Inorganic Chemistry

An Alkali-Metal Ion Extracted Layered Compound as a Template for a Metastable Phase Synthesis in a Low-Temperature Solid-State Reaction: Preparation of Brookite from $K_{0.8}Ti_{1.73}Li_{0.27}O_4$

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We have designed a new approach to synthesize brookite, i.e., to extract alkali-metal ions from $K_{0.8}Ti_{1.73}Li_{0.27}O_4$ (KTLO) and to apply simultaneous heat treatment to the remaining lepidocrocite-type layers of TiO_6 octahedra. For the alkali-metal ion extraction and the simultaneous heat treatment, KTLO was heated at 400 °C with polytetrafluoroethylene (PTFE) in flowing Ar. PTFE has been found to be an effective agent to extract strongly electropositive alkali-metal ions from KTLO because of the strong electronegativity of F as its component. The product of this reaction consists of a mixture of brookite, K_2CO_3, LiF, and PTFE derivatives, indicating the complete extraction of K^+ and Li^+ from KTLO and formation of brookite from the lepidocrocite-type layer of TiO_6 octahedra as a template. This brookite has a partial replacement of O^{2-} with F^- and/or slight oxygen deficiency; thus, its color is light-bluish gray. Fully oxidized brookite formation and complete decomposition of PTFE derivatives have been achieved by further heating in flowing air, and coproduced alkali-metal salts have been removed by washing in water. Powder X-ray diffraction, Raman spectroscopy, and chemical analysis results have confirmed that the final brookite product treated at 600 °C is single phase, and it is white. The method to extract alkali-metal ions from a crystalline material using PTFE is drastically different from the common methods such as soft-chemical and electrochemical reactions. It is likely that this new synthetic approach is applicable to other layered systems to prepare a diverse family of compounds, including novel metastable ones.

Introduction

Titania (TiO_2) has extensively been investigated because of its practical properties for a diverse range of applications including use in pigments,[1] photocatalysts,[2] dye-sensitized solar cells,[3] oxygen sensors,[4] and antimicrobial coatings.[5] They have three primary polymorphs in nature namely anatase, brookite and rutile.[6-13] Among the naturally occurring polymorphs, fewer studies on brookite, which is metastable,[7,14] have been reported even though brookite exhibits excellent properties favorable to some applications such as use in photocatalysts,[13,15-20] photoinduced hydrophilic films,[6] and dye-sensitized solar cells.[21] One of the reasons for this limited number of studies on brookite is because its synthesis is more difficult than that of the other polymorphs.[12,13,16] A few approaches to synthesize brookite,

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utilizing liquid phase processes involving hydrolysis,[8,17,22] thermolysis,[21,23,24] hydrothermal[8,11–13,16,25–27] and/or solvo-thermal reactions,[19] have been reported. However, synthesis of single-phase brookite still remains difficult especially in bulk reactions.[11,12,17,28] Therefore, it is interesting and important to investigate a new approach, which is easily scalable, to synthesize brookite.

Gateshki et al. predicted that brookite evolves from a lepidocrocite-type layer of TiO_6 octahedra as an intermediate phase in the case of a solvothermal reaction based on the total XRD coupled to atomic pair distribution function (PDF) analysis.[19] Because $K_{0.8}Ti_{1.73}Li_{0.27}O_4$ (KTLO) is a compound whose structure consists of such lepidocrocite-type layers of TiO_6 octahedra (with partial occupation of Li^+ in the Ti^{4+} site) interspersed with K^+,[29,30] we expected that extraction of the alkali-metal ions from KTLO with appropriate heat treatment might also yield brookite.

Extraction of alkali-metal ions from a host structure is generally performed using traditional methods such as soft-chemical[30–34] or electrochemical[35] reactions. These reactions, especially the soft-chemical approaches, are quite advantageous to synthesize metastable phases because only a part of a host structure is modified and the fundamental atomic framework of the host is retained topochemically in their low-temperature reactions. Such metastable phases can hardly be synthesized by typical calcination reactions because high-temperature reactions mainly lead to the formation of thermodynamically stable phases.[34] However, for those general alkali-metal ion extraction reactions, the positive charge of extracted alkali-metal ions is compensated by ion-exchanged cations or oxidation of other metal ions in the host. We expect that such a charge compensation is neither necessary nor preferable to form brookite from KTLO. In addition, investigation of a completely new approach to synthesize metastable materials is desired in order to open a new field to explore in synthetic chemistry.

