Journal of the Korean Ceramic Society
Vol. 40, No. 1, pp. 5~10, 2003.

Effect of the Sintering Temperature on Electrical Properties of Porous Barium-strontium Titanate Ceramics

Jun-Gyu Kim, Jae-Hwang Sim,* and Won-Seung Cho*,†
Institute of Advanced Materials, Inha University, Inchon 402-751, Korea
**School of Materials Science and Engineering, Inha University, Inchon 402-751, Korea*
(Received November 13, 2002; Accepted November 27, 2002)

ABSTRACT

Porous barium-strontium titanate ceramics were fabricated by adding corn- or potato-starch (are referred to as starch). The effect of sintering temperature on the microstructure and electrical properties of the porous ceramics was investigated. The room-temperature electrical resistivity of the barium-strontium titanate ceramics decreased with sintering temperature. The porosity and pore size were decreased and the grain size was increased with increasing the sintering temperature. The porosity and grain size of the barium-strontium titanate ceramics with corn-starch sintered at 1300 and 1450°C were 28.5, 22.6% and 3.2, 6.2 μm, respectively. The average pore sizes of the barium-strontium titanate ceramics with corn-starch sintered at 1300, 1400 and 1450°C were 0.5, 0.3 and 0.2 μm, respectively. The decrease in the room-temperature resistivity with increasing sintering temperature is attributed mainly due to the increase of grain size and the decrease of the electrical barrier height of grain boundaries as well as the partial decrease of porosity.

Key words : Porous barium-strontium titanate ceramics, PTCR, Electrical property, Sintering temperature, Starch

1. Introduction

Commercially pure barium titanate($BaTiO_3$) is known to have high electrical resistivity at room temperature, but its electrical resistivity can be dramatically lowered by some dopants, like rare earth elements.[1-5] Donor doped polycrystalline barium titanate($BaTiO_3$) exhibits Positive Temperature Coefficient of Resistivity(PTCR) characteristics, which is usually controlled by grain-boundary related effect.[6-14] PTCR characteristics originate from the existence of an electrical potential barrier, corresponding to the presence of a two-dimensional surface layer of acceptor state, e.g. segregated acceptor ions, or adsorbed oxygen at the grain boundaries.[8,10] The magnitude of the PTCR also varies as a function of the composition, sintering temperature, sintering time, atmosphere and annealing conditions.[15,16] These factors are further found responsible for changing the PTCR characteristics of barium titanate($BaTiO_3$) ceramics through the variation of the room temperature resistivity and microstructure.

Porous barium titanate($BaTiO_3$) showing a large PTCR effects generally prepared by the thermal decomposition of barium titanyl oxalate $BaTiO(C_2O_4)_2 \cdot 4H_2O$ or by the incorporation of graphite, Polyvinylalcohol(PVA), Polyvinylbutyral(PVB), borides, silicides, carbides and partially oxidized Ti powders to barium titanate($BaTiO_3$).[17-22] Porous structure in the $BaTiO_3$ ceramics promotes to incorporate the oxygen in the grain boundary and to form surface acceptor states in comparison with ordinary dense ceramics.[23]

Porous thermistors show better heat resistance than dense ones and, thus, can be used as overcurrent protectors in electric circuits[19] and they are also potential candidates as humidity and gas sensor. In this study, porous barium-strontium titanate ceramics were fabricated by adding corn- or potato-starch and investigated effect of sintering temperature on the microstructure and electrical properties of the porous ceramics.

2. Experimental Procedure

The barium-strontium titanate ceramics powder consisting of highly pure $BaTiO_3$, 0.1 mol% Sb_2O_3 and 30 mol% SrO (Kyoritsu Yogyo Co. Ltd, Japan) was utilized. This powder is referred to as $(Ba,Sr)TiO_3$. The mean particle size and ferroelectric curie temperature of the powder were 1.0 μm and 55°C, respectively. The corn-starch (Shinyo Pure Chemicals Co. Ltd, Japan) as the starting material is agglomerated particle observed by Scanning Electron Microscopy (SEM: S-4200, Hitachi), while the potato-starch (Shinyo Pure Chemicals Co. Ltd, Japan) is the dispersed particle (mean particle size: 25 μm).

The starch (corn- and potato-starch), with amounts ranging from 5−15 wt% was added to the $(Ba,Sr)TiO_3$ powder and then mixed in a mortar for 1 h. The mixed powders were pelletized at a pressure of 40 MPa resulting in green compacts of dimension : 15×12×7 mm^3. The green com-

† Corresponding author : Won-Seung Cho
E-mail : wscho@inha.ac.kr
Tel : +82-32-860-7528 Fax : +82-32-874-3382

pacts were sintered at 1300–1450°C for 1 h in air. The samples were heated up to the sintering temperature with a rate of 3°C/min and cooled with a rate of 10°C/min from the sintering temperature to 300°C and then furnace cooled.

