# Facile synthesis of >?99% phase-pure brookite TiO2 by hydrothermal conversion from Mg2 TiO4

# Facile synthesis of >99% phase-pure brookite TiO$_2$ by hydrothermal conversion from Mg$_2$TiO$_4$

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**Abstract:**

The synthesis of pure brookite is generally much more difficult than that of pure anatase. The hydrothermal conversion, recently developed by Kozawa et al., is a facile method to synthesize brookite TiO$_2$ from inverse spinel-type Mg$_2$TiO$_4$ under a mild hydrothermal condition *e.g.* in 1 M HCl solution at 100°C. However, slight rutile TiO$_2$ is usually co-existed under the reported conditions. The aim of this study is to prepare a high-purity brookite TiO$_2$ powder by the hydrothermal conversion from Mg$_2$TiO$_4$. We investigated the conditions of Mg$_2$TiO$_4$ preparation and hydrothermal conversion, and it was found that the most important factor for the high-purity brookite synthesis, *i.e.* decreasing the co-existing rutile TiO$_2$, was to prepare the Mg$_2$TiO$_4$ precursor without MgTiO$_3$. Using an MgO-rich composition and adding a second calcination step for the Mg$_2$TiO$_4$ preparation yielded a high-purity (99.3 wt %) brookite powder with a surface area of 27.7 m$^2$/g. Under the current experimental conditions, addition of a surfactant or an alcohol for the hydrothermal treatment was not apparently effective for the high-purity brookite synthesis.

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## 1. Introduction

Titanium dioxide ($TiO_2$) is a representative photocatalyst with several useful functions, such as antibacterial [1,2], deodorizing [3], antifouling [4], $NO_x$ removal [5], self-cleaning [6,7], and antifogging. $TiO_2$ has three naturally occurring polymorphs, i.e., rutile, anatase and brookite. Rutile and anatase are widely used for practical applications since they are easily synthesized and cost-effective. In our previous study [8], we reported that the excessive oxidizing ability of anatase $TiO_2$ caused some problems in the self-cleaning; it formed $CaSO_4$ white precipitates on a window from atmospheric pollutants. Hence, in our recent study [9], we have focused on brookite $TiO_2$ with a *mild* oxidizing ability, which is suitable for the self-cleaning.

The synthesis of pure brookite is generally much more difficult than that of pure anatase. Several groups used $TiCl_4$ as a precursor for the brookite synthesis [10-12]. However, $TiCl_4$ is relatively difficult to handle, and in many cases, the resulting $TiO_2$ became a mixture of brookite and rutile. Meanwhile, Tomita et al. [13] developed an excellent protocol to synthesize a single-phase brookite powder using a hydrothermal treatment of a water-soluble complex precursor, $(NH_4)_6[Ti_4(C_2H_2O_3)_4(C_2H_3O_3)_2(O_2)_4O_2]\cdot4H_2O$, but this protocol required many experimental steps.

Recently, Kozawa et al. [14] have reported another protocol using a hydrothermal treatment of a simple double-oxide precursor, $Mg_2TiO_4$. The hydrothermal conversion of $Mg_2TiO_4$ to brookite proceeds under a mild hydrothermal condition, *e.g.* in 1 M HCl solution even at 100 °C. The advantages of the Kozawa method are to use stable and cost-effective ingredients and its easy experimental operations. It is practical to obtain brookite $TiO_2$ powder, but its phase purity is not as prominent as the Tomita method [13]. In our recent work on the self-cleaning [9], we have synthesized brookite powders via the Kozawa method. Actually, the obtained $TiO_2$ was a mixture of brookite and rutile, and the highest purity of brookite was 97.2 wt % [9]. Such residual rutile $TiO_2$ can be also seen in the original report by Kozawa et al. (Fig. 1(b) [14]).

Here, we investigated a synthetic condition for high-purity brookite (>99%) by optimizing the $Mg_2TiO_4$ preparation and the hydrothermal conversion. The additive effects of a surfactant and an alcohol for the hydrothermal treatment are also reported.

