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Synthesis and characterization of $BaTiO_3$ fine particles by hydrothermal process

Dong-Sik Bae, Gi-Tae Joo, Kyong-Sop Han and Sang-Heul Choi*

Division of Ceramics, Korea Institute of Science and Technology, Seoul 136-791, Korea
**Department of Inorganic Materials Engineering, Hanyang University, Seoul 133-791, Korea*

수열합성법에 의한 미립의 $BaTiO_3$ 분말합성 및 특성

배동식, 주기태, 한경섭, 최상흘*

한국과학기술연구원 세라믹스 연구부, 서울, 136-791
*한양대학교 무기재료공학과, 서울, 133-791

Abstract $BaTiO_3$ fine particles were prepared by hydrothermal process from titanium tetra-isoproproxide ($Ti(OiPr)_4$) and barium hexa-hydroxide ($Ba(OH)_2 \cdot 8H_2O$) as raw materials. The fine particles were obtained at the temperature range of 160 to 185℃. The properties of $BaTiO_3$ particles were studied as a function of various parameters such as reaction temperature, reaction time and Ba/Ti ratio, etc. The average particle size of $BaTiO_3$ increased with increasing reaction temperature and time. After hydrothermal treatment at 170℃ for 8 h, the average particle size of $BaTiO_3$ was about 30 nm and the particle size distribution was narrow.

요 약 $BaTiO_3$ 분말은 티타늄 수산화물 용액과 바륨수산화물 용액을 혼합하여 적당한 온도와 압력하에서 합성되었다. 미 분말이 얻어진 온도는 160~185℃, 압력은 5~10 kgf/cm²이였다. 분말의 모양과 크기는 주사전자현미경, 결정 상은 X-선 회절로 분석하였다. 분말합성온도, 반응시간, 및 농도변화에 따르는 분말의 물성을 조사하였다. $BaTiO_3$ 분말의 평균입자크기는 반응온도 및 시간이 증가함에 따라 증가하였다. 170℃에서 8시간 반응시킨 경우의 평균입자크기는 약 30 nm이고, 입도 분포는 균일하였다.

1. Introduction

Synthesis of high-purity fine $BaTiO_3$ powders have been studied for electronic applications. $BaTiO_3$ is commonly synthesized by solid-state reaction of barium carbonates and titanium dioxide and oxaltes, citrates, and carbonates are thermally decomposed to the oxides [1-4]. This kind of synthesis methods have not yet achieved consistent results in producing in a high-purity fine $BaTiO_3$ powders.

There is advantage in the hydrothermal preparation of fine ceramic powders. Homogeneous, submicrometer, narrow-size distribution, anhydrous multicomponent powders can be obtained directly from solution at temperature far below those required for conventional powders preparation. The moderate temperature employed during this technique not only reduce the energy costs but also enhance the reactivity of the products. High purity and stoichiometric particles of ceramic powders can be obtained at relatively faster rates under elevated water vapour pressures and temperatures [5]. It has been demonstrated that such powders are composed of much softer agglomerates and could be densified much better than those prepared by calcination decomposition of the same oxides [6]. These powders could be sintered at low temperature without calcination and milling steps [7].

In this work we studied the processing of fine $BaTiO_3$ particles by hydrothermal synthesis of solution prepared from $Ba(OH)_2$ and $Ti(OiPr)_4$.

2. Experimental Procedure

$BaTiO_3$ fine powders were prepared by hydrothermal method using titanium tetra-isoproproxide ($Ti(OiPr)_4$) and barium hexa-hydroxide ($Ba(OH)_2 \cdot$

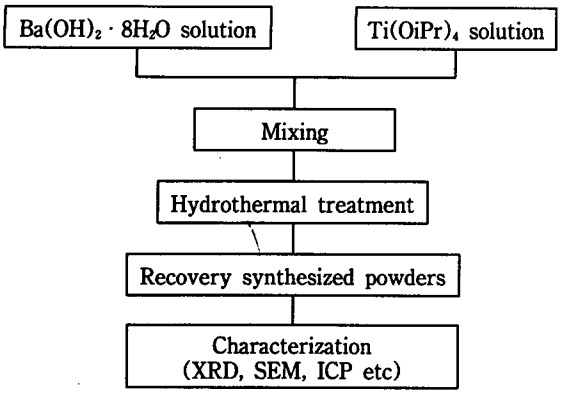

Fig. 1. Processing flow diagram of preparation of fine $BaTiO_3$ powders.

$8H_2O$) as raw materials. The process for preparing $BaTiO_3$ by hydrothermal treatment is schematically illustrated in Fig. 1. The titania sol was obtained by dissolving titanium tetraisopropoxide, $Ti(OiPr)_4$, in isopropanol followed by hydrolysis with excess water. Mixed solution was prepared by dissolving barium hexa-hydroxide in water and by adding titania sol to the solution under reflux condition.

