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Effect of oleic acid on morphologies of BaTi₅O₁₁ nanocrystals synthesized by hydrothermal method

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Abstract: BaTi₅O₁₁ nanocrystals were synthesized by a hydrothermal method, and the effect of oleic acid (OA) in the Ba–Ti precursors on morphologies of BaTi₅O₁₁ nanocrystals was investigated. As the OA/(Ba²⁺ + Ti⁴⁺) molar ratio ranged from 0 to 8, single-phase BaTi₅O₁₁ nanocrystals were synthesized at 260 °C for 20 h. When OA reagent was not added to the precursors, rice-like BaTi₅O₁₁ nanocrystals were obtained. As the OA/(Ba²⁺ + Ti⁴⁺) molar ratio was 1, elongated lath-like BaTi₅O₁₁ nanocrystals were synthesized with the width of about 130 nm, thickness of about 50 nm and length of about 400 nm. With increasing the OA/(Ba²⁺ + Ti⁴⁺) molar ratio from 1 to 6, the grain size of elongated lath-like BaTi₅O₁₁ nanocrystals gradually decreased. As the OA content increased, the amount of adsorbed OA molecules on the surface of Ti(OH)_x nucleus increased and hindered the reaction of Ba²⁺ ions with Ti(OH)_x nucleus, which caused the decrease of grain size of lath-like BaTi₅O₁₁ nanocrystals. When the BaTi₅O₁₁ nanocrystals were synthesized at OA/(Ba²⁺ + Ti⁴⁺) molar ratio of 1, they had the largest dielectric constant (ϵ_r) of 40.9 at 5 GHz.

Keywords: BaTi₅O₁₁ nanocrystals; Hydrothermal method; Oleic acid; Morphology; Microwave dielectric constant

1 Introduction

As a typical microwave dielectric material, the BaTi₅O₁₁ compound with monoclinic structure has been widely studied for application in microwave communications [1].

Tillmanns firstly reported the existence of BaTi₅O₁₁ phase by melting BaO:4TiO₂ composition between 1400 and 1500 °C [2]. Negas et al. [3] failed to prepare the BaTi₅O₁₁ compound in the subsolidus by melting BaTiO₃:TiO₂. O'Bryan and Thomson sintered a mixture of BaO:5TiO₂ at 1100 °C, and the major phase of BaTi₅O₁₁ was obtained [4]. Ritter et al. [5] firstly synthesized a pure BaTi₅O₁₁ phase via an organic precursor route, and predicated that the single-phase BaTi₅O₁₁ ceramics should have excellent microwave dielectric properties. Javadpour and Eror also synthesized the single-phase BaTi₅O₁₁ compound by a liquid mix technique between 700 and 1100 °C for 4 h [6]. Fukui et al. [7] prepared BaTi₅O₁₁ ceramics from an alkoxide-derived powder. The BaTi₅O₁₁ ceramics with more than 99 % theoretical density were synthesized by sintering at 1120 °C for 48 h, their dielectric constant (ϵ_r) and Q volume were 42 and 6100 at 9.7 GHz, respectively, and the temperature coefficients of the resonant frequency (τ_f) was 39.3 ppm/°C at 7 GHz. Zhou et al. [8] prepared BaTi₅O₁₁ ceramics by a reaction-sintering process at 1100 °C for 6 h with CuO addition, and the BaTi₅O₁₁ ceramics had good microwave dielectric properties (ϵ_r of 41.2, $Q \times f$ of 47,430, and τ_f of 36 ppm/°C). Jang et al. [9] deposited the BaTi₅O₁₁ thin films on poly-Si/SiO₂/Si substrates by a magnetron sputtering method, and ϵ_r of BaTi₅O₁₁ thin film measured at 100 kHz was about 35. Guo et al. [10] prepared the BaTi₅O₁₁ thick films on Pt/Ti/SiO₂/Si substrates by a laser chemical vapor deposition method, and ϵ_r of BaTi₅O₁₁ thick film measured at 1 MHz was only 21.4. In our previous research, rice-like BaTi₅O₁₁ nanocrystals were synthesized by the hydrothermal method, and ϵ_r of rice-like BaTi₅O₁₁ nanocrystals was measured to be about 38.9 at 8 GHz [11]. The nanocrystals possess unique physical and chemical properties that are strongly related to their size, shape, and surface chemistry [12]. Oleic acid (OA) has been widely used as a surfactant to tune the shape of BaTiO₃ and SrTiO₃ nanocrystals synthesized by the hydrothermal method [13]. In our previous reports [11, 14, 15], rice-like BaTi₅O₁₁ nanocrystals were synthesized by the hydrothermal method without the surfactant in the precursors.

