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Preparation of porous *n*-BaTiO$_3$ ceramics by adding polyethylene glycol

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Addition of donor dopants (Sb^{5+}, La^{3+}, etc.) at a relatively low concentration (<0.4 at%) leads to semiconducting BaTiO$_3$ ceramics with positive temperature coefficient of resistivity (PTCR) characteristics, whereas higher dopant content lead to insulating materials [1–26]. The donor doped BaTiO$_3$ (n-BaTiO$_3$) ceramics sintered in air or oxidizing atmosphere exhibit an anomalous increase in electrical resistivity near the ferroelectric Curie temperature (∼120 °C) [8, 9]. 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 n-BaTiO$_3$ PTCR thermistors are used in a variety of applications, including current limiting, temperature sensing, degaussing and protection against overheating in equipment such as electric motors.

Porous n-BaTiO$_3$ has been prepared by the incorporation of graphite, borides, silicides, carbides, partially oxidized Ti powders, corn- and potato-starch to BaTiO$_3$ [27–31]. The porous ceramics exhibit large PTCR effects, since oxygen can be adsorbed 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 [31]. Porous thermistors show better heat resistance than dense ones, and thus can be used for overcurrent protectors in electric circuits [27]. In this study, porous n-BaTiO$_3$ ceramics are prepared by adding poly (ethylene glycol) (PEG). PEG is a very cheap material compared with the above-mentioned additives. The effect of PEG on the microstructure and electrical properties was investigated.

The n-BaTiO$_3$ ceramic powder was commercially obtained from high-purity BaTiO$_3$ powder containing 25 mol% SrO (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 PEG (Shinyo Pure Chemicals Co. Ltd., Japan) of 1–20 wt% was added to the n-BaTiO$_3$ powders and then mixed in a mortar for 1 h. The green compacts were sintered at 1350 °C for 1 h in air.

Table I shows the porosity and grain size of all the n-BaTiO$_3$ ceramics containing PEG. As the content of PEG in n-BaTiO$_3$ ceramics increased, the porosity and grain size are increased and decreased, respectively. For example, the porosity and grain size of the n-BaTiO$_3$ ceramics containing PEG of 5 wt% are 10.4% and 6.3 μm respectively, and the porosity and grain size of the n-BaTiO$_3$ ceramics containing PEG of 20 wt% are 25.2% and 5.0 μm respectively. The porosity of the n-BaTiO$_3$ ceramics containing the PEG content was increased with increasing PEG. This can be explained by the fact that the cavities formed due to the burning-out of PEG during sintering act as the sites of the pore generations, leading to a increase in the porosity.

Fig. 1 shows SEM micrographs of the fractured surfaces for the n-BaTiO$_3$ ceramics containing (a) 0, (b) 5, (c) 10 and (d) 20 wt% PEG. It is confirmed that the porosity and grain size are increased and decreased with increasing PEG content, respectively.

Fig. 2 shows the electrical resistivity as a function of temperature for the n-BaTiO$_3$ ceramics containing various amount of PEG. It is found that all the n-BaTiO$_3$ ceramics containing PEG showed PTCR behavior, and PTCR jump was slightly increased with increasing PEG content. As an example, the PTCR jump of the n-BaTiO$_3$ ceramics containing PEG of 1 and 20 wt% is 2.84×10^5, 6.76×10^5, respectively. This is due to an increase in porosity, and can be explained by the barrier model proposed by Heywang [12, 13]. However, the room-temperature electrical resistivity of the porous n-BaTiO$_3$ ceramics containing PEG is higher than that of the n-BaTiO$_3$ ceramics without PEG, and increased with increasing PEG content. Based on the above microstructures and porosity, this can be explained by the fact that the increase of room-temperature resistivity in the n-BaTiO$_3$ ceramics containing PEG results from increase of porosity and decrease of grain size with increasing PEG.

Consequently, it was found that the addition of PEG into n-BaTiO$_3$ ceramics gave rise to porous ceramics, and the porosity increased and the grain size decreased with increasing PEG content. It was also found that the n-BaTiO$_3$ ceramics showed excellent PTCR characteristic by adding 1–20 wt% of PEG. It is believed that newly prepared n-BaTiO$_3$ ceramics can be used for humidity and gas sensors [32–35].

