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Compare of liquid-state methods synthesizing Nano-$BaTiO_3$

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ABSTRACT

Nano-$BaTiO_3$ powder is synthesized with $TiCl_4$ and $Ba(OH)_2$ by different liquid-state methods, such as atmospheric method, high-pressure thermal method and microwave method. Its phase, shape and capacity is investigated by XRD, TEM, SEM, SAXS, LCR. XRD of the series of the nanometer powder demonstrates that $BaTiO_3$ of cubic system has been prepared. Through TEM we found 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.

KEYWORDS

Nano-$BaTiO_3$;
Atmospheric method;
Thermal method;
Microwave method.

INTRODUCTION

Nano-ceramic material is the associative outcome of modern chemistry and advanced technology, which will be one of the most important materials in the new century. Thereinto, $BaTiO_3$ ceramic has always been placed emphasis on in this voluminous family of nano-ceramic material. It cuts a brilliant figure as industry raw material in technical production and daily life. The linchpin to synthesize nano-ceramic is to prepare little grain-size powder with uniform shape. It is significant to explore a preparation method of $BaTiO_3$ nano-powder.

With the grain size of $BaTiO_3$ nano-powder diminishing, the grain quantity for given quality will increase and exterior area will enlarge. Thus the boundary layer effect functions markedly, which endue $BaTiO_3$ nano-powder with inimitable physical and chemical property. Therefore, nano-$BaTiO_3$ ceramic material turns into new type and high-powered material to 21 century, especially as excellent dielectric material with merits of low cost, stable property and innocuity. In this article, three liquid-state methods, such as atmospheric method, high-pressure thermal method and microwave method are researched. Different reaction conditions are discussed to confirm the optimal synthesis technique.

EXPERIMENTAL

Material and apparatus

$TiCl_4$, $Ba(OH)_2$, $8H_2O$, NH_3, H_2O are of analytical grade. All experiments were carries out in double-distilled water.

Rigaku D/MAX-RC-X-ray diffractometer(Jp), TEM-1000SX Transmission Electrical Microscope(Jp), 769YP-242 TABLE Oil Press(Tianjin), RJXG-5-13 Electrical Stove, Automatic LCR Meter(En), Whirlpool microwave stove(Am) and reactor etc.

Synthesis of $BaTiO_3$ nano-powder

1. Atmospheric liquid-state method

Hydrolysis of $TiCl_4$ is similar to the literature[3,4]. H_2TiO_3 is launched into water and conducted into serum of 250ml, then commixed with 200ml alkaline solution of $Ba(OH)_2$. Then the mixture mixed up by a beater is lain on a electric cooker to react below 100^0C for 3~5h. The solid powder of $BaTiO_3$ is obtained after filtering, washing and drying at 100^0C. Reaction principle as follows:

$$TiCl_4 + H_2O \rightarrow H_2TiO_3 + HCl$$

$$H_2TiO_3 + Ba(OH)_2\ Ba(OH)_3 + 2H_2O$$

2. High-pressure thermal method

Calculated $TiCl_4$ is hydrolyzed into H_2TiO_3, launched into water and conducted into serum of 250ml, then commixed with 200ml alkaline solution of $Ba(OH)_2$. Afterward, the mixture is poured into high-pressure thermal reactor to react at 150 ^0C for 2h. The solid powder of $BaTiO_3$ is obtained after filtering, washing and drying at 100^0C.

3. Microwave method[5,6]

Hydrolysis of $TiCl_4$ is similar to the literature[3,4]. H_2TiO_3 is launched into water and conducted into serum of 250ml, then commixed with 200ml alkaline solution of $Ba(OH)_2$. Then the mixture placed in a beaker (The beaker is full of water) is lain in the microwave stove. The heating power is turned to 10 by regulating the heating-power knob for 5 min, then turned to 2 for 15 min, so that the reactant maintains slightly boiled at 100^0C. The solid powder of $BaTiO_3$ is obtained after filtering, washing and drying at 100^0C.