In this study, BaTi₅O₁₁ nanocrystals were synthesized by the hydrothermal method, and the effect of OA content

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2 Experimental details

The phase composition of the precipitates was measured by an X-ray diffractometer (XRD, D/MAX-RB, Japan) with scanning speed of 2° min^{-1} . Their morphologies were characterized by a field emission scanning electron microscope (FESEM, ZEISS-ULTRA, Germany) and a high-resolution transmission electron microscope (TEM, JEM-2100F, Japan). The infrared spectra of the samples were measured by a Fourier transform infrared spectrophotometer (FT-IR, Thermo Fisher Nicolet 6700, USA). To measure the microwave dielectric properties of $\text{BaTi}_5\text{O}_{11}$ nanocrystals, a practical medium theory based on the Bruggeman equation was applied to extract the ϵ_r values of $\text{BaTi}_5\text{O}_{11}$ nanocrystals in composites [16]. The detail of preparing $\text{BaTi}_5\text{O}_{11}$ nanocrystals/paraffin wax composites was reported in our previous report [11]. The microwave dielectric properties of $\text{BaTi}_5\text{O}_{11}$ nanocrystals/paraffin wax composites were measured using an Agilent N5230A vector network analyzer (USA) with measuring frequencies ranging from 0.1 to 5 GHz.

3 Results and discussion

phase was formed. It indicated that the high OA concentration in the precursor could hinder the reaction of Ba^{2+} and Ti^{4+} ions to form $\text{BaTi}_5\text{O}_{11}$ phase.

Figure 3 displays typical TEM images of elongated lath-like nanocrystals synthesized at OA/(Ba²⁺ + Ti⁴⁺) molar ratios of 1 and 6, and the crystal structure of BaTi₅O₁₁ phase. When the nanocrystals were synthesized at OA/(Ba²⁺ + Ti⁴⁺) molar ratio of 1, a typical lath-like nanocrystal was observed, as shown in Figure 3a. The lath-like nanocrystal had width of about 140 nm and length of about 480 nm,