A new possible approach to extract alkali-metal ions from a host structure is to use a F-containing organic agent. Because alkali metals are very electropositive, they are expected to easily react with an agent containing a very electronegative element such as F to form alkali fluorides. In addition, charge compensation for the extracted alkali-metal

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Scheme 1. Brookite Preparation via Alkaline-Metal Ion Extraction from Lepidocrocite-Type KTLO and Heat Treatment
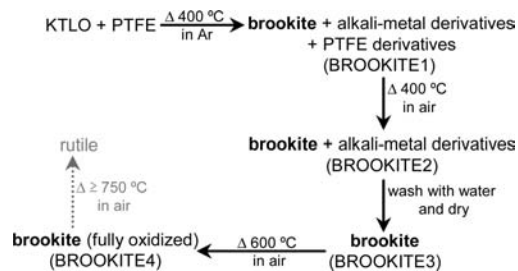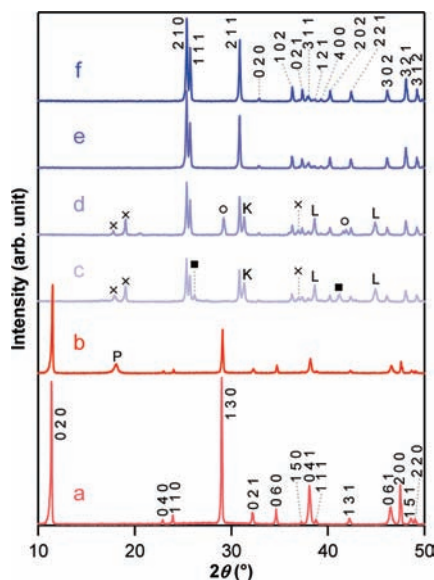

ions in the oxide host is expected to take place with the simultaneous extraction of excess O from the oxide host to maintain the charge balance in the alkali-metal ion extracted oxide product, where the O is consumed to oxidatively decompose the alkali-metal ion extraction agent, if it is organic and the reaction takes place in an inert atmosphere. Furthermore, derivatives of such an organic agent formed after the reaction can be oxidatively decomposed by subsequently heating them in O_2 gas or air. Utilization of these series of reactions in solid state synthesis is a novel approach, which is likely to be applicable to producing a diverse family of compounds from various layered-compound precursors.

One of the candidates for such agents to extract alkali-metal ions from KTLO is polytetrafluoroethylene (PTFE). The reason why PTFE becomes a candidate is because it consists of C and F only. Thus, it must be ideal to extract alkali-metal ions as alkali fluorides and excess O for charge compensation. In this paper, we report successful brookite synthesis via alkali-metal ion extraction from KTLO with simultaneous heat treatment using PTFE as the extraction agent. The detailed synthetic procedure and results of characterizations of the brookite product and its intermediate phases are discussed.

Experimental Procedure

Materials. The brookite synthesis from KTLO was performed by multistep reactions as indicated in Scheme 1. First, KTLO was prepared as a precursor by the solid state reaction of K_2CO_3, TiO_2, and Li_2CO_3 as described elsewhere.[30] Second, extraction of the alkali-metal ions from KTLO was performed using PTFE as a source of F for the fluoride salt formation. Thoroughly mixed KTLO/PTFE (1:1.8 in mol) for the following expected reaction was heated at 400 °C in a 100 mL/min flow of Ar for 12 h:

$$K_{0.8}Ti_{1.73}Li_{0.27}O_4 + 0.535CF_2 \rightarrow 1.73TiO_2 + 0.8KF + 0.27LiF + (0.535 - x)CO_y + xC \quad (1)$$
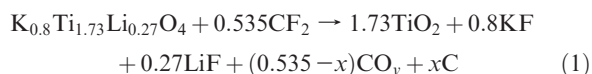
where the CF_2 monomer unit was used to represent PTFE in this stoichiometry. The excess amount of PTFE was necessary in order to achieve the complete alkali-metal ion extraction from KTLO. In addition, heating in the inert atmosphere was necessary in order to avoid the excessive oxidative decomposition of PTFE at this stage. The product of this reaction is denoted as BROOKITE1. Third, BROOKITE1 was heated at 400 °C in a 300 mL/min flow of air for 24 h with one intermittent grinding in order to oxidatively decompose the PTFE derivatives. The brookite product after this heat treatment is denoted as BROO-KITE2. Fourth, BROOKITE2 was washed with copious amount of water in order to dissolve and rinse out the copro-duced alkali-metal derivatives. This washed phase was dried in air, and it is denoted as BROOKITE3. Finally, BROOKITE3

Figure 1. Powder XRD patterns of (a) KTLO, (b) KTLO + PTFE, (c) BROOKITE1, (d) BROOKITE2, (e) BROOKITE3, and (f) BROOKITE4.

was heated at 600 °C in a 300 mL/min flow of air in order to fully oxidize the brookite product. This final product is denoted as BROOKITE4.

Characterizations. The powder X-ray diffraction (XRD) patterns of the product and all its intermediates were obtained using Cu Kα radiation on a Rigaku RINT2200V/PC diffractometer. The diffraction peaks were indexed, and the lattice parameters were refined using APPLEMAN software.[36] The structural data of the previously reported brookite phase were used as starting parameters for these processes.[37] The elemental compositions of the brookite products were analyzed by flame atomic absorption spectrometry (FAAS), inductively coupled plasma-optical emission spectrometry (ICP-OES), and the lanthanum-alizarin complexone method for alkali metals (K and Li), Ti and F, respectively. For FAAS and ICP-OES, samples were dissolved in a mixture of H_2SO_4 and HF, and for the lanthanum-alizarin complexone method, samples were dissolved in molten Na_2CO_3. Morphology analysis of the brookite product and its intermediates was performed using a Keyence VE-8800 scanning electron microscope (SEM) at an accelerating voltage of 5 kV. Finally, Raman spectra of BROOKITE3 and BROOKITE4 were obtained using the 514-nm output from a krypton/argon laser as the excitation source. The spectrometer was calibrated using the silicon Raman mode.

Results and Discussion

The powder XRD pattern of KTLO is shown in Figure 1a. All the reflections can be well indexed on the basis of the orthorhombic structure of KTLO reported previously.[30] Figure 1b shows the diffraction pattern of KTLO mixed with PTFE before heating. PTFE exhibited a broad diffraction hump around 18° as indicated with "P" in the figure.

The powder XRD patterns of BROOKITE1, BROO-KITE2, BROOKITE3, and BROOKITE4 are shown in Figure 1c–f. All the peaks from KTLO disappeared after heating it with PTFE in Ar, and most of the major peaks in

the diffraction patterns can be indexed on the basis of the structure of brookite reported previously.[37] This confirms that brookite was undoubtedly formed from KTLO. However, several peaks that cannot be attributed to the brookite structure were observed for BROOKITE1 and BROO-KITE2. Among them, the highest intensity peak around 31°, which is marked with "K", corresponds to a reflection from a few polymorphs of K_2CO_3,[38,39] and the second and third highest intensity peaks around 39 and 45°, which are marked with "L", correspond to reflections from LiF.[40] Our original intention to react KTLO with PTFE was to convert all alkali-metal ions (K^+ and Li^+) in KTLO into their fluoride salts such as KF and LiF as in eq 1. The diffraction patterns of BROOKITE1 and BROOKITE2 did indicate that Li^+ was certainly reacted to form LiF as expected. This LiF formation is attributed to the strong electropositivity of Li and strong electronegativity of F. However, K^+ was converted into K_2CO_3, and no trace of KF was observed. Because the reaction took place in a flow of high purity Ar ($> 99.999\%$), we expect that the O in the carbonate ions was from partial replacement of O^{2-} with F^- and/or the formation of oxygen deficiencies in the brookite product as discussed in later sections. In addition, the source of C in carbonate ions must be PTFE. We expect that this preferential reaction of K^+ with carbonate ions originates from the fact that its interlayer site is more accessible than the intralayer site of Li^+, and K_2CO_3 formation likely took place before LiF formation because Li^+ is in the less accessible octahedral site in the host layer. These reflections marked with "K" and "L" of BROOKITE1 and BROOKITE2 disappeared upon washing them with water, as shown in the diffraction pattern of BROOKTITE3 (Figure 1e). However, those peaks did not disappear upon heating them in flowing air during the conversion from BROOKITE1 to BROOKITE2. These results also indicated that those reflections were from water-soluble alkali-metal salts rather than PTFE derivatives, which were expected to oxidatively decompose in air at the reaction temperature and not to dissolve in water. In addition, other diffraction peaks marked with "×" of BROOKITE1 and BROOKITE2 behaved similarly to those marked with "K" and "L". Therefore, those peaks are also considered to be from some sort of unidentified water-soluble alkali-metal compounds. Previously, F-containing compounds such as PTFE were often used to partially replace O^{2-} in oxides or to fill in the oxygen deficiency with F^-.[41–45] However, the results from the present study indicate that PTFE can also be used to extract alkali-metal ions from a layered compound.

