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Fabrication and PTCR Characteristics of Porous Barium Titanate Thermistors using Graphite Powders

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New porous $BaTiO_3$ thermistors were fabricated using graphite powders (0 to 10 wt.%) and their porosities were in the range of 9.1% to 16.2%. As results of impedance analysis, it was confirmed that the pores affected the grain-boundary resistance and the bulk (grain interior) resistance was constant as about 25 Ω at room temperature. The magnitude of PTCR effect (ρ_{max}/ρ) markedly increased from 3 orders to 7 orders without addition of any acceptor dopant such as Mn or Cr.

Key words : PTC thermister, $BaTiO_3$, Impedance spectra

I. Introduction

It is well known that the doped barium titanate ($BaTiO_3$) shows a distinct positive temperature coefficient of resistivity (PTCR) effect in a certain temperature range near the Curie temperature.[1-3] In this phenomenon, the grain boundary plays an important role because single crystals of the same composition do not have these characteristics, but the details of the PTCR mechanism is not yet clear.[4] These PTC thermistors are widely used as constant temperature resistors, current-limiting resistors, temperature sensors, etc.

In general, to control and/or improve PTCR properties of $BaTiO_3$ ceramics, various kinds of additives are used; Sb, La, Nb, or Y element for semiconduction and resistivity adjustment, Si, Ge or Al for liquid-phase sintering and to produce lower sintering temperatures, and Mn, Cr, Fe, or Cu for barrier layer control and a high PTCR magnitude, respectively.[5-7]

According to the reports of many investigators,[8-10] a Mn dopant yields high PTCR effects (approximately 7 orders of magnitude). In this case, Mn forms acceptor levels at the grain boundary layers of $BaTiO_3$ and the resulting high concentration of acceptor levels contributes to the increase in magnitude of the PTCR effect.[8,11] However, M. Kuwabara[11,12] reported that porous $BaTiO_3$ prepared from $BaTi(C_2O_4)_2 \cdot 4H_2O$ without addition of any acceptor dopant such as Mn or Cr, exhibited a PTCR effect of more than 7 orders of magnitude. It is believed that the porosity of the sintered body is one of the important factors for improvement of PTCR effects.

The objective of the present study is to fabricate new porous $BaTiO_3$ thermistors using graphite powders instead of a Mn acceptor dopant and to confirm the improvement of PTCR effects. The basic composition of the $BaTiO_3$ thermistors was the $BaTiO_3$-0.1 mol.% Sb_2O_3-0.25 wt.% SiO_2 system and various amounts of graphite were added into the basic composition. For the porous $BaTiO_3$ thermistors using graphite, the density, porosity, microstructure, impedance spectra, and resistivity-temperature characteristics were investigated, systematically.

II. Experimental Procedure

Reagent-grade $BaTiO_3$, tetraethyl orthosilicate (TEOS) and graphite, and high-purity (99.9%) Sb_2O_3 were used as raw materials. Thermistors of five batches shown in Table 1 were fabricated by the processing shown in Fig. 1.

First of all, the powders added 0.1 mol.% Sb_2O_3 in $BaTiO_3$ were mixed with ethanol in a ball mill and dried in air. Secondly, the appropriate amount of insoluble TEOS as a 0.25 wt.% SiO_2 source was diluted by means of ethanol to react easily with water. This diluted TEOS was stirred at 60°C for 30 minutes using a sol-gel processing apparatus and then stirred again after adding the appropriate amounts of HCl and distilled water. TEOS becomes a sol with high viscosity by hydrolysis and dehydration-condensation reactions. At this time, after stirring the mixed sol was added to the already prepared powders of $BaTiO_3$ and 0.1 mol.% Sb_2O_3, the graphite powders (-100 mesh) were finally added, mixed and then gelled. The reason for adding graphite during gelation after stirring for some time is to achieve a uniform distribution of graphite powders of relatively low density.

After drying, the adequate amount of a 1.5 wt.% aq. solution of PVA was added to the powders and mixed by using an agate mortar. The powders were then uniaxially pressed into pellets of 10 mm in diameter and 2 mm in thickness, under a pressure of 700 kg/cm². These samples were sintered at 1260°C for 1 hour in air.

For comparison of the density and porosity in the sintered samples, the bulk density (d) and the porosity (p, %) were calculated by equations $d=W_d/(W_{sat}-W_{sus})$ and $p=(W_{sat}-W_d)/(W_{sat}-W_{sus})\times 100$, respectively, where W_d is the dry weight, W_{sat} is the saturated weight, and W_{sus} is the suspended weight. The microstructure for the fracture surface of the samples was observed with a scanning electron microscopy (SEM, JXA-8600, JEOL).

The polished samples for electrical measurements were electroded with Ag-In-Ga paste for ohmic contact by the silk-screen printing method and thermally treated at 600°C for 10 minutes. The impedance analysis (1260 Impedance/Gain Phase Analyzer, Solatron Instrument) was performed at room temperature over the frequency range of 100 mHz to 10 MHz. The resistivity versus temperature characteristics of the samples were measured from 0°C to 240°C in air at a rate of about 0.2°C/min using a two-probe method.

Table 1. Composition and PTCR Effect (ρ_{max}/ρ) of 0.1 mol.% Sb_2O_3 and 0.25 wt.% SiO_2-Doped $BaTiO_3$ Thermistors Containing 0, 3, 5, 7 and 10 wt.% Graphite, respectively

Sample	Composition (wt.%)				Magnitude of PTCR effect $(\frac{\rho_{max}}{\rho})^*$
	$BaTiO_3$	Sb_2O_3	SiO_2	Graphite	
G0	99.6266	0.1246	0.2494	0	4.52×10^3
G3	96.7313	0.1210	0.2421	2.9056	1.35×10^7
G5	94.8932	0.1187	0.2375	4.7506	1.36×10^7
G7	93.1236	0.1165	0.2331	6.5268	1.10×10^7
G10	90.5897	0.1133	0.2268	9.0703	1.31×10^7

*ρ_{max} is the maximum resistivity attained slightly above T_c and ρ is the minimum resistivity below T_c.

