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Preparation of porous $BaTiO_3$-based ceramics by high-energy ball-milling process

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Abstract

Porous $BaTiO_3$-based ceramics containing potato-starch (0–15 wt.%) were prepared by wet mixing and the effect of high-energy ball-milling time (1–20 h) on the electrical property and microstructure of the porous ceramics has been investigated. With increasing potato-starch content and ball-milling time, the porosity of the $BaTiO_3$-based ceramics containing potato-starch increased and decreased, respectively. The grain size decreased and increased, with increasing potato-starch content and ball-milling time, respectively. The room-temperature electrical resistivity of the porous ceramics slightly increased with increasing potato-starch content, and decreased with increasing ball-milling time. PTCR jump of the porous ceramic was slightly increased with increasing potato-starch content, while it was slightly decreased with increasing ball-milling time.

Keywords: Porous $BaTiO_3$-based ceramics; High-energy ball-milling; Potato-starch; PTCR; Electrical properties; Sintering

1. Introduction

Pure $BaTiO_3$ is an insulator and no positive temperature coefficient of resistance (PTCR) characteristics can be observed [1–6]. The additives play a crucial role in the fabrication of $BaTiO_3$-based PTCR ceramics. The semiconducting ceramic grains can be achieved by donor doping, which is a prerequisite for preparing PTCR ceramics. The donor additives are usually trivalent (La^{3+}, Y^{3+}) or pentavalent (Nb^{5+}, Ta^{5+}) ions. Semiconducting $BaTiO_3$-based ceramic shows a PTCR characteristic [7–9]. The PTCR characteristic in $BaTiO_3$-based ceramic is widely regarded as a grain boundary-controlled phenomenon [8–13]. Various theories of the PTCR characteristic have been proposed, commencing with the model of Heywang [14,15].

Porous $BaTiO_3$-based ceramics exhibit large PTCR effect [16–19], and various fabrication techniques have been attempted to investigate the PTCR characteristics and improve the thermistors performance [20], in particular, porous electronic ceramics prepared by the incorporation of polymer [16–18,21]. The potato-starch, utilized as a new porous additive, is a very cheap material. It can be considered that the ball-milling of powder influences the PTCR characteristics and microstructure in the porous $BaTiO_3$-based ceramic. In this study, the effects of potato-starch content (0–15 wt.%, 1 h) and high-energy ball-milling time (1–20 h, 15 wt.%) on the

Table 1
Summary of the samples obtained in this study

Sample	Potato-starch (wt.%)	Ball-milling time (h)
S01	0	1
S51	5	1
S101	10	1
S151	15	1
S155	15	5
S1510	15	10
S1515	15	15
S1520	15	20

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Table 2
Porosity and grain size of samples produced by high-energy ball-milling

Sample	Porosity (%)	Average grain size (μm)
S01	7.18	6.71
S51	15.86	5.76
S101	20.95	5.01
S151	25.87	4.68
S155	24.71	5.52
S1510	22.83	6.45
S1515	17.75	7.43
S1520	15.53	7.91

electrical property and microstructure of the porous ceramics have been investigated.

2. Experimental

The $BaTiO_3$-based ceramic powder was commercially obtained from high-purity (>99.99%) $BaTiO_3$ powder containing 25 mol% SrO and 0.2 mol% Y_2O_3 (Toho Titanium Co. Ltd, Japan). The mean particle size and ferroelectric Curie temperature of the powder are 0.7 μm and 61 °C, respectively. The potato-starch (purity: >99.9%, Shinyo Pure Chemicals Co. Ltd, Japan) as the starting material is the dispersed particle (mean particle size: 25 μm) observed by scanning electron microscopy (SEM: S-4200, Hitachi). The potato-starch of 0–15 wt.% was added to the $BaTiO_3$-based powder. The mixed powder was ball-milled in planetary mill (Fritsch, German, 500 rpm) with ethanol media (40 ml) using ZrO_2 balls (ϕ 2 mm, 90 g) for 1–20 h. And then this powder dried at 100 °C for 4 h. The dried powder was compacted by die-pressing at a pressure of 40 MPa to prepare the green compacts ($15 \times 12 \times 7$ mm^3). The green compacts were sintered at 1350 °C for 1 h in air. The samples obtained in this study are summarized in Table 1. The microstructure of the porous $BaTiO_3$-based ceramics was analyzed by scanning electron microscopy (SEM: S-4200, Hitachi), and the average grain size of the $BaTiO_3$-based ceramics was estimated by the line-intersection method. The electrical resistance was measured with a digital multi-meter.

