PTCR characteristics of porous Y-doped \((\text{Ba},\text{Sr})\text{TiO}_3\) ceramics prepared using nano-size carbon black as a pore precursor

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Carbon black (0 to 60 vol%) was added to \((\text{Ba},\text{Sr})\text{TiO}_3\) powder. The resulting mixture was treated by sonication and freeze drying. The effects of the carbon black content on the microstructure and PTCR characteristics of the resulting porous \((\text{Ba},\text{Sr})\text{TiO}_3\) ceramics were investigated. The combined process of sonication and freeze drying was an effective method for preparing a homogeneous dispersion of nano-size carbon black. The porosities of all \((\text{Ba},\text{Sr})\text{TiO}_3\) ceramics were < 10%. The PTCR jump of the \((\text{Ba},\text{Sr})\text{TiO}_3\) ceramics prepared with carbon black was > 10⁶, and increased slightly with increasing carbon black content. Carbon black is an effective additive for \(\text{BaTiO}_3\)-based ceramics, showing excellent PTCR characteristics. The change in the resistivity of porous \((\text{Ba},\text{Sr})\text{TiO}_3\) ceramics can be explained in terms of the change in potential barrier height due to the chemisorption/desorption of oxygen atoms at the grain boundaries.

Key words: Carbon black, Freeze drying, Y-doped \((\text{Ba},\text{Sr})\text{TiO}_3\) ceramics, PTCR.

Introduction

\(\text{BaTiO}_3\) is a representative ferroelectric ceramic with a perovskite structure that can be transformed to an n-type semiconductor by doping with \(\text{La}^{3+}\) or \(\text{Nb}^{5+}\), etc. The resistance of semiconducting \(\text{BaTiO}_3\) increases dramatically above the Curie temperature (\(T_c\)), which is known as positive temperature coefficient of resistivity (PTCR) behavior. The Heywang-Jonker model is the model most commonly used to explain the PTCR characteristics in semiconducting \(\text{BaTiO}_3\) [1]. According to the Heywang-Jonker model, the PTCR characteristics can be explained by the formation of a double Schottky barrier due to an acceptor level formed at the grain boundaries in \(\text{BaTiO}_3\). Specifically, it is a phenomenon related to the nature of interfaces. The PTCR characteristics can be improved by controlling the grain size (i.e. grain boundary area) and pore distribution.

Many studies have attempted to improve the PTCR characteristics in \(\text{BaTiO}_3\)-based ceramics [2-6]. Kuwabara reported that porous \(\text{BaTiO}_3\)-based ceramics exhibit larger PTCR characteristics than dense ceramics [7, 8]. Takahashi et al. reported that the potential barrier of semiconducting \(\text{BaTiO}_3\) was formed by oxygen adsorbed at the grain boundaries [9]. Porous \(\text{BaTiO}_3\)-based ceramics have been prepared by the incorporation of pore precursors, thermal decomposition, etc. [7, 10-12].

In a previous study [13], porous \((\text{Ba},\text{Sr})\text{TiO}_3\) ceramics were prepared by the addition of nano-size carbon black as a pore precursor by dry mixing. The microstructure revealed many agglomerates consisting of carbon black, which is inevitable in dry mixing. This means that the homogeneous dispersion of nano-size carbon black requires an alternative processes, such as wet mixing. On the other hand, nano-size carbon black tends to agglomerate when mixed into a liquid. Effective means of deagglomeration and dispersion are needed to overcome the bonding forces of carbon black in a slurry. Sonication is an effective method for preparing a homogeneous dispersion of nano-size carbon black in a slurry. Ultrasonication can breakup any agglomerated structures in aqueous suspensions. Cavitation, which is a process of bubble formation, growth and collapse, is responsible for the strong shear force that can deagglomerate carbon black during sonication [14]. Nevertheless, nano-size carbon black will form strong agglomerates if dried inappropriately meaning that the initial homogeneous dispersion state created by sonication cannot be sustained. Therefore, special attention should be paid to keep the nanoparticles apart during the drying step. The freeze-drying technique [15, 16] is effective for maintaining a homogeneous mixture because only a water-based solvent is removed by sublimation after rapid freezing of the slurry in a short time.

