

# Solvothermal Preparation of CaTiO<sub>3</sub> Prism and CaTi<sub>2</sub>O<sub>4</sub>(OH)<sub>2</sub> Nanosheet by a Facile Surfactant-Free Method

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Calcium titanate (CaTiO<sub>3</sub>) with prism-like-shaped and CaTi<sub>2</sub>O<sub>4</sub>(OH)<sub>2</sub> nanosheet-like morphology were synthesized by a simple solvothermal route without any surfactants. X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and Fourier transform infrared spectroscopy (FT-IR) were employed to investigate the microstructure of the samples. The experimental results showed that NaOH concentration played a key role for the formation of CaTiO<sub>3</sub> prisms. With increasing NaOH concentrations, the obtained sample changed from CaTi<sub>2</sub>O<sub>5</sub> aggregated particles to CaTi<sub>2</sub>O<sub>4</sub>(OH)<sub>2</sub> nanosheets, and then to CaTiO<sub>3</sub> prisms. When NaOH concentration was 7 M, CaTiO<sub>3</sub> morphology is mainly composed of regular prisms. A rational mechanism was proposed to illustrate the morphology evolution of the samples synthesized at various NaOH concentrations. And the CaTi<sub>2</sub>O<sub>4</sub>(OH)<sub>2</sub> interlaminar structure was illustrated.

**Keywords:** solvothermal preparation, surfactant-free, CaTiO<sub>3</sub> prisms, CaTi<sub>2</sub>O<sub>4</sub>(OH)<sub>2</sub> interlaminar structure.

## 1. INTRODUCTION

Due to its widespread potential applications in a lot of fields, calcium titanium oxide has been considered as one of the most important inorganic materials [1, 2]. Gibbs-Curie-Wulff theorem or Wulff facets argument suggests that crystal shape depends on the relative specific surface energy of each face or facet of the crystal [3]. However, our experiment results show that these pure thermodynamics can not be the only explanation. It can be the concentration of existing monomers by tuning NaOH concentration that plays a key role for the evolution of the shapes and phases of the calcium titanium oxide crystals [4, 5]. If the pH values can be well-controlled, the growth of crystals with different morphologies should be possible. According, the concentration of the remaining precursor solution after nucleation depends on the number of nucleation. To maintain the correct pH of the solvothermal system, it is necessary to use alkaline or acidity mineralizers i.e. pH adjusting agents such as NaOH or HNO<sub>3</sub>, which are most convenient for this purpose. However, intermediates are often observed during the preparation of CaTiO<sub>3</sub>. The presence of this impurity phase significantly affects the material's properties and, thus, it should be avoided. Therefore, it is worthwhile to compare NaOH concentration that is necessary to obtain phase-pure calcium titanium oxide. Recently, some nanostructures of calcium titanate were synthesized via hydrothermal reaction routes by controlling the amount of alkali hydroxide. Rectangular prism-like CaTiO<sub>3</sub> were prepared by a practical microwave-induced hydrothermal reaction method with the mixture of CaCl<sub>2</sub> and TiO<sub>2</sub> as starting materials, and NaOH as mineralizer [5]. CaTiO<sub>3</sub> dendrite and prism were also obtained by Huang and his co-workers

via adjusting the stirring rate under N<sub>2</sub> atmosphere with Ca(OH)<sub>2</sub> and titanium tetraisopropoxide as starting materials and with NaOH as mineralizer [6].

To the best of our knowledge, this kind of novel CaTiO<sub>3</sub> prisms has not been reported by a simple solvothermal approach without template or surfactant up to now. Calcium titanium oxide was prepared by tuning NaOH concentration via a facile surfactant-free method. A rational growth mechanism of CaTiO<sub>3</sub> prisms is illustrated. And the CaTi<sub>2</sub>O<sub>4</sub>(OH)<sub>2</sub> interlaminar structure is analysed by XRD, FESEM and FT-IR.

## 2. EXPERIMENTAL DETAILS

**General procedure:** The CaTiO<sub>3</sub> crystals were synthesized in a water-ethanol medium by a solvothermal route. In a typical synthesis, 0.01 mol Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub> (Sigma Aldrich, 99 %) were mixed with molar ratio of water/ethanol = 10/10. And concentrated nitric acid (65–68 %) was added to control the deionized water at pH = 1. Then added to 10 ml of 1 M CaCl<sub>2</sub>·5H<sub>2</sub>O solution under vigorous stirring at room temperature. After the solution was stirred for 5 min, various NaOH concentrations (0.005 M, 0.01 M, 1 M, 3 M, 5 M, 7 M) were added to adjust the pH to a certain value, which is 5.3, 7.9, 8.5, 9.8, 10.6, 13.8, respectively. Subsequently, the autoclave was sealed and maintained at 180 °C for 36 h, followed by natural cooling to room temperature. Afterward, the final samples were centrifuged, washed with distilled water and absolute ethanol several times, and then dried at 80 °C for 15 h in air.