A commercial ohmic paste (Ag-7 mass% Ni) of ~10 μm thickness was spread on two opposite sides of the sintered samples (15×12 mm^2). After the paste was dried at room temperature, Ag paste of ~10 μm in thickness was applied to the ohmic paste layers. The samples were baked at 580°C for 5 min with a heating rate of 10°C/min in air. Subsequently, copper wire leads of 0.58 mm diameter were joined to the central portion of the surfaces of baked samples with solder (Pb-2 mass% Sn). Pastes with Ga-40 mass% In composite were also spread for Capacitance-applied Voltage(C-V) and complex impedance measurements. The samples obtained in this study are summarized in Table 1(a) and (b).

The microstructure of the $(Ba,Sr)TiO_3$ ceramics was analyzed by SEM. The average grain size and porosity of the ceramics were estimated by the line-intersection method and porosimetry (mercury penetration method), respectively. The electrical resistance was measured with a digital multi-meter under air atmosphere. Capacitance-Voltage(C-V) characteristics were measured with an impedance analyzer at room temperature in a frequency of 10 kHz in order to calculate the electrical potential barrier of grain boundaries and the donor concentration of grains.

Table 1. (a),(b) Summary of the Samples Prepared in This Study

(a)

Sample	Corn-starch content (wt%)	Potato-starch content (wt%)	Sintering temp. (°C)
A	0	0	1350
C1	5	0	1350
C3	10	0	1350
C6	15	0	1350
P1	0	5	1350
P3	0	10	1350
P6	0	15	1350

(b)

Sample	Corn-starch content (wt%)	Potato-starch content (wt%)	Sintering temp. (°C)
C2	10	0	1300
C3	10	0	1350
C4	10	0	1400
C5	10	0	1450
P2	0	10	1300
P3	0	10	1350
P4	0	10	1400
P5	0	10	1450

3. Results and Discussion

Table 2(a) shows the room-temperature electrical resistiv-

Table 2. (a),(b) Room-temperature Electrical Resistivity ($\rho_{25°C}$), Maximum Electrical Resistivity (ρ_{max}) and PTCR Jumps ($\rho_{max}/\rho_{25°C}$) as well as Calculated Donor Concentrations and Electrical Potential Barriers at 25°C for all the Samples

(a)

Sample	$\rho_{25°C}$ (Ω·cm)	ρ_{max} (Ω·cm)	PTCR jump ($\rho_{max}/\rho_{25°C}$)	Donor concentration of grains (N_d : #/cm^3)	Electrical potential barrier of grain boundaries (Φ : eV)
A	3.41×10	5.69×10^6	1.67×10^5	5.61×10^{18}	0.006
C1	3.35×10^2	$>3\times10^8$*	$>8.95\times10^5$	4.52×10^{18}	0.058
C3	4.29×10^2	$>3\times10^8$*	$>6.99\times10^5$	4.33×10^{18}	0.074
C6	5.41×10^2	$>3\times10^8$*	$>5.54\times10^5$	4.43×10^{18}	0.094
P1	1.19×10^3	$>3\times10^8$*	$>2.52\times10^5$	3.73×10^{18}	0.206
P3	3.22×10^3	$>3\times10^8$*	$>9.32\times10^4$	2.67×10^{18}	0.557
P6	6.44×10^3	$>3\times10^8$*	$>4.66\times10^4$	2.63×10^{18}	1.116

*Higher than the measuring limit (3×10^8 Ω·cm) of the multi-meter used.

(b)

Sample	$\rho_{25°C}$ (Ω·cm)	ρ_{max} (Ω·cm)	PTCR jump ($\rho_{max}/\rho_{25°C}$)	Donor concentration of grains (N_d : #/cm^3)	Electrical potential barrier of grain boundaries (Φ : eV)
C2	1.50×10^3	$>3\times10^8$*	$>2.00\times10^5$	3.65×10^{18}	0.259
C3	4.29×10^2	$>3\times10^8$*	$>6.99\times10^5$	4.33×10^{18}	0.074
C4	1.72×10^2	$>3\times10^8$*	$>1.74\times10^5$	4.68×10^{18}	0.030
C5	8.42×10	5.25×10^7	6.23×10^5	5.31×10^{18}	0.014
P2	6.82×10^3	$>3\times10^8$*	$>4.39\times10^4$	2.58×10^{18}	1.177
P3	3.22×10^3	$>3\times10^8$*	$>9.32\times10^4$	2.67×10^{18}	0.557
P4	9.52×10^2	1.62×10^8	1.70×10^5	3.27×10^{18}	0.164
P5	5.75×10^2	1.23×10^8	2.14×10^5	4.01×10^{18}	0.099

