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Materials

Characterization and growth dynamics of barium titanate crystallite on nanometer scale

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Abstract: Barium titanate powder on nanometer scale was synthesized by means of co-precipitation. The thermal mass loss, crystal grain growth and phase transition of the barium titanate nanometer powder were investigated by TG (Thermogravimetric)-DTA (Differential scanning calorimetric) and XRD (X-ray powder diffractometer) at different heat treatment temperatures. The results show that amorphous barium titanate powder can transfer into tetragonal symmetry structure after heat treatment. When the heat treatment temperature is below 900°C, the grains grow rapidly because the activation energy at low temperature is greatly less than that at high temperature. By controlling the heat treatment temperature, the optimization of the barium titanate crystallite size and formation of tetragonal phase can be realized.

Key words: barium titanate; nanoscale powder; phase transition; activation energy

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1 Introduction

Barium titanate plays a very important role in electronic ceramic field because of its high dielectric constant and excellent ε-t character, by which it has become the most important dielectric of multiplayer chip capacitor (MLCC). Since high permittivity and small size are the main trend of MLCC development at present [1], the manufacturer must try to reduce the thickness of unit dielectric layer to even thinner than 1 μm and keep its high dielectric constant at the same time. In order to improve the reliability of MLCC and reduce the probability of short circuit, the dielectric layer between two inner electrodes must contain more than five $BaTiO_3$ grains [2], and correspondingly the average grain size of the $BaTiO_3$ smaller than 200 nm should be satisfied. Of the several phases, only tetragonal $BaTiO_3$ is fit for MLCC dielectric [3]. It is not only of great theoretical meaning but also of practical meaning to study the grain growth and tetragonal phase formation of $BaTiO_3$ on nanometer scale. Many papers about synthesis method of barium titanate have been published so far, but seldom on the characterization of nanometer barium titanate powder, especially papers about the growth mechanism of the barium titanate crystallite and the formation of tetragonal barium titanate on nanometer scale have not been found. The purpose of this work is to study the grain growth and formation dynamics of tetragonal barium titanate at different heat treatment temperatures. In addition, to acquire the relationship between the particle size and formation of tetragonal barium titanate.

2 Experimental

Analytical-grade $TiCl_4$, ethanol, $BaCl_2{\cdot}2H_2O$, $H_2C_2O_2{\cdot}6H_2O$ were used as starting materials. The flowchart of the sample processing by oxalic acid co-precipitation method is shown in **figure 1**.

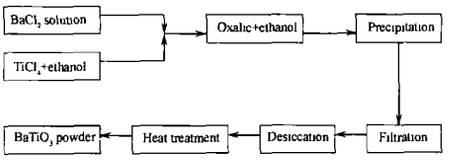

Figure 1 Flowchart for the preparation of $BaTiO_3$ powder.

Thermogravimetric (TG) and differential scanning calorimetric (DSC) curves were obtained using NETZSCH STA409C in a dynamic N_2 atmosphere at a heating rate of 10 °C/min. Morphological analysis of

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samples was performed by scanning electron microscopy (SEM) using a Cambridge S320 microscope. X-ray powder diffractometer (XRD) were obtained using a Rigaku D/ Max-RB diffractometer.

3 Results and discussion

3.1 TG/DSC analysis

Figure 2 indicates TG and DSC curves of the precursor after heat treatment below 1000°C with a heat rate of 10 °C/min. The total mass loss of the precursor terminated at 950°C and four discrete regions of mass loss occurred at temperature ranges of 30-180°C, 180-400°C, 400-550°C and 550-950°C, respectively. Below 180°C, the mass loss is due to the evaporation of the absorbed water and part of organic materials. Above 80°C, the mass loss can be ascribed to the loss of hydroxylated water and the decomposition of organic and carbonate constituents of the precursor powder. Corresponding to the mass loss regions, there are five obvious peaks in the DSC curve, two exothermic peaks at 314.9 and 503°C and three endothermic peaks at 140.8, 695 and 803°C respectively. The first exothermic peak at 314.9°C can be explained as the combustion of carbonaceous in the precursor, and the second exothermic peak at 503°C can be explained as the recrystallization of the precursor. Three endothermic peaks, the first at 140.8°C, the second at 695°C and the third at 803°C respectively, are associated with the removal of structure water and the decomposition of carbonate and the formation of tetragonal phase $BaTiO_3$.