Preparation of ceramics

The ceramic is prepared by the powder synthesized and their properties are studied. The sample is mixed with suitable amount of adherent (8% PVA aqueous solution) and grounded evenly, then bolted by the screen with its aperture of 0.45mm (40 meshes). The resulting powder is pressed into disc whose diameter is 1.5 cm and thickness is 0.2cm at a pressure of 6~8 MPa. The binder is removed by firing at 600^0C in air. After cooling, the discs are sintered by heating to 1150^0C. After layered with Ag electrodes, their electric capacity value (C) and dielectric loss (tanδ) are measured by Automatic LCR Meter at different temperatures, their thickness and diameter are measured with micrometer, and their dielectric constants are calculated from the formula as follows, where C is capacity value of sample, h the thickness of disc, S the electrode area, ε_o the vacuum dielectric constants, $\varepsilon_o = 1/4\pi \times 9 \times 10^{11}$ F/cm.

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

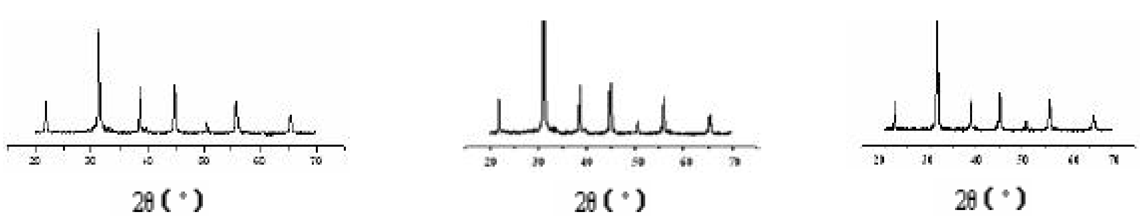
RESULTS AND DISCUSSION

XRD analyses of $BaTiO_3$ nano-powder

$BaTiO_3$ powder synthesized by three methods is analyzed with XRD respectively. It has the same XRD pattern as pure $BaTiO_3$ phase and all of them belong to the cubic system in figure 1(a. atmospheric liquid-state method, b. high-pressure thermal method, c. microwave method). But from the aspects of kurtosis and peak value, the powder synthesized by different methods differs from each other appreciably. The peak value of powder synthesized by high-pressure thermal method is topmost, while kurtosis of powder synthesized by microwave method is widest.

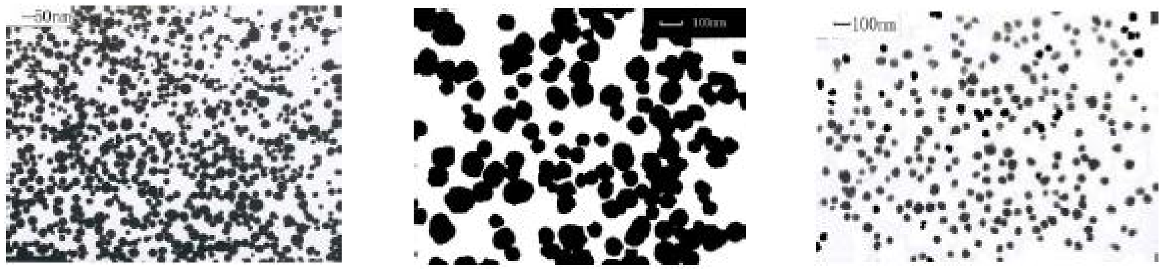
TEM analyses of $BaTiO_3$ powder

Through TEM, an observation of the $BaTiO_3$ powder synthesized by different methods reveals as follows: Grain size of atmospheric liquid-state method is 70~80nm with a spheroidic shape. Grain size of high-pressure thermal method is 120~150nm with a



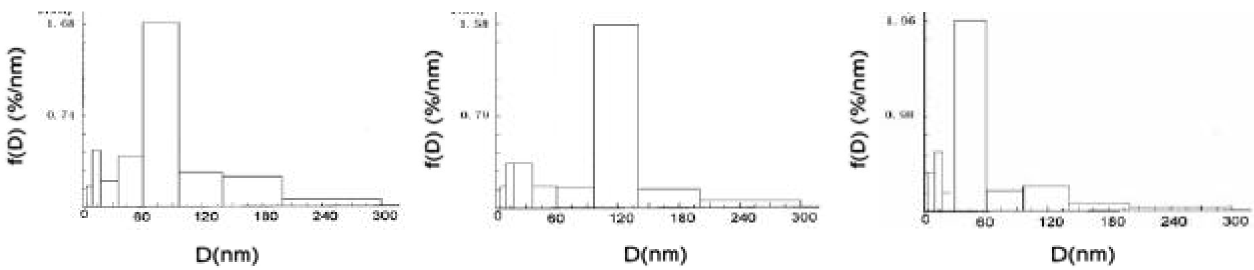
(a) Atmospheric liquid-state method **(b) High-pressure thermal method** **(c) Microwave method**