## 2. Experimental procedures

### 2.1 $Mg_2TiO_4$ preparation

The experimental conditions were similar to our previous report [9]. At first, $Mg_2TiO_4$ powder was synthesized by a solid-state reaction between $MgCO_3$ (basic) [or more precisely, $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$] and anatase $TiO_2$ powders (both 99.9% purity, Kojundo Chemical Laboratory). Prior to weighing, TG-DTA analysis (up to 1000 °C, DTA-50, Shimadzu) was conducted on the $MgCO_3$ (basic) powder to determine the weight-loss during the heating. Taking into account the compositional calibration using the TG-DTA results, the $MgCO_3$ (basic) and the anatase $TiO_2$ powders were weighed to be stoichiometric ratio of $MgO:TiO_2$=2:1: sample **(a)**. The other was weighed so as to be 5 wt % excessive MgO rather than the stoichiometric $Mg_2TiO_4$ composition: sample **(b)**.

These powders were planetary ball-milled (acceleration: 4 G, Pulversette 6, Fritsch) with $ZrO_2$ balls in ethanol (EtOH) for 2 h. The mixed slurries were vacuum dried, and the dried powders were placed in an oven at 80 °C for 1 h. The mixed powders were calcined at 1250 °C for 2 h in air. As for the powder sample **(b)**, after calcination at 1250 °C for 2 h, it was pulverized in an agate mortar, and then it was re-calcined at 1270 °C for 2 h in air: sample **(c)**.

### 2.2. Hydrothermal treatment and phase analysis

**Table 1** summarizes typical compositions for the hydrothermal treatment. Note that to emphasize the effects of hydrothermal conditions, 2 g loading (instead of 1 g [9]) of $Mg_2TiO_4$ was mainly tested; i.e., if the hydrothermal conversion was not sufficient, the brookite yield became much smaller. The synthesized $Mg_2TiO_4$ powder, namely sample **(a)**, **(b)** or **(c)**, and HCl aq. solution were put into an autoclave with a polytetrafluoloethylene inner container, and the hydrothermal conversion was conducted at 150 °C for 24 h in a static condition. Each resulting product was collected using a membrane filter, washed with distilled water, and dried at 80 °C.

Since a surfactant may act as a structure-directing agent to preferentially yield brookite during the hydrothermal treatment, laurylamine hydrochloride (LAHC) was added to the above sample **(a)** or **(c)** so that the weight ratio of $Mg_2TiO_4$:LAHC was 4:1. These powders and HCl aq. were put into an autoclave, and the hydrothermal conversion was also conducted at 150 °C for 24 h.

Also, since an alcohol addition to hydrothermal conversion may shorten the reaction time (via a solvothermal effect) with reducing the nucleation and growth of rutile $TiO_2$, EtOH was added to HCl aq. so that the volume ratio of HCl aq.:EtOH was 2:1. Sample **(a)** or **(c)** and the mixture of HCl aq./EtOH were put into an autoclave, and the solvothermal treatment was conducted at 150 °C for 8 h.

The constituent phases of the samples were analyzed by X-ray diffraction (XRD, Multiflex, Cu-K$\alpha$, 40 kV and 40 mA, Rigaku) at a scanning rate of 4 °/min. The microstructure of the brookite $TiO_2$ powders was observed by scanning electron microscopy (SEM, SU-70, Hitachi High-Technologies). Specific surface area of the brookite powder was determined by BET method using a nitrogen gas sorption analyzer (Autosorb-3-AG, Quantachrome).

## 3. Results and discussion

**Figure 1** shows XRD patterns of the powders before the hydrothermal treatment. Main peaks of the sample **(a)** were identified to $Mg_2TiO_4$. Sample **(b)** was quite similar to sample **(a)**. However, there were several peaks corresponding to $MgTiO_3$ at $2\theta \sim 33°$, $41°$, and $49.5°$. Therefore, strictly speaking, the samples **(a)** and **(b)** were $Mg_2TiO_4$/$MgTiO_3$ mixtures. Although excess MgO was added to the sample **(b),** $MgTiO_3$ could not be fully removed. Meanwhile, the sample **(c)**, which was re-calcined at 1270 °C of sample **(b)**, did not contain the $MgTiO_3$ peaks. Hence, sample **(c)** consisted of single-phase $Mg_2TiO_4$, at least under the standard XRD resolution. Excess MgO may exist as amorphous $Mg(OH)_2$ and $MgCO_3$ (by reactions with atmospheric $H_2O$ and $CO_2$). Also $Mg_2TiO_4$ with inverse spinel structure may accommodate some excess MgO, although a report MgO-$TiO_2$ phase diagram depicts $Mg_2TiO_4$ as a line compound (without a solid solution) [15]. From this result, in order to prepare single-phase $Mg_2TiO_4$, it is effective to add excess amount of MgO and to add a second calcination step.