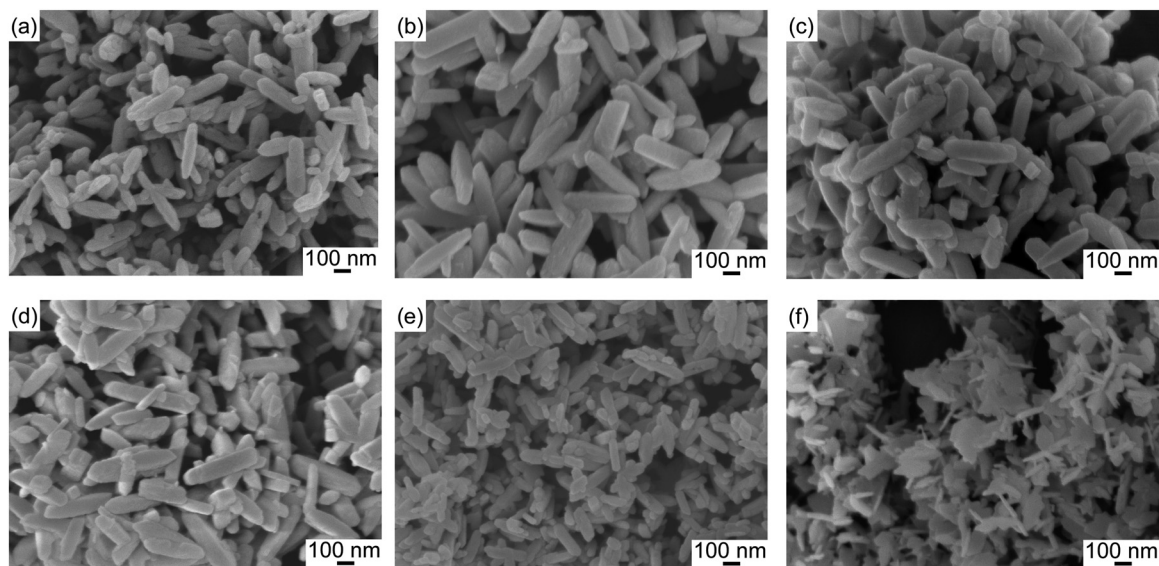


Figure 2: Morphologies of $\text{BaTi}_5\text{O}_{11}$ nanocrystals synthesized at different molar ratios of $\text{OA}/(\text{Ba}^{2+} + \text{Ti}^{4+})$: (a) 0, (b) 1, (c) 2, (d) 4, (e) 6, and (f) 8.

