Preparation of porous, Y-doped $BaTiO_3$ ceramics produced by wet mixing

J.-G. KIM
Institute of Advanced Materials, Inha University, Inchon 402-751, Korea
E-mail: jgkim@inha.ac.kr

Donor doped $BaTiO_3$ ceramics are widely used in positive temperature coefficient resistors (PTCR) [1–7]. Semiconducting $BaTiO_3$ ceramics sintered in air or oxidizing atmosphere exhibit an anomalous increase in electrical resistivity near the Curie temperature (∼120° C) [8, 9]. It is well known that PTCR characteristics originate from the existence of an electrical potential barrier arising from the presence of a two-dimensional surface layer of acceptor state, e.g., segregated acceptor ions, or adsorbed oxygen at the grain boundaries [8–13]. The Curie point of $BaTiO_3$ ceramics can be shifted to lower temperatures by substituting strontium for barium, or zirconium for titanium, and to higher temperatures by substituting lead for barium [14, 15].

Since oxygen can be adsorbed at the grain boundaries due to the presence of pores in the porous ceramics, the porous ceramics exhibit large PTCR effects [16–20]. These ceramics are more favorable to form surface acceptor states compared with ordinary dense ceramics [20]. Porous thermistors show better heat resistance than dense ones, and thus can be used for overcurrent protectors in electric circuits [16]. In this study, porous $BaTiO_3$ ceramics are prepared by adding corn-or potato-starch (are referred to as starch) and by wet mixing, and the electrical properties in the porous $BaTiO_3$ ceramics were investigated.

The Y-doped $BaTiO_3$ ceramic powder was commercially obtained from high-purity $BaTiO_3$ 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 starch (Shinyo Pure Chemicals Co. Ltd., Japan) of 1–20 wt% was added to the Y-doped $BaTiO_3$ powder. The mixed powder was ball-milled in planetary mill (Fritsch, German, 500 rpm) with ethanol media (40 ml) using ZrO_2 balls (ϕ2 mm, 90 g) for 3 h. And then these powder dried at 100°C for 4 h. The dried powder were compacted by die-pressing at a pressure of 40 MPa to prepare the green compacts ($15 \times 2 \times 7$ mm^3). The green compacts were sintered at 1350°C for 1 h in air. The samples were heated up to the sintering temperature at a rate of 3°C/min, and cooled at a rate of 10°C/min from the sintering temperature to 800 °C, and then furnace cooled. The ohmic (Ag-7 mass% Ni) and cover (Ag) paste were baked at 580°C for 5 min with a heating rate of 10°C/min in air. The microstructure of the porous ceramics was analyzed by scanning electron microscopy (SEM: S-4200, Hitachi), and the average grain size of the ceramics was estimated by the line-intersection method. The electrical resistance was measured with a digital multi-meter. The samples obtained in this study are summarized in Table I.

Table II shows the porosity and grain size of all the porous ceramics containing starch. The porosity and grain size of the porous ceramics are increased and decreased, as the content of starch increased, respectively. For example, the porosity and grain size of the sample C5 are 13.45% and 6.52 μm respectively, and the porosity and grain size of the sample C20 are 20.57% and 5.66 μm respectively. The porosity of the porous ceramics containing the starch content was increased with increasing starch. This can be explained by the fact that the cavities formed due to the burning-out of starch during sintering act as the sites of the pore generations, leading to an increase in the porosity.

Fig. 1 shows the SEM micrographs of the fractured surfaces for samples (a) A0, (b) C5, (c) C10 and (d) C15. It is confirmed that the porosity and grain size are increased and decreased with increasing starch content, respectively.

TABLE I Summary of the samples obtained in this study

Sample	Corn-starch (wt.%)	Potato-starch (wt.%)
A0	0	0
C5	5	0
C10	10	0
C15	15	0
C20	20	0
P5	0	5
P10	0	10
P15	0	15

TABLE II Porosity and grain size of samples produced by wet mixing

Sample	Porosity (%)	Average grain size (μm)
A0	7.18	6.71
C5	13.45	6.52
C10	15.15	6.35
C15	17.59	5.94
C20	20.57	5.66
P5	15.86	5.76
P10	20.95	5.01
P15	25.87	4.68

