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Notes

Synthesis of nano-$BaTiO_3$ by liquid-state methods

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Nano-$BaTiO_3$ powder has been synthesized with $TiCl_4$ and $Ba(OH)_2$ by different liquid-state (atmospheric, hydrothermal and microwave) methods. Its phase, shape and capacity have been investigated by X-ray diffraction, transmission electron microscopy, scanning electron microscopy, small-angle X-ray scattering and LCR data. XRD pattern of the series of the nanometer powders demonstrates that $BaTiO_3$ has cubic structure. TEM shows that the products have a shape of uniform, substantially spherical particles. Powder synthesized by microwave method has the least grain size, the lowest sintering temperature, and the best dielectric capacity. Microwave method requires less reaction time, little grain size, and narrow grain size distribution.

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Nano-ceramic materials are expected to be one of the most important materials during the present century. There has been enhanced emphasis on all of the nano-ceramic $BaTiO_3$ materials[1]. Thus, preparation of the $BaTiO_3$ nano-powder is very important.

With the grain size of $BaTiO_3$ powder diminishing, the grain quantity for given weight will increase and exterior area will enlarge[1,2]. Thus, the boundary layer effect functions markedly, which endows $BaTiO_3$ nano-powder with superexcellent physical and chemical property. Therefore, nano-$BaTiO_3$ ceramic material turns into a new type and high-powered material, especially as excellent dielectric material with merits of low cost, stable property and avirulence. We report herein the synthesis of nano-$BaTiO_3$ powder using three liquid-state methods, viz. the atmospheric method, hydrothermal method and microwave method. The optimal synthesis technique is proposed after studying different reaction conditions.

Experimental

The chemicals $TiCl_4$, $Ba(OH)_2.8H_2O$, NH_4OH were of analytical grade. All experiments were carried out in double-distilled water. Rigaku D/MAX-RC-X-ray diffractometer, TEM-1000SX transmission electrical microscope, 769YP-242 table oil press (Tianjin), RJXG-5-13 electrical stove, Automatic LCR meter, Whirlpool microwave stove and reactor were used.

$BaTiO_3$ nano-powder was synthesized by the following methods.

Atmospheric liquid-state method

Hydrolysis of $TiCl_4$ is done as reported[3, 4]. 0.1 mol H_2TiO_3 is put into water in a beaker (250 mL), then mixed with 200 mL alkaline solution of 0.1 mol $Ba(OH)_2$. Then, the mixture is stirred by a magnetic stirrer placed on a electric hot plate to react below 100°C for 3-5 h. The solid powder of $BaTiO_3$ is obtained after filtering, washing and drying at 100°C. The reaction may be described by:

$$TiCl_4 + H_2O \rightarrow H_2TiO_3 + HCl$$
$$H_2TiO_3 + Ba(OH)_2 \rightarrow BaTiO_3 + 2H_2O$$

Hydrothermal method

0.1 mol $TiCl_4$ is hydrolyzed into H_2TiO_3, diluted with distilled water and slurried into 250 mL, and then comixed with 200 mL alkaline solution of 0.1 mol $Ba(OH)_2$. The mixture is then poured into hydrothermal reactor to react at 150°C for 2 h. The solid powder of $BaTiO_3$ is obtained after filtering, washing and drying at 100°C.

Microwave method[5,6]

0.1 mol H_2TiO_3 is diluted with water and slurried into 250 mL, then comixed with 200 mL alkaline solution of 0.1 mol $Ba(OH)_2$. Then, the mixture is placed into the microwave stove. The heating power is turned to 2450 MHz by regulating the heating-power knob for 5 min, then turned to 500 MHz for 15 min, so that the reactant maintains slight boiling at 100°C. The solid powder of $BaTiO_3$ is obtained after filtering, washing and drying at 100°C.

Preparation of ceramics

The ceramic is prepared using the powder synthesized and its properties are studied. The sample is mixed with suitable amount of adhesive (8% PVA aqueous solution) and grounded evenly, then sieved by the sifter with its cell of 0.45 mm (40 meshes). The resulting powder is pressed into disc whose diameter is 1.5 cm and thickness is 0.2 cm at a pressure of 6-8 MPa. The adhesive is removed when heated to 600°C in air.

After cooling, the discs are sintered into ceramic by heating to 1150°C. After layered with Ag electrodes, their electric capacity value (*C*) and dielectric loss (tan δ) are measured by Automatic LCR meter at different temperatures, their thickness and diameter measured with micrometer, and their dielectric constants calculated from the formula as following:

$$\varepsilon = \frac{Ch}{\varepsilon_0 s} = 1.4395 \times 104 \times \frac{CL}{d^2} = 14400CL/d^2$$

where C is capacity of the sample, h the thickness of disc, S the electrode area, ε_o the vacuum dielectric constants, and $\varepsilon_o = 1/4\pi \times 9 \times 10^{11}$ F/cm.