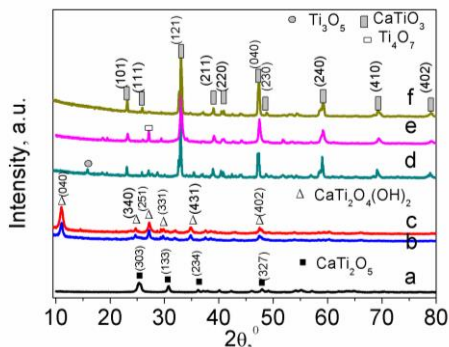
**Detection Method:** The crystal phases of the samples were characterized by XRD, PANalytical X'Pert Pro, Holland), in a 2θ range from 10° to 80°, using Cu-Kα radiation. The microstructure of the samples was investigated by field emission scanning electron microscopy (FESEM, Hitachi S-4800, Japan). Infrared

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spectra of the samples were obtained using a Nicolet Nexus 470 Fourier transform infrared (FT-IR) spectrometer in the 400–4000  $\text{cm}^{-1}$  region by KBr pellet.

### 3. RESULTS AND DISCUSSION

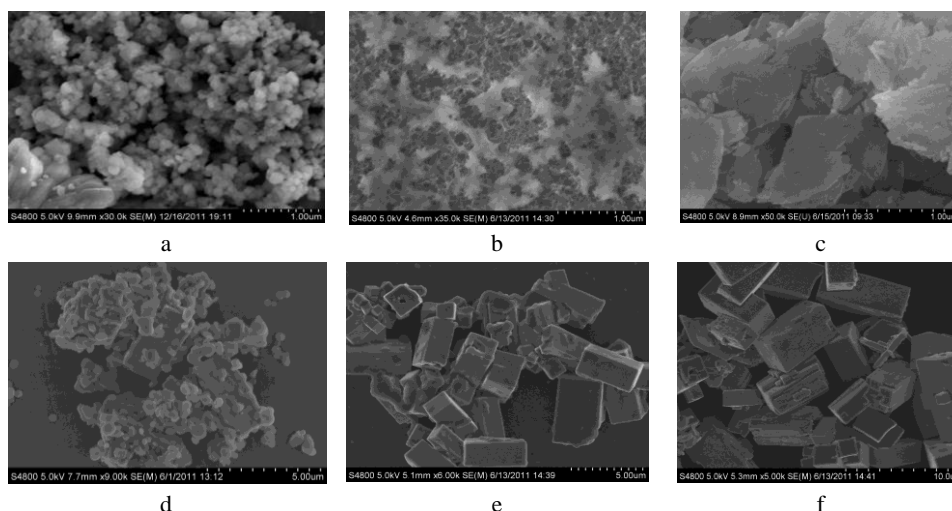
We have systematically investigated the system in various NaOH concentrations while keeping the other reaction conditions unchanged, as shown in Fig. 1 and Fig. 2.



**Fig. 1.** XRD patterns of the samples solvothermal synthesized at 180 °C for 36 h with different NaOH concentrations: a–0.005 M; b–0.01 M; c–1 M; d–3 M; e–5 M; f–7 M

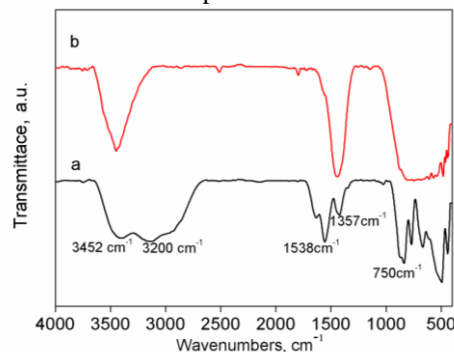
Fig. 1 shows the XRD patterns of the samples solvothermal synthesized in various NaOH concentrations. When NaOH concentration is 0.005 M, the sample is  $\text{CaTi}_2\text{O}_5$  (JCPDS card 22-0153) phase (Fig. 1 a). When NaOH concentration is 0.01 M, the sample is pure  $\text{CaTi}_2\text{O}_4(\text{OH})_2$  (JCPDS card 39-0357) phase (Fig. 1 b). When NaOH concentration increases to 1 M, intensity of  $\text{CaTi}_2\text{O}_4(\text{OH})_2$  phase increases (Fig. 1 c). Further increasing NaOH concentration to 3 M,  $\text{CaTi}_2\text{O}_4(\text{OH})_2$  phase disappears and  $\text{CaTiO}_3$  (JCPDS card 42-0423) appears with a little trace of  $\text{Ti}_3\text{O}_5$  and  $\text{Ti}_4\text{O}_7$  (Fig. 1 d). When NaOH concentration is above 5 M, pure  $\text{CaTiO}_3$  is obtained and peak intensity of  $\text{CaTiO}_3$  further increases (Fig. 1 e–f), which indicates well crystallized.