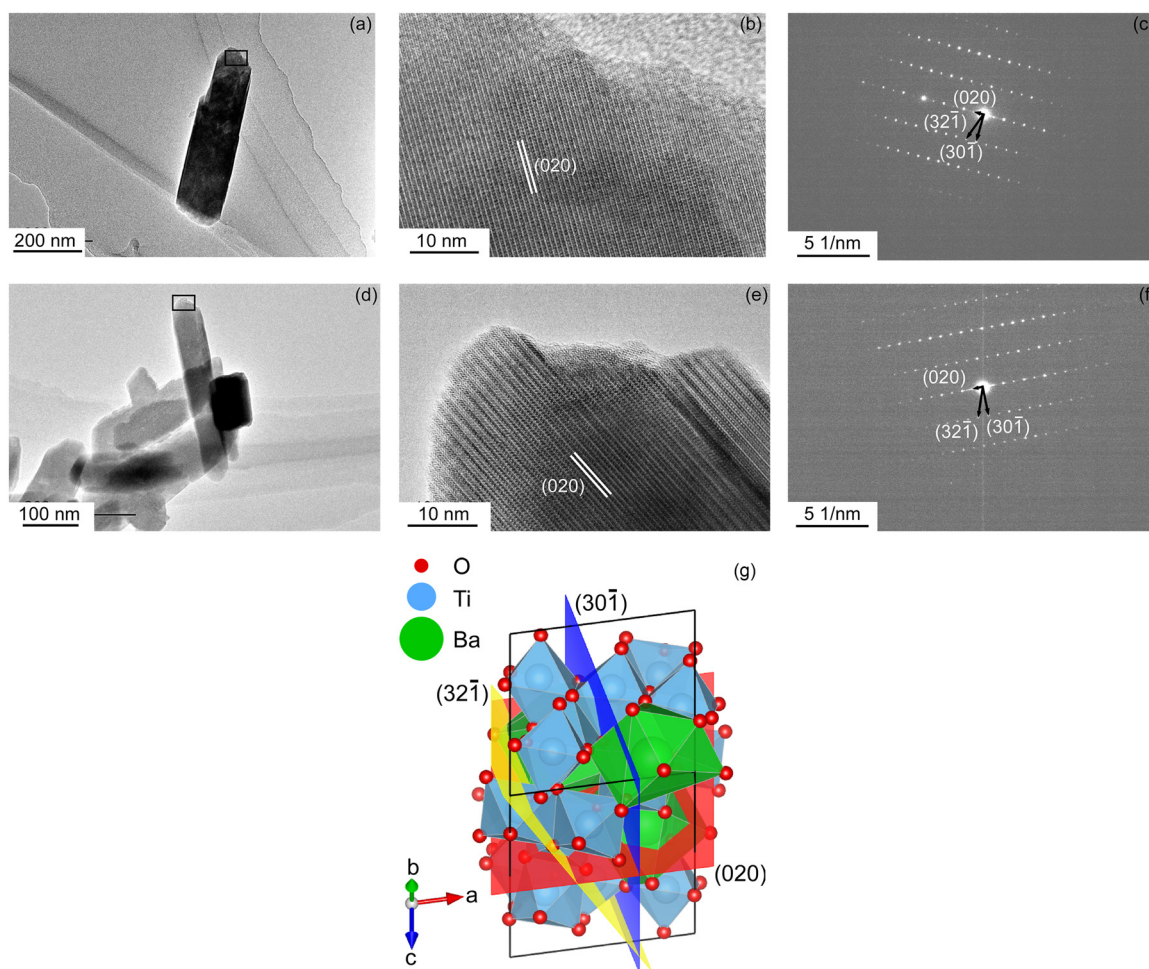


Figure 3: TEM images, high-resolution TEM images and their corresponding selected area electron diffraction (SAED) patterns of $\text{BaTi}_5\text{O}_{11}$ nanocrystals synthesized at different molar ratios of $\text{OA}/(\text{Ba}^{2+} + \text{Ti}^{4+})$: (a, b and c) 1, (d, e and f) 6, and (g) the crystal structure of $\text{BaTi}_5\text{O}_{11}$ compound.

which was close to the results as shown in Figure 2b. Figure 3b shows a high-resolution TEM image of the circled area in Figure 3a. The interplanar spacing with 0.7087 nm corresponded to the (020) plane (0.7021 nm) of the monoclinic BaTi₅O₁₁ phase. Its corresponding selected area electron diffraction (SAED) pattern is shown in Figure 3c. The included angles between the (020) and (30 $\bar{1}$) planes, (020) and (32 $\bar{1}$) planes were measured to be 89.43° and 69.92°, respectively. The included angles between the (020) and (30 $\bar{1}$) planes, (020) and (32 $\bar{1}$) planes were calculated to be 90° and 70.34° based on the monoclinic BaTi₅O₁₁ phase (JCPDS No. 35–0805). The theoretical included angles were consistent with the measured angles, which confirmed that single-crystal BaTi₅O₁₁ nanocrystal with lath-like morphology was formed. When the nanocrystals were synthesized at OA/(Ba²⁺ + Ti⁴⁺) molar ratio of 6, a single lath-like nanocrystal with width of about 50 nm and length of about 300 nm is shown in Figure 3d. It indicated that the nanocrystals became slimmer with increasing the OA content in the precursors. Figure 3e displays a high-resolution TEM image of the circled area in Figure 3e. The interplanar spacing with 0.7051 nm corresponded to the (020) plane of the monoclinic BaTi₅O₁₁ phase, and its corresponding SAED pattern is displayed in Figure 3f. According to the Figure 3f, the included angles between the (020) and (30 $\bar{1}$) planes, (020) and (32 $\bar{1}$) planes were measured to be 90.73° and 70.39°, respectively. The measured angles were close to the calculated angles based on the monoclinic BaTi₅O₁₁ phase, which indicated that the lath-like nanocrystal belonged to the monoclinic BaTi₅O₁₁ phase. Figure 3g shows the crystal structure of monoclinic BaTi₅O₁₁ phase with (020), (30 $\bar{1}$) and (32 $\bar{1}$) planes. It was drawn with VESTA software [17]. The TEM results confirmed that the BaTi₅O₁₁ nanocrystals with lath-like morphology were formed due to the additive of OA reagent.

OA reagent is considered as a typical surfactant to tune the shape of nanocrystals in the hydrothermal process [13]. To identify the effect of OA on the formation of BaTi₅O₁₁ nanocrystals, FT-IR spectra of OA and BaTi₅O₁₁ nanocrystals synthesized at OA/(Ba²⁺ + Ti⁴⁺) molar ratios of 0 and 6 were measured, as shown in Figure 4. When the BaTi₅O₁₁ nanocrystals were synthesized with the OA additive, the peaks at 2923 and 2853 cm^{−1} corresponded to the C–H stretching mode of methyl and methylene groups within OA molecules, and the absorption bands of 1541 and 1420 cm^{−1} represented the stretching frequency of the carboxylate group [18]. This result evidently indicated that the OA molecule's carboxylate group chemically bonded with the surface of BaTi₅O₁₁ nanocrystals during the hydrothermal process.