0022-2461

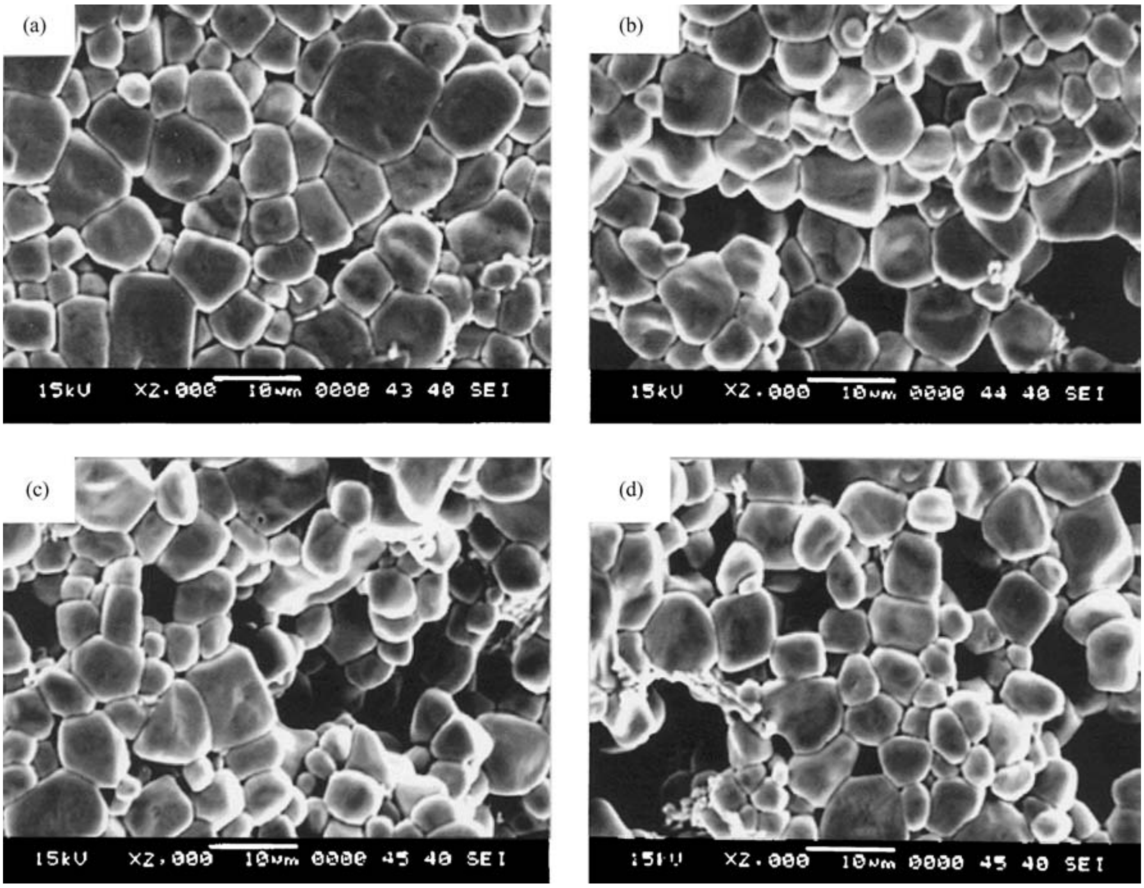

Figure 1 SEM micrographs of the fractured surfaces for the samples (a) A0, (b) C5, (c) C10 and (d) C15.

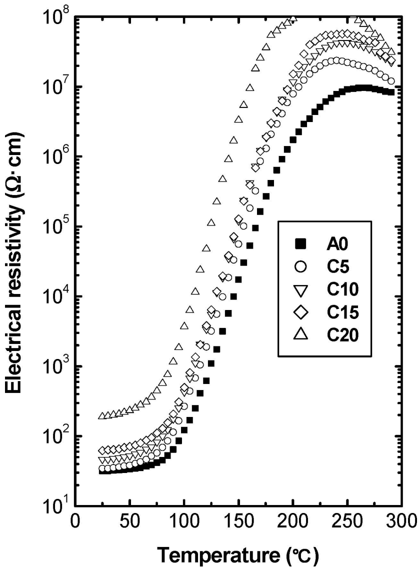

Figure 2 Electrical resistivity as a function of temperature for the samples (A0, C5, C10, C15, C20) produced by wet mixing.