When NaOH concentration is 0.005 M,  $\text{CaTi}_2\text{O}_5$  aggregated particles are obtained (Fig. 2 a). When NaOH concentration is 0.01 M,  $\text{CaTi}_2\text{O}_4(\text{OH})_2$  porous needle like and floating irregular clouds-like particles are obtained (Fig. 2 b).



**Fig. 2.** FESEM images of the samples solvothermal synthesized at 180 °C for 36 h with different NaOH concentrations: a – 0.005 M; b – 0.01 M; c – 1 M; d – 3 M; e – 5 M; f – 7 M

When NaOH concentration is 1 M,  $\text{CaTi}_2\text{O}_4(\text{OH})_2$  morphology is mainly composed of overlap leaves (Fig. 2 c). When NaOH concentration is 3 M, nanosheets disappear, and a lot of aggregated particles with a little trace of prisms are obtained (Fig. 2 d). Whereas NaOH concentrations are above 5 M,  $\text{CaTiO}_3$  rectangular prisms are formed (Fig. 2 e–f). To provide the characteristic oscillations in  $\text{CaTi}_2\text{O}_4(\text{OH})_2$  and  $\text{CaTiO}_3$  compounds, infrared spectra of the samples are obtained using FT-IR spectrometer. Fig. 3 shows FT-IR spectra in the range of 400–4000  $\text{cm}^{-1}$  of the samples.



**Fig. 3.** FT-IR spectra in the range of 400–4000  $\text{cm}^{-1}$  of the samples: a– $\text{CaTi}_2\text{O}_4(\text{OH})_2$ ; b– $\text{CaTiO}_3$  solvothermal synthesized in 1 M and 7 M NaOH concentrations, respectively

Fig. 3 a shows FT-IR spectrum in the range of 400–4000  $\text{cm}^{-1}$  of  $\text{CaTi}_2\text{O}_4(\text{OH})_2$  sample. The peaks at 3425  $\text{cm}^{-1}$  can be attributed to the O-H stretching. Compared with free –OH (3600  $\text{cm}^{-1}$ ), the absorption peak shifts to low wavelength, which is due to the coordinated water molecules via hydrogen bonding interaction to the  $\text{CO}_3^{2-}$  of the interlamination [7]. The broad absorption band observed at 3200  $\text{cm}^{-1}$  is originated from the presence of hydroxyl groups of water [8]. The absorption peak at 1538  $\text{cm}^{-1}$  attributes to H-O-H bending of the lattice water [8]. The sharp absorption peak at 1357  $\text{cm}^{-1}$  attributes to C-O-C bending of carbonate ion. A band centred at 750  $\text{cm}^{-1}$ , which is attributed to isolated tetrahedron  $\text{TiO}_4$  stretching vibration. The absorption bands below 500  $\text{cm}^{-1}$ , i. e. bands centred at 495 and 425  $\text{cm}^{-1}$  can be ascribed to Ca-Ti-O bending vibrations.

CaTiO<sub>3</sub> prism-like sample exhibits the similar the absorption bands with those of CaTiO<sub>3</sub> in our reference [4], as shown in Fig. 3 b.