In this study, powder mixtures with different carbon black contents were prepared using the combined process of sonication and freeze-drying. Porous \((\text{Ba},\text{Sr})\text{TiO}_3\) ceramics were prepared by burning carbon black out during the sintering process. The microstructure, PTCR and reducing gas sensing characteristics of the porous \((\text{Ba},\text{Sr})\text{TiO}_3\) ceramics were examined.

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Experimental Procedure

High-purity Y-doped (Ba,Sr)TiO$_3$ (Toho Titanium Co., Ltd., Japan) and nano-size carbon black (HIBLACK 170, 58 nm, Korea Carbon Black Co. Ltd., Korea) were used as the starting powders. The Y-doped (Ba,Sr)TiO$_3$ powders contained SrTiO$_3$ (19.2 mol%) and Y$_2$O$_3$ (0.2 mol%). The mean particle size and ferroelectric Curie temperature of the Y-doped (Ba,Sr)TiO$_3$ powder were 0.18 µm and 61 ºC, respectively. Y-doped (Ba,Sr)TiO$_3$ powders were ball-milled for 72 h in an ethanol medium using a plastic pot and ZrO$_2$ balls.

As a pore precursor, 0 vol% to 60 vol% carbon black was added to the Y-doped (Ba,Sr)TiO$_3$ powders. Table 1 lists the samples prepared in this study. As the nano-size carbon black tends to agglomerate, ultrasonic treatment and freeze drying were attempted simultaneously to obtain a uniform dispersion of carbon black within the (Ba,Sr)TiO$_3$ powders. To prevent the agglomeration of nano-size carbon black, the slurries were prepared by adding Y-doped (Ba,Sr)TiO$_3$ powders and carbon black to distilled water, followed by the addition of two types of ammonium salts of polycarboxylic acid (Cerasperse 5468-CF, HS-dispersant 5801, San Nopco Korea Ltd., Korea) were used as the starting powders. The Y-doped (Ba,Sr)TiO$_3$ ceramics was estimated using the Archimedes principle and the relative density was calculated from the relationship between the measured and theoretical densities.

The microstructure and crystalline structure of the samples were analyzed by scanning electron microscopy (SEM : JSM-5500, Jeol) and X-ray diffraction (XRD : PW-1710, Philips), respectively. The mean grain size of the (Ba,Sr)TiO$_3$ ceramics was estimated using the linear intercept method [17] after thermal etching at 1270 ºC for 30 minutes in air. The open pore size distribution was examined using mercury porosimetry (Poresizer 9320, Micromeritics).

Commercial paste (Ag-Zn, Daejoo Electronic Materials Co. Ltd., Korea) was spread thinly on both surfaces of the samples using a screen printing method to maintain Ohmic contact during the electrical resistivity measurements. The paste was then dried at 150 ºC for 20 minutes. Ag paste was then coated onto the Ohmic paste layers. The resulting pastes were baked at 560 ºC in air for 10 minutes at a heating rate of 5 K/min. The real-time electrical resistivity of the (Ba,Sr)TiO$_3$ ceramics was measured at various temperatures ranging from room temperature to 300 ºC using a data-acquisition system equipped with a digital multimeter (10$^{-4}$-10$^{-12}$ Ω). The effects of the measuring gas atmospheres on the PTCR characteristics of the BST/CB40 sample were investigated to determine the gas sensing characteristics. Finally, complex impedance analysis was carried out using an impedance analyzer (HP LF 4192A) at room temperature over the frequency range, 5 Hz to 13 MHz.

Table 1. Compositions and symbols of the samples.