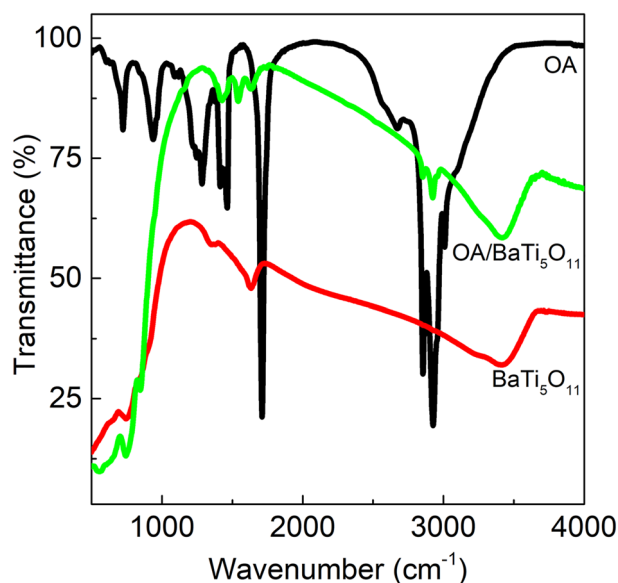


Figure 4: FT-IR spectra of OA, and BaTi₅O₁₁ nanocrystals synthesized at OA/(Ba²⁺ + Ti⁴⁺) molar ratios of 0 and 6.

A schematic illustration of BaTi₅O₁₁ nanocrystal formation in the hydrothermal process with the OA additive is shown in Figure 5. As the NaOH solution was added to the Ba–Ti precursors, Ti(OH)_x nuclei were formed. In the hydrothermal process, Ba²⁺ ions reacted with Ti(OH)_x nuclei to form the rice-like BaTi₅O₁₁ nanocrystals due to its monoclinic crystal structure (Figure 3g). When the OA reagent was added into the Ba–Ti precursors, OA molecules were hydrophobic and adsorbed on the surface of Ti(OH)_x nuclei to offer the protecting role [19], and the elongated lath-like BaTi₅O₁₁ nanocrystals with flat surface were formed. With increasing OA content, the amount of adsorbed OA molecules on the surface of Ti(OH)_x nucleus increased and hindered the reaction of Ba²⁺ ions with Ti(OH)_x nucleus, which caused the decrease of the grain size for lath-like BaTi₅O₁₁ nanocrystals. When the OA/(Ba²⁺ + Ti⁴⁺) molar ratio reached 8, irregular BaTi₅O₁₁ nanoflakes were formed. At high OA/(Ba²⁺ + Ti⁴⁺) molar ratio of 10, the Ti(OH)_x nuclei were completely coated with OA molecules,

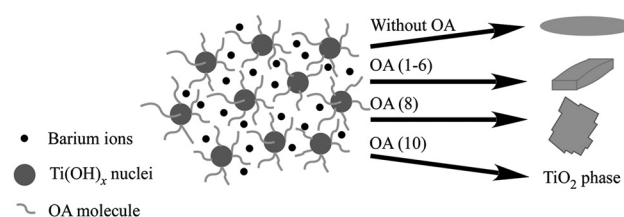


Figure 5: Schematic illustration of formation of BaTi₅O₁₁ nanocrystals in the hydrothermal process with OA additive.

Ba²⁺ ions could not react with Ti(OH)_x nuclei, and only TiO₂ phase was formed.

The ϵ_r values of BaTi₅O₁₁ nanocrystals were calculated based on the Bruggeman effective medium theory using the measured dielectric constant of the BaTi₅O₁₁ nanocrystals/paraffin wax composites [16]. The Bruggeman equation for effective ϵ_r values can be expressed by

$$(1-f) \frac{\epsilon_m - \epsilon_{\text{eff}}}{\epsilon_m + 2\epsilon_{\text{eff}}} + f \frac{\epsilon_p - \epsilon_{\text{eff}}}{\epsilon_p + 2\epsilon_{\text{eff}}} = 0 \quad (1)$$

