Research on Preparation of Nano-Barium Titanate and Dielectric Property of Barium Titanate Ceramic Capacitor

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ABSTRACT

A mild alcohol-thermal synthesis of nano-$BaTiO_3$ from $H2TiO_3$ and $Ba(OH)_2$ at an Atmospheric Press was systematically studied and the optimized preparation conditions were obtained. When the reaction is carried out at a temperature of 79℃,an atmospheric press for 6h, the moral ratio of $Ba(OH)_2$: H_2TiO_3=1.0, pH=11, the cubic crystal structure of nano-$BaTiO_3$ was obtained. The dielectric ceramic was fabricated with nano-$BaTiO_3$. By comparison with ordinary ceramic, the ceramic with nano-$BaTiO_3$ from alcohol-thermal method could lower sintering temperature from 1300℃ to 1150℃, change Courier point to 70℃,make dielectric constant 20000.

Keywords: nanometer powder, Barium titanate, solvent-thermal method, dielectric property

1 INTRODUCTION

Barium titanate is increasing importance in the preparation of dielectric capacitors or transducers due to its high dielectric constants, ferroelectric properties, piezoelectric properties and positive temperature coefficient (PTC)effect [1-5]. In particular, nano-$BaTiO_3$ exhibits unique features that strongly differ from those of bulk phase, such as switch of Curie temperature and increase in dielectric constant [6-7]. Many authors emphasized the importance of their synthesis process on the properties of BaTiO3 powder ,thus many methods have been developed to synthesize $BaTiO_3$ with specific size, such as solid state method, sol-gel process, precipitation and hydrothermal. Solid-state method[8] did not satisfy the needs of electronic ceramic industries due to lack of uniform nanocrystalline $BaTiO_3$.Sol-gel process[9] needs high temperature over 700℃ and expensive alkoxides, which goes against practical application. Precipitation[10] using inorganic salts has shown success in producing $BaTiO_3$, but it also need high temperature during sintering. Hydrothermal methods[11-15] with inorganic salts offers a promising approach to prepare $BaTiO_3$, whereas it needs high temperature(160-300℃) and high pressure(4-8MPa). Michael Z-C[16] reported that hydrothermal proceeded at temperature 100℃,but the reaction time is as long as 24h-72h,the particle size is 0.2-1um.The reports concerning low temperature alcohol-thermal synthesis of nano-$BaTiO_3$ with low-priced H_2TiO_3 at ambient pressure to prepare nano-$BaTiO_3$ has not been published.

Qinghua University reported in 2006 that ceramic based nano-$Ba(Zr,Ti)O_3$ powder exhibits 23000 of dielectric constant, but the high dielectric constant ceramic based pure nano-$BaTiO_3$ powder have not been reported heretofore.

In this paper we report a mild alcohol –thermal route to $BaTiO_3$ nanoparticles;the mole ratio of Ba to Ti in precursor and reaction time are used as variable.The formation process of Barium titanate ,the sinterring temperature of ceramic and the dielectric property are discussed.

2 INTRODUCTION

H_2TiO_3 was scattered in alcohol at room temperature (marked A); $Ba(OH)_2$ was scattered in alcohol in a closed bottle at 79℃ (marked B).Aqueous ammonia and A were gradually added to B respectively, which were stirred and refluxed for some time at 79℃. The suspension were cooled to room temperature, separated by centrifugation, washed with the acid, distilled water and alcohol, dried at ambient temperature. Thus the $BaTiO_3$ powders were gained.

$BaTiO_3$ powders were characterized with TEM (JEM-2010 model, JEOL Corporation, Japan) and X-ray diffraction(XRD) model D/MAX-ⅡP, Tokyo, Japan.. $BaTiO_3$ capacitor were characterized with SEM (SEM-5900LV,JEOL Corparation) and the capacitance at different temperature was tested by LCR apparatus (Tianjin No.6 radio Factory,China).

3 RESULTS AND DISCUSSION

3.1 The Effect of Ba/Ti Molar Ratio

When the reaction is carried out at pH=1, 79℃,6h,the effect of Ba/Ti molar ratio in the precursors on the products is shown in Fig.1.

It can be seen from Fig.1 that with the increase Ba/Ti moral ratio in the precursors, the Ba/Ti moral ratio in the powders all the while increased.The XRD patterns of the sample prepared by the different moral ratio of Ba/Ti in reactants at 79℃for 6h were showed in Fig.2.

