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SYNTHESIS OF $BaTiO_3$ POWDER BY SOL-GEL METHOD

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ABSTRACT

Pure tetragonal phase barium titanate nanograin with an average diameter of about 54 nm has been synthesized via a sol-gel route starting from soluble precursors of barium and titanium and without surfactant. The gel was peptized and crystallized in water under a refluxing condition. The effect of pH value on the properties of $BaTiO_3$ powder was investigated. $BaTiO_3$ samples were characterized by X-ray diffraction, BET analysis, transmission electron microscope and thermal gravimetric analysis. It was found that the pH value of solvent had a great influence on the calcination temperature of powders while $BaTiO_3$ crystallites were formed at 800 ºC by acidic catalyst process and at 1000 ºC by using basic additives. Higher initial pH led to smaller crystallite sizes of $BaTiO_3$ powders. As-prepared powder has perovskite tetragonal structure with an average grain size of 54 nm and a high BET value of 25 m^2/g for pH = 9. Sol gel route has shown many distinctive advantages in the preparation of high purity $BaTiO_3$ nanopowders without Ba and Ti losses and hazardous wastes.

KEY WORDS

Sol gel Process; Nano Structure; Ceramics

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INTRODUCTION

Barium titanate has been one of the best known and widely used materials for electric ceramics due to its excellent dielectric [1], ferroelectric [2], and piezoelectric properties [3,4]. Because of wide applications of barium titanate ($BaTiO_3$) in such parts, there is much literature on the preparation of this material [5,8].

The synthesis of nanoparticles with controlled sizes and compositions is of fundamental and technological interest. The effort to understand the physics of ever smaller structures has been paralleled by attempts to exploit their beneficial properties. Nanomaterials, which exhibit size-dependent optical, magnetic, electronic, and catalytic properties, have been heralded as the next generation of electronic devices in the design of advanced materials [9]. Because nano-phase materials possess unusual properties compared to traditional materials, studies upon obtaining nano-sized powder of $BaTiO_3$ gradually becomes attractive, and more and more attentions have been paid to this area [10]. In the past decades, extensive studies have been conducted to produce nanosized $BaTiO_3$ powders with narrow particle size distribution, controlled morphology, and high purity [11].

$BaTiO_3$ nanocrystals have been synthesized by various techniques such as; conventional solid state reaction, coprecipitation, hydrothermal technique and sol–gel. The most popular methods for preparing $BaTiO_3$ nanoparticles are liquid phase methods, such as hydrothermal method [12] and sol–gel method [13,14].

Sol-gel method presents some particular advantages through a low-temperature process avoiding contamination of the materials. It also yields better stoichiometric control and the possibility of grain-size and grain-shape control. It is a complex process of synthesizing powders by a sol-gel method [15]. All stages, including the formation of colloid particles to form gel-net, drying of wet gel, and calcinations 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. Compared to other fabrication methods, the sol-gel process offers low capital investment cost. On the other hand, it is compatible with continuous manufacturing techniques for the production of powders.

In this work, we present a study of the $BaTiO_3$ nanocrystalline powder fabricated by a simple sol-gel method. pH value dependence on the characteristics of $BaTiO_3$ powders was also evaluated.

EXPERIMENTAL

Powder preparation

A sol-gel method was used to prepare nanocrystalline $BaTiO_3$ powder. Titanium alkoxide (Merck 99%) as the source of Ti ions, and $BaCO_3$ (Merck 99%) as a source of barium titanate were used. The synthesis procedure is as follows; barium carbonate was dispersed in water with the ratio of 1:1 and stirred for 2 h at 70ºC. Titanium alkoxide was also dissolved in absolute ethanol (Merck 99.99%) with the ratio of 1:1, and water was added to this solution in the ratio of 1:20 after 1 h. Then

these two solutions were mixed and stirred to form a sol which contained barium and titanium in a ratio of 1:1. The basic (NaOH, Merck 99.99%) and acidic (HCl, Merck 99.99%) catalysts were added to the sol to investigate the effect of pH on the calcination temperature of pure $BaTiO_3$. After a certain time, a clear gel was formed. The Ba and Ti precursor was dried in an oven at 100ºC for 24 h and then was ground and heat-treated to obtain the crystalline $BaTiO_3$ powder. For all samples the calcinations treatment was performed in the temperature 400ºC, 800ºC, 1000ºC at rate of 10º/min.