*Higher than the measuring limit (3×10^8 Ω·cm) of the multi-meter used.

ity ($\rho_{25°C}$), maximum resistivity (ρ_{max}) and PTCR jump ($\rho_{max}/\rho_{25°C}$) for the $(Ba,Sr)TiO_3$ ceramics with starch. It was found

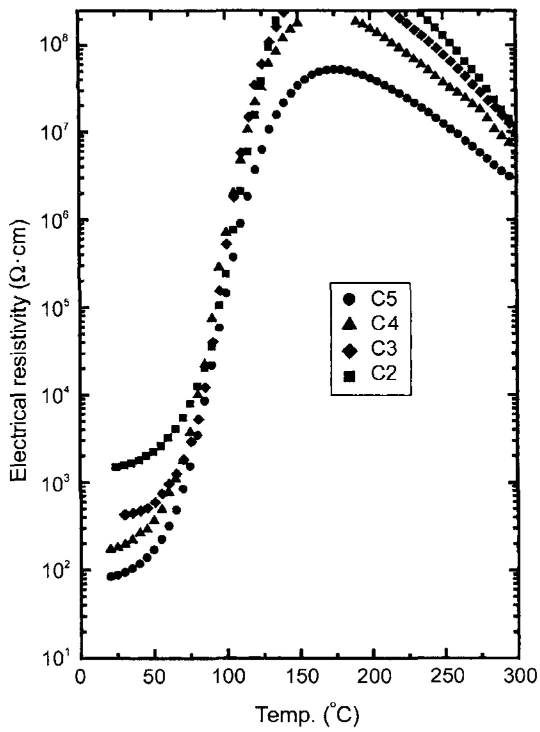

Fig. 1. Electrical resistivity as a function of temperature for the various $(Ba,Sr)TiO_3$ ceramics with corn-starch of 10 wt% sintered at 1300–1450°C.

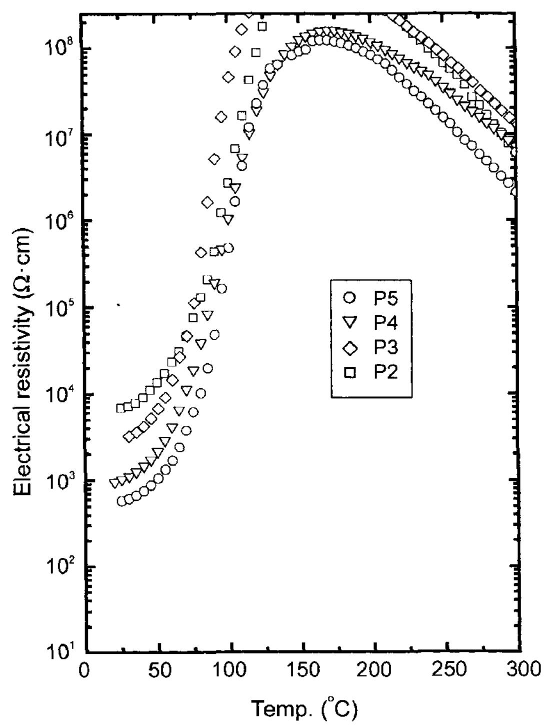

Fig. 2. Electrical resistivity as a function of temperature for the various $(Ba,Sr)TiO_3$ ceramics with potato-starch of 10 wt% sintered at 1300–1450°C.

the PTCR behavior in the $(Ba,Sr)TiO_3$ ceramics with starch showed. The PTCR jump was slightly increased with increasing starch content and was about 1-2 orders higher than that of $(Ba,Sr)TiO_3$ ceramics without starch. The enhancement in the PTCR jump is due to the porosity and can be explained by the barrier model.[8,11] However, the room-temperature electrical resistivity of the porous $(Ba,Sr)TiO_3$ ceramics with starch is higher than that of the $(Ba,Sr)TiO_3$ ceramics without starch.

In order to reduce the room-temperature resistivity of the starch added $(Ba,Sr)TiO_3$ ceramics, sintering temperature was varied and examined its effect.