Results and discussion

XRD analyses of $BaTiO_3$ nano-powder

$BaTiO_3$ powders synthesized by three methods mentioned above have been analyzed by XRD studies. The $BaTiO_3$ powders have the same XRD pattern as pure $BaTiO_3$ phase and all of them belong to the cubic system shown in Fig. 1 (a: atmospheric liquid-state method; b: hydrothermal method; c: microwave method). From the aspects of spectral pattern and intensity, the powders synthesized by different methods differ from each other appreciably. The peak value of powder synthesized by hydrothermal method is topmost, while spectral width of powder synthesized by microwave method is widest.

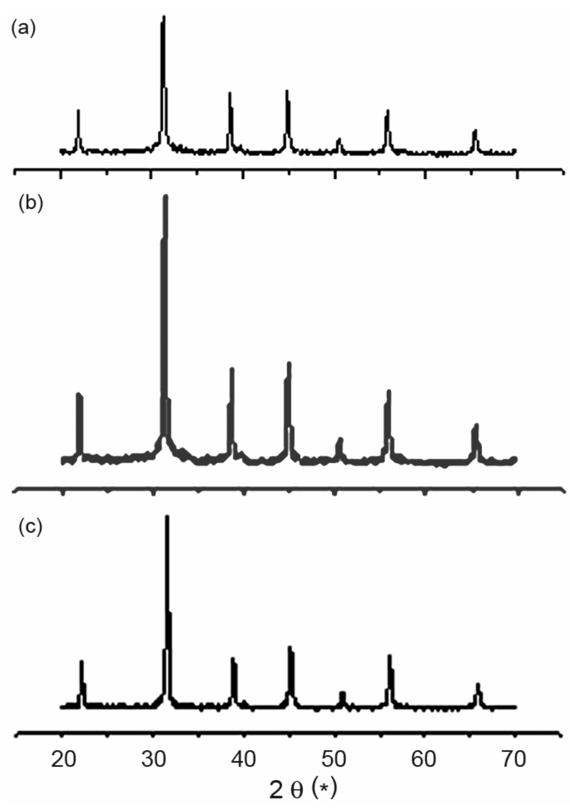

Fig. 1—XRD patterns of nano-$BaTiO_3$: (a) Atmospheric liquid-state method; (b) hydrothermal method; and (c) microwave method.

TEM analyses of $BaTiO_3$ powder

TEM of the $BaTiO_3$ powder synthesized by different methods reveals that: (i) Grain size of atmospheric liquid-state method is 70-80 nm with a spherical structure; (ii) Grain size of hydrothermal method is 120-150 nm with a cubic structure; and (iii) Grains of microwave method are regularly spherical with the average size of 40 nm in diameter, which is shown in

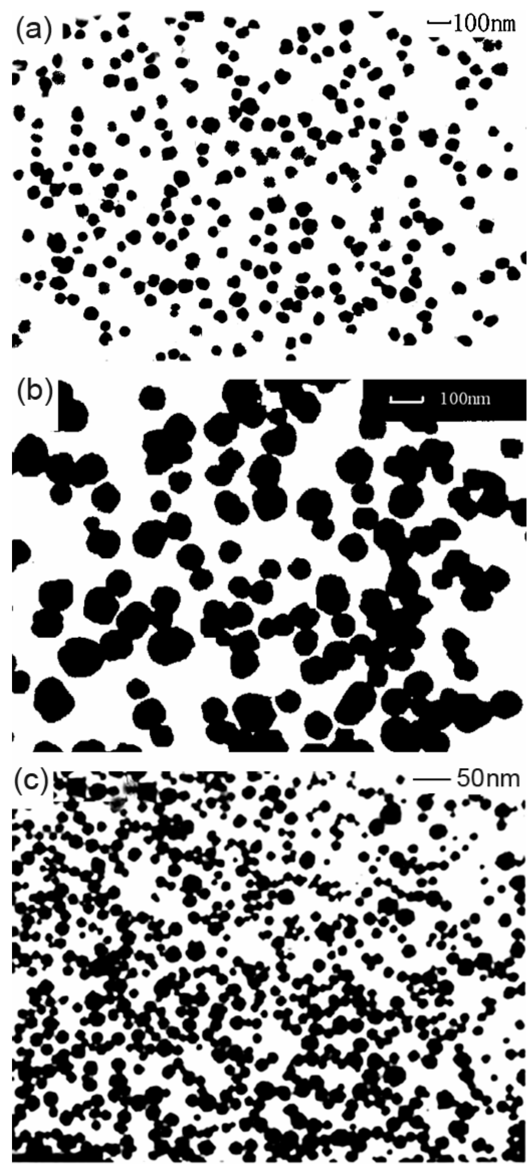

Fig. 2—TEM photographs of nano-$BaTiO_3$: (a) atmospheric liquid-state method; (b) hydrothermal method; and, microwave method.

Fig. 2.

Atmospheric liquid-state method has the merits of low reaction temperature, below 100°C. But, it needs long reaction time, and artificial control throughout the whole preparing process. Otherwise, it is difficult to control the heating temperature precisely with electric stove, so that the powder synthesized by this method is asymmetric. Hydrothermal method needs slashing reaction conditions such as high temperature and high pressure. So, it results in the defects of large energy consumption and high cost. Grains grow to micro-meter under these conditions and will never be used to prepare nano-ceramic. The microwave method is the best method of the three by virtue of its simple operation and short reaction time. It utilizes cavitation effect to obtain high rate constant of heating and radio frequency heating from inside to outside which induces creating velocity of the powder much faster than growing velocity. So the grain size is as small as 40 nm, and has a homogeneous distribution.