Characterization
The thermal stability of the product was evaluated using thermal analysis method. The phase purity and phase structure of as-prepared samples were characterized by X-ray powder diffraction (XRD), using a Philips X'pert X-ray diffractometer equipped with Cu Kα radiation (40 kV, 20 mA) at a scanning speed of 10º/min over a range of 20–100º at room temperature.

The morphological characteristics of the crystallized powders, after calcination, was examined by transmission electron microscope (TEM, JEM-200CX, Jeol), To prepare TEM samples, a tiny amount of $BaTiO_3$ powder was dispersed into isopropanol by grinding in an agate mortar. A copper grid with a supported thin carbon film was dipped into the suspension, removed and dried on a filter paper. 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.

Results and Discussion

Thermal analysis
Thermal analysis was carried out on dried gel of the sample with pH=3 in order to investigate different phenomena occurring during calcinations process. The TG curve (Fig 1) revealed that the decomposition occurred in four different weight loss steps.

The first main step, corresponding to 4.45% weight loss, is due to the vaporization of water and some organic compound at temperature between 25 and 293 ºC as reported elsewhere [16]. The second step, corresponding to weight loss of 16.24%, was observed from 293 to 445ºC. It is related to the decomposition of $BaCO_3$ and dissociation of the alkoxide. The third step, corresponding to 5.18% weight loss at temperature between 445 and 690ºC, is probably due to the transformation of $BaCO_3$, and a small amount of $BaTiO_3$ was produced. Finally, the peak, between 690 and 800 ºC in the TG curve with a weight loss of 1.56%, was attributed to the formation of $BaTiO_3$. In this step, nearly all of $BaCO_3$ reacted with Ti-complex to produce $BaTiO_3$ and release CO_2.

In the gelation step followed by drying, almost all Ti–OR (without reacting with H_2O) and –Ti–OH (intermediate species) could be replaced by $Ti–OR^-$ or $–O–Ba–OR^-$ (R-=CH_3CO), and the final polymerization molecules became the stable network of metal-organic groups linked by –O–. The stable compounds with O–M–O (M = Ba, Ti) bonds and C - O bonds led to on increase in the calcinations temperature and $BaTiO_3$ formation.[10]

Effect of pH and calcinations temperature on the result product

In this work, we studied several kinds of specimens with various pH values including 1, 3, 4, 5 and 9. These pHs were chosen based on this fact that the acidic pH can increase the production rate, so we chosen 4 acidic pHs. We evaluated one basic pH to compare its production properties with acidic catalyst too. It is found that the alkalinity and acidity have a great influence on the properties of the powder. Although Luan and Gao [17] reported that the specimen with pH = 4 could not form a gel, the present study showed that the gel formation could occur in this pH and below it. For all samples the calcination treatment was performed in the temperatures of 400, 600, 800 and 1000 ºC. Figs 2, 3, 4, 5 and 6 show the XRD patterns of the samples with different pH values.

The XRD patterns showed that $BaTiO_3$ phase with a cubic structure could be formed at 400ºC, but there was impure peak located at 2θ=23.8 and 2θ=28 which could attributed to one of the main strong peaks of $BaCO_3$ and Ti. At 800ºC for pH=1 and 3, $BaCO_2$ and Ti disappeared and high purity $BaTiO_3$ phase could be obtained. However at pH= 4, 5 and 9 the single phase $BaTiO_3$ product was formed at a temperature of 1000 ºC.

It is clear that for pH= 4, 5 and 9 the calcination temperature for preparing pure $BaTiO_3$ was 1000 ºC but pure $BaTiO_3$ was prepared at a calcination temperature of 800ºC for pH = 1 and 3. Harizonov [18] reported that cubic $BaTiO_3$ was obtained at 600ºC-900ºC for 1 hour in air and tetragonal product was observed after heating at 1000ºC for 1 hour.