Figs. 1 and 2 show the effect of sintering temperature (1300–1450°C) on the electrical resistivity of the $(Ba,Sr)TiO_3$ ceramics with 10 wt% corn-starch (Fig. 1) and potato-starch (Fig. 2), respectively. The room-temperature electrical resistivity of the $(Ba,Sr)TiO_3$ ceramics with corn-starch decreased with increasing sintering temperature. The sample C5 sintered at 1450°C showed the lowest room-temperature resistivity (8.42×10 Ω·cm) with the high ratio of maximum resistivity to room-temperature electrical resis-

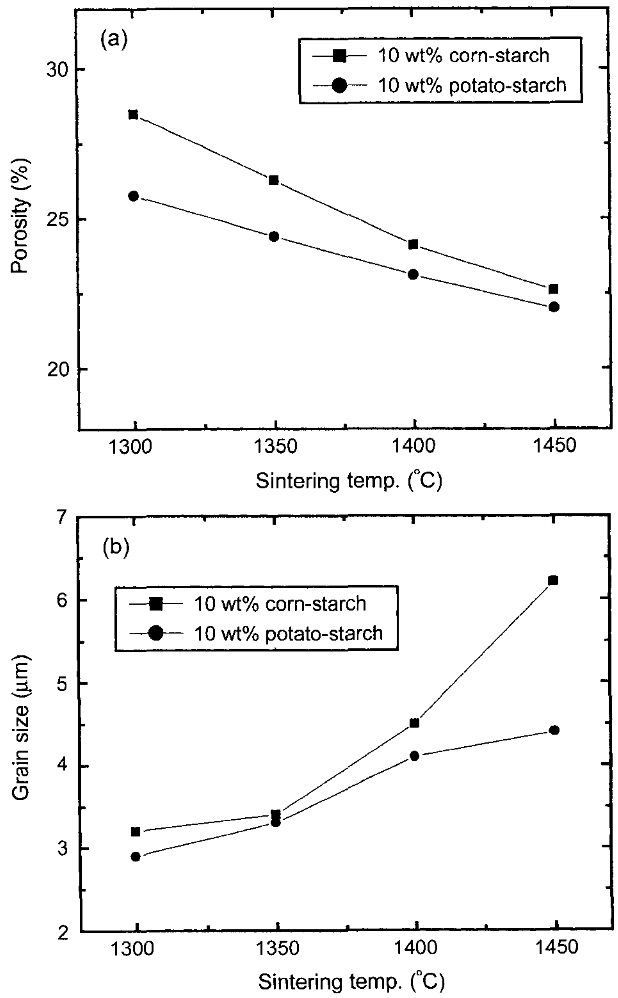

Fig. 3. Porosity (a) and grain size (b) of $(Ba,Sr)TiO_3$ ceramics with starch of 10 wt% sintered at different temperature.

tivity (6.23×10^5). The room-temperature electrical resistivity ($\rho_{25^\circ C}$), maximum resistivity (ρ_{max}) and PTCR jump ($\rho_{max}/\rho_{25^\circ C}$) for the samples are summarized in Table 2(b). It was also found that the room-temperature electrical resistivity of the $(Ba,Sr)TiO_3$ ceramics with potato-starch decreased with increasing sintering temperature.

In order to investigate the reason for the decrease of the room-temperature electrical resistivity of the samples, with increasing sintering temperature, the grain size, porosity, donor concentration of grains (N_d) and electrical barrier height of grain boundaries (Φ) of the samples were calculated. Fig. 3 shows the porosity (a) and grain size (b) of $(Ba,Sr)TiO_3$ ceramics with starch of 10 wt% sintered at different temperature. With increasing sintering temperature, the porosity and grain size decreased and increased, respectively. For example, the porosity and grain size of the samples C2 and C5 were 28.5, 22.6% and 3.2, 6.2 μm, respectively. The difference of porosity may have been resulted by the burning-out content of corn-starch during sintering which act as the sites of the pore generations. The grains of the $(Ba,Sr)TiO_3$ ceramics with corn-starch were grown with increasing sintering temperature.

Fig. 4 shows the pore diameter distribution of the samples C2 (a), C4 (b) and C5 (c). The pore size for the samples with starch decreased with increasing sintering temperature. For example, the average pore sizes of the samples C2, C4 and C5 were 0.5, 0.3 and 0.2 μm, respectively.

Figs. 5 and 6 show the SEM micrographs of the fractured surfaces for the samples C3 (a), C4 (b), P3 (c) and P4 (d) at magnification ×500 (Fig. 5) and ×2000 (Fig. 6). It is confirmed that the grain size and porosity increased and decreased respectively, with increasing sintering temperature.

