Sintering condition and PTCR characteristics of porous *n*-BaTiO$_3$ ceramics by adding poly(ethylene glycol)

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

Semiconducting barium titanate ceramics exhibit an anomalous electrical resistivity increase above the Curie temperature (T_c) [1–5]. This increase is well known as the positive temperature coefficient of resistivity (PTCR) [6–10]. The PTCR characteristic has been utilized as PTCR thermistors for temperature sensing and overcurrent limiting [11–13]. In such applications, especially in the latter, low resistivity at room temperature and high resistivity jump at T_c are important. The PTCR characteristic can be controlled by various factors such as dopant concentration, sintering temperature, sintering time and cooling rate, and so on [14, 15].

Porous BaTiO$_3$ has been reported to exhibit large PTCR effects [16–20]. Oxygen can adsorb at the grain boundaries due to the presence of pores in the porous ceramics, which are more favorable to form surface acceptor states compared with ordinary dense ceramics [21]. In this study, donor (Y) doped BaTiO$_3$ (n-BaTiO$_3$) ceramics were fabricated by adding poly(ethylene glycol) (PEG) and the influence of sintering temperature and time on the PTCR characteristics of the porous ceramics was investigated.

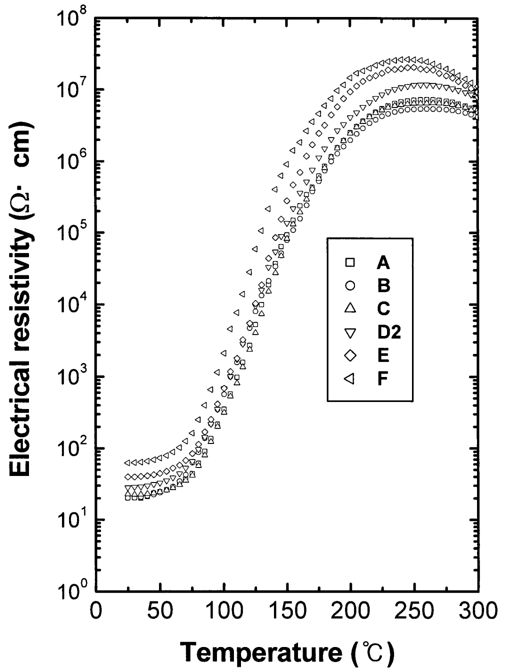
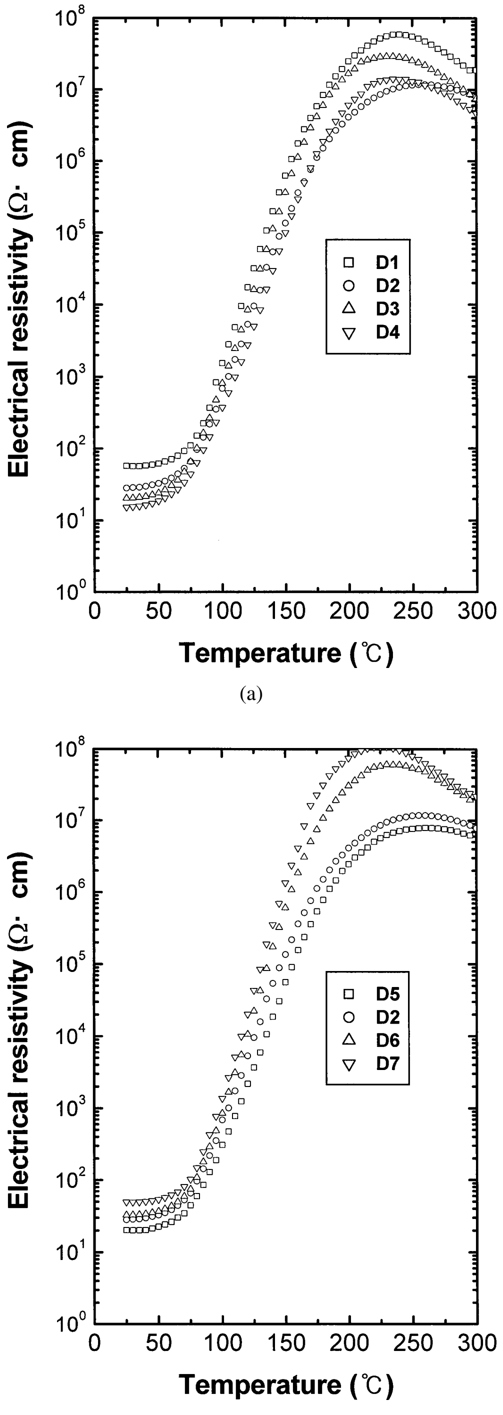


Figure 1 Electrical resistivity as a function of temperature for the n-BaTiO$_3$ ceramics containing various amounts of PEG.