At low pH values, the uncompleted polymerization process lead to a weaker polymeric network compared to the samples prepared at high pH values. Hence, the phase transformation occurred in lower temperature.

According to JCPDS cards, the single peak (200) located in the range of 44-46° indicated only cubic crystal phase of $BaTiO_3$. Although the calcinations temperature of 1200°C was reported by Li et al. [10] for producing the $BaTiO_3$ single phase product, in this study, by using the best pH values for making the gel, the calcinations temperature was reduced to 800°C to 1000°C.

The phase compositions of the samples with different pH are presented in Table 1. In all cases the '$BaTiO_3$ gel' started to crystallize at 400 ºC with a secondary phase of $BaCO_3$. The XRD patterns of sintered powder in proper temperature showed peaks of an apparently tetragonal perovskite structure with its (001), (002) and other certain diffraction peaks splitting, which match very well with the published patterns.

The effect of pH and calcinations temperature on the grain size

The grain size of $BaTiO_3$ powders with different pH values and different calcinations temperature are presented in Table 2. The crystallite size of $BaTiO_3$ powders was calculated by the Scherer's equation;

$dx = 0.94\lambda/\beta\cos\theta$

Where dx is the crystallite size, λ is the X-ray wavelength, β is the full-width at half-maximum (FWHM), and θ is the diffraction angle. The (2 0 0) peak was used to

calculate the crystallite size. Scanning speed of 5°/min was used for preparing the XRD pattern.
The line broadening effects of XRD pattern is caused by the finer grains. Table 2 shows that in all cases the nanocrystalline powders with grain size in the range of 50 – 100 nm were synthesized.

It is believed that there is a critical crystallite size for $BaTiO_3$ phase transition from cubic to tetragonal. If the crystallite size is less than the critical grain size, the phase should be cubic [19]. Normally the $BaTiO_3$ bulk body retains its ferroelectricity unless the average grain size is less than its critical size, 50 nm [20]. Since all powders have grain size higher than 50 nm, the tetragonal crystallographic structure could be observed in all samples.
It can be concluded that the increase in the pH can reduce the grain size significantly but it has negative effect on the calcination temperature. At a pH of 3, the nanocrystalline powder having a calcination temperature of 800 ºC can be obtained, and complete polymerization in high pH values lead to form pure products with lower grain size.
The BET result is considered to be more descriptive of the performance of the powder. The change of BET surface area with pH value is shown in Table 3. The BET measurement of crystalline powder prepared at pH=1 had a very low specific surface area of 3.7 m^2/g. When the pH value was increased to 5, the BET value consequently increased to 12.68 m^2/g. A high BET value of 25.76 m^2/g was obtained with the continuous increment of pH value at 9.

The micrographs of the as-synthesized $BaTiO_3$ (pH=3 and 9) nanoparticles are shown in Fig.7. From the TEM image, it can be seen that the as-synthesized product is mainly composed of $BaTiO_3$ nanoparticles with an average diameter of less than 100nm for pH =3 and 9.

Mechanism of powder synthesis
The pH value of the solvent has a great effect on the process and properties of the final product. It is known that titanium alkoxide has a strong tendency to react with H_2O. Under alkaline condition, alkoxide ions react with water molecule to form the complexion $[Ti(OH)_6]^{2-}$, which will neutralize with the Ba ion, then polymerize to $Ba^{2+}[Ti(OH)_6]^{2-}$. [18] The formation of the Ti complexion must be carried out under alkaline condition. The mechanisms for various routes the evolution of crystalline $BaTiO_3$ is distinctly different and has 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^-. When the hydrolysis speed is faster than that of polymerization, the hydrolysis is completed 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. 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 Ti complexion. Therefore, in order to obtain a fine powder with good properties, the pH value of the solvent should be adjusted to above 9 [9,19]

It is clear that wet chemical method by sol-precipitation has some advantages over the conventional solid-state reaction process. In the sol-precipitation, all reactions occurring on the atomic scale lead to a final nanoparticle with high degree of crystallization, stoichiometric composition and homogeneity. Therefore, in our reaction system, Ba^{2+} cations are able to homogeneously diffuse into hydrolyzed precursor of Ti by mixing the molecular solution, leading to the optimized component homogeneity.