3. Results and discussion

Table 2 shows the effects of potato-starch content (0, 5, 10 and 15 wt.%) and ball-milling time (1, 5, 10, 15 and 20 h) on the porosity and grain size in the porous $BaTiO_3$-based ceramics containing potato-starch. It is seen that with increasing potato-starch content, the porosity increased and the grain size decreased. In addition, the porosity decreased and grain size of the porous $BaTiO_3$-based ceramics increased with increasing ball-milling time.

For example, the porosity and grain size of the sample S51 are 15.86% and 5.76 μm, respectively, and those of the sample S151 are 25.87% and 4.68 μm, respectively. The porosity and grain size of the sample S1510 are 22.83% and 6.45 μm, respectively, while those of the sample S1520 are 15.53% and 7.91 μm, respectively.

The porosity of the porous ceramics increased with increasing potato-starch content, since the cavities formed due to the burning-out of starch during sintering act as the sites of the pore generations. It is found that the grain size of the porous ceramics decreased with

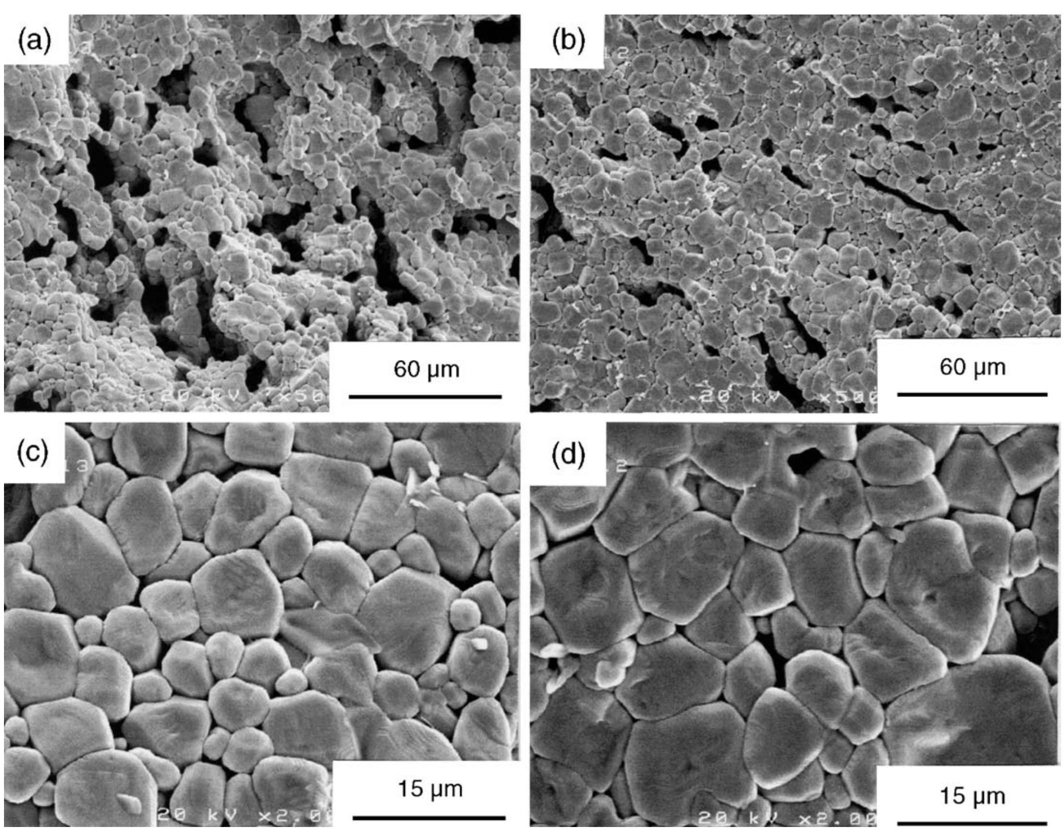

Fig. 1. SEM micrographs of the fractured surfaces for the sample S155 at magnification (a) ×500, (c) ×2000 and the sample S1520 at magnification (b) ×500, (d) ×2000.