The resulting suspension was placed in a 1000 ml stainless steel pressure vessel. The vessel was then heated to the desired temperature at a rate of 5℃/min. During heating, the autogenous pressure gradually increased to 4.5 kgf/cm^2 and was usually maintained below 10 kgf/cm^2 during the holding period. The reaction products were washed at least two times by repeated cycles of centrifugation and redispersion in methanol. The recovered powders were analyzed for phase composition using X-ray diffraction (Phillips, PW 1825/00) over the 2 theta range from 10~70° at rate of 2.5°/min. The morphology of the synthesized particles was observed using scanning electron microscopy (SEM, Hitachi S-4200). The rinse supernatants were diluted in a controlled manner and analyzed for dissolved barium and titanium using an inductively coupled plasma spectrometer (Model polyscan 61E).

3. Results and Discussion

The value of the starting suspension and consequently the aqueous suspension of already formed $BaTiO_3$ nuclei after the hydrothermal synthesis are very important for the successful preparation of $BaTiO_3$ powder. After the formation of $BaTiO_3$ nuclei from supersaturated solution, the aqueous suspension of formed nuclei is stable only when the pH value exceeds 13. The calculation of stability diagrams outlining that successful processing of $BaTiO_3$ required at least a pH $\geq$ 13 [8].

The pH value of the $Ti(OiPr)_4$ solution and $Ba(OH)_2$ solution were around 1 and $\geq$ 14, respectively. But, the pH value of the mixed solution was decreased about 12. In order to adjust pH value, 1 M NH_4OH solution was added in the mixed solution which pH value exceeds 13.

Figure 2 shows the scanning electron micrographs of synthesized fine $BaTiO_3$ powders at 160 to 180℃ for 8 h. The shape of synthesized $BaTiO_3$ powders nearly sphere. The mean particle size of synthesized $BaTiO_3$ were increased from 30 to 100 nm with reaction temperature increasing from 160 to 180℃. The reaction temperature has an effect on the size of the synthesized $BaTiO_3$ powder in solution. As shown the figure, the average particle size of $BaTiO_3$ increased with reaction temperature increasing. The reaction temperature had a great effect on the grain size of the products and the agglomeration among grains. $Ba(OH)_2$ react with $Ti(OH)_4$ particles under hydrothermal conditions to form $BaTiO_3$ through the dissolution-deposition route. During this process the concentrations of cations and hydroxide have to increase to the supersaturation range where the nucleation products are stable. Then the monodispersed grains are formed by subsequent uniform growth on the existing nuclei, which were provided by adsorption of solute species, agglomeration and Ostwald ripening. Thus, the dissolution of TiO_2 particles affects the supersaturation range, the nucleation and the growth of $BaTiO_3$ particles. The dissolution rate of titania and its constitution to a great extent governs the formation of $BaTiO_3$ monodispersed grains.

The state of agglomeration is important in oxides powders synthesized by wet chemical means. Alcohol has been used to control agglomeration during wet milling of powders [9]. Although alcohol washing is commonly used, little work has been reported on the mechanism involved in producing soft agglomerates. Aging of hydrous zirconia gels in water has been shown to lead to consolidation of the gel structure due to continued condensation reactions [10]. It is possible that the higher surface tension of water compared to alcohol leads to higher capillary forces and thus hard agglomerates in water washed

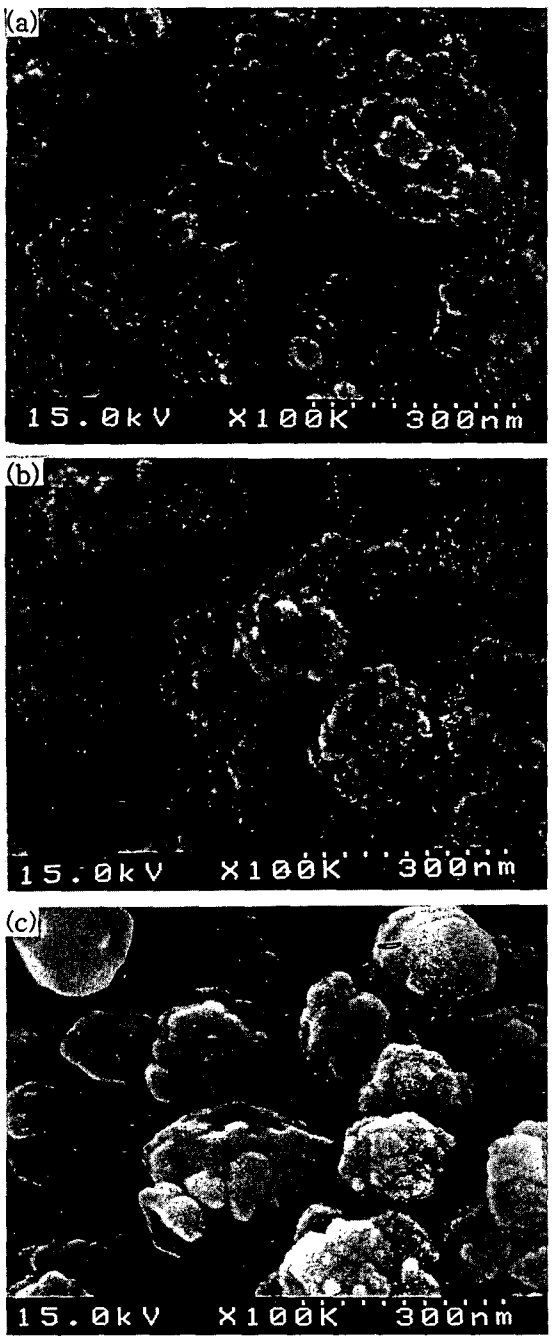

Fig. 2. SEM micrographs of the BaTiO powders were synthesized by hydrothermal processing as a function of reaction temperature at (a) 160℃, (b) 170℃, and c) 180℃ for 8 h.

powders.