<table>
<thead>
<tr>
<th>Symbol of samples</th>
<th>Composition (vol%)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>(Ba,Sr)TiO$_3$</td>
</tr>
<tr>
<td>BST</td>
<td>100</td>
</tr>
<tr>
<td>BST/CB10</td>
<td>90</td>
</tr>
<tr>
<td>BST/CB20</td>
<td>80</td>
</tr>
<tr>
<td>BST/CB30</td>
<td>70</td>
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<tr>
<td>BST/CB40</td>
<td>60</td>
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<tr>
<td>BST/CB50</td>
<td>50</td>
</tr>
<tr>
<td>BST/CB60</td>
<td>40</td>
</tr>
</tbody>
</table>

Table 2. Conditions for preparing mixed powders of (Ba,Sr)TiO$_3$ and carbon black.

<table>
<thead>
<tr>
<th>Powder</th>
<th>(Ba,Sr)TiO$_3$ (17 g basis)</th>
<th>Carbon black (3 g basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount of dispersant</td>
<td>1 g (Cerasperse 5468-CF)</td>
<td>1 g (HS-dispersant 5801)</td>
</tr>
<tr>
<td>Amount of DI-water</td>
<td>20 ml</td>
<td>30 ml</td>
</tr>
</tbody>
</table>

Fig. 1 shows SEM images of the mixed powder for the freeze-dried BST/CB30 sample. Fig. 1(a) shows cross-section views of the freeze-dried sample. Directional pore channels, ~ few tens of µm in width, were observed. These channels were formed by the sublimation of columnar ice formed during freezing. Fig. 1(b) and (c) shows images of the mixed powder taken at the pore channels that had been stirred for 12 h and sonicated for 3 minutes before freeze-drying. As shown in Fig. 1(b), agglomerated carbon black was observed frequently. In contrast, there was no agglomerated carbon black in Fig. 1(c). This shows
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that the combined sonication and freeze-drying process is an effective means of dispersing nano-size carbon black.

Fig. 2 shows the DTA and TGA data for mixed powders of (Ba,Sr)TiO$_3$ and 30 vol% carbon black to determine the appropriate burning-out conditions of the dispersants and carbon black after freeze-drying. A slight weight loss was observed from room temperature to 200 °C, which was attributed to the vaporization of moisture and organic compounds absorbed on the power surface. Two small peaks at approximately 300 °C were assigned to the burning out of the dispersants (ammonium salts of polycarboxylic acid) added to disperse (Ba,Sr)TiO$_3$ and carbon black during the slurry fabrication process. A large and broad exothermic peak was also observed at 534 °C due to the following reactions [18]:

\[
\begin{align*}
C(s) + O_2 (g) \rightarrow CO_2 (g) \uparrow & \quad \Delta H = - 393.5 \text{ kJ/mol} \\
C(s) + 1/2O_2 (g) \rightarrow CO (g) \uparrow & \quad \Delta H = - 110.5 \text{ kJ/mol}
\end{align*}
\]

Based on DTA/TGA analysis, the dispersants and carbon black were burnt out at 750 °C for 5 h in air.

Fig. 3 shows SEM images of the thermally etched surfaces of (Ba,Sr)TiO$_3$ ceramics. The pores in the BST sample were small but increased gradually in size with increasing carbon black content because the pores, which had formed at earlier carbon black sites between the (Ba,Sr)TiO$_3$ grains, remained after sintering. The size and shape of the residual pores between BST/CB20 and BST/CB40 were similar, and the area of those increased gradually. The grain sizes of the (Ba,Sr)TiO$_3$ ceramics decreased slightly with increasing carbon black content. The mean grain size of the (Ba,Sr)TiO$_3$ ceramics was estimated using the linear intercept method.

