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An organic-inorganic solution technique for fabrication of nano-sized CaTiO₃ powder

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Nano-sized $CaTiO_3$ powder was fabricated by planetary milling with porous particles. A steric entrapment route employing ethylene glycol was used for the preparation of the porous $CaTiO_3$ particles. Titanium isopropoxide and calcium nitrate were dissolved in liquid-type ethylene glycol without any precipitation. With the optimum amount of the polymer, the metal cations were dispersed in the solution and a homogeneous polymeric network was formed. The organic-inorganic precursor gels were turned to porous powder through an explosive oxidation reaction during a calcination process. The porous powders were crystallized to single phase of $CaTiO_3$ at about 800 °C and the crystalline powders were planetary milled to nano-size.

Key words: CaTiO₃ powder, Ethylene glycol, Porous particles, Organic-inorganic solution technique, Nano-sized powder, Planetary milling.

Introduction

Ceramic processing is evolving in the direction of chemical synthesis of powders [1]. Methods based on soft-solution processing provide powders with the desired properties such as high purity and homogeneity. Recently, as one of the soft-solution processing routes, an organic-inorganic solution technique using PVA (polyvinyl alcohol), PEG (polyethylene glycol) or EG (ethylene glycol) as a polymer carrier has been developed to make soft-solution processing easier and more highly productive [2-10]. The PVA ensures a homogeneous distribution of the metal ions in its polymeric network structure and inhibits their segregation and/or precipitation from the solution. In the solution involving polymer and nitrate ions, the long chain polymer prevents contact between cations and limits their agglomeration and precipitation. In particular, the amount of polymer and its molecular length can affect the distribution of cations in the solution [6, 9, 10]. The PVA process also produces carbonaceous material that gives heat through its combustion, so that fine and single-phase powders can be formed at a relatively low external temperature [4, 6, 9, 11-13].

The powder synthesis method used in this study is based on a steric entrapment route using ethylene glycol as an organic carrier. In the organic-inorganic solution technique, the PVA polymer only works with systems that are water soluble. However, by applying the ethylene glycol polymerizing agent to an organicinorganic solution technique, the process can be extended to chemicals that decompose in water, such as titanium isopropoxide. In particular, the ethylene glycol can act as an effective solvent for wet chemical synthesis of titanate powder because water-soluble titanium salt is not available commercially [11, 14]. The ethylene glycol in this method, acts to capture the metal ions through a steric entrapment mechanism as in the PVA method. This serves to decrease the mobility of metal ions and constrain the system to prevent precipitation of cation species and agglomeration. With the optimum amount of polymer, the metal ions are dispersed in solution and a homogeneous polymeric network is formed. Recently, BaTiO₃ and Ba₂TiO₄ powders have been successfully synthesized by the ethylene glycol method [14]. The $BaTiO_3$ powder synthesized by the ethylene glycol method had a particle size of 100 nm and crystallized from amorphous to the tetragonal phase on calcining at 700 °C.

In the present study, CaTiO₃ powder is prepared by the ethylene glycol method, and the effect of polymer content and distinct calcination behavior are examined. In addition, synthesized, porous CaTiO₃ powder is planetary milled to break up agglomerates and to reduce particle size. The effects of planetary milling on the porous powder are also examined.

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Experimental Procedure

Powder Synthesis

Titanium(IV) isopropoxide $(Ti(OC_3H_7)_4, reagent grade,$ (Alfa Aesar Chem. Co., Ward Hill, MA) and calcium nitrate (Ca(NO₃)₂·4H₂O, reagent grade, (Aldrich Chem. Co., Milwaukee, WI), were dissolved in stoichiometric proportions in liquid-type ethylene glycol (Fisher Chemical, FW:62.07, Fair Lawn, NJ). The amount of ethylene glycol was calculated using a ratio of total weight of metal ions from cation sources to weight of ethylene glycol. Several ratios of 1:1, 1:5 and 1:7 were tried. The transparent solution was then allowed to gel for 48 h in a drying oven at 80 °C. The dried gels were then calcined at various temperatures. The inside of the furnace was monitored through a window in the low temperature range (100 °C~300 °C) to observe the explosive reaction. Finally, the calcined powders were planetary milled with ϕ 5 mm zirconia media for 10 h. Isopropyl alcohol was used as a solvent for milling and the milling speed was 200 rpm.