(a)

(b)

Figure 2 (a) and (b). Effects of sintering temperature (a) and time (b) on the electrical resistivity of the various n-BaTiO$_3$ ceramics containing PEG of 10 wt%.

High-purity $BaTiO_3$ ceramic powder was utilized in this study (Toho Titanium Co. Ltd., Japan). The powder was commercially obtained as $BaTiO_3$ powder containing $SrTiO_3$ (19.2 mol%) and Y_2O_3 (0.2 mol%). The mean particle size and ferroelectric Curie temperature of the powder were 0.7 μm and 61 °C, respectively. The PEG (powder form, mean particle size: 50 μm, Shinyo Pure Chemicals Co. Ltd., Japan), with amount ranging from 1–20 wt% was added to the n-$BaTiO_3$ powder and then mixed in a mortar for 1 hr. The mixed 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 1300–1450 °C for 1–4 hr in air. The samples obtained in this study are summarized in Table I.

The microstructure of the n-$BaTiO_3$ ceramics was analyzed by scanning electron microscopy (SEM: S-4200, Hitachi). The average grain size and porosity of the ceramics were estimated by the line-intersection method and mercury porosimeter, respectively. The electrical resistance was measured with a digital multi-meter under-air atmosphere. Four samples were measured and plots obtained from averaged measurements.

Fig. 1 shows the electrical resistivity as a function of temperature for the n-$BaTiO_3$ ceramics containing various amounts of PEG. All samples containing PEG