Fig. 4 shows the porosities and grain sizes of the porous (Ba,Sr)TiO$_3$ ceramics. The porosities of the samples increased slightly with increasing carbon black content. For example, the porosities of the BST and BST/CB60 samples were 7.3% and 8.7%, respectively. On the other hand, the grain sizes of the BST samples decreased slightly from 7.9 µm to 5.2 µm by the addition of 60 vol% carbon black content. This means that the pores generated by burning-out carbon black inhibits (Ba,Sr)TiO$_3$ grain growth. The grain boundary area in porous (Ba,Sr)TiO$_3$ ceramics was calculated using the linear intercept method because the area of the grain boundaries is inversely proportional to the grain size. The grain boundary area in porous (Ba,Sr)TiO$_3$ ceramics increased with increasing carbon content...
black content. For example, grain boundary area in the BST, BST/CB40 and BST/CB60 samples were 0.25\,\mu m^2/\mu m^3, 0.37\,\mu m^2/\mu m^3 and 0.39\,\mu m^2/\mu m^3, respectively.

Fig. 5 shows the pore size distributions of porous (Ba,Sr)TiO$_3$. The samples except for the BST/CB60 sample consisted mainly of submicrometre-sized pores ranging 0.2\,\mu m to 0.6\,\mu m. For the BST/CB60 sample, the pore size showed a bimodal distribution with two peaks at 20\,\mu m and 160\,\mu m. The large pores in the BST/CB60 sample were attributed to the agglomeration of carbon black during the powder mixing process. The mean pore sizes in the samples ranging from BST to BST/CB40 increased slightly with increasing carbon black content. The mean pore sizes of the BST, BST/CB40 and BST/CB60 samples were 0.34\,\mu m, 0.42\,\mu m and 24.4\,\mu m, respectively.

Fig. 6 shows XRD patterns of the porous (Ba,Sr)TiO$_3$ ceramics measured at room temperature. In all samples, the (Ba,Sr)TiO$_3$ phase was observed as the major phase with the Ba$_2$TiSi$_2$O$_8$ (fresnoite) phase as a minor phase detected at 27.0$^\circ$ and 28.9$^\circ$. The Ba$_2$TiSi$_2$O$_8$ phase might have formed by a reaction between BaO, TiO$_2$ and SiO$_2$, which were added as sintering aids during powder production. This suggests that the carbon black had been burnt out completely and there was no reaction between the carbon black and (Ba,Sr)TiO$_3$ during the sintering process. The XRD patterns of the samples was also measured at a high angle (73-78$^\circ$) because it was difficult to analyze the crystalline structure due to the structural similarities between the cubic and tetragonal phases in (Ba,Sr)TiO$_3$ ceramics. The split between the two peaks corresponding to the (103) and (310) planes at approximately 75$^\circ$, indicates that the (Ba,Sr)TiO$_3$ ceramics have a tetragonal crystalline structure. The lattice parameters ($a$, $c$) and tetragonality ($c/a$ ratio) of the tetragonal phases were calculated from the XRD patterns using the Nelson-Riley extrapolation method [19]. The lattice parameters, $a$ and $c$ of BST sample were 3.966\,\AA{} and 4.025\,\AA{}, respectively. The tetragonality of BST sample was 1.015. There was no appreciable difference in the lattice parameters and tetragonality with the carbon
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black content, indicating that carbon was not dissolved in the tetragonal structure. Carbon cannot occupy the interstitial sites of (Ba,Sr)TiO$_3$ ceramics easily due to the large difference between the size of the octahedral site surrounding the O$^2_{\text{ions}}$ and the atomic radius of carbon (0.58 Å and 0.77 Å [18], respectively).

Fig. 7 shows the electrical resistivity of the porous (Ba,Sr)TiO$_3$ ceramics as a function of temperature. Typical PTCR behaviors were observed in all samples. The PTCR jump is defined as the ratio of the maximum resistivity ($\rho_{\text{max}}$) to the room temperature resistivity ($\rho_{\text{min}}$). The PTCR jump of all samples increased with increasing carbon black content. In particular, the PTCR jumps of the BST and BST/CB40 samples were $1.54 \times 10^5$ and $4.98 \times 10^6$, respectively. On the other hand, the maximum resistivity of the BST/CB60 sample could not be measured due to the limit in the measuring range of the multi-meter ($< 10^8$). The increase in resistivity at room temperature was attributed mainly to the increase in porosity. The resistivity of the samples increased linearly with temperature from 100 $^\circ$C to 150 $^\circ$C. The slope of the resistivity vs. temperature curve ($\log_{10}\rho/T$) was calculated from 100 $^\circ$C to 150 $^\circ$C. The slope of the porous (Ba,Sr)TiO$_3$ ceramics prepared by the addition of carbon black was larger than that of the BST sample. In particular, the slope of the BST/CB60 sample was the largest of the samples assessed. This is in the same order as that observed for the PTCR jump. The increased PTCR jump was attributed to the increased grain boundary area and pore size. The porous microstructure enables the adsorption of oxygen at the grain boundaries, which can increase the potential barrier at the grain boundaries, as explained by the barrier model proposed by Heywang.