A photograph of BROOKITE1 is shown in Figure 2b. The starting mixture of KTLO (Figure 2a) and PTFE was white, but the heat treatment at 400 °C in Ar turned it black. This black color is mainly attributed to carbon or other PTFE

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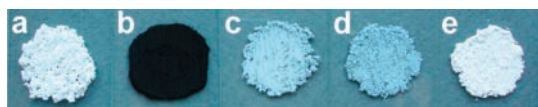
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Figure 2. Photograph of (a) KTLO, (b) BROOKITE1, (c) BROO-KITE2, (d) BROOKITE3, and (e) BROOKITE4.

Table 1. Analytically Determined Molar Elemental Compositions of the Intermediate and Final Brookite Products

	K	Ti	Li	F
KTLO[a]	0.46	1	0.16	
BROOKITE1	0.45	1	0.16	1.86[b]
BROOKITE3	0.016	1	0.005[c]	0.080
BROOKITE4	0.016	1	0.005[c]	0.035

[a] The elemental composition of KTLO is nominal based on its chemical formula, $K_{0.8}Ti_{1.73}Li_{0.27}O_4$. [b] For the analysis, the sample had to be dissolved in Na_2CO_3. However, it decomposed at a temperature below the melting point of Na_2CO_3. Thus, not all F from the sample might have been dissolved in Na_2CO_3, and the analytically determined F content might be lower than the actual one. [c] These values are within the background range of the analysis.

derivatives that tend to form when PTFE is heated in an inert atmosphere. As mentioned before, PTFE exhibited a broad diffraction feature around 18° as indicated with "P" in Figure 1b, but it disappeared upon heating at 400 °C in Ar (Figure 1c). This result suggested that PTFE was totally reacted to extract alkali-metal ions from KTLO and to form the alkali-metal and PTFE derivatives by this first heat treatment. In addition, the result of the elemental analysis indicated that a significant amount of F was remaining in the BROOKITE1 sample (Table 1). Because no KF formation was detected by powder XRD of BROOKITE1, we believe that a large portion of remaining F was in the PTFE derivatives. Furthermore, diffraction peaks from unidentified phases marked with "■" were observed in the XRD pattern of BROOKITE1 (Figure 1c), and those peaks disappeared upon further heat treatment in flowing air to form BROOKITE2 (Figure 1d). This result suggested that those peaks were from the PTFE derivatives coexisting with brookite, and they oxidatively decomposed by heat treatment in air. The black color of BROOKITE1 could also arise if Ti^{4+} in brookite is significantly reduced to the 3+ oxidation state, which might originate from a partial replacement of O^{2-} with F^- and/or oxygen deficiency. However, our preliminary investigation of such a possibility by XPS on BROOKITE1 indicated no clear sign of Ti^{3+} existence. That is another reason why we believe that the black color of BROOKITE1 is mainly due to the color of the PTFE derivatives.