Lee and Readey proposed that agglomerates strength is determined by the extent to which water molecules, hydrogen bonded to surface hydroxyl

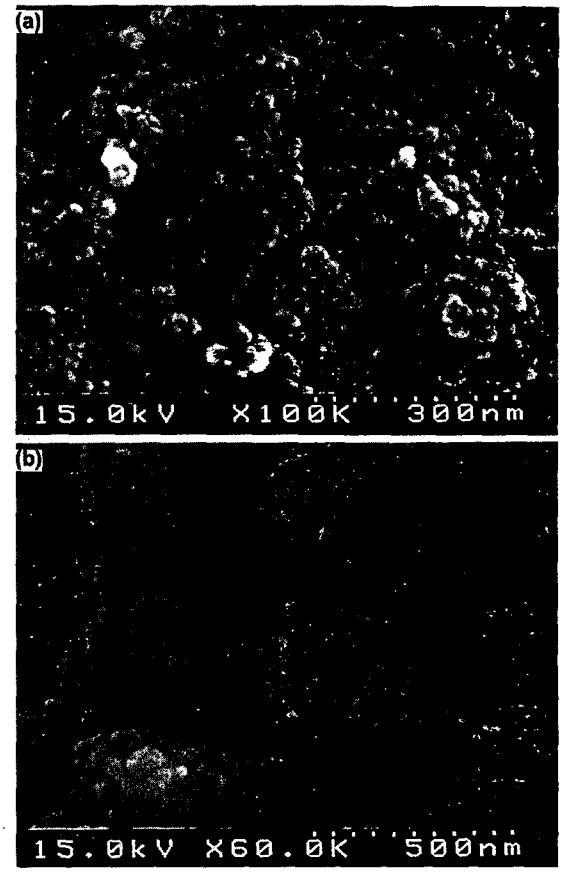

Fig. 3. SEM micrographs of the $BaTiO_3$ powders were prepared by deionized water washing (a) and methanol washing (b).

groups, are able to form bridges between adjacent particles. During washing, ethanol was postulated to hydrogen bond to surface hydroxyls, but could not cause particle-particle interaction. Thus, the possibility of any chemical bonds forming between particles during drying is significantly reduced, inhibiting formation of hard agglomerates [11].

The $BaTiO_3$ powders were prepared by methanol or deionized water washing. The effect of washing solution was shown in Fig. 3. As shown it figures, the agglomeration of synthesized $BaTiO_3$ powders decreased by methanol washing.

The sharp diffraction peaks consistant with the well defined and crystallized particles shown Fig. 4. The crystal structure of the synthesized $BaTiO_3$ particle is cubic. XRD pattern of the synthesized $BaTiO_3$ powder indicates the absence of hydroxides and carbonates of barium. However, the result of inductively coupled plasma spectrometer shows small

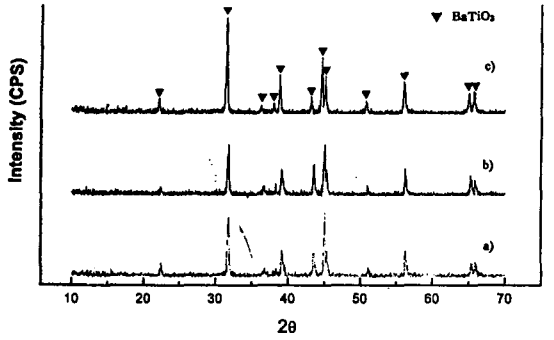

Fig. 4. X-ray diffraction patterns of the $BaTiO_3$ powders were synthesized by hydrothermal processing: a) 160℃, b) 170℃ and c) 180℃.

amount of excess TiO_2 contained. The Ba/Ti ratio of the synthesized $BaTiO_3$ powder was approach to 1 by using excess $Ba(OH)_2$ solution.

Thus, the hydrothermal method used here led to fine spherical particles which may be useful applications for various field.

4. Conclusions

$BaTiO_3$ fine powders were synthesized by hydrothermal process from titanium tetra-isoproproxide ($Ti(OiPr)_4$) and barium hexa-hydroxide ($Ba(OH)_2 \cdot 8H_2O$). The fine particles were obtained at the temperature range of 160 to 180℃. The average particle size of $BaTiO_3$ increased with increasing reaction temperature and time. After hydrothermal treatment at 170℃ for 8 h, the average particle size of $BaTiO_3$ was about 30 nm and the particle size distribution was narrow.

It is possible to control the size of the $BaTiO_3$ particles such as reaction temperatures and time are carefully controlled.

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