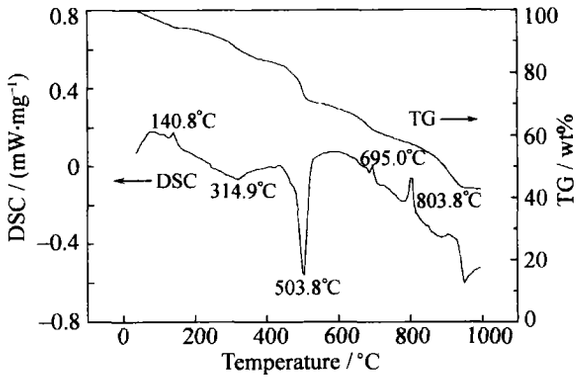

Figure 2 TG/DSC curves of burnt powders.

3.2 Powder X-ray analysis

XRD patterns of the barium titanate powders after four different temperature treatments are shown in **figure 3**.

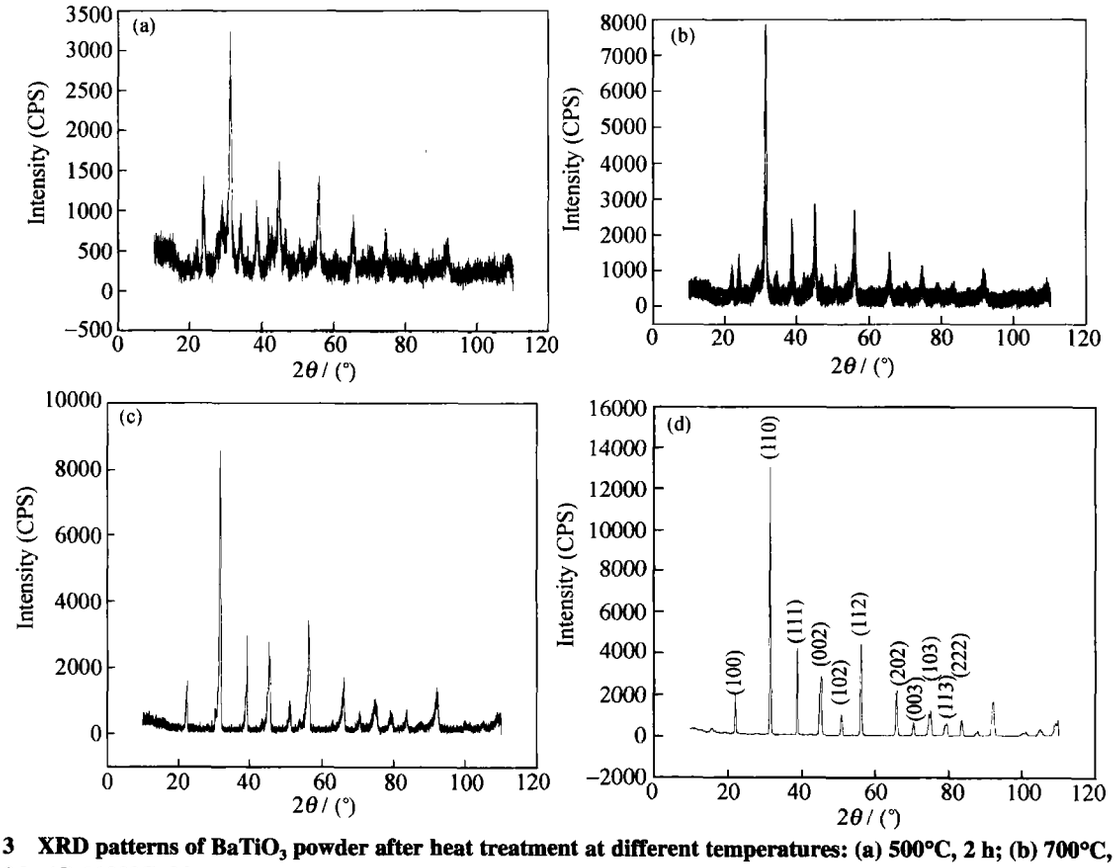

Figure 3 XRD patterns of $BaTiO_3$ powder after heat treatment at different temperatures: (a) 500°C, 2 h; (b) 700°C, 2 h; (c) 900°C, 2 h; (d) 1100°C, 2 h.