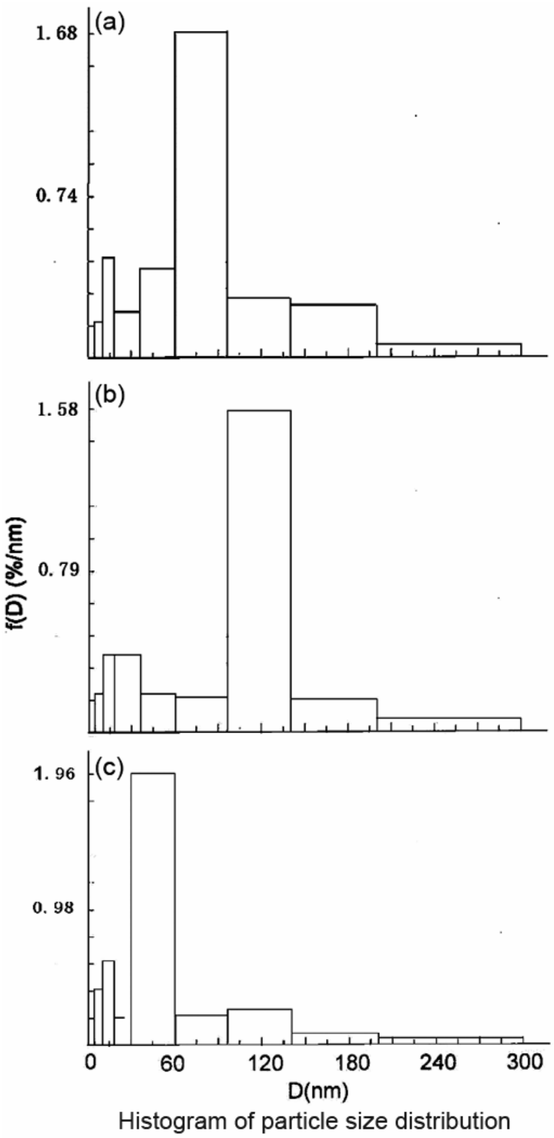

Fig. 3—SAXS patterns of nano-$BaTiO_3$: (a) atmospheric liquid-state method; (b) hydrothermal method; and (c) microwave method.

SAXS analyses of $BaTiO_3$ nano-powder

By TEM analyses, the larger the quantity of determined grains, the more accurate the average grain size is reflected. Nevertheless, it cannot reflect the powder's distribution which is an important index to estimate powder property. In contrast, SAXS analysis has the merits of excellent repetitiveness and few artificial error to character powder property. From the patterns of grain size distribution (Fig. 3), microwave method can prepare the powder with homogeneous grain size distribution.

Sintering capability of $BaTiO_3$ powder

The powder synthesized by different methods is compacted into ceramic discs and analyzed by SEM. The photographs of SEM analyses reveal that disc diameter prepared by microwave is much less than disc by hydrothermal method, because grain size of powder synthesized by microwave is less than the latter. Figure 4 compares the two kinds of discs prepared from powders by hydrothermal method and microwave method, respectively. Ceramic crystalline size has direct relation with powder size. Under the same ceramic preparation process, the less the raw powder grain size is, the less the ceramic crystalline size made from the powder is.

Measure of dielectric properties

Discs made from powder synthesized by different methods are tested to compare their properties, as shown in Table 1. It reveals that ceramic properties prepared by microwave method are much better than those prepared by the other two methods. It is because of small grain size and homogeneous grain size distribution. Powder synthesized by microwave method

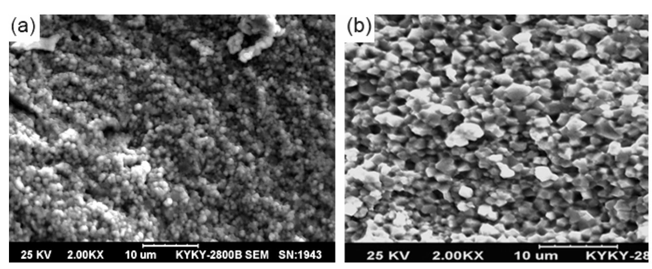

Fig. 4—SEM photographs of discs synthesized from the different raw materials: (a) hydrothermal method; (b) microwave method.

Table 1—The dielectric capacity of $BaTiO_3$ synthesized by different methods

Desc.	Atmospheric method	Hydrothermal method	Microwave method
Sintering temperature (°C)	1250-1300	1300	1150
Dielectric capacity	4000	2500	7200
Dielectric loss	0.1	0.1	0.01

can be compacted into discs without bond, which avoids bond remained in the process of sintering. So, it is much easier to decrease pores among grains. Thus, it is easy to be prepared into compact ceramic.

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