CONCLUSION

In summary, were successfully synthesized $BaTiO_3$ nanoparticles via sol-gel route. In the process of $BaTiO_3$ nanocrystalline powder synthesis using a sol-gel method, pH value of the solvent had a great effect on the colloid formation, gel structure, grain size distribution and degree of aggregates. With the results obtain from XRD, BET and TEM measurements the microstructure of powders with various pH values were described. The mechanism for the evolution of crystalline $BaTiO_3$ has been studied in the paper and optimal pH value is proposed. The formation of the single-crystal $BaTiO_3$ nanoparticles occurred through a diffusion mechanism of Ba^{2+} ions into the gel at strong alkaline condition.

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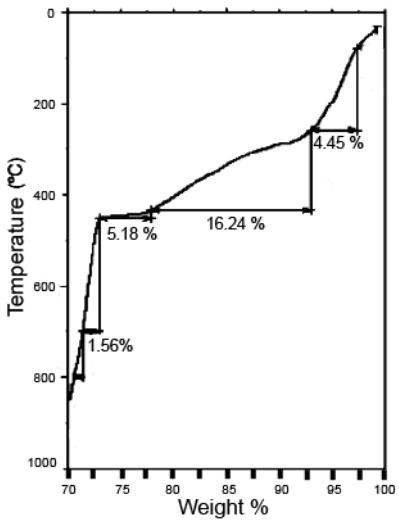


Fig1. TG curve of the $BaTiO_3$ precursor gel.

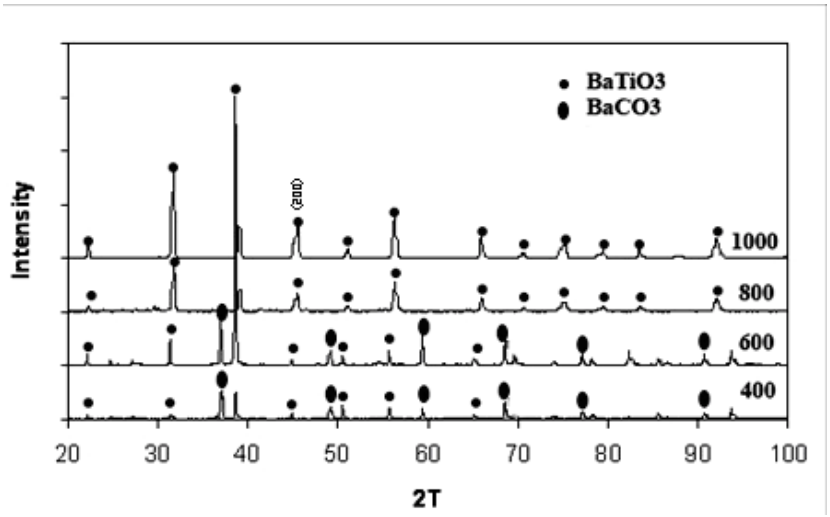


Fig. 2.XRD patterns of powder prepared at pH=1.

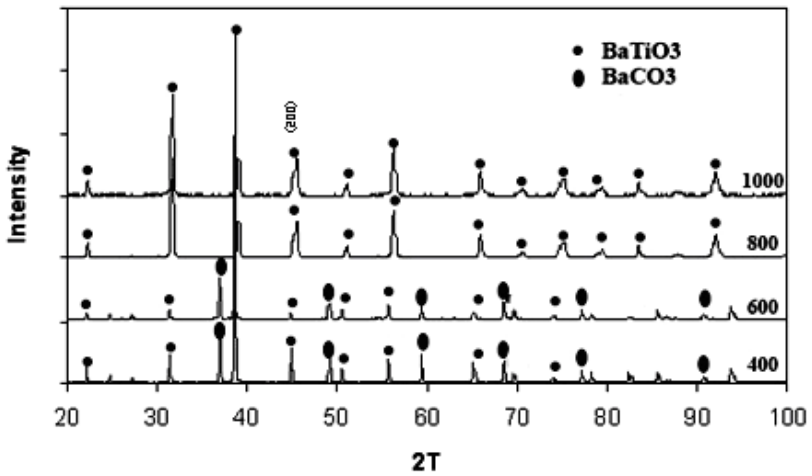


Fig. 3.XRD patterns of powder prepared at pH =3.