Characterization

The crystallization behavior of the gel-type precursor powders was examined as functions of temperature and ethylene glycol content, using an X-ray diffractometer (Dmax 2200, Rigaku/USA, Danvers, MA) with CuKa radiation (40 kV, 30 mA). The measurements were made with a scanning speed of 10°/minute and a sampling interval of 0.02°. Five-point analysis from nitrogen gas absorption (Model Autosorb-1, Boynton Beach, FL) was conducted to obtain BET specific surface areas of the crystalline powders. The pyrolysis and decomposition behavior of the organic-inorganic precursor were monitored by simultaneous differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) (DSC/ TGA, Model STA 409, Netzsch GmbH, Selb, Germany) up to 1200 °C at a heating rate of 10 °C/minute in an air atmosphere. Fourier transform infrared spectroscopy (FTIR, Model Bomen MB 102, Hartmann & Brown) was used to examine the distinct calcination behavior accompanying the explosive expansion reaction. The morphologies of the porous, crystallized powder and planetary milled powders were examined by scanning electron microscopy, (SEM, Hitachi S3500N, Hitachi, Japan) and transmission electron microscopy (TEM, Hitachi H-600, Hitachi, Japan). The powders were sprayed on an aluminum stub and Au-Pd sputtered for SEM examination. The preparation of the powder sample for TEM work followed standard procedures.

Results and Discussion

The ethylene glycol solution with dissolved titanium isopropoxide and calcium nitrate was pale yellow colored and transparent. During the drying process at 80 °C, the transparent sol turned to a soft solid gel.

Table 1 lists the XRD results of the calcined precursor powders at different temperatures and ethylene glycol contents. Amorphous and CaTiO₃ phases coexisted at 700 °C. However, at 800 °C, all powders were fully crystallized to CaTiO₃ except the 1:1 ratio. In the 1:1 ratio, free CaO and TiO₂ phases were observed. It is speculated that insufficient ethylene glycol caused an inhomogeneity in the metalic cation distribution due to a deficiency of steric entrapment by the polymer chains. This resulted in agglomerated metal ions in the solution and residual free CaO and TiO₂ after calcination. In case of the 1:7 ratio powder, the crystallization behavior was similar to the 1:5 case. The precursors containing excess ethylene glycol content (over 1:7 ratio) resulted in longer burn-out time and waste of the polymer, but showed similar crystallization behavior to the 1:5 case.

The crystallization temperatures for the production of single phase CaTiO₃ and specific surface areas of the crystallized CaTiO₃ powders at each ethylene glycol content are listed in Table 2. The powder derived from the 1:1 ratio crystallized to single phase CaTiO₃ at 950 °C without free CaO. The polymer content also affected the specific surface area of the crystallized powders. The BET measurement of crystalline powder prepared from the 1:1 ratio precursor had the lowest specific surface area of 10.6 m²/g in comparison with the 1:5 and 1:7 cases. This result means that insufficient polymer caused agglomeration of metal cations in the precursor

Table 2. Summary of $CaTiO_3$ powder prepared by ethylene glycol method at each ethylene glycol content

Amount of EG§	Crystallization temp. (°C)	Specific surface area (m ² /g)
1:1	950	10.6
1:5	800	19.7
1:7	800	21.2

[§]total weight of metal ions from cation sources: weight of ethylene glycol

Table 1. Observed crystalline phases at each heating temperature and ethylene glycol content

Amount of EG§	700 °C	800 °C	900 °C
1:1	amorphous	CaTiO ₃ , CaO, TiO ₂	CaTiO ₃ , (CaO) ^{\$}
1:5	CaTiO ₃ , amorphous	CaTiO ₃	CaTiO ₃
1:7	CaTiO ₃ , amorphous	CaTiO ₃	CaTiO ₃

[§]total weight of metal ions from cation sources: weight of ethylene glycol

^{\$}(): minor phase



Fig. 1. TGA/DSC curves for $CaTiO_3$ precursor prepared by ethylene glycol method (ethylene glycol content is 1:5).

derived from the 1:1 ratio, and resulted in an increase of the crystallization temperature and a low specific surface area.

The CaTiO₃ precursors showed a distinct calcination behavior. The crisp, dried precursor gels were quite hydrophilic and produced a vigorous exothermic reaction at about 300 °C. The exothermic reaction was accompanied with an abrupt volume expansion. This reaction occurred in all the precursors, regardless of the ethylene glycol content. However, the reaction occurred more vigorously as the amount of ethylene glycol was increased. This means that the amount of ethylene glycol has an influence to some extent on the exothermic reaction. After the reaction, the precursor gel changed to a soft, porous solid with a significant volume expansion. In the precursor derived from the 1:5 ratio, the thermal analysis plot is shown in Fig. 1. In the TGA curve, the mass loss occurred in the range 200 °C~550 °C indicating the release of $N_x O_y$ gases from the nitrate salt and the burn out of the ethylene glycol [14]. The DSC spectrum showed two exothermic peaks at 280 °C and 550 °C. The first exothermic peak was caused by degradation of the polymeric structure by pyrolysis of ethylene glycol, which is then followed by oxidation of residual carbon. The second peak indicates the oxidation reaction. The reaction involved a volume expansion and occurred at about 300 °C. The relatively high intensity of the exothermic peak at 280 °C could be a result from the overlapping of the oxidation reaction with the exothermic peak accompanying volume expansion. The reaction was more vigorous as the heating rate was increased.