For BROOKITE2, in addition to the peaks marked with "K", "L", and "×" for BROOKITE1, peaks marked with "○" around 29 and 42° were observed in its diffraction pattern (Figure 1d). These peaks disappeared after washing it with water to form BROOKITE3 (Figure 1e); thus, we believe that those peaks were also from some kind of water-soluble alkali-metal compounds. Furthermore, the color of BROOKITE2 was light-bluish gray as in Figure 2c. Disappearance of the black color of BROOKITE1 by the heat treatment in air indicated that the PTFE derivatives, which were black, were oxidatively decomposed. A white color is generally expected for pure and fully oxidized brookite. The fact that the color of BROOKITE2 was light-bluish gray suggested that a small fraction of Ti^{4+} in BROOKITE2 was
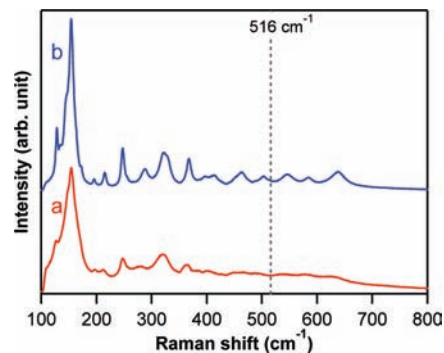

Figure 3. Raman spectra of (a) BROOKITE3 and (b) BROOKITE4.

reduced to a 3+ state as occasionally observed for reduced oxides. This reduction of Ti^{4+} might arise from the formation of an oxygen deficiency in the brookite product due to the carbonate ion formation as mentioned above. In addition, partial replacement of O^{2-} with F^- from PTFE might also have reduced Ti^{4+} in the brookite product.

The powder XRD pattern of BROOKITE3 is shown in Figure 1e. All diffraction peaks observed were from the brookite phase, and no trace of peaks from other phases was observed. It is well-known that most of the intense diffraction peaks from brookite overlap with those from anatase. However, some peaks of anatase such as the 1 0 3 reflection around 37° do not significantly overlap with the peaks of brookite.[46] No such unique peak from anatase was observed in the diffraction pattern of BROOKITE3. Furthermore, all the peaks in the Raman spectrum of BROOKITE3 corresponded well with those expected from single-phase brookite, and unique Raman-shift peaks of anatase, such as that expected around 516 cm^{-1} for A_{1g} and B_{1g} modes, were not observed as in Figure 3a.[9,10,12,13,15,47,48] Therefore, these powder XRD and Raman spectroscopy results confirmed that brookite, which was single-phase within the phase detection limit of the experiments, was successfully formed by alkali-metal ion extraction from KTLO with simultaneous heat treatment. However, the color of BROOKITE3 was not white, but light-bluish gray (Figure 2d), as also described in the previous section for BROOKITE2. This suggests the partial existence of Ti^{3+} in BROOKITE3 due to the possible reduction of Ti^{4+}. Results of the elemental analysis indicated that the K, Li, and F contents in BROOKITE3 were much lower than those in BROOKITE1. This means that alkali-metal ions were successfully extracted from KTLO (Table 1). However, a small but measurable amount of F remained in BROOKITE3. Considering the fact that BROOKITE3 is crystallographically single phase, it is rational to believe that F^- is partially occupying the O^{2-} site of brookite produced in this study. Thus, Ti^{4+} in the brookite product is likely to be partially reduced to the 3+ state in order to balance the charge.

The powder XRD pattern of BROOKITE4 is shown in Figure 1f. The diffraction pattern of BROOKITE4 remained virtually identical to that of BROOKITE3. However, the light-bluish gray color of BROOKITE3 turned into the white of BROOKITE4 after heat treatment at 600 °C in

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Table 2. Lattice Parameters of the Intermediate and Final Brookite Products

	a (nm)	b (nm)	c (nm)
BROOKITE1	0.9178(3)	0.5451(2)	0.5138(2)
BROOKITE2	0.9176(3)	0.5448(2)	0.5135(2)
BROOKITE3	0.9169(2)	0.5451(1)	0.5138(1)
BROOKITE4	0.9172(2)	0.5445(1)	0.5133(1)

flowing air, as in Figure 2e. This result indicated that full oxidation of brookite in BROOKITE4 was achieved upon this heat treatment. The results of the elemental analysis (Table 1) agreed with this observation. The remaining F content in BROOKITE4 became less than a half of that in BROOKITE3 by this final heat treatment. It is likely that a still remaining trace amount of alkali metals and F can further be reduced to the desired level by additional washing in water and repeated and/or prolonged heat treatment in flowing air. In addition, peaks in the Raman spectrum of BROOKITE4 became sharper than those in BROOKITE3 (Figure 3). We expect that this change is mainly due to the significant enhancement of the crystallinity and full oxidation of the brookite product by the heat treatment at 600 °C.