Figure 1 : XRD patterns of nano-$BaTiO_3$



(a) Atmospheric liquid-state method **(b) High-pressure thermal method** **(c) Microwave method**

Figure 2 : TEM photos of nano-$BaTiO_3$



(a) Atmospheric liquid-state method **(b) High-pressure thermal method** **(c) Microwave method**

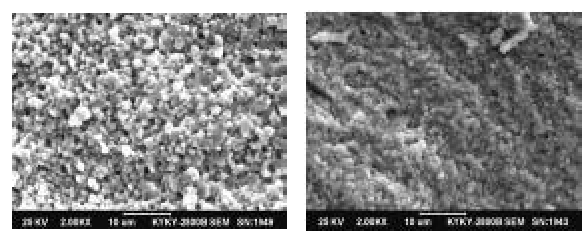
Figure 3 : SAXS patterns of nano-$BaTiO_3$

squareoidic shape. Grains of microwave method are substantially spherical with the average size of 40 nm in diameter, which is shown in figure 2.

Atmospheric solid-state method has the merits of low reaction temperature, below 100^0C. But it needs long reaction time, and artificial control throughout the whole preparing process. Otherwise, temperature is difficult to control heated by stove, so that the powder synthesized by this method is asymmetric. High-pressure thermal method needs slashing reaction conditions such as high temperature and high pressure, so it has the defects of large energy consumption, high cost. Grains grows to micro-meter under these conditions which are impossible to be used into nano-ceramic preparation. While microwave method is the best method in the three in virtue of simple operation, short reaction time. It utilizes cavitation effect to obtain high calefactive velocity and calefaction from inside to outside which induce creating velocity faster than growing velocity of the powder. So the grain size is as small as 40nm, and has a homogeneous distribution.

SAXS analyses of $BaTiO_3$ nano-powder

By TEM analyses, the larger the quantity of determined grains is, the more actually the average grain size is reflected. Nevertheless, it can not reflect the powder distribution which is an important index to estimate powder property. In contrast, SAXS analysis has the merits of excellent statistic and little artificial error. So it has better determining repeat to character powder property. From the patterns of grain size distribution as figure 3 show, microwave method can prepare the powder with the most homogeneous grain size distribution.



(a) High-pressure thermal method **(b) Microwave method**

Figure 4 : SEM photos of discs synthesized from different raw material

Sintering capability of $BaTiO_3$ powder

The powder synthesized by different methods is processed into ceramic discs, which are analyzed by SEM. The photos of SEM analyses reveal that disc diameter prepared by microwave is much less than disc by high-pressure thermal method, because grain size of powder synthesized by microwave is less than the latter.

TABLE 1 : The dielectric capacity of $BaTiO_3$ synthesized by different methods

Disc	Atmospheric method	High-pressure thermal method	Microwave method
Sintering temperature/^{0}C	1250~1300	1300	1150
Dielectric capacity	4000	2500	7200
Dielectric loss	0.1	0.1	0.01

Figure 4 is compared the tow kinds of discs prepared from different powder. Ceramic crystalline size has the near and near 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 showed in TABLE 1. It reveals that ceramic properties prepared by microwave method are much better than those prepared by other tow methods. It is because of little grain size and homogeneous grain size distribution. Powder synthesized by microwave method can be pressed into discs without bond, which avoids bond remained in the sintering course. So it is much easier to decrease pores among grains. That is, it is easy to compact.

CONCLUSION

In this article, three liquid-state methods used to synthesize $BaTiO_3$ powder are compared with each other, in the aspects of experimental process, grain size, sintering capability and dielectric properties. Microwave method has the merits of short reaction time, easy control, little grain size, narrow grain size distribution. It is in favor to prepare capability-excellent dielectric ceramic. It will realize miniaturization and integration of electron implement as an outstanding technique to prepare nano-ceramic.

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