where ϵ_{eff} , ϵ_m , ϵ_p , and f represent the effective ϵ_r values of the composites, the ϵ_r values of matrix (paraffin wax), the ϵ_r values of BaTi₅O₁₁ nanocrystals, and the volume fraction of BaTi₅O₁₁ nanocrystals, respectively. When the f value is between 20 and 50 vol.%, the measured ϵ_{eff} is creditable [16]. The ϵ_r values of BaTi₅O₁₁ nanocrystals were calculated, and the results are shown in Figure 6. With increasing the measuring frequency from 0.1 to 0.5 GHz, the ϵ_r values of BaTi₅O₁₁ nanocrystals obviously decreased. When the measuring frequency ranged from 0.5 to 5 GHz, the ϵ_r values of BaTi₅O₁₁ nanocrystals slightly changed. The ϵ_r values of BaTi₅O₁₁ nanocrystals at a measuring frequency of 5 GHz are listed in Table 1. As the BaTi₅O₁₁ nanocrystals were synthesized at OA/(Ba²⁺ + Ti⁴⁺) molar ratio of 1, they had the largest ϵ_r value of 40.9 at 5 GHz. With increasing the OA content, the ϵ_r values decreased. In our previous report, the ϵ_r value of rice-like BaTi₅O₁₁ nanocrystals was about 38.9 (8 GHz), when they were synthesized by hydrothermal

Table 1: Dielectric properties of BaTi₅O₁₁ nanocrystals at 5 GHz based on the Bruggeman equation.

OA/(Ba ²⁺ + Ti ⁴⁺) molar ratios in the precursors	Volume fraction of BaTi ₅ O ₁₁ nanocrystals (f , vol.%)	Dielectric constant of BaTi ₅ O ₁₁ nanocrystals (ϵ_p)
1:1	23.89	40.9
1:4	24.05	39.0
1:6	23.80	37.4
1:8	24.05	38.8

method without the additive of OA in the precursors [11]. The ϵ_r value of BaTi₅O₁₁ ceramic is about 41, which indicates that the ϵ_r value of lath-like BaTi₅O₁₁ nanocrystals is almost the same as that of the bulk BaTi₅O₁₁ ceramics [20].

4 Conclusions

BaTi₅O₁₁ nanocrystals were synthesized by the hydrothermal method, and their morphology was tuned by the addition of OA reagent in the Ba–Ti precursors. As the OA/(Ba²⁺ + Ti⁴⁺) molar ratio ranged from 0 to 8, the single-phase BaTi₅O₁₁ nanocrystals were synthesized. When the OA/(Ba²⁺ + Ti⁴⁺) molar ratio was 1, elongated lath-like BaTi₅O₁₁ nanocrystals with the width of about 130 nm, the thickness of about 50 nm and the length of about 400 nm were synthesized. With increasing the OA/(Ba²⁺ + Ti⁴⁺) molar ratio from 1 to 6, the grain size of elongated lath-like BaTi₅O₁₁ nanocrystals decreased, and the morphological uniformity of BaTi₅O₁₁ nanocrystals worsened. Irregular BaTi₅O₁₁ nanoflakes with thickness of about 20 nm were formed at high OA/(Ba²⁺ + Ti⁴⁺) molar ratio of 8. As the BaTi₅O₁₁ nanocrystals were synthesized at OA/(Ba²⁺ + Ti⁴⁺) molar ratio of 1, they had the largest ϵ_r value of 40.9 at 5 GHz, which was almost the same as that of bulk BaTi₅O₁₁ ceramics.

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Competing interests: The authors state no conflict of interest.

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Data availability: The raw data can be obtained on request from the corresponding author.

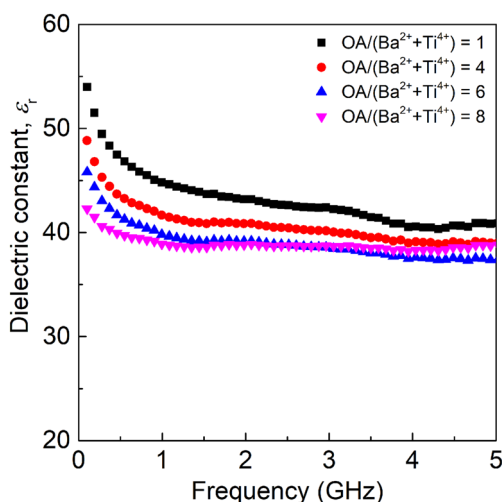


Figure 6: Microwave dielectric constant (ϵ_r) of BaTi₅O₁₁ nanocrystals synthesized at different molar ratios of OA/(Ba²⁺ + Ti⁴⁺) in the precursors.

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