discussed above. These differences may affect the properties of the final products, which should be further investigated with regard to the application-specific requirements.

4. MATERIALS AND METHODS

4.1. Chemicals. Titanium(IV) oxysulfate hydrate (TiOSO₄·xH₂O—commonly referred to as titanyl sulfate—TS, min. 29% Ti as TiO₂ basis, technical grade purity, Sigma-Aldrich) was used as a starting material for the syntheses. In addition to the normally used aqueous ammonia solution (NH₃·H₂O, 25–29% p.a.; Penta, Ltd.), the following bases served for precipitation of the precursor: lithium hydroxide (LiOH), sodium hydroxide (NaOH), and potassium hydroxide (KOH) (all analytical grade purity; Penta, Ltd.).

4.2. Preparation of TiO₂ Microsheets. TiO₂ microsheets were prepared with several modifications according to our recent published papers. In the first step of the preparation, 7.2 g of titanyl sulfate was dissolved in 250 mL of deionized water under stirring at 35 °C until the transparent solution was obtained. The solution was then cooled and precipitated by gradual addition of aqueous solution of KOH/NaOH/LiOH, and potassium hydroxide (KOH) (all analytical grade purity; Penta, Ltd.).

4.3. Samples' Labeling System. Samples were labeled with the name of the cation used in their preparation, and the abbreviation LYO for lyophilized samples, or, for the annealed samples, the value of the annealing temperature (230 or 800 °C) (e.g., Li_LYO, Li_230, Li_800).

4.4. Methods of Characterization. Samples were inspected with an FEI Nova NanoSEM 450 high-resolution scanning electron microscope (HRSEM) equipped with an Everhart–Thornley secondary electrons detector and a through-lens detector. Measurements were made in high vacuum with a low acceleration voltage of 5–10 kV. Powdered samples were mixed with ethanol, and the suspension was pipetted on the silicon chip substrate and allowed to dry at ambient temperature. Just before conducting observations in SEM, the samples were treated in UV Prep for SEM by an SPI Supplies device to remove possible contaminants (thin hydrocarbon film) from the specimens' surface.

The morphological and structural details of the material were studied by high-resolution transmission electron microscopy (HRTEM). Cathode LaB₆ was used as a source of electrons. HRTEM is carried out at an accelerating voltage of 300 kV and a theoretical resolution of 1.7 Å. The microscope is equipped with CCD GATAN MULTISCAN (model 794) and an EDS spectrometer (INCA X-stream module OXFORD). Electron diffraction patterns were evaluated using the ProcessDiffraction software. The examined samples for HRTEM were dispersed in ethanol, and a drop of very dilute suspension was placed on a holey-carbon-coated copper grid and allowed to dry by evaporation at ambient temperature.

Atomic force microscopy (AFM) was used to evaluate surface microstructure and thickness of layers. The AFM images were obtained using a Bruker Icon Dimension microscope in ScanAsyst-air contact mode. A silicon tip on a nitride lever was employed for the measurement. An aqueous suspension was pipetted onto an atomically smooth synthetic mica support and spread over the substrate.

XRD measurements were carried out using a PANalytical X’Pert PRO diffractometer equipped with a conventional X-ray tube (Cu Kα radiation, 40 kV, 30 mA, line focus) in transmission mode. An elliptic focusing mirror, a divergence slit of 0.5°, an anticatter slit of 0.5°, and a Soller slit of 0.02 rad were used in the primary beam. A fast-linear position-sensitive detector PIXcel with an anticatter shield and a Soller slit of 0.02 rad were used in the diffracted beam. All patterns were collected in the 2θ range of 4–80° (step of 0.013° and 400 s/step producing a scan of about 2.5 h). The samples were ground in an agate mortar in a suspension with cyclohexane. The suspension was then placed on top of mylar foil. After evaporation of solvent, a thin layer of sample was then covered with the second mylar foil.

In situ high-temperature X-ray powder diffraction (HT-XRD) measurements were carried out in a Bragg–Brentano arrangement using a PANalytical X’Pert PRO diffractometer with a conventional X-ray tube (Co Kα radiation, 40 kV, 30 mA, line focus) and a multichannel detector X’Celerator with an anticatter shield. The diffraction patterns were recorded from 25 to 1000 °C with a step of 50 °C in the 2θ range of 10–76° (step of 0.0334, loading time of 40 s/step, and heating rate of 60 °C/min). An Anton Paar HTHK1600 high-temperature chamber and a platinum holder were used for high-temperature measurements. Preparation of samples before measurement was as follows: samples were ground in an agate mortar in a suspension with cyclohexane. The suspension was then placed on top of the platinum heating element and dried by evaporation at ambient temperature.