Complex impedance analysis was carried out as a function of frequency to determine the grain interior and grain boundary resistance. Fig. 8 shows the complex impedance spectra of the samples measured at room temperature. No remarkable difference in grain interior resistivity was observed between the samples, whereas the grain boundary resistivity increased with increasing carbon black content. The sintered compact resistivity of the BST, BST/CB40 and BST/CB60 samples at room temperature was 14.4, 21.8 and 642 $\Omega$cm, respectively. The corresponding grain boundary resistivity ($\rho_{\text{GB,RT}}$) was 11.7, 18.3 and 634 $\Omega$cm. This suggests that the resistivity of a sintered compact depends mainly on the grain boundaries.

The effect of a reducing gas on the PTCR characteristics of (Ba,Sr)TiO$_3$ ceramics was examined by heating the BST/CB40 sample from 25 $^\circ$C to 300 $^\circ$C followed by cooling from 300 $^\circ$C to 25 $^\circ$C. Fig. 9 shows the electrical resistivity in the BST/40CB sample measured in a H$_2$ atmosphere. The PTCR characteristics in a H$_2$ atmospheres during cooling are significantly different from those during heating. This can be explained by the fact that hydrogen atoms diffuse along the grain boundaries and react with chemisorbed oxygen.
atoms. Hence, chemisorbed oxygen atoms are consumed and conduction electrons are released. This leads to a decrease in the potential barrier due to an increase in the number of conduction electrons. This suggests that (Ba,Sr)TiO$_3$ ceramics are strongly reduced and the pores are important factors in this process.

The complex impedance spectra of the BST/CB40 sample were measured at room temperature to examine the change in grain boundary resistance due to the adsorption/desorption of oxygen (Fig. 10). The grain boundary resistivity at room temperature after the heating and cooling cycles in air and H$_2$, were 18.7 and 10.6 $\Omega$cm, respectively. The change in grain boundary resistivity may originate from a change in acceptor-state level concentration accompanied by the adsorption and desorption of oxygen at the grain boundary regions. The low grain boundary resistivity in porous (Ba,Sr)TiO$_3$ ceramics achieved after the heating and cooling cycles in a reducing atmosphere decreased the potential barrier due to an increase in the number of conduction electrons caused by the desorption of oxygen chemisorbed at the grain boundaries.

Conclusions

A mixture of (Ba,Sr)TiO$_3$ and carbon black was prepared by sonication and freeze drying. Porous Y-doped (Ba,Sr)TiO$_3$ ceramics were prepared by sintering. The microstructure, PTCR characteristics and reducing gas sensing characteristics of the porous Y-doped (Ba,Sr)TiO$_3$ ceramics were investigated. The results can be summarized as follows:

1. The combined mixing process of sonication and freeze drying is an effective method for preparing a homogeneous dispersion of nano-size carbon black.

2. The porosity of the burnt-out (Ba,Sr)TiO$_3$ ceramics increased with increasing carbon black content. The PTCR jump of the (Ba,Sr)TiO$_3$ ceramics prepared by adding carbon black was $>10^4$, which increased slightly with increasing carbon black.

3. The change in the resistivity of the porous (Ba,Sr)TiO$_3$ ceramics can be explained in terms of the change in potential barrier height due to the chemisorption/desorption of oxygen atoms at the grain boundaries.

Acknowledgements

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References