**Figures 2** and **3** show XRD patterns of the powders after the hydrothermal treatment of

the samples **(a)** and **(b)**, and the sample **(c)**, respectively. The weight fractions of brookite and rutile $TiO_2$ can be estimated from the following empirical equation proposed by Zhang and Banfield [16, 17]:

$$W_B = \frac{2.721 A_B}{A_R + 2.721 A_B} \tag{1}$$

where $W_B$ represents the weight fraction of brookite, and $A_B$ and $A_R$ represent the integrated intensities of the peaks of brookite 121 and rutile 110, respectively. **Table 1** summarizes the weight fractions estimated using the Eq. 1. Because the sample **(d)** was synthesized using the same conditions in our previous report [9], the XRD pattern and the brookite fraction of sample **(d)** (97.2 wt %) are used as the benchmarks in **Figs. 2**, **3** and **Table 1**.

In the XRD pattern of sample **(e)**, synthesized from the MgO-rich $Mg_2TiO_4$ precursor (sample **(b)**), the rutile 110 peak appears larger than the sample **(d)**. The brookite fraction (92.8 wt %) of the sample **(e)** was smaller than that of the sample **(d)**. In the XRD pattern of sample **(f)**, synthesized with LAHC surfactant, the rutile 110 peak appears a little broader and lower height than the sample **(d)**. The brookite fraction (95.0 wt %) of the sample **(f)** was smaller than that of the sample **(d)**. In the XRD pattern of sample **(g)**, synthesized with EtOH (for 8 h), the rutile 110 peak seems clearly higher than the sample **(d)**. The brookite fraction (92.8 wt %) of the sample **(g)** was smaller than that of sample **(d)**.

In the XRD pattern of sample **(h)**, synthesized from the sample **(c)**, the rutile 110 peak was the smallest. The brookite fraction of the sample **(h)** was 99.3 wt %, which was the highest purity brookite powder we had ever synthesized. As for sample **(j)** synthesized with LAHC surfactant, and sample **(k)** synthesized with EtOH, these powders had smaller brookite fractions, similarly to the samples **(f)** and **(g)**. However, by comparison between same hydrothermal conditions, the use of the sample **(c)** as a precursor became larger brookite fraction than that of the sample **(a)**. Throughout this study, the purity of $Mg_2TiO_4$ is a dominant factor to synthesize purer brookite powder.

**Figure 4** shows a SEM micrograph of the brookite powder, sample **(h)**, with the surface area of 27.7 $m^2/g$. Similarly to the previous work [9], the brookite powder retained macroscopic shape of micrometer-sized $Mg_2TiO_4$ particles, but was actually composed of a large number of

minute particles (ca. 50-100 nm). Facetted growth with dipyramidal idiomorphs of brookite $TiO_2$ was observed.

## 4. Conclusions

To prepare a high-purity brookite $TiO_2$ powder by the hydrothermal conversion from $Mg_2TiO_4$, improved conditions of the $Mg_2TiO_4$ preparation and the hydrothermal conversion were investigated. The most important factor for the high-purity brookite synthesis is to prepare the $Mg_2TiO_4$ precursor without $MgTiO_3$. It is effective to use an MgO-rich composition and to add a second calcination step for the $Mg_2TiO_4$ preparation, which yielded a high-purity (99.3 wt %) brookite $TiO_2$.

## Acknowledgements

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## Tables

**Table 1** Hydrothermal conditions and final weight fractions of brookite and rutile.

| Samples | Precursor powder | Surfactant (LAHC) | Alcohol (EtOH) | HCl aq. | Hydrothermal duration (h) | Brookite (wt %) | Rutile (wt %) |
|---|---|---|---|---|---|---|---|
| (d) | 1 g (a) | | | 1M 30 mL | 24 | 97.2 | 2.8 |
| (e) | 2 g (b) | | | 2M 30 mL | 24 | 92.8 | 7.2 |
| (f) | 2 g (a) | 0.5 g | | 2M 30 mL | 24 | 95.0 | 5.0 |
| (g) | 0.5 g (a) | | 10 mL | 2M 20 mL | 8 | 92.8 | 7.2 |
| (h) | 2 g (c) | | | 2M 30 mL | 24 | **99.3** | **0.7** |
| (j) | 1 g (c) | 0.25 g | | 2M 30 mL | 24 | 95.9 | 4.1 |
| (k) | 0.5 g (c) | | 10 mL | 2M 20 mL | 8 | 96.6 | 3.4 |