For BROOKITE1, BROOKITE2, and BROOKITE3, we have attempted to elucidate the difference in their F content (and/or amount of Ti^{3+}) and the amount of possible oxygen deficiency by comparing their lattice parameters. However, no significant difference in their lattice parameters was observed, as seen in Table 2. These close lattice parameter values reflect the fact that ionic radii of O^{2-} and F^- are not significantly different, and the amounts of F^- and possible oxygen deficiency in brookite produced in this study were small.

In addition, morphologies of the brookite products were analyzed by SEM because they are quite important for some applications. As-prepared KTLO crystallites have a plate-like morphology reflecting its layered structural nature, as in Figure 4a. The crystallite sizes are approximately 1 μm, and they have well-defined smooth surfaces. After the reaction to form BROOKITE1, the surface of those crystallites became rough (Figure 4b). It is likely that small particles of the PTFE and alkali-metal derivatives were covering the surface of the brookite crystallites to make them rough. However, the crystallite sizes of BROOKITE1 seemed to remain the same as those of as-prepared KTLO. Further heat treatment in an air flow and subsequent washing in water to form BROOKITE3 made the surface of the crystallites more well-defined than that of BROOKITE1, indicating the removal of the PTFE and alkali-metal derivatives (Figure 4c), and the sizes of the BROOKITE3 crystallites became smaller than those of BROOKITE1. The final heat treatment at 600 °C to form BROOKITE4 further reduced the crystallite sizes down to a few hundred nanometers (Figure 4d). It is likely that a rearrangement of TiO_6 octahedral connectivity for the transformation of KTLO to brookite induced cracks in the brookite crystallites, and those cracks became more pronounced by repeated heating at higher temperatures,
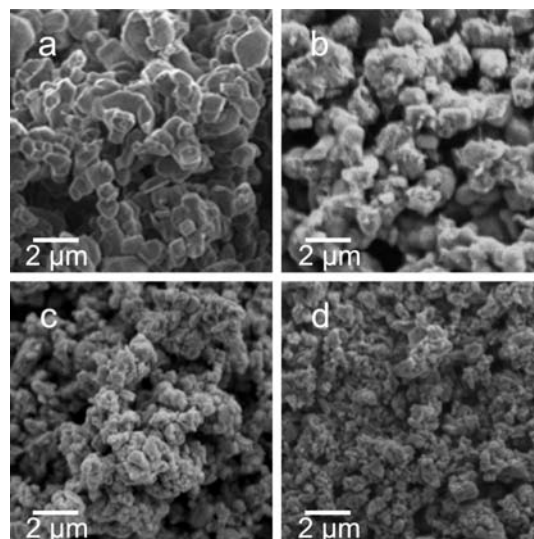
Figure 4. SEM images of (a) KTLO, (b) BROOKITE1, (c) BROOKITE3, and (d) BROOKTITE4.

resulting in the reduced crystallite sizes. Because higher performance in photocatalytic applications is expected for brookite with smaller particle sizes, brookite produced in this study might be suitable for such an application.[16]