The above experimental results show that the presence of NaOH concentration in the solution is necessary for the formation of calcium titanium oxides. From the effect of the chemical composition, NaOH concentration may influence the combination of free Ca<sup>2+</sup> and release Ti<sup>4+</sup> ions of TiO<sub>2</sub> in the solvothermal process [4, 6]. When NaOH concentration is 0.005M, due to the small solubility of titanium dioxide soluble species in low NaOH concentration, and a shortage of TiO<sub>2</sub> soluble species near Ca<sup>2+</sup> will stop the reaction to form CaTiO<sub>3</sub>. Instead, owing to the small solubility of titanium dioxide in the acid condition, CaTi<sub>2</sub>O<sub>5</sub> forms. Increasing NaOH to 0.01 M, the solvothermal processing accelerates TiO<sub>2</sub> formation and promotes TiO<sub>2</sub> to transform small amounts of Ti<sup>4+</sup> ions [4, 5, 9], which are involved in a reaction with Ca<sup>2+</sup>, leading to the formation of CaTi<sub>2</sub>O<sub>4</sub>(OH)<sub>2</sub> crystallites. However, when NaOH concentration is increased to 1 M, a large amount of Ti(OH)<sub>4</sub> is formed, and O-H group of TiO<sub>6</sub> octahedron free end decreases, thus, the probability of Ca<sup>2+</sup> ions into the lattice increases the formation of tetragonal CaTiO<sub>3</sub> particles. With the increase of NaOH concentration to 5 M, i. e. in the high OH<sup>-</sup> ion concentration, because of CaTiO<sub>3</sub> crystal defects and grain size effect, CaTiO<sub>3</sub> particles are formed. For the cubic phase CaTiO<sub>3</sub>, (110) and (100) surfaces can exist at the same time, gamma (110) is slightly larger than the gamma (100) crystal [4, 5], which makes the tetragonal CaTiO<sub>3</sub> nanocrystals along (110) plane and (100) surface growth, so CaTiO<sub>3</sub> particles will give priority to the relatively low surface energy (100) surface growth, resulting in the formation of prism. Further increasing NaOH concentration to 7 M, the sample further Ostwald ripens and forms distinct edges and corners of CaTiO<sub>3</sub> prisms [4, 5]. In previous researches [10], our work found that CaTi<sub>2</sub>O<sub>4</sub>(OH)<sub>2</sub> may have photocatalytic and electrochemical properties. On view of the potential application, the interlaminar structure of CaTi<sub>2</sub>O<sub>4</sub>(OH)<sub>2</sub> is explored. From XRD and FT-IR results, the interlamination contains CO<sub>3</sub><sup>2-</sup>, H<sub>2</sub>O, isolated tetrahedron TiO<sub>4</sub> and -OH ions, Fig. 4 shows diagrammatic sketch of CaTi<sub>2</sub>O<sub>4</sub>(OH)<sub>2</sub> sample.

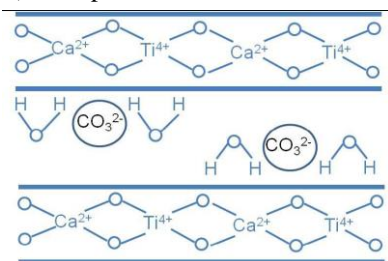


Fig. 4. Diagrammatic sketch of CaTi<sub>2</sub>O<sub>4</sub>(OH)<sub>2</sub> sample

A detailed time study is obvious for the growth process of the CaTiO<sub>3</sub> prism in the case of 7 M NaOH. Unfortunately, due to the fast growth rate, the CaTiO<sub>3</sub> prisms form too fast, which prevent direct observation of its detailed growth process. However, based on the morphology evolution (Fig. 2 a – f), the morphology evolution of the samples synthesized at various NaOH concentrations is simply illustrated in Fig. 5.

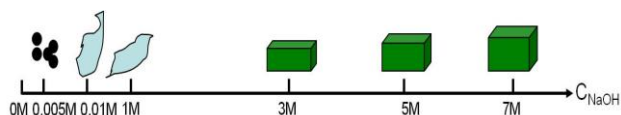


Fig. 5. Schematic diagram of morphology evolution of the samples synthesized at various NaOH concentrations

## 4. CONCLUSIONS

In summary, we report here a simple solvothermal process for the formation of pure calcium titanium oxide without any surfactants or templates. It is also found that the appropriate concentration of NaOH is vital for the formation of CaTiO<sub>3</sub> prism. When NaOH concentration was 0.005 M, the morphology of CaTi<sub>2</sub>O<sub>5</sub> was composed of aggregated particles. With increasing NaOH concentrations from 0.01 M to 1 M, CaTi<sub>2</sub>O<sub>4</sub>(OH)<sub>2</sub> nanosheets formed. When NaOH concentration was 7 M, CaTiO<sub>3</sub> regular prisms was observed. The synthetic process here could be extended to other perovskite oxides. And the CaTi<sub>2</sub>O<sub>4</sub>(OH)<sub>2</sub> interlaminar structure was illustrated.

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