(a) Stoichiometric $Mg_2TiO_4$, (b) 5% MgO-rich $Mg_2TiO_4$, and (c) re-calcination at 1270 °C for 2 h of sample (b).
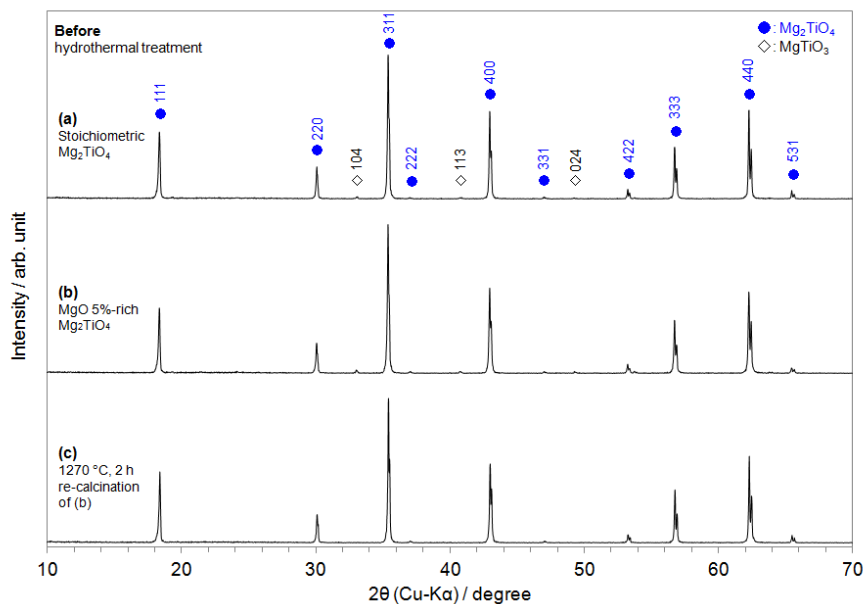
(d) Best conditions in Ref. 9.

**Figures**



**Fig. 1**  XRD patterns of the samples before the hydrothermal treatment: (a) stoichiometric $Mg_2TiO_4$, (b) 5% MgO-rich $Mg_2TiO_4$ and (c) re-calcination at 1270 °C for 2 h of sample (b).
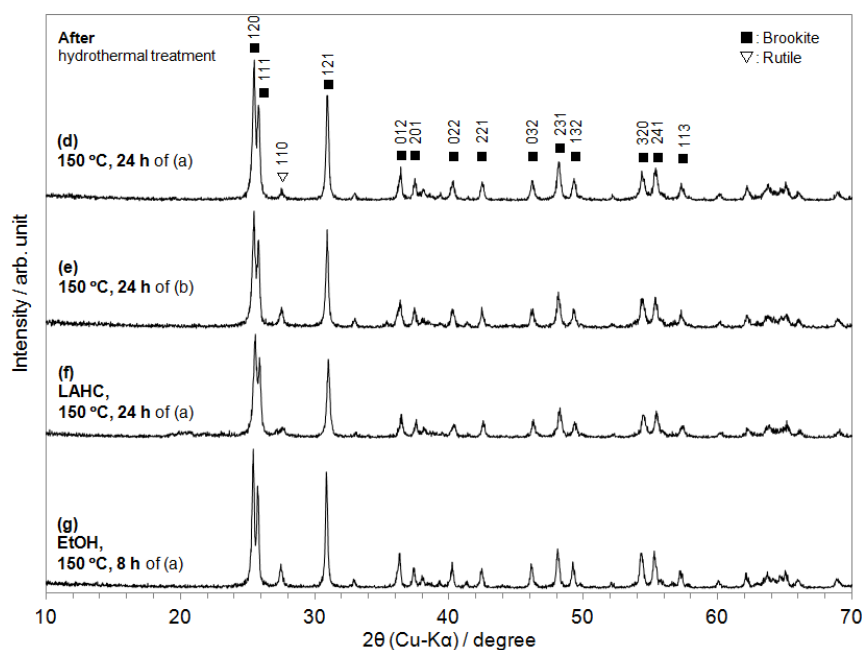


