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Influence of pH value on properties of nanocrystalline $BaTiO_3$ powder

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Abstract

Nanocrystalline $BaTiO_3$ powders were prepared by a simple sol-gel method starting from comparatively cheap raw materials. The effect of pH value on the properties of $BaTiO_3$ powder was investigated. It was found that the pH value of solvent has a great influence on the process of powder fabrication, including colloid formation, gel structure and agglomerates. The mechanism was discussed and the optimal powder preparing condition was proposed in this paper. As-prepared powder was pseudo cubic structure with an average grain size of 13 nm (TEM) and a high BET value of 33 m^2/g. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: Nanostructures; Ferroelectrics; Nanofabrication

1. Introduction

Barium titanate ($BaTiO_3$), which has good dielectric properties, is widely utilized in the manufacture of thermistors, multilayer capacitors (MLCs) and electro-optic devices. Properties, such as high purity, superfine and narrow size distribution of powder are the general trends of high-tech applications. Traditional mixed-oxide routes preparation of powder is coarse, impure, inhomogeneous and multiphase. Nowadays, wet chemical methods appear very attractive in synthesising high purity, ultrafine and homogeneous powder.

Nanocrystalline $BaTiO_3$ powder has been prepared by various methods [1–4], but sol-gel methods present some particular advantages through a low-temperature process avoiding contamination of the materials. They also yield better stoichiometric control and the possibility of grain-size and grain-shape control [5]. It is a complex process of synthesising powders by a sol-gel method [6]. All stages, including the formation of colloid, particles connected to form gel-net, the dry of wet gel and calcination stage can all lead to grain growth and formation of agglomerates. Hence, to carefully control the process is very essential in preparing high performances and high reliability powders.

In this work, we present a study of the pH value dependence on the characteristics of $BaTiO_3$ nanocrystalline powder obtained by a simple sol-gel method starting from comparatively cheap raw materials. It was found that the pH value not only affected the reaction process, but also the formation of aggregates and the characteristics of the powder.

2. Experimental

A modified sol-gel method was used to fabricate nanocrystalline $BaTiO_3$ powder. The synthesis procedure is as follow: barium oxyhydrate and tetrabutyl titanate were separately dissolved in ethylene glycol monomethyl ether and ethanol. Then these two solutions were mixed and stirred the mixture to form a sol which contains barium and titanium in a ratio of 1:1. Water diluted ethylene glycol monomethyl ether was slowly added to the sol. After a certain time, a clear gel was formed. The Ba, Ti precursor was dried in an oven at 110°C and then was ground and heat-treated to obtain the crystalline $BaTiO_3$

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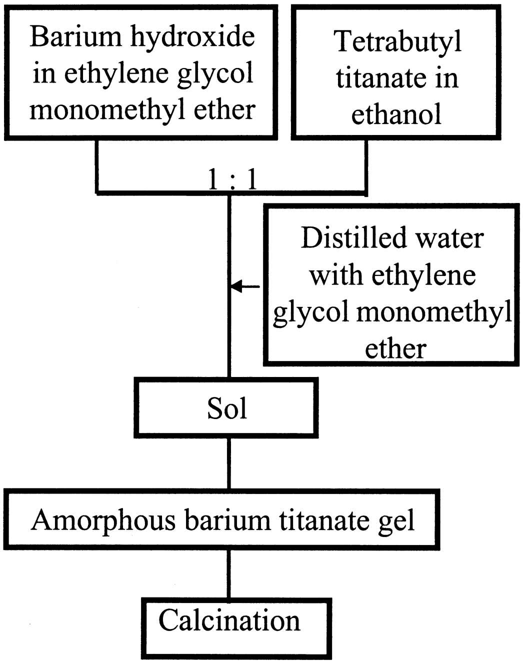

Fig. 1. Flow sheet for $BaTiO_3$ synthesis of a sol-gel process.

powder. These processes are shown in a schematic sketch in Fig. 1.

The pH value of solvents was adjusted by adding ammonia or nitric acid into the solution. The ζ potential of powder was measured using Zeta plus potential instrument (Brookhaven company, using 1 mM KCl solution as suspension,). The crystal structure of powder calcined at 600°C was investigated by XRD with CuK_α radiation (40 kV, 20 mA) at a scanning speed of 10°/min over a range of 10–70° at the room temperature. The morphological characteristics of the crystallized powders after calcination was examined by transmission electron microscope (TEM, JEM-200CX, Jeol), eight-point Brunauer–Emmett–Teller (BET) analysis from nitrogen gas absorption (ASAP 2010, Micromeritics) was used to obtain the BET-specific surface area of the crystalline powders.