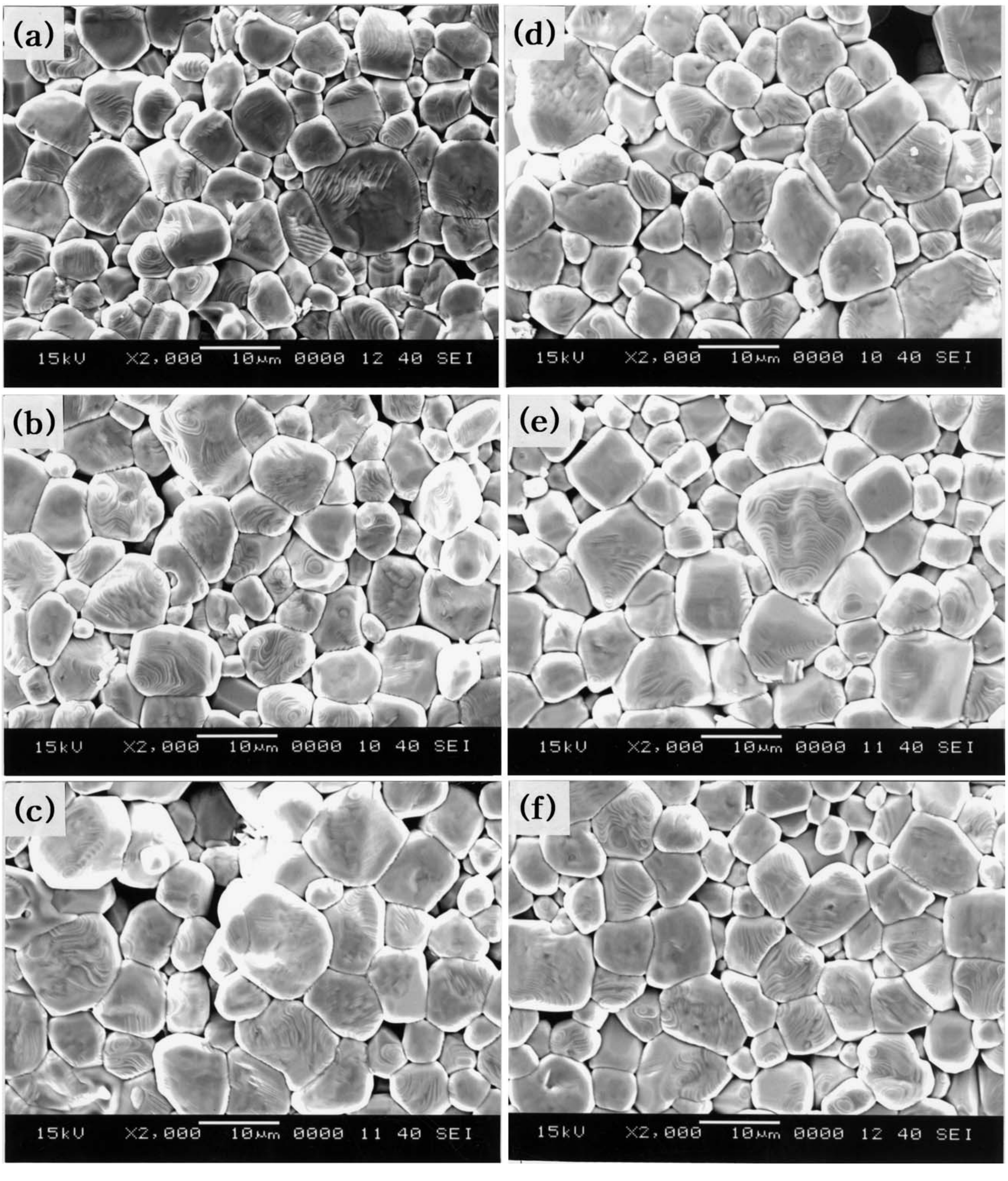


Figure 3 SEM micrographs of the fractured surfaces for the samples (a) D1, (b) D3, (c) D4, (d) D5, (e) D6 and (f) D7.

TABLE I Summary of the samples obtained in this study

		Sintering condition	
Sample	PEG content (wt%)	Temperature (°C)	Time (hr)
A	0	1350	1
B	1	1350	1
C	5	1350	1
D1	10	1350	1
D2	10	1350	1
D3	10	1400	1
D4	10	1450	1
D5	10	1350	0.5
D6	10	1350	2
D7	10	1350	4
E	15	1350	1
F	20	1350	1

TABLE II (a) and (b). Porosity and grain size of n-BaTiO$_3$ ceramics containing PEG sintered at various temperatures and times

Sample	Porosity (%)	Grain size (μm)
	(a)	
A	6.1	7.2
B	8.5	6.8
C	10.4	6.3
D2	12.8	5.8
E	18.6	5.4
F	25.2	5.0
	(b)	
D1	14.5	5.3
D2	12.8	5.8
D3	11.4	6.1
D4	9.6	6.4
D5	13.1	5.6
D6	12.5	5.9
D7	11.8	6.0

showed PTCR characteristic and the PTCR jump of the ceramics containing PEG was higher than that of samples without PEG. The enhancement in the PTCR jump is due to the porosity (Table IIa) and can be explained by the barrier model [12, 13]. However, the room-temperature electrical resistivity of the porous ceramics containing PEG is higher than that of the ceramics without PEG (sample A).

To reduce the room-temperature resistivity of the ceramics containing PEG, they were sintered at different temperatures (1300–1450 °C) and times (0.5–4 hrs).

Fig. 2a and b show the effects of sintering temperature (a) and time (b) on the electrical resistivity of the various n-BaTiO$_3$ ceramics containing PEG of 10 wt%. The room-temperature electrical resistivity of the n-BaTiO$_3$ ceramics slightly decreased with increasing sintering temperature, while that of the ceramics slightly increased with increasing sintering time. For example, the room-temperature electrical resistivity of the n-BaTiO$_3$ ceramics for the samples D1 and D4 is 5.7×10^2 and 1.5×10^2 $\Omega \cdot$cm, respectively, while that of the ceramics is 2.0×10^2 and 4.9×10^2 $\Omega \cdot$cm, respectively for the samples D5 and D7. The sample D4 showed the lowest room-temperature resistivity: 1.5×10^2 $\Omega \cdot$cm and the high ratio of maximum resistivity to minimum resistivity: 1.1×10^5.

Table IIa and b show the porosity (error range: ±5%) and grain size (error range: ±1%) of n-BaTiO$_3$ ceramics containing PEG sintered at various temperature and time, to investigate the reason for the change of room-temperature electrical resistivity of the samples. The porosity and grain size slightly decreased and increased, respectively with increasing sintering temperature and with increasing sintering time. For example, the porosity and grain size of the samples D1 and D4 were 14.5, 9.6% and 5.3, 6.4 μm, respectively, while those of the samples D5 and D7 were 13.1, 11.8% and 5.6, 6.0 μm, respectively.

Fig. 3 shows the SEM micrographs of the fractured surfaces for the samples (a) D1, (b) D3, (c) D4, (d) D5, (e) D6 and (f) D7. It is confirmed that the grain size slightly increased with increasing sintering temperature and time.

It is concluded that a decrease in the room-temperature resistivity with increasing sintering temperature is attributed mainly to the increase in the grain size as well as the partial decrease in the porosity, while, an increase in the room-temperature resistivity with increasing sintering time is mainly due to the increase of the porosity.

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