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Low-temperature sintering of $BaTiO_3$ powders prepared by a hydrothermal process with ball milling system

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Abstract

In this work, a hydrothermal process with ball milling system was developed to produce nanosized $BaTiO_3$ powders with low-temperature sintering capability. By using this apparatus, it was possible to synthesize nanosized $BaTiO_3$ powders from $Ba(OH)_2$ and titanium alkoxides at 100 °C after 2 h. The primary particle size was determined to be about 20 nm. Moreover, nanosized $BaTiO_3$ particles were uniformly agglomerated to about 150 nm. The green bodies prepared from these powders were densified above 95% at 900 °C, which is fairly lower than the ordinary sintering temperature. The densification was about 60% at 900 °C in the green bodies fabricated from powders synthesized by the hydrothermal reaction without ball milling system. The sinterability was found higher for the $BaTiO_3$ powders synthesized by ball milling-assisted hydrothermal process. The characterization of the synthesized powders and the sintered compacts was carried out by X-ray diffraction, scanning electron microscopy and transmission electron microscopy. For the electrical properties, room temperature dielectric constants as high as 4000 were measured.

Keywords: Hydrothermal synthesis; $BaTiO_3$; Low-sintering temperature; Ball milling

1. Introduction

Barium titanate ($BaTiO_3$) has excellent dielectric properties, which makes it the most important composition of ceramic capacitors, especially for the manufacture of multilayer ceramic capacitors (MLCCs) [1]. In general, $BaTiO_3$ powder is prepared using solid-state synthesis from barium carbonate and titania, and then the mixture is calcined at high temperature. It is known, however, that the solid-state reaction method causes some drawbacks, such as a large particle size, wide particle distribution, aggregation and high impurity content, which results from repetitive calcination and grinding treatments [2]. At present, the need for nanosized pure $BaTiO_3$ powders has led to the development of many alternative low-temperature chemical synthesis methods such as hydrolysis of barium titanate alkoxides [3], sol–gel processing [4–6], and hydrothermal processing [7–15]. Sol–gel processing with metal alkoxides allows fabricating monodispersed fine ceramic powders, but calcination is required both to form pure crystalline phase and to remove unreacted organics. Recently, hydrothermal process has been proposed to be an effective method for synthesizing fine ceramic powders. In general, hydrothermal processing is a technique that can produce either large single crystals or fine ceramic powders. The process progresses in a closed system at a high autogenous pressure. The temperature required for synthesizing ceramic powders can be greatly reduced by the benefit of the closed system operating under a high pressure because of the enhanced reactivity of the species in a liquid environment. Therefore, fine particles exhibiting high sinterability can be produced. The hydrothermal process has received a particular emphasis related to the possibility of synthesizing highly pure and nanosized $BaTiO_3$ powders. However, shaping of nanosized powders with high green density is difficult because of the agglomeration, which, in turn, gives rise to lower densification after sintering.

In this work, the ball milling-assisted hydrothermal processing of nanosized $BaTiO_3$ powders with low-temperature sintering property is reported. A novel hydrothermal apparatus with ball milling system is developed. The morphologies of the powders prepared by hydrothermal reaction with/without ball milling system are investigated. The low-temperature sintering

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of the green compacts prepared from the synthesized powders is studied and dielectric properties are measured. The effect of ball milling during hydrothermal reaction on the sinterability of the powders is demonstrated.

2. Experiment procedure

All chemicals were used as received without further purification. The $BaTiO_3$ powders were prepared from $Ba(OH)_2{\cdot}8H_2O$ (Wako Pure Chemical Industries, Japan) and titanium tetraisopropoxide ($Ti(i\text{-}OPr)_4$, TTIP, Wako, Japan). The high pH necessary for the reaction was provided by introducing an excess of $Ba(OH)_2{\cdot}8H_2O$ (Ba/Ti > 1.00) [9,16]. $Ba(OH)_2{\cdot}8H_2O$ was dissolved in hot water at 80 °C and quickly filtered to remove $BaCO_3$. TTIP was diluted in isopropyl alcohol and then dropped slowly into the $Ba(OH)_2$ solution under vigorous stirring. The mole ratio of Ba to Ti before the removal of $BaCO_3$ was adjusted to 1.5:1. $BaTiO_3$ powders were produced by a novel hydrothermal synthesis apparatus with ball milling system developed for this study (Fig. 1). The mixed starting solution was transferred to a Teflon vessel and 5 mm ZrO_2 balls were added. Then, the sealed Teflon vessel was put into a stainless-steel vessel. Heating was maintained for 2 h at one of the studied temperatures (100, 125, 150 °C) and the vessel was rotated at 150 rpm during the reaction. The suspension was centrifuged and the resulting solid was washed several times in water to remove unreacted Ba ions. The solid was finally freeze-dried. The particle size distribution of the synthesized powders was measured by a laser particle size analyzer (Horiba LA-920, Japan). Green bodies were fabricated by first uniaxial dry-pressing at 20 MPa in a steel die and then cold isostatic pressing (CIP) under 150 MPa for 5 min. Then, the green bodies were sintered at 800, 850, 880, 900, 950, 1000 or 1100 °C for 5 h. Green bodies using powders synthesized by hydrothermal reaction without ball milling were also prepared for the sake of comparison.