A brookite-to-rutile transition generally takes place directly[9,14,15,49,50] without forming another polymorph, such as anatase, as an intermediate, except for in one rare case.[51] This trend is consistent with the relative thermal stability order: rutile > brookite > anatase.[8] In addition, according to Li and Ishigaki, the brookite-to-rutile transition takes place in the wide temperature range ~400−1000 °C depending on a variety of factors including crystallite size, size distribution, contact area of the crystallites in powder forms, the impurity type and its concentration, and atmosphere.[15] However, low-temperature phase transition to rutile is quite limited, and most of the previously reported brookite-to-rutile transformation took place above 600 °C.[8,17] We have taken the powder XRD patterns of BROOKITE3 heated at 700, 750, 800, and 850 °C in 300 mL/min flowing air (Figure 5). A sign of the rutile formation was observed at 750 °C (Figure 5b). At 800 °C, very low intensity peaks, which were attributed to a trace amount of K-extracted titania $K_{0.0}Ti_8O_{16}$ (also called as $TiO_2(H)$), were observed.[52,53] Finally, single-phase rutile was formed at 850 °C (Figure 5d). In the case where anatase emerges as an intermediate phase, the relative intensities of the two peaks around 25° are expected to change upon heating because anatase exhibits a strong intensity peak in this region.[13] However, no such change in the relative intensities of those peaks was observed. Considering the fact that the diffraction peak intensities from the intermediate $TiO_2(H)$ phase at 800 °C were negligibly small, BROOKITE3-to-rutile transition was virtually direct. Thus, the thermal phase transformation behavior of brookite produced in this study was similar to that of the general brookite products reported previously.

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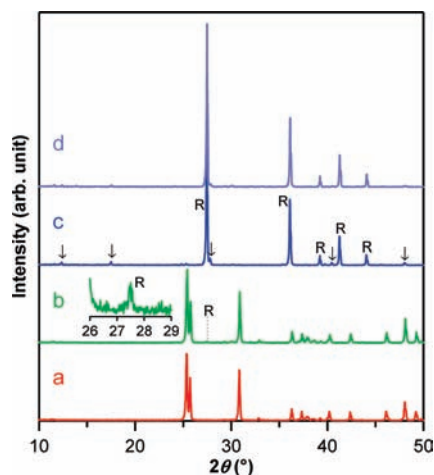
Figure 5. Powder XRD patterns of BROOKITE3 heated at (a) 700, (b) 750, (c) 800, and (d) 850 °C. The peaks marked with "R" are from rutile, and "↓" indicates the positions of very low intensity peaks from a trace amount of an intermediate phase, $TiO_2(H)$. (Inset) The expanded diffraction pattern of BROOKITE3 heated at 750 °C.
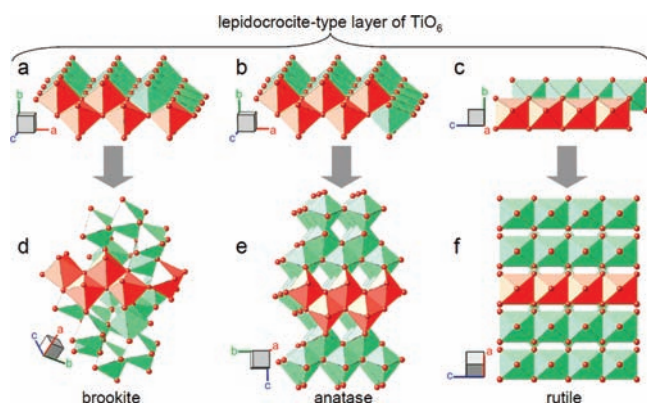

Figure 6. Structures of (a−c) the lepidocrocite-type layers in KTLO, (d) brookite, (e) anatase, and (f) rutile. The similar linkages of TiO_6 octahedra in these structures are exemplified in red color.

On the basis of the PDF analysis, Gateshki et al. suggested that the brookite, anatase, and rutile phases all evolve from the lepidocrocite-type layer of TiO_6 octahedra as an intermediate phase in case of the solvothermal synthesis, and a particular polymorph can be synthesized in a controlled manner by selecting the solvent type and adjusting its acidity (pH).[19] The lepidocrocite-type layer of TiO_6 octahedra, brookite, anatase, and rutile all consist of corner- and/or edge-shared TiO_6 octahedral linkages (see Figure 6, which is based on the model by Gateshki et al.).[19] The connectivity similarity of TiO_6 octahedra between the rutile and the lepidocrocite-type layer is limited only to the edge-shared linear chains of TiO_6 octahedra, and other parts of the rutile structure, consisting of corner-shared linkages of TiO_6 octahedra, are rather different. This should be the reason why the rutile formation requires higher energy, in other words, higher temperature, in order to accomplish a relatively higher degree of structural rearrangement.[19] On the other hand, both edge- and corner-shared linkages of TiO_6 octahedra in brookite and anatase are similar to those in the lepidocrocite-type layer. Thus, less rearrangement of the structural units within the lepidocrocite-type layer of TiO_6 octahedra is expected in order to transform it into brookite and anatase