To examine the cause of the explosive reaction involving volume expansion, the variations of chemical bonding of the powders obtained at each calcination step were studied. Figure 2 shows the FTIR spectra for CaTiO₃-type powders obtained at each processing step. The powder samples from before and after expansion were obtained from the powders calcined at 200 °C and 400 °C, respectively. Also the depolymerization sample was calcined at 550 °C, the terminal point of weight loss in TGA curve (Fig. 1). The powder heated to 800



Fig. 2. FTIR spectra for $CaTiO_3$ type powders obtained at each processing step.

°C was used for the crystallization sample. O-H bond groups in calcium nitrate and ethylene glycol are seen at 3500 cm⁻¹. Also C-H bond groups in ethylene glycol and titanium isopropoxide are seen at 2900 cm⁻¹ and 1400 cm⁻¹, respectively. The peaks shown at 1600 cm⁻¹ indicate N=O groups in calcium nitrate. From the literature, Ti-O groups are seen at about 500 cm⁻¹~700 cm^{-1} [15]. The peaks showed a significant difference before and after expansion. Organic bonding groups almost disappeared after expansion. This suggests that ethylene glycol was burned out and some organic groups from the nitrate salt were pyrolysed. C-O bond groups, which are seen at 1100 cm⁻¹, have almost disappeared after expansion. This means that calcium cations formed Ca-O bonds by reaction with the titanium gel as a result of the pyrolysis of the C-O bond, which come from O-C₃H₇ and are derived from the terminal group of titanium gel. The Ca-O peak can not be checked in Fig. 2, because that peak occurs at $300 \text{ cm}^{-1} \sim 400 \text{ cm}^{-1}$. However, the reaction is confirmed from the literature [16]. Also the Ti-O peak was activated after expansion. Finally, it may be speculated that the reaction between titanium gel and calcium cations resulted in the vigorous exothermic reaction involving oxidation of calcium cations, and simultaneously the reaction made extensive voids in the powder structure by the volume expansion and the burn-out of organic substances. The peak observed from the crystallization step may be explained by the formation of an intermediate substance derived from amorphoustype CaTiO_x resulting from a change in the Ti-O peak position. From the literature, the Ti-O peak moves its position in the range 500 cm⁻¹~900 cm⁻¹ according to the surrounding bonding conditions [15, 17, 18].

The powder morphologies of the crystalline $CaTiO_3$ derived from the 1:5 ratio material and the planetary ball milled $CaTiO_3$ powder are shown in Fig. 3. The SEM micrograph of the crystalline $CaTiO_3$ revealed soft and porous powder structure (Fig. 3(a)). The powder



Fig. 3. SEM micrographs of (a) crystalline $CaTiO_3$ powder (ethylene glycol content is 1:5) and (b) planetary ball milled powder for 5 h.



Fig. 4. TEM micrograph of nano-sized $CaTiO_3$ powder planetary ball milled for 10 h.

milled for 5 h showed submicrometre particles with severe agglomeration (Fig. 3(b)). In the milling process, the efficiency was improved by the soft and porous powder structure in comparison with non-porous powders. The milling process was conducted for 10 h, and the powder morphology is represented in Fig. 4. In this TEM micrograph for the 10 h planetary ball milled powder, a significantly reduced particle size of about 50~60 nm was observed.

Conclusions

The ethylene glycol method was successfully used for fabrication of titanate powder of CaTiO₃. The new method employing water-insoluble chemicals as a source of titanium ions has a distinct advantage over other chemical synthesis methods in that it is easier and cheaper. The simple, processable precursor could be synthesized by steric entrapment of cations by the ethylene glycol polymer to avoid selective precipitation and the method produced homogeneous mixing on a molecular scale. In particular, an exothermic reaction involving volume expansion in the calcination process contributed to form a soft and porous powder. The porous powder was capable of being ground to nanosized powder by powerful planetary ball milling. The ethylene glycol method is expected to find application for the synthesis of many other titanate powders because of its merits, such as being a cheap and simple process, allowing easy control of the crystalline form and particle size.

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