The XRD data given in figure 3 indicate that an initial heat treatment temperature is found to be 500°C for the formation of the barium titanate crystallite, which is close to the recrystallization temperature in-

dicated in the DSC curve in figure 2. The most intensive diffraction peaks in the four XRD patterns appeared at 2θ= 31.6°, which is corresponding to the surface (110) of tetragonal $BaTiO_3$ unit cell according to JCPDS data. In the samples after heat treatment at 500 and 700°C, except tetragonal $BaTiO_3$, there are other phases such as cubic phase and undecomposed constituents. When the heat treatment temperature is higher than 900°C, all the diffraction peaks in the XRD pattern can match satisfactorily well with the known data tetragonal $BaTiO_3$ from JCPDS. With increasing of heat treatment temperature, the intensity of diffraction peaks of the tetragonal phase $BaTiO_3$ increases rapidly, which is also an indication of the decrease of non-tetragonal or cubic phase $BaTiO_3$. There is no cubic phase $BaTiO_3$ in the XRD pattern after 1100°C heat treatment. The grain size of $BaTiO_3$ crystallite, which is an important factor that will influence the phase of $BaTiO_3$, will increase with heat treatment temperature increasing. When the size of $BaTiO_3$ grain is at the critical value, $BaTiO_3$ crystallite will transfer from cubic phase to tetragonal phase [4]. The average critical size and growth mechanism of grains will be discussed in next section.

3.3 Microstructure

Figure 4 shows the morphological features of the barium titanate powders revealed by the scanning electron microscopic after four different heat treatment temperatures.

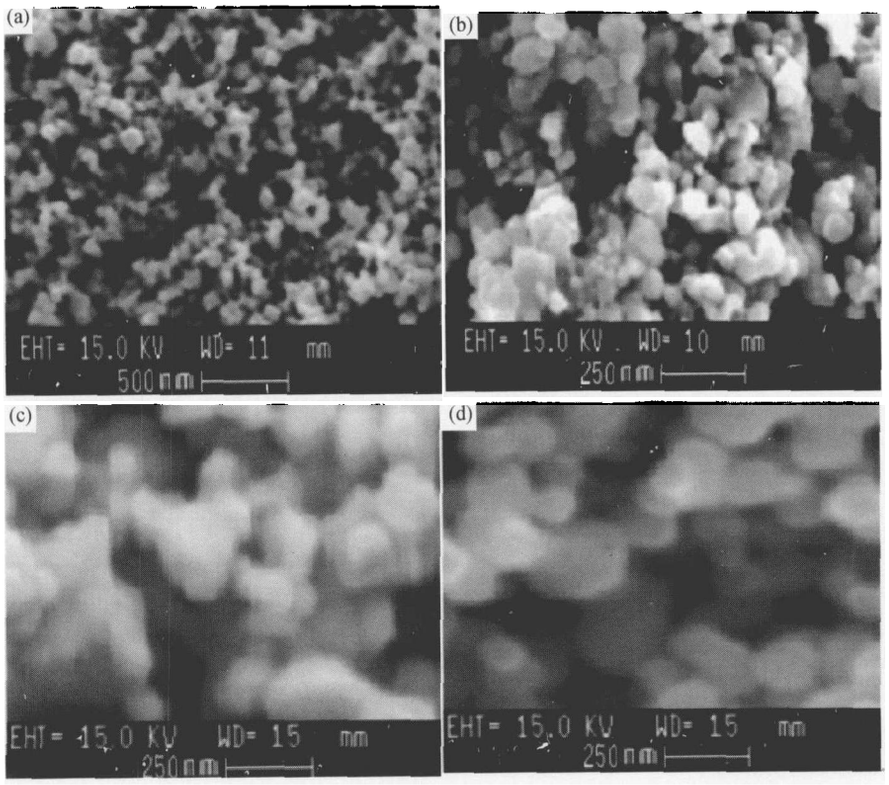

Figure 4 SEM micrographs of $BaTiO_3$ powder: (a) 500°C, 2 h; (b) 700°C, 2 h; (c) 900°C, 2 h; (d) 1100°C, 2 h.

The dried powder obtained by co-precipitation disperses uniformly and no strong agglomeration has been found in the samples. $BaTiO_3$ powders calcined at 900°C have an average grain size of 210 nm in diameter with a spherical micrograph. With increasing of heat treatment temperature, the particles of $BaTiO_3$ continue to grow because of the fusion of interparticle neck. At the same time, a tetragonal morphology of the particles come into being and the particles loss their spherical morphology as showed by figure 4(d).

The grain size, expressed by D, can be estimated by Scherrer' formula,

$$D=0.89\lambda/\beta\cos\theta$$

where λ is the X-ray wavelength, β is a constant, and θ is the diffraction angle. The temperature-average grain size relation is summarized by **figure 5**.

The result above is somewhat different with the average particle size got from SEM. Maison argued that there is an internal structure of the particles consisting of twinned domains and crystallite boundaries, which cannot be found by SEM but can be detected by X-ray [5].

