Synthesis of nano-BaTiO₃ by solid-state reaction at 80°C

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Abstract. Nano-BaTiO₃ powder was synthesized by solid-state reaction at 80°C. The method is high productive and can be easily operated. XRD pattern demonstrates that the powder is pure cubic phase. And TEM photograph of the powder shows that the particles are uniform and spherical with average size of 50nm in diameter. Furthermore we confirmed that chemical reaction is the rate-determining step.

1. Introduction
The outstanding dielectric, ferroelectric and piezoelectric properties of BaTiO₃ make it the desirable material for a variety of applications including multilayer capacitors, thermistors and electrooptic devices[1]. Because of its properties, many methods were explored to synthesize BaTiO₃. Traditional solid-state reaction needs high temperature up to 1200°C, which not only makes the grains bulky, but also easily introduce some impurities into the product[2]. And sol-gel method has attracted many researcher’s attention, but this method can't also be for application because its original material price is too expensive. We have used hydrothermal method[3,4], but it makes environment polluted and needs higher quality for equipment. In our present work, a new method called solid-state reaction at low temperature[5,6,7] has been explored to synthesize BaTiO₃. This method has many advantages, such as no solvents, little pollution and high productive.

2. Experimental

2.1 Chemicals and Instruments
TiCl₄, Ba(OH)₂·8H₂O and NH₃·H₂O are analytical reagents made in China. All experiments were carried out in the deionized water.

Y-2000 X-ray Diffractometer (Dandong), JEM-100SX Transmission Electrical Microscope (Japan), etc.

2.2 Synthesis of BaTiO₃ Powder
A suitable amount of TiCl₄ was slowly dropped to 100 mL water. The pH value of the solution was
adjusted to 6~8 by dropping 1:1 \( \text{NH}_3\cdot\text{H}_2\text{O} \) to form \( \text{H TiO}_3 \) (or \( \text{TiO}_2\cdot\text{H}_2\text{O} \)). Then it was filtered and washed with deionized water until the \( \text{Cl}^- \) could not be detected. Subsequently it was mixed with needed \( \text{Ba(OH)}_2\cdot8\text{H}_2\text{O} \) (molar ratio is Ti:Ba=1:1). The mixture was milled for 60min at room temperature, then dried at 80\( ^\circ \text{C} \) for 5.5h.

3. Results and Discussion

3.1 XRD Analysis of \( \text{BaTiO}_3 \) Powder
Comparing XRD pattern of synthetical \( \text{BaTiO}_3 \) powder with JCPDS Card (31-0174), it can be seen that synthetical \( \text{BaTiO}_3 \) powder is pure cubic phase. (shown in figure 1)

![Figure 1 XRD pattern of synthetical \( \text{BaTiO}_3 \)](image)

3.2 TEM Analysis of \( \text{BaTiO}_3 \) Powder
TEM photograph of the powder shows that the particles are uniform and spherical with average size of 50nm in diameter. (shown in figure 2)

![Figure 2 TEM photograph of sample](image)

3.3 Influence of Reaction Temperature
The mixture was divided into seven parts, then dried respectively at room temperature, 40\( ^\circ \text{C} \), 60\( ^\circ \text{C} \), 70\( ^\circ \text{C} \), 80\( ^\circ \text{C} \), 100\( ^\circ \text{C} \) and 120\( ^\circ \text{C} \) for 6d, 48h, 34h, 28h, 24h, 5.5h and 4h in order to be dried completely. XRD patterns of the dried powder are shown in figure 3.

In figure 3, 1, 2, 3, 4, 5, 6, 7 are respectively XRD pattern of dried powder at room...
temperature, 40°C, 60°C, 70°C, 80°C, 100°C and 120°C.

It is can be seen that dried powder at room temperature has no BaTiO₃ phase, only has some impurities, such as BaCO₃, Ba(OH)₂·8H₂O and Ba(OH)₂. As temperature rising, Ba(OH)₂·8H₂O disappears at 40°C, Ba(OH)₂ and BaCO₃ decrease gradually. At 80°C, the main phase is BaTiO₃ with little impurities. So we confirmed the reaction temperature is 80°C.

3.4 Influence of Reaction Time

In order to definite how long the mixture needs to form BaTiO₃ at 80°C, the mixture react respectively for 1h, 2h, 3h, 4h, 7h, 10h, 13h under 80°C, and then dried at room temperature. Their XRD patterns are shown in figure 4.

3.5 Reaction Mechanism
Diffusion, reaction, nucleation and growth are the four steps of the solid-state reaction. In the past, diffusion or nucleation is considered to be the rate-determining step of the high temperature solid-state reaction. From figure 3, it can be seen that the strength of the Ba(OH)$_2$ diffraction peaks is very small from the start to the end, so we can know the diffusion from Ba(OH)$_2$ to H$_2$TiO$_3$ is very quick. In figure 3, reaction under 80°C just exhibits the BaTiO$_3$ diffraction peaks and in figure 4, reaction for 4h under 80°C just begins to exhibit the BaTiO$_3$ diffraction peaks with high strength. From the above, we draw a conclusion that diffusion, nucleation and growth is quick. So, we confirmed that reaction is the rate-determining step of the solid-state reaction at low temperature.

4. Conclusions
(1) It is the first time to use solid-state reaction at low temperature to synthesize cubic BaTiO$_3$. The method is high productive and partly process achieving economic atom reaction according to the ideas of green chemistry.
(2) In the solid-state reaction at low temperature, chemical reaction is the rate-determining step.

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