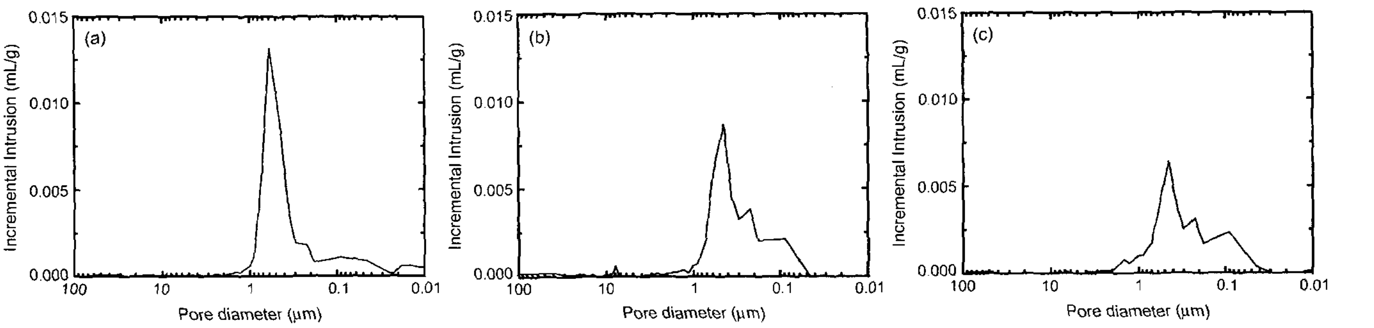

Fig. 4. Pore diameter distribution of the samples C2 (a), C4 (b) and C5 (c).

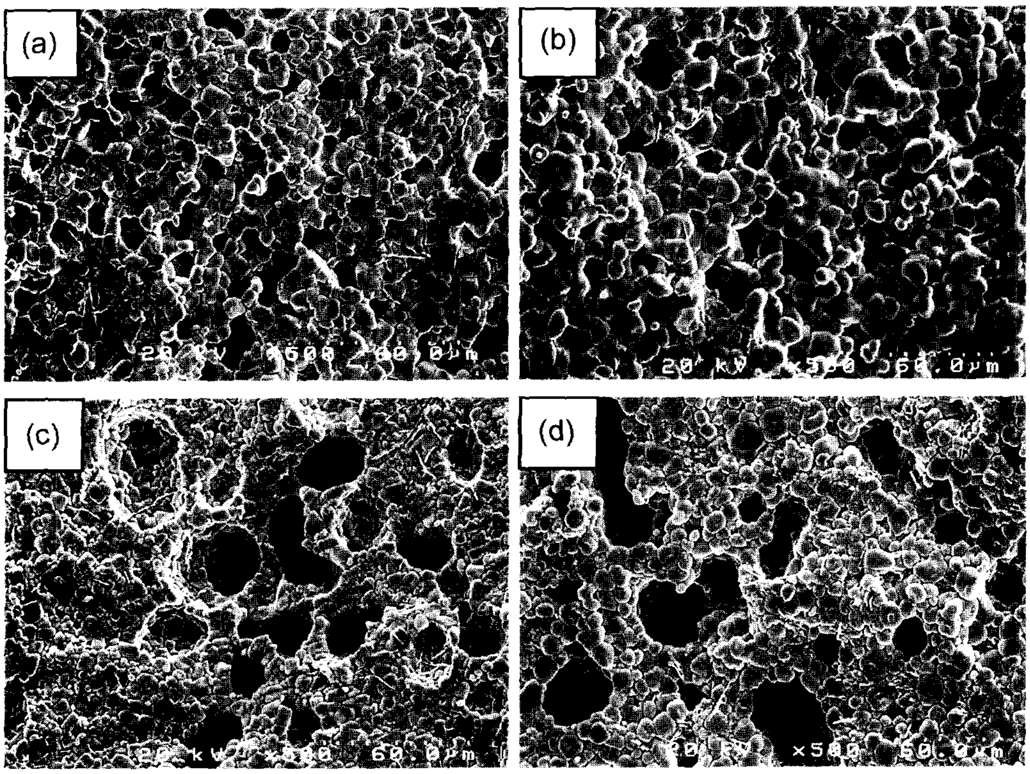

Fig. 5. SEM micrographs of the fractured surfaces for the samples C3 (a), C4 (b), P3 (c) and P4 (d) (×500).