3.4 Phase transition and grain growth of the powder

Tetragonal phase $BaTiO_3$ appears when $BaTiO_3$ grain size obtained by Scherrer' formula is 84 nm cor-

responding to the heat treatment temperatures of 500°C. It has been reported that 100 nm is the limited diameter of the cubic phase $BaTiO_3$ [6]. When greater than this critical size, $BaTiO_3$ will be in tetragonal phase. Another report argued that this critical size is at 120 nm [4]. We found that an even smaller size particle of 84 nm can present tetragonal phase. This difference on critical size of cubic-tetragonal transition likely comes from the different synthesis method. Figure 5 shows that growth rate of the particle depends on the heat treatment temperature, the particle size increases rapidly with the heat temperatures from 500 to 900°C, but increase slowly over this temperature range. The growth rate of the crystallite grain can be described as follow [7]:

$$\mu=K[\exp(-Q/RT)][1-\exp(-\Delta F_v/RT)] \quad (1)$$

where μ is the growth rate of the crystallite grain, K is a constant, Q is the growth activation energy, ΔF_v is the energy difference between crystalline $BaTiO_3$ and amorphous $BaTiO_3$, R is a constant.

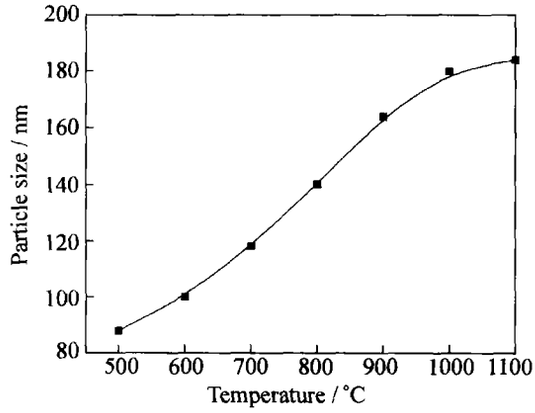

Figure 5 Relationship between annealing temperature and particle size.

Because $\Delta F_v >> RT$ in this case, the formula above can also be described as follow:

$$\mu=K[\exp(-Q/RT)] \quad (2)$$

Then the grain size D can be described as follow:

$$D=K[\exp(-Q/RT)]t \quad (3)$$

where t is the heat treatment time. Since all the samples are heated by the same time, the grain size D has direct proportion with $\exp(-Q/RT)$ term , namely,

$$D \propto \exp(-Q/RT) \quad (4)$$

This formula can be substituted into the formula in a logarithmic form:

$$\ln D=-Q/RT+C \quad (5)$$

where C is a constant.

Figure 6 shows the plot of the size of $BaTiO_3$ grain *vs* the reciprocal temperature based on formula (5). Obviously, the plot can be divided into two parts by the different slopes, which is in proportion to the activation energy Q. Activation energies in different temperature ranges obtained by this method are Q_1 and Q_2 respectively. Q_1 responds to the activation energy obtained below 900°C, and Q_2 responds to the activation energy obtained over 900°C. From the result above, a conclusion can be made that the grain growth below 900°C is more rapid than that over 900°C since the activation energy at low heat treatment temperature is far lower than the one at higher temperature.

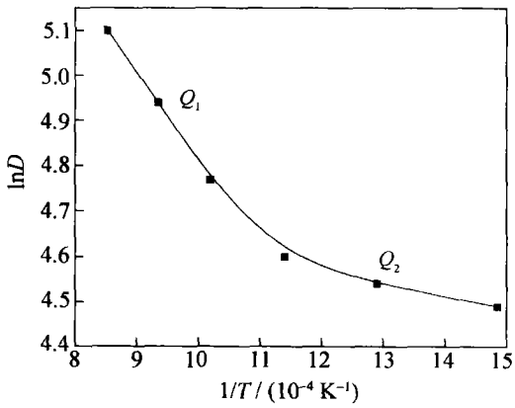

Figure 6 Relationship between ln$D$ and 1/T.

4 Conclusions

(1) The mass loss of barium is due to the evaporation of residual water and the decomposition of organic and carbonate constituents in the precursor powder.

(2) The cubic and tetragonal phase $BaTiO_3$ come into being when the heat treatment temperature near 500°C. XRD powder diffraction indicates that the cubic phase is stable up to 500°C. After that, cubic phase $BaTiO_3$ begin to decrease and tetragonal phase $BaTiO_3$ begin to increase with increasing the heat treatment temperature.

(3) The calculated result showed that the grain growth rate and grain size depend on the heat treatment temperature. It has been pointed out that the grain growth rate, as a function of the heat treatment temperature, is controlled by a high activation energy at high temperature and a low activation energy at low temperature respectively.

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