**Fig. 2**  XRD patterns of the samples after the hydrothermal treatment using sample (a) or (b): (d) at 150 °C for 24 h, (e) at 150 °C for 24 h, (f) at 150 °C for 24 h with LAHC, and (g) at 150 °C for 8 h with EtOH.
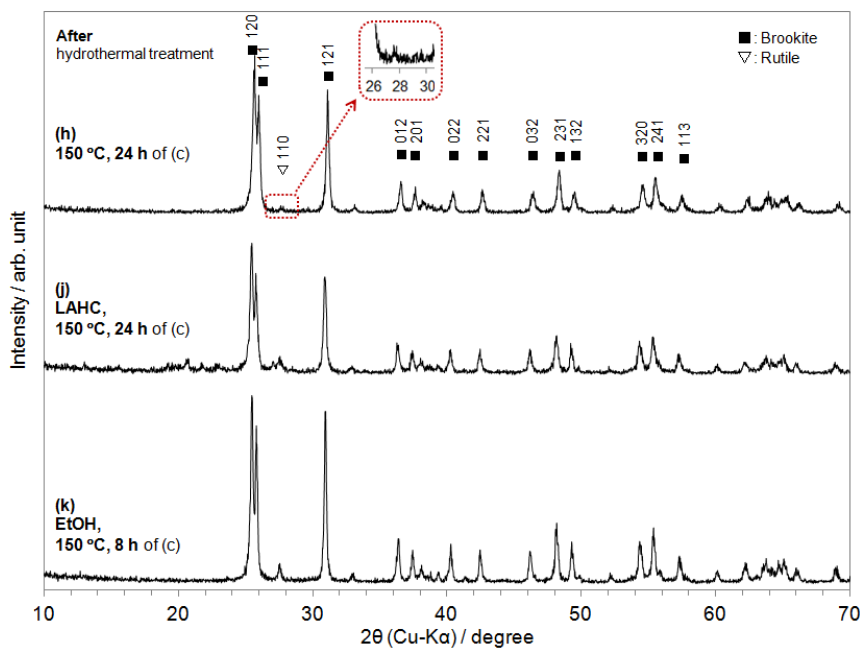
**Fig. 3** XRD patterns of the samples after the hydrothermal treatment using sample (c): (h) at 150 °C for 24 h, (j) at 150 °C for 24 h with LAHC, and (k) at 150 °C for 8h with EtOH.
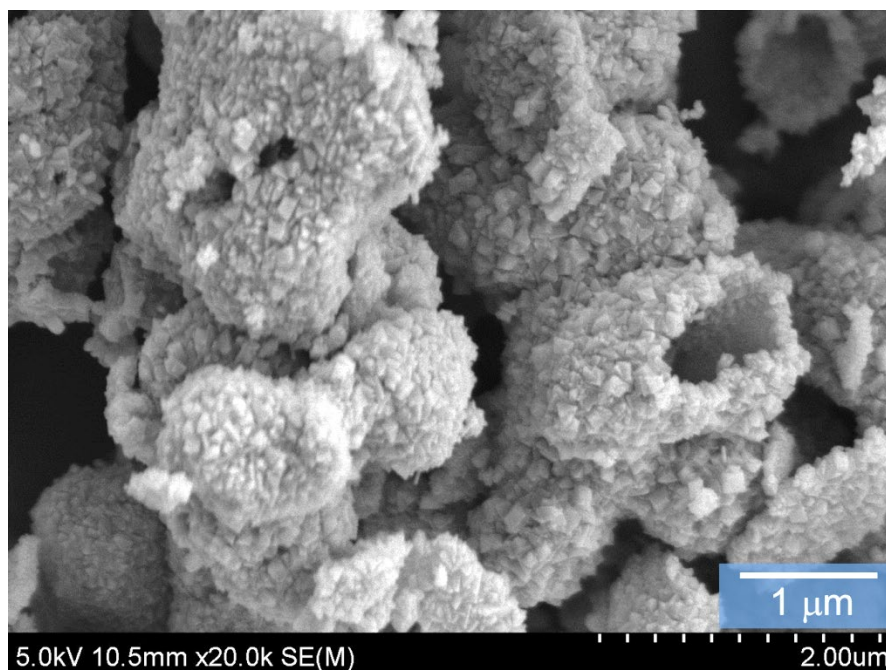


**Fig. 4** SEM micrograph of the brookite powder, sample **(h)**, with the surface area of 27.7 m$^2$/g.