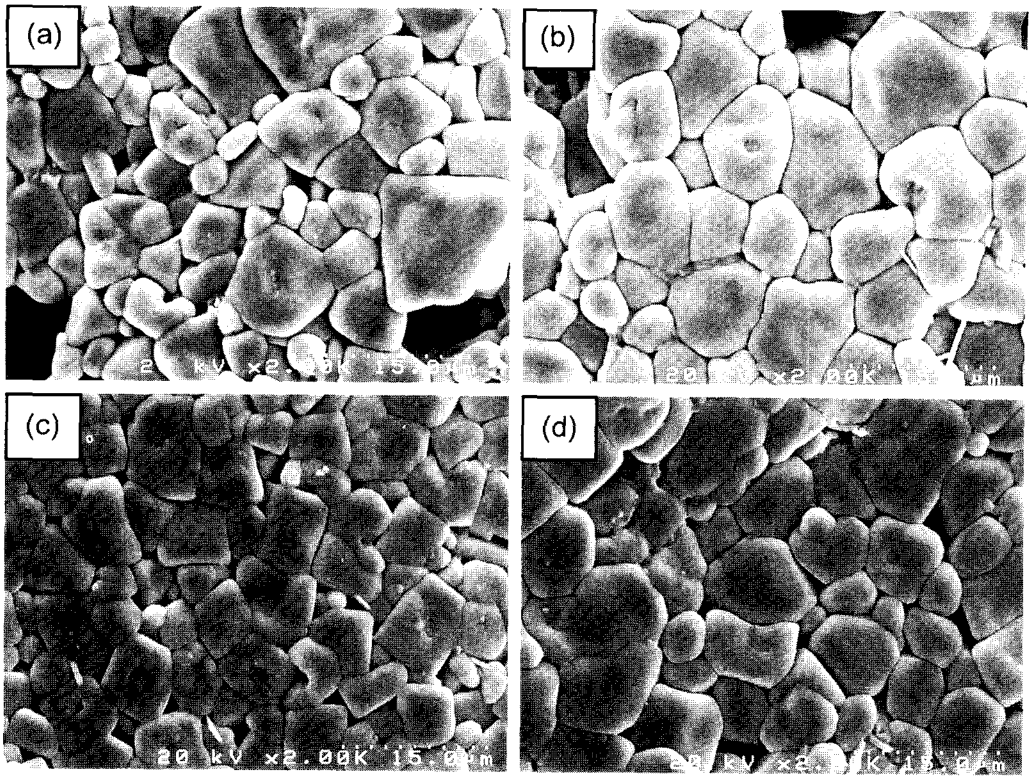

Fig. 6. SEM micrographs of the fractured surfaces for the samples C3 (a), C4 (b), P3 (c) and P4 (d) (×2000).

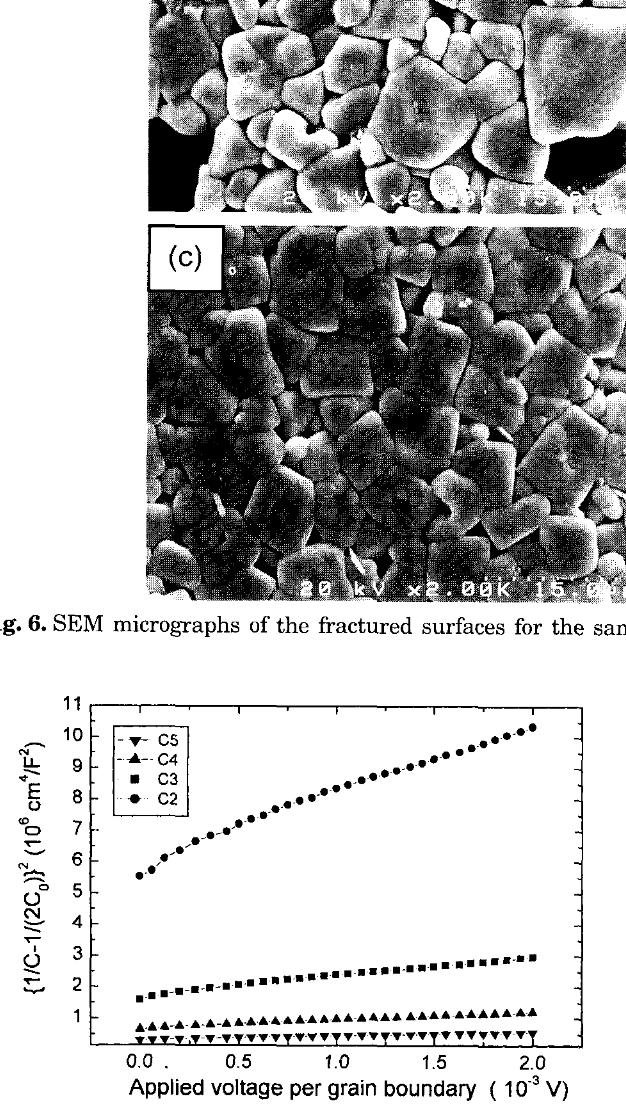

Fig. 7. Capacitance-applied voltage relation at room temperature for the samples C2, C3, C4 and C5.