rather than into rutile.[19,54] Brookite was formed at 400 °C in the present study. As a matter of fact, such a low-temperature reaction should limit phase transformations to only those involving relatively small rearrangements of the structural units, especially in the case of solid state reactions.[31,32,55] As mentioned above, the relative thermal stability order, brookite > anatase, has been reported,[8] and brookite prepared in this study was stable in a wide temperature range from 400 to 700 °C. These suggest that a possible factor of the preferential formation of brookite rather than anatase from KTLO in this study is their relative thermal stabilities.

In addition, as in the case for the selectively formed brookite via controlled reaction conditions in liquid media, a kinetic factor might also be involved in the selective formation of brookite in this present study.[56] According to the PDF analysis by Gateshki et al., atomic ordering in the lepidocrocite-type layer of TiO_6 octahedra is structurally closer to brookite than that of rutile and anatase.[19] On the basis of such similarity in atomic ordering between the lepidocrocite-type layer of TiO_6 octahedra and brookite, we believe that kinetically favored structural evolution takes place by nucleation of the brookite phase from a partial structural unit in the lepidocrocite-type layer, such as that indicated in Figure 6a in red, as a template.

Furthermore, possible F^- substitution into the O^{2-} site and/or oxygen deficiency formed in the alkali-metal ion extracted KTLO host (the lepidocrocite-type layer of TiO_6 octahedra) in this study might be crucial factors realizing its transformation into brookite rather than anatase. It has been reported that KTLO can be protonated to $H_{1.07}Ti_{1.73}O_4 \cdot H_2O$ (HTLO), and HTLO can be exfoliated into $Ti_{0.87}O_2$ nanosheets soft-chemically.[30,57] In the structure of these KTLO derivatives, the lepidocrocite-type layers of TiO_6 octahedra are retained without substitution of O^{2-} with other ions and/or formation of oxygen deficiency. The topotactic nature of the transformation of KTLO into HTLO and $Ti_{0.87}O_2$ nanosheets is attributed to the result of charge compensation during the room-temperature soft-chemical processes. These HTLO and $Ti_{0.87}O_2$ nanosheets, which completely retain the lepidocrocite-type layers of TiO_6 octahedra, transform into anatase upon heating.[58] On the contrary, alkali-metal ion extraction in the present study takes place at 400 °C. In such a midtemperature range, F^- substitution into the O^{2-} site and/or oxygen deficiency might arise in the lepidocrocite-type layer of the KTLO host during the alkali-metal ion extraction and simultaneous heating processes rather than after the formation of brookite. Such slight modification of the lepidocrocite-type layer might be essential for it to become a template for the brookite formation.

Conclusion

Brookite was successfully prepared from KTLO by alkali-metal ion extraction with simultaneous heat treatment.

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To the best of our knowledge, this is the first solid state synthesis of brookite under ambient pressure. This synthetic approach can easily be scaled up for bulk brookite production and enable characterizations and practical utilization of brookite. Our experimental results proved that the lepidocrocite-type layer of TiO_6 octahedra in KTLO is a useful template for brookite formation as previously predicted by PDF analysis.[19] In addition, with appropriate modifications of reaction conditions, such as reaction atmosphere, the source of F, and its amount, other polymorphs of titania might also be formed from the lepidocrocite-type layer of TiO_6 octahedra in KTLO in a controlled manner, just like the case for the solvothermal approach.[19] Furthermore, PTFE was found to be an effective agent to extract alkali-metal ions from KTLO at a temperature as low as 400 °C. The new synthetic approach utilized in this study is likely to be applicable to other layered systems to prepare a diverse family of compounds, including novel ones; thus, it would open a new field to explore in synthetic chemistry.

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