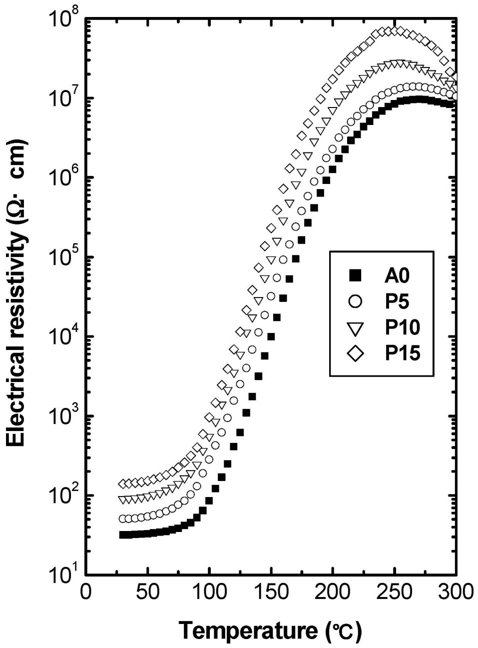

Figure 3 Electrical resistivity as a function of temperature for the samples (A0, P5, P10, P15) produced by wet mixing.

Figs 2 and 3 show the electrical resistivity as a function of temperature for the porous ceramics containing various amount of corn-starch (Fig. 2) or potato-starch (Fig. 3). These figures show that all the samples showed PTCR behavior, and PTCR jump was slightly increased with increasing starch content. As an example, the PTCR jump of the sample A0, C5 and C15 is 2.85×10^5, 6.91×10^5 and 9.22×10^5, respectively. This is due to an increase in porosity, and can be explained by the potential barrier height [12]. Namely, with increasing porosity, an increase of the PTCR jump is due to the increase in potential barrier height, which originates from a decrease in the number of electrons owing to the adsorption of chemisorbed oxygen atoms at the grain-boundaries [13]. However, the room-temperature electrical resistivity of the porous ceramics containing starch is higher than that of the ceramics without starch, and increased with increasing starch content.

Based on the above microstructures and porosity, this can be explained by the fact that the increase of room-temperature resistivity in the porous ceramics containing starch results from increase of porosity and decrease of grain size with increasing starch.

Consequently, it is found that the wet mixing of the Y-doped $BaTiO_3$ ceramics containing starch can produce to porous ceramics, and the porosity of the porous ceramics increased and the grain size decreased with increasing starch content.

References

1. H. NAGAMOTO, H. KAGOTANI and T. OKUBO, *J. Am. Ceram. Soc.* **76** (1993) 2053.
2. H. EMOTO and J. HOJO, *J. Ceram. Soc. Jpn.* **100** (1992) 555.
3. I. C. HO, *J. Am. Ceram. Soc.* **77** (1994) 829.
4. I. C HO and H. L. HSIEH, *ibid.* **76** (1993) 2385.
5. H. F. CHENG, T. F LIN and C. T. HU, *ibid.* **76** (1993) 827.
6. B. C LACOURSE and V. R. W. AMARAKOON, *ibid.* **78** (1995) 3352.
7. O. SABURI, *J. Phys. Soc. Jpn.* **14** (1959) 1159.
8. W. HEYWANG, *J. Mater. Sci.* **6** (1971) 1214.
9. G. H. JONKER, *Solid State Elec.* **7** (1964) 895.
10. J. DANIELS and R. WERNIKE, *Philips Res. Rep.* **31** (1976) 544.
11. T. R. N. KUTTY, P. MURUGARAJ and N. S. GAJBHIYE, *Mater. Res. Bull.* **20** (1985) 565.
12. W. HEYWANG, *J. Am. Ceram. Soc.* **47** (1964) 484.
13. *Idem., Solid State Elec.* **3** (1961) 51.
14. T. F. LIN, C. T HU and I. N. LIN, *J. Am. Ceram. Soc.* **73** (1990) 531.
15. I. C HO and S. L. FU, *ibid.* **75** (1992) 728.
16. S.-M. SU, L.-Y. ZHANG, H.-T. SUN and X. YAO, *ibid.* **77** (1994) 2154.
17. T. R. SHROUT, D. MOFFATT and W. HUEBNER, *J. Mater. Sci.* **26** (1991) 145.
18. J. H. LEE, J. J. KIM and S. H. CHO, in "Research Report" (Kyungpook National University, Korea, 1990) 115.
19. T. TAKAHASHI, Y. NAKANO and N. ICHINOSE, *J. Ceram. Soc. Jpn* **98** (1990) 879.
20. M. KUWABARA, *J. Am. Ceram.* Soc. **64** (1981) C-170.

Received 11 August
and accepted 17 November 2004