TABLE I Porosity and grain size of the n-BaTiO$_3$ ceramics containing various amount of PEG

PEG (wt%)	Porosity (%)	Grain size (μm)
0	6.1	7.2
1	8.5	6.8
5	10.4	6.3
10	12.8	5.8
15	18.6	5.4
20	25.2	5.0

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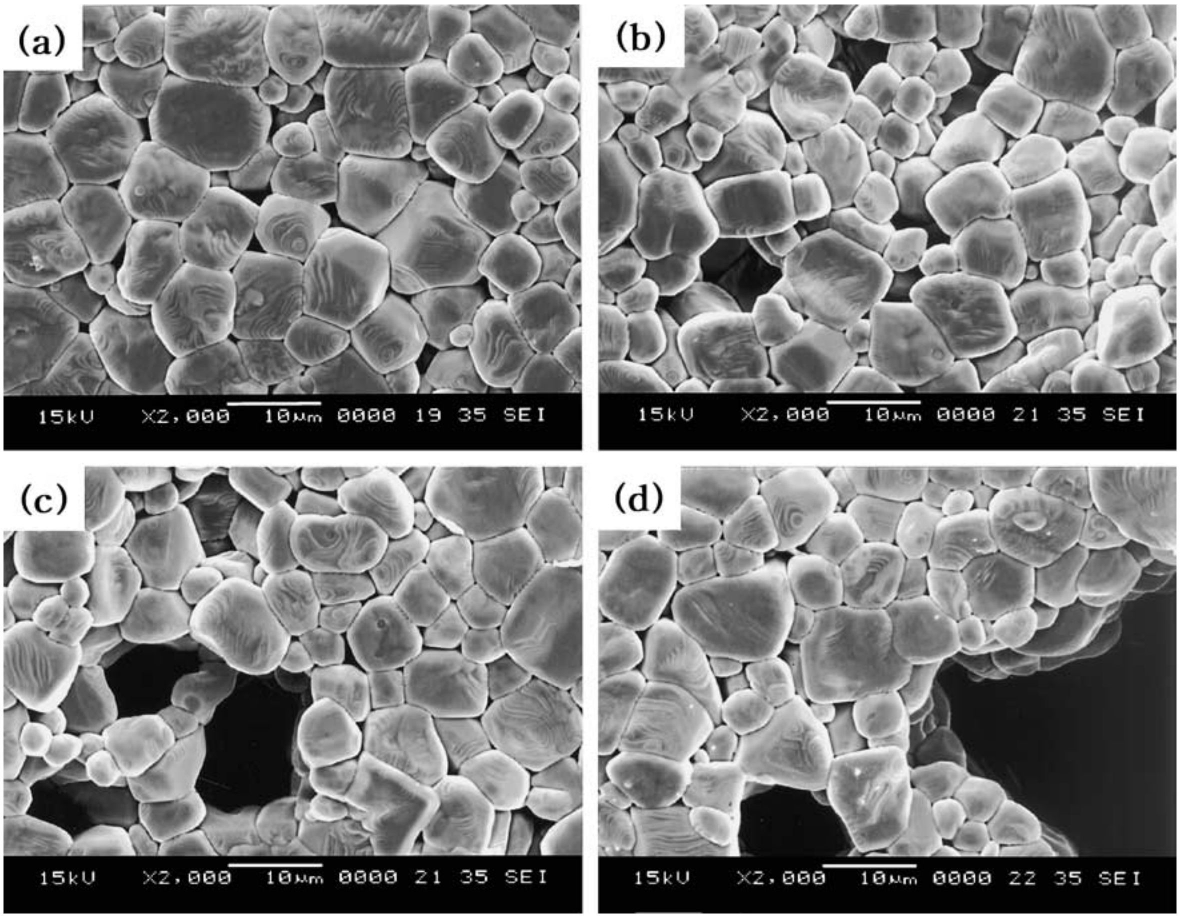

Figure 1 SEM micrographs of the fractured surfaces for the n-BaTiO$_3$ ceramics containing: (a) 0, (b) 5, (c) 10, and (d) 20 wt% PEG.

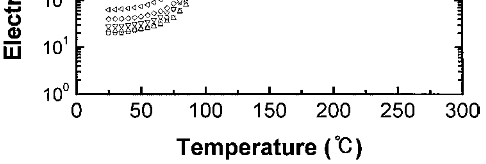

Figure 2 Electrical resistivity as a function of temperature for the n-BaTiO$_3$ ceramics containing various amount of PEG.

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