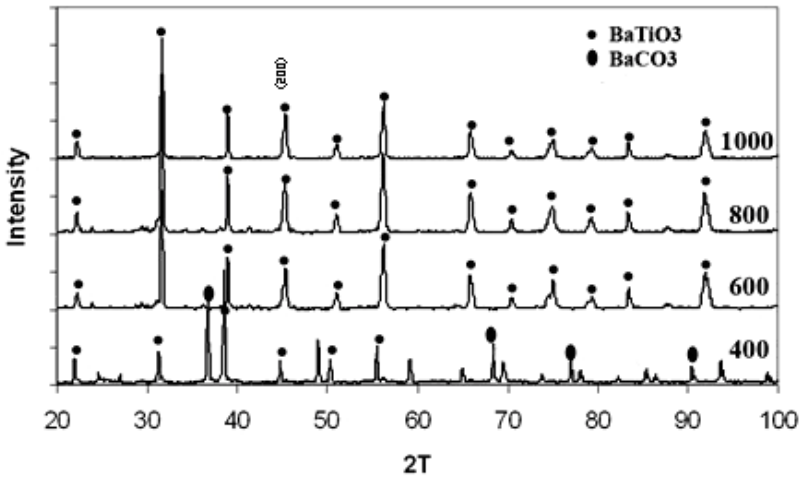


Fig. 4.XRD patterns of powder prepared at pH=4.

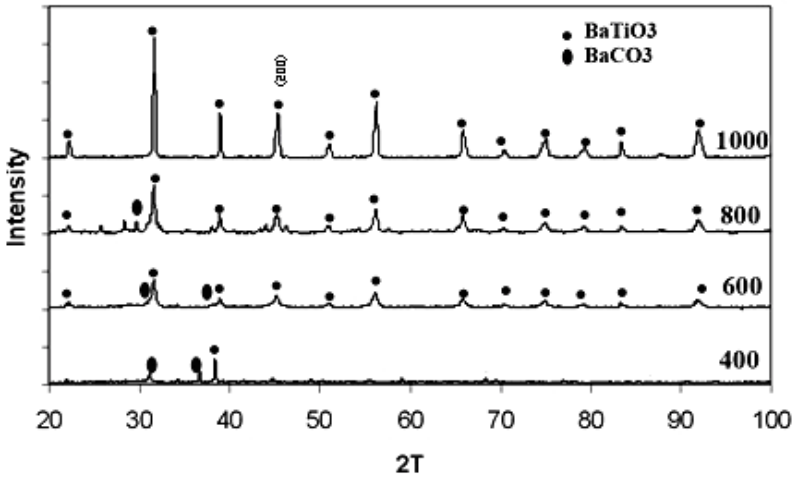


Fig. 5.XRD patterns of powder prepared at pH=5.