The donor concentration of grains (N_d) and electrical barrier height of grain boundaries (Φ) of the $(Ba,Sr)TiO_3$ ceramics were calculated using the following equation:[24]

$$[1/C-1/(2C_o)]^2=[2(\Phi+qV)/(q^2\varepsilon_s N_d)] \quad (1)$$

where, C is the capacitance per unit area of a grain boundary, C_o is the capacitance at zero applied voltage, ε_s is the dielectric constant of $(Ba,Sr)TiO_3$, V is the applied voltage per grain boundary and q is the electronic charge. If the barrier model of grain boundary region is acceptable, plotting the left-hand term of Eq. (1) with the applied voltage yields a straight line. N_d and Φ can be obtained from the slope of the line and the intercept of the line on the voltage axis, respectively. The capacitance-applied voltage variations at room temperature for the samples are shown in Fig. 7. The calculated donor concentrations of grains and the electrical potential barriers of grain boundaries for the samples are summarized in Table 2(b). With increasing sintering temperature, the donor concentration of grains did not almost change, but the electrical barrier height of grain boundaries of the samples decreased. The decrease in the electrical barrier height of grain boundaries is found to be due to the increase in the number of electrons, which originates from a decrease of chemisorbed oxygen atoms at grain boundaries.

Based on the above results, it is found that the decrease in the room-temperature resistivity with increasing sintering temperature is attributed mainly due to the increase of grain size and the decrease of the electrical barrier height of grain boundaries as well as the partial decrease of porosity.

The porous ceramics fabricated here are potential candidates as humidity and gas sensor.[25-27]

4. Conclusion

Porous barium-strontium titanate ceramics were successfully prepared by adding starch and the effect of sintering temperature on the microstructure and electrical properties of the porous ceramics was investigated. The results obtained were as follows:

1. The room-temperature electrical resistivity of the bar-

ium-strontium titanate ceramics decreased with increasing sintering temperature. The sample sintered at 1450°C showed the excellent PTCR characteristics, i.e. the lowest room-temperature resistivity ($8.42\times10\ \Omega\cdot cm$) with the high ratio of maximum resistivity to room-temperature electrical resistivity (6.23×10^5).

2. As the sintering temperature increased, the porosity and pore size were decreased and the grain size was increased. The porosity and grain size of the barium-strontium titanate ceramics with corn-starch sintered at 1300 and 1450°C were 28.5, 22.6% and 3.2, 6.2 μm, respectively. The average pore sizes of the barium-strontium titanate ceramics with corn-starch sintered at 1300, 1400 and 1450°C were 0.5, 0.3 and 0.2 μm, respectively.

3. The decrease in the room-temperature resistivity with increasing the sintering temperature is attributed mainly due to the increase of grain size and the decrease of the electrical barrier height of grain boundaries as well as the partial decrease of porosity.

4. The porous barium-strontium titanate ceramics fabricated here are potential candidates as humidity and gas sensor.

Acknowledgements

This work was supported by Inha University Research Grant through the Special Research Program in 2002 (INHA-22523).