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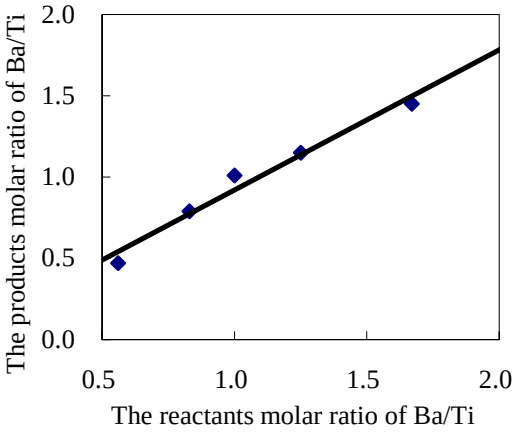


（reaction conditions：pH:11, reaction time:6h,temperature:79℃）

Figure 1 :The curves of molar ratio of Ti/ Ba

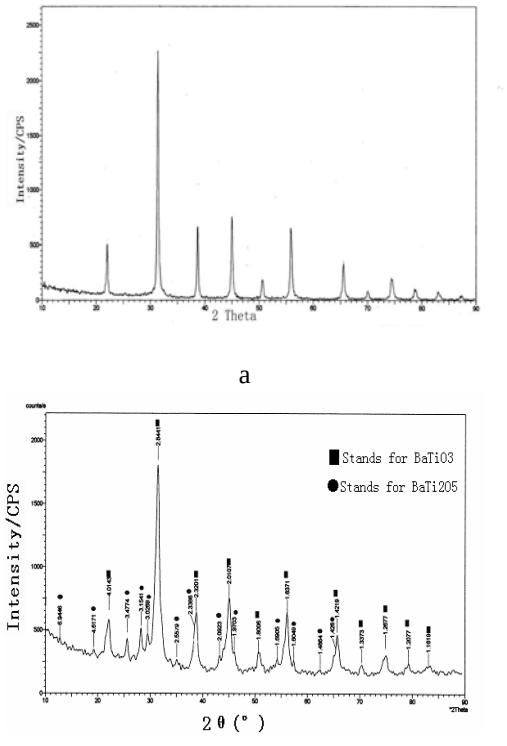


Figure 2: XRD patterns of Barium Titanate

a:Ba/Ti moral ratio 1.0;b Ba/Ti moral ratio 0.8;

Fig.2.a is the XRD patterns of sample from reactants moral ratio of Ba to Ti：1.0, it is clear that all diffraction peaks can be indexed to the cubic structure of $BaTiO_3$, Fig.2.b is the XRD patterns of sample from reactants moral ratio of Ba to Ti： 0.8,there are peaks of $BaTi_2O_5$ (moniclinic) and $BaTiO_3$ (cubic) ,which suggest the reactants moral ratio of Ba to Ti affected the constitute of products. To obtain pure $BaTiO_3$, it is necessary to control reactants moral ratio of Ba to Ti., that is the optimum Ba/Ti moral ratio in the precursors is 1.0.

The reaction process abides by the following steps:

$$H_2TiO_3 + Ba(OH)_2 \longrightarrow BaTiO_3 + 2\,H_2O \quad (1)$$

when H_2TiO_3 is excess,the reactiom is as follows

$$H_2TiO_3 + BaTiO_3 \longrightarrow BaTi_2O_5 + H_2O \quad (2)$$

3.2 The Effect of Reaction Time on Products

Table 1 showed the effect of reaction time on products. It is clearly seen that Ba/Ti molar ratio and the content of $BaTiO_3$ in the products increased with the increase of reaction time from table 1.The increase extent was not large after 6h, which indicated the reaction can complete when the reaction is 6h .

Time(h)	Ti/Ba in product	$BaTiO_3$（%）
1	0.32	-
3	0.48	30.8
5	0.98	80.4
6	1.01	92.1
10	1.02	93.5

（reactants moral ratio of Ba / Ti:1.0, temperature:79℃）

Table 1: The effect of reaction time on powder

3.3 TEM Analysis

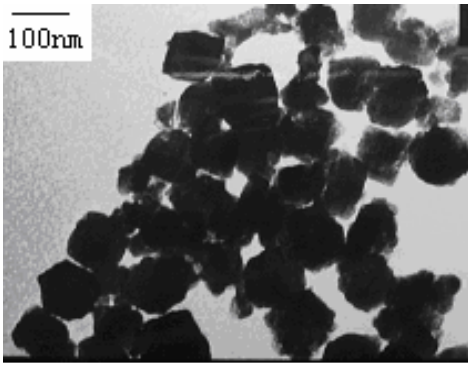
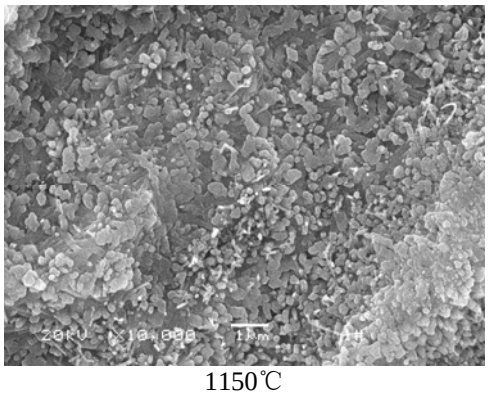