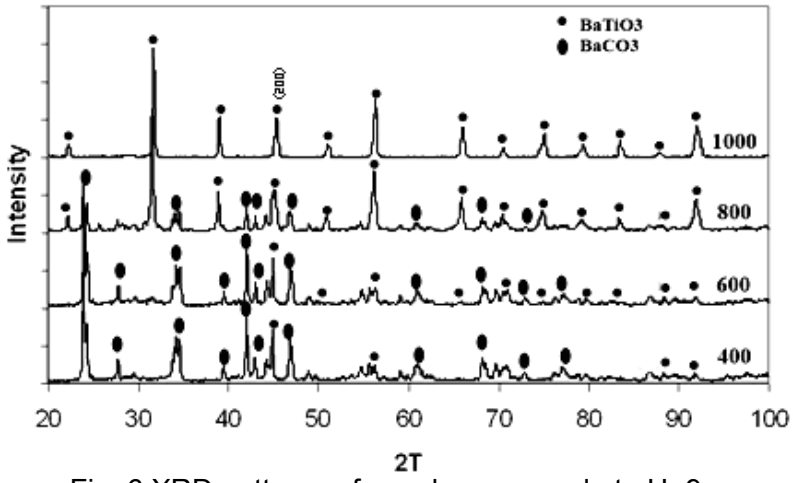
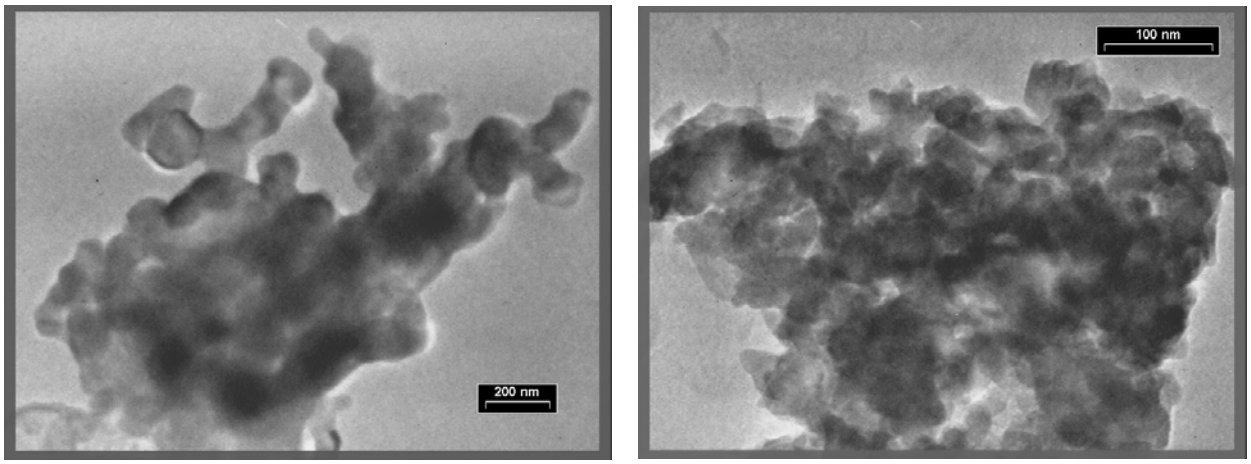


Fig. 6.XRD patterns of powder prepared at pH=9.



a b

Fig 7. TEM micrograph of the powders prepared at; a) pH = 3, b) pH = 9

Table 1. The phase composition of the samples prepared at different pH values.

	pH = 1	pH = 3	pH = 4	pH = 5	pH = 9
400 ºC	Ti, $BaCO_3$, $BaTiO_3$	Ti, $BaCO_3$, $BaTiO_3$	Ti, $BaCO_3$, $BaTiO_3$	Ti, $BaCO_3$, $BaTiO_3$	Ti, $BaCO_3$
600 ºC	Ti, $BaCO_3$, $BaTiO_3$	Ti, $BaCO_3$, $BaTiO_3$	Ti, $BaCO_3$, $BaTiO_3$	Ti, $BaCO_3$, $BaTiO_3$	Ti, $BaCO_3$, $BaTiO_3$
800 ºC	$BaTiO_3$	$BaTiO_3$	Ti, $BaTiO_3$	Ti, $BaCO_3$, $BaTiO_3$	Ti, $BaCO_3$, $BaTiO_3$
1000 ºC	$BaTiO_3$	$BaTiO_3$	$BaTiO_3$	$BaTiO_3$	$BaTiO_3$

Table 2. The grain size of the samples prepared at different pH values.

pH	pH = 1	pH = 3	pH = 4	pH = 5	pH = 9
Grain size (nm)	100	85	74	60	54
Calcination Temperature (ºC)	600	600	1000	1000	1000

Table 3. BET measurement of the samples prepared at different pH values.

pH	1	3	4	5	9
BET (m^2/g)	3.7	7.04	9.27	12.68	25.76