REFERENCES

1. H. Nagamoto, H. Kagotani, and T. Okubo, "Positive Temperature Coefficient Resistivity in $Ba_{1-x}Sr_xPb_{1+y}O_{3-\delta}$ Ceramics," *J. Am. Ceram. Soc.*, **76** [8] 2053-58 (1993).
2. H. Emoto and J. Hojo, "Sintering and Dielectric Properties of $BaTiO_3$-Ni Composite Ceramics," *J. Ceram. Soc. Jpn.*, **100** [4] 555-59 (1992).
3. I. C. Ho, "Semiconducting Barium Titanate Ceramics Prepared by Boron-containing Liquid-phase Sintering," *J. Am. Ceram. Soc.*, **77** [3] 829-32 (1994).
4. I. C. Ho and H. L. Hsieh, "Influence of Potassium on Preparation and Performance of PTC Resistors," *J. Am. Ceram. Soc.*, **76** [9] 2385-88 (1993).
5. H. F. Cheng, T. F. Lin, and C. T. Hu, "Effect of Sintering Aids on Microstructures and PTCR Characteristic of $(Sr_{0.2}Ba_{0.8})TiO_3$ Ceramics," *J. Am. Ceram. Soc.*, **76** [4] 827-32 (1993).
6. B. C. Lacourse and V. R. W. Amarakoon, "Characterization of the Firing Schedule for Positive Temperature Coefficient of Resistance $BaTiO_3$," *J. Am. Ceram. Soc.*, **78** [12] 3352-56 (1995).
7. O. Saburi, "Semiconducting Bodies in the Family of Barium Titanates," *J. Am. Ceram. Soc.*, **44** [2] 54-63 (1961).
8. W. Heywang, "Semiconducting Barium Titanate," *J. Mater. Sci.*, **6** 1214-26 (1971).
9. G. H. Jonker, "Some Aspects of Semiconducting Barium Titanate," *Solid State Electron.*, **7** 895-903 (1964).
10. J. Daniels, K. H. Hardtl, and R. Wernike, "The PTC Effect of Barium Titanate," *Philips Tech. Rev.*, **38** [3] 73-82 (1978/79).
11. W. Heywang, "Resistivity Anomaly in Doped Barium Titanate," *J. Am. Ceram. Soc.*, **47** [10] 484-90 (1964).
12. Y. G. Li and S. G. Cho, "Determination of Potential Barrier Heights at the Grain Boundaries of PTC Ceramics," *J. Kor. Ceram. Soc.*, **38** [7] 639-42 (2001).
13. J.-H. Lee, Y.-K. Choi, C. W. Won, and C. S. Kim, "Formation Rate of Tetragonal $BaTiO_3$ Powder by Hydrothermal Synthesis and its Dielectric Property," *J. Kor. Ceram. Soc.*, **39** [7] 628-34 (2002).
14. B. K. Kim, D. Y. Lim, J. S. No, and S. B. Cho, "Preparation of Nano-size $BaTiO_3$ Powders Using Glycothermal Method," *J. Kor. Ceram. Soc.*, **39** [7] 642-48 (2002).
15. J. G. Fagan and V. R. W. Amarakoon, "PTC Thermistors," *Am. Ceram. Soc. Bull.*, **72** [2] 69-76 (1993).
16. J. B. Macchesney and J. F. Potter, "Factors and Mechanisms Affecting the Positive Temperature Coefficient of Resistivity of Barium," *J. Am. Ceram. Soc.*, **48** 81-8 (1965).
17. M. Kuwabara, "Effect of Microstructure on the PTCR Effect in Semiconducting Barium Titanate Ceramics," *J. Am. Ceram. Soc.*, **64** [11] 639-44 (1981).
18. M. Kuwabara, "Influence of Stoichiometry on the PTCR Effect in Porous Barium Titanate Ceramics," *J. Am. Ceram. Soc.*, **64** [12] C170-71 (1981).
19. S.-M. Su, L.-Y. Zhang, H.-T. Sun, and X. Yao, "Preparation of Porous $BaTiO_3$ PTC Thermistors by Adding Graphite Porosifiers," *J. Am. Ceram. Soc.*, **77** [8] 2154-56 (1994).
20. T. R. Shrout, D. Moffatt, and W. Huebner, "Composite PTCR Thermistors Utilizing Conducting Borides, Silicides and Carbide Powders," *J. Mater. Sci.*, **26** 145-54 (1991).
21. J.-G. Kim, W.-S. Cho, and K. Park, "PTCR Characteristics in Porous $(Ba,Sr)TiO_3$ Ceramics Produced by Adding Partially Oxidized Ti Powders," *Mater. Sci. Eng. B*, **77** [3] 255-60 (2000).
22. T. Takahashi, Y. Nakano, and N. Ichinose, "Influence of Reoxidation on PTC Effect of Porous $BaTiO_3$," *J. Ceram. Soc. Jpn.*, **98** [8] 879-84 (1990).
23. M. Kuwabara, "Determination of the Potential Barrier Height in Barium Titanate Ceramics," *Sol. State Elect.*, **27** [11] 929-35 (1984).
24. K. Mukae, K. Tsuda, and I. Nagasawa, "Capacitance-vs-voltage Characteristics of ZnO Varistors," *J. Appl. Phys.*, **50** [6] 4475-76 (1979).
25. T. J. Hwang and G. M. Choi, "Humidity Response Characteristics of Barium Titanate," *J. Am. Ceram. Soc.*, **76** [3] 766-68 (1993).
26. J. Wang, B. Xu, G. Liu, Y. Liu, F. Wu, X. Li, and M. Zhao, "Influence of Doping on Humidity Sensing Properties of Nanocrystalline $BaTiO_3$," *J. Mater. Sci. Lett.*, **17** 857-59 (1998).
27. A. C. Caballero, M. Villegas, J. F. Fernandez, M. Viviani, M. T. Buscaglia, and M. Leoni, "Effect of Humidity on the Electrical Response of Porous $BaTiO_3$ Ceramics," *J. Mater. Sci. Lett.*, **18** 1297-99 (1999).