Figure 3 : TEM micrograph of $BaTiO_3$

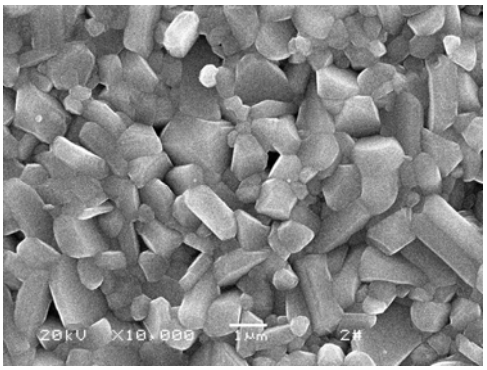
TEM photos showed that the $BaTiO_3$ nanoparticles were square in shape, the size was about 50nm .Particle size distribution was in narrow range, and no agglomerates were observed.

3.4 SEM Analysis

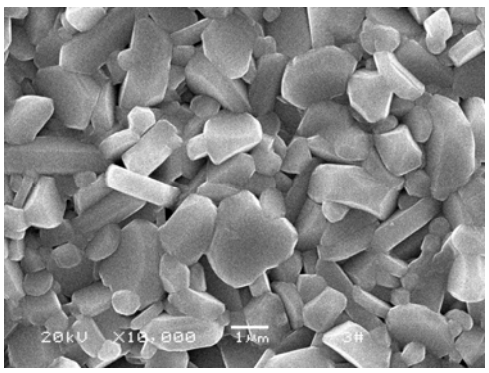
The micrograph of $BaTiO_3$ ceramic at different sinterring temperature are showed in figure 4.



1150℃



1200℃



1250℃

Figure 4: SEM micrograph of $BaTiO_3$ ceramic

It can be seen that the diameter of $BaTiO_3$ in ceramic increased with increaing temperature,which conform with the relationship between sinterring temperature and the diameter.

SEM photos showed that the particle size in $BaTiO_3$ ceramic sinterred at 1150℃ was about 200nm,Particle size distribution was in narrow range.

3.5 DielectricConstant of $BaTiO_3$ Capacitor

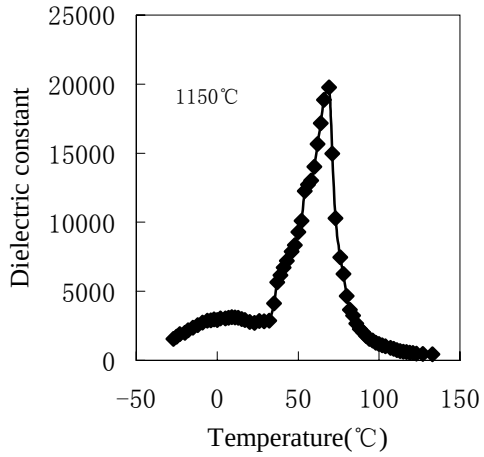


Figure. 5 Temperature dependence of dielectric constant of $BaTiO_3$ capacitors

The relationship between temperature and dielectric constant is nonline,which indicated the ceramic sinterred at 1150℃ from nano-$BaTiO_3$ is ferroeletric ceramic. By comparison with ordinary $BaTiO_3$ ceramic capacitor, the ceramic capacitor fabricated by nano-$BaTiO_3$ could not only lower sintering temperature from1300℃ to1150℃, but also change Courier point from 130 to 70℃, improve dielectric constant from 6000 to 20000,which can satisfy the development of microdevies.

4 CONCLUSION

When Ba/Ti moral ratio in the precursors is 1.0 and the reaction time is 6h, the reaction of synthesis pure $BaTiO_3$ has completed. one step synthesis $BaTiO_3$ particles without sintering are cubic structure and the size is 50nm. The ceramic capacitor fabricated by this kind of $BaTiO_3$ is ferroeletric ceramic , sintering temperature is 1150℃, Courier point is 70℃, dielectric constant at Curie point is 20000.

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