The morphologies of the synthesized powders and the microstructures of the sintered bodies were observed by field emission scanning electron microscopy (FE-SEM, Hitachi S-4300, Japan) and transmission electron microscopy (TEM, JEM-2010, JEOL, Japan). The crystalline phase of synthesized powders was characterized by X-ray diffractometry (XRD; Cu Kα, RINT 2000; Rigaku, Japan). Ba/Ti ratio in the synthesized $BaTiO_3$ powders was determined using inductively coupled plasma spectroscopy (ICP, IRIS Advantage, Thermo Electron K.K., Japan) and Energy dispersive spectroscopy (TEM-EDS, JEM-2010, JEOL, Japan). Sintering behavior was evaluated by measuring the relative density of the sintered bodies. Five pellets were prepared for characterizations.

For the electrical characterization of the ceramics, 1 mm thick samples were prepared by polishing. Electrodes were deposited on both parallel faces by serigraphy of a silver paste. The electrodes were baked at 700 °C. The dielectric constant was measured from room temperature to 200 °C (Model 1658 RLC Digibridge, 1 kHz, GenRad) at a heating rate of 0.5 °C/min.

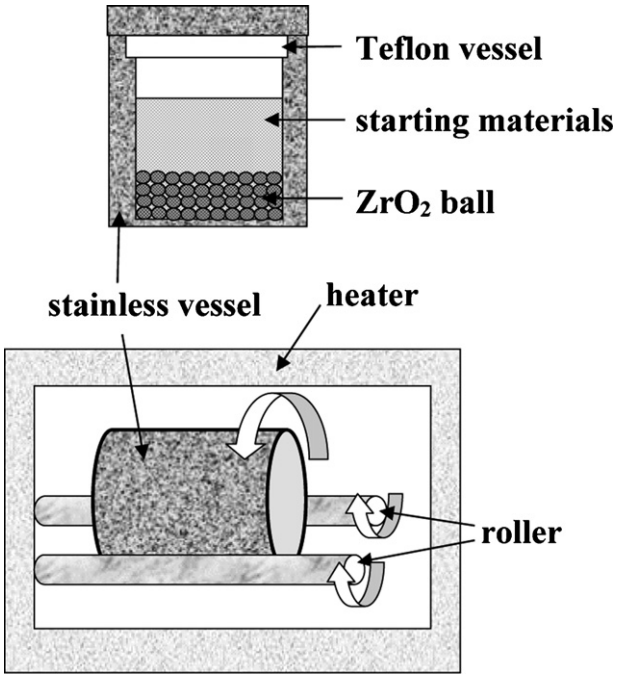

Fig. 1. Hydrothermal apparatus with ball milling system.

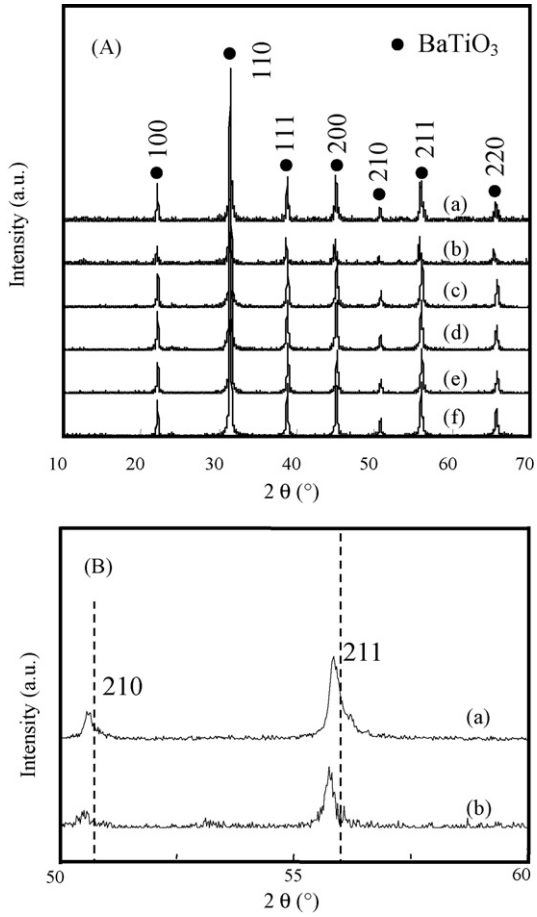

Fig. 2. (A) XRD patterns of the powders synthesized by a hydrothermal reaction without ball milling system ((a), (c) and (e))/with ball milling system ((b), (d) and (f)). Hydrothermal temperature: (a) and (b) 100 °C, (c) and (d) 125 °C, (e) and (f) 150 °C. (B) XRD diffraction profiles of 2 1 0 and 2 1 1 Bragg peaks given in (a) and (b) in (A).