Qualitative analysis was performed with HighScorePlus software package (PANalytical, the Netherlands, version 4.8.0), DiffracPlus software package (Bruker AXS, Germany, version 8.0), and JCPDS PDF-4 database. For quantitative phase analysis, DiffracPlus Topas (Bruker AXS, Germany, version 4.2) with structural models based on ICSD database was used. This software allows us to estimate the weight fractions of crystalline phases by means of Rietveld refinement procedure. The estimation of the size of crystallites was...
performed on the basis of the Scherrer formula, as implemented within the DiffracPlus Topas software.

Simultaneous thermogravimetry (TG) and differential scanning calorimetry (DSC) were carried out on apparatus Netzsch STA449 F1. Decomposition of samples (initial mass was approximately 5 mg) was studied in an argon atmosphere (flow rate, 50 mL/min) in a crucible with Al$_2$O$_3$ covered with a lid. The samples were heated at a rate of 10 °C/min up to 1000 °C. The data of the analysis of evolved gases were collected by a single-quadrupole mass selective detector (Agilent Technologies 5977 MSD) coupled with a thermal analyzer through a preheated transfer line. Specified fragments of interest were analyzed in multiple-ion mode type of detection with a dwell time of 50 ms. Observed $m/z$ (mass-to-charge ratio) fragments were selected according to the expected gaseous products known from the literature water (27, 18), oxygen (16, 32), nitrogen oxides (30, 44), carbon dioxide (44), and residual sulfates (64).

Fourier transform infrared (FTIR) spectra were recorded on a Thermo Nicolet Nexus 670 FTIR spectrometer in the region 4000−400 cm$^{-1}$ at a resolution of 4 cm$^{-1}$ using KBr pellets.

The Raman spectra were collected using a DXR Raman microscope (Thermo Scientific); 256 two-second scans were accumulated with 532 nm laser (0.1; 1 or 2 mW), 25 or 50 μm slit under 10X objective of Olympus microscope in full range.

To study the elemental composition of the obtained products, pellets from prepared samples were inspected with a JEOL scanning electron microscope (SEM) JSM-6510LV equipped with an energy-dispersive spectrometer (EDS) by Oxford Instruments with a silicon-drifted detector. EDS measurements were carried out in high vacuum with an accelerating voltage of 20 kV, working distance of 10 mm, and acquisition time of 100 s. Quantitative analyses with EDS were executed after quant optimization on Co standard. The EDS spectra were analyzed with INCA software by Oxford Instruments. The values were normalized to 100% for samples K$_2$$_{2}$O and Na$_2$$_{2}$O. The un-normalized quantitative analysis of Ti in sample Li$_2$$_{2}$O was performed with an electron probe microanalyzer JEOL JXA-8230 with the tungsten source of electron equipped with energy-dispersive spectrometer Bruker QUANTAX 200. The data were calculated with ESPIRIT 2.2a according to the quantification model Phi(Rho, Z) with TiO$_2$ as standard.

Laser ablation inductively coupled mass spectrometry (LA-ICP-MS) was applied to detect lithium content in the pellet prepared from sample Li$_2$$_{2}$O. A NexION 300 inductively coupled plasma mass spectrometer (PerkinElmer, Canada) equipped with the LSX-213 laser ablation system (CETAC) was used during LA-ICP-MS measurements with argon (Ar) as the carrier gas. Three ablation lines were selected on the surface of the sample ($E = 5.0$ mJ; $\phi = 100$ μm; SR = 50 μm/s; $20$ Hz). Transient signals were recorded for $^7$Li and $^{49}$Ti isotopes. They were registered, background-corrected, and integrated using Microsoft Excel with recalculation versus SRM NIST 610 as the external standard. The final results were normalized versus Ti (which was measured with an electron probe microanalyzer as the internal standard).

CHNS elemental analysis (CHNS) was performed in a Thermo Scientific FlashSmart 2000 elemental analyzer (USA). The combustion tube packing was supplied with the instrument and consisted of the following components: EA-2000 chromium oxidizer, high-quality copper reducer, and silver cobaltous-cobaltic oxide. Portions of samples with mass around 1 mg were weighed in tin containers together with vanadium pentoxide ($10$ mg). The concentration of each element in the CHNS analyzer was calculated after the measurement of the corresponding peak areas in the chromatogram.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02570.

Detailed HRSEM micrographs of lyophilized samples (Figure S1), annealed at 230 °C (Figure S2) and 800 °C (Figure S3); TEM observations of samples annealed at 230 °C (Figure S4) and 800 °C (Figure S5); and electron diffraction patterns obtained from samples Li$_2$$_{2}$O (Figure S6) and Li$_2$$_{2}$ (Figure S7), as well as NH$_4$$_{800}$ (Figure S8) (PDF)

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### Notes

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