3. Results and discussion

3.1. Characterization of powders

In this work we studied three kinds of specimens with various pH values such as 4, 7 and 9. It is found that the alkalinity and acidity have a great influence on the properties of the powder. The specimen with pH = 4 can not form a gel, a white precipitation was observed after the two precursors was mixed. XRD measurement was carried out after the precipitation was calcined at 600°C (Fig. 2). The XRD patterns of calcined powder showed peaks of apparently tetragonal perovskite structure with its (001), (002) and other certain diffraction peaks splitting, which match very well with the published patterns [7]. This powder was seriously agglomerate based on the study of TEM (Fig. 3). Most of the grains are clustered with only a few separate grains left. When the pH value was increased to 7, the obtained gel was turbid white. Powder calcined at 600°C was pure $BaTiO_3$ of tetragonal phase, just as that of pH = 4. Some degree of agglomerates were found in this specimen, and the clusters consisted of many small grains. This case changed when the pH value was adjusted to 9, where a clear gel was obtained. Powder after being calcined is very fine and homogeneous with the average grain size of 13 nm (TEM). Its XRD patterns showed that the powder was a quasi-stable, pseudo-cubic system at room temperature, while the tetragonal structure is more stable in the bulk crystal. The line broadening effects of XRD pattern is caused by the finer of grains. It has been noted that the stability of the tetragonal phase results from the delicate cancellation of the long-range electrostatic force from the ionicity of barium, titanium and oxygen ions by a short-range overlap force from the covalency of Ti–O bonds. Normally the $BaTiO_3$ bulk body retains its ferroelectricity unless the average grain size is less than its critical size, ~50 nm [8]. While the particles are fine, the energetic gain from long-range electrostatic interaction may be reduced and the cubic phase may become stable [9].

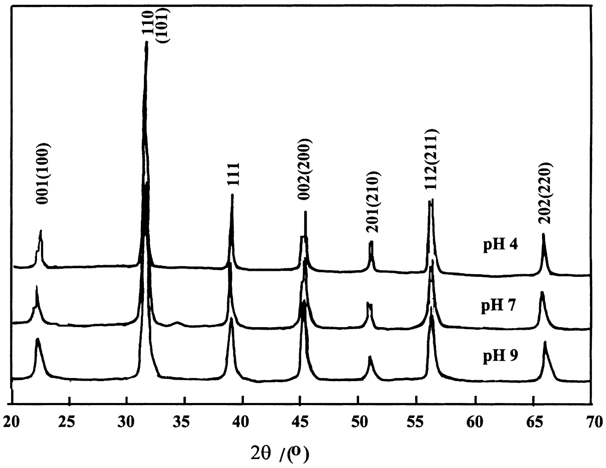

Fig. 2. XRD patterns of $BaTiO_3$ powder after calcination at 600°C.

The BET result is considered to be a more descriptive of the performance of the powder. The change of BET surface area with pH value is shown in Table 1. The BET measurement of crystalline powder prepared at

Table 1
Relationship between pH value and BET of $BaTiO_3$ powder

pH value of solvent	4	7	9
BET (m^2/g)	3.76	16.03	33.27

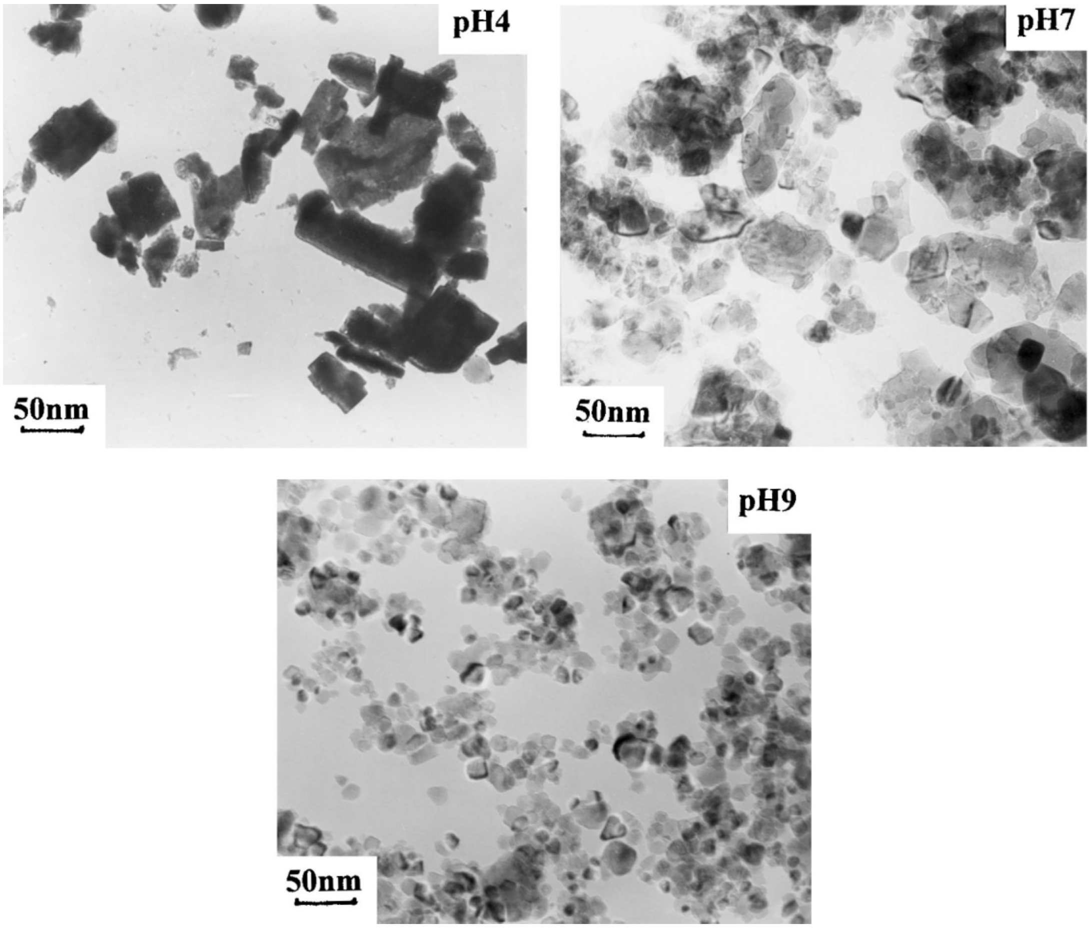

Fig. 3. The micrographs of a $BaTiO_3$ powder prepared at different pH value.

pH = 4 had a very low specific surface area of 3.76 m^2/g. When the pH value was increased to 7, the BET value consequently increased to 16.03 m^2/g. A high BET value of 33.27 m^2/g was obtained with the continuous increment of pH value at 9.

The dependence of the zeta potential on pH value is shown in Fig. 4. It can be found that the IEP (isoelectric point) of this powder is between 1.7 and 1.9. On the low side of the IEP, the ζ potential increases rapidly with the reduction of pH value. While above the IEP, the ζ potential decreases slowly with the increase of pH value and remains steady when the pH value is above 8.

3.2. Mechanism of powder synthesis

The pH value of the solvent has a great effect on the process and properties of the final product. As we know, titanium propoxide has a strong tendency to react with H_2O to form $Ti(OH)_4$ precipitation. Under alkaline condition, hydroxide ions react with tetrabutyl titanate and water molecule to form the complexion $[Ti(OH)_6]^{2-}$, which will neutralize with the Ba ion, then polymerize to $Ba^{2+}[Ti(OH)_6]^{2-}$. The above mentioned reactions can be described as:

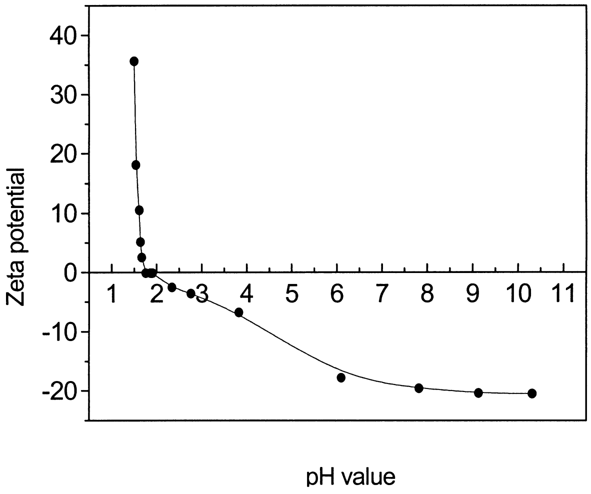

Fig. 4. The zeta potential vs pH value for a sol-gel $BaTiO_3$ powder.

$$Ti(OR)_4 + 4H_2O + Ba^{2+} + 2OH^- \xrightarrow{60\text{–}100^\circ C} [Ti(OH)_6]^{2-} + Ba^{2+} + 4ROH \rightarrow BaTiO_3 + 3H_2O + 4ROH$$

in which the formation of the Ti complexion must be carried out under alkaline condition. The mechanisms for the evolution of crystalline $BaTiO_3$ of various routes are distinctly different and have important effects on the microstructure of the powder. When the pH value of the solvent is 9, the hydrolysis is caused by the nucleophilic replacement of OH^-. As the hydrolysis speed is faster than that of polymerization, the hydrolysis can complete more rapidly than polymerization. The formation of gel is mostly controlled by polycondensation, so the performance of gel structure is very good at a pH value of 9. On the other hand, based on the double layers theory [10], we know that since its pH value is far away from the IEP, the high repel potential energies among colloidal particles have reduced the degree of agglomerates. Hence, the obtained powder at this pH value is homogeneous and fine.

When the pH value is reduced below 7, for the polycondensation speed is much higher than the hydrolytic speed, and the hydrolysis is caused by the electrophilic mechanism of H_3O^+, the polycondensation has already started before the completion of hydrolysis. The product is hydrate TiO_2 instead of the Ti complexion. Because the pH value is near the IEP, the possibility for gel particle agglomerates is much higher.

In the neutral solvent, the ionization of water molecules provides OH^- for the reaction, so a high quality gel skeleton can be got. But because of the low concentration of OH^-, some hydrated titania precipitation can form during the process, which was contained in the gel and made the gel turbid and white.

Therefore, in order to obtain a fine powder with good properties, the pH value of the solvent should be adjusted to above 8.

4. Conclusions

In the process of synthesising $BaTiO_3$ nanocrystalline powder using a sol-gel method, pH value of the solvent has a great effect on the colloid formation, gel structure, grain size distribution and degree of aggregates. When the pH value is below 7, no gel can form and the obtained powder has a strong degree of aggregates. Increasing the pH value above 8 and the powder is homogenous and fine with an average grain size of 13 nm (TEM). The XRD, BET and TEM measurements were given in describing the microstructure of powders with various pH value. The mechanism for the evolution of crystalline $BaTiO_3$ has been studied in the paper and optimal pH value is proposed.

References

[1] K.S. Mazdiyasni, Fine particle pervoskite processing, Am. Ceram. Soc. Bull. 63 (1984) 591–594.

[2] T.T.N. Kutty, R. Balachandranm, Direct precipitation of lead zirconate titanate by the hydrothermal method, Mater. Res. Bull. 19 (1984) 1479–1488.

[3] P.P. Phule, S.H. Risbud, Sol-gel synthesis of $BaTiO_3$ powders using barium acetate and titanium isopropoxide, Adv. Ceram. Mater. 3 (1988) 183–185.

[4] X. Li, H. Zhang, J. Guan, L. Xiao, Z. Wang, M. Zhao, Synthesis of nanocrystalline materials of composite oxides based on $BaTiO_3$ by using stearic acid-sol method, Nano. Mater. 2 (1993) 457–462.

[5] R.N. Das, P. Aramanik, Chemical synthesis of nanocrystalline lead zirconate-titanate powders using tartarate precursor, Mater. Lett. 40 (1999) 251–254.

[6] F. Chaput, J.P. Boilot, Alkoxide-hydroxide route to synthesize $BaTiO_3$-based powders, J. Am. Ceram. Soc. 73 (4) (1990) 942–948.

[7] ASTM Pattern No. 5-0626, American Society for Testing and Materials, Philadelphia, PA.

[8] S. Schlag, H.F. Ecke, Size driven phase transition in nanocrystalline $BaTiO_3$, Solid State Commun. 91 (1994) 883–887.

[9] R.E. Cohen, H. Krakauer, Lattice dynamics and origin of ferroelectricity in $BaTiO_3$: linearized-augmented-plane-wave total-energy calculations, Phys. Rev. B: Condens. Matter B42 (1990) 6416–6423.

[10] A. Bleier, C.G. Weamoreland, Effects of pH and particle size on the processing of and the development of microstructure in alumina-zirconic composite, J. Am. Ceram. Soc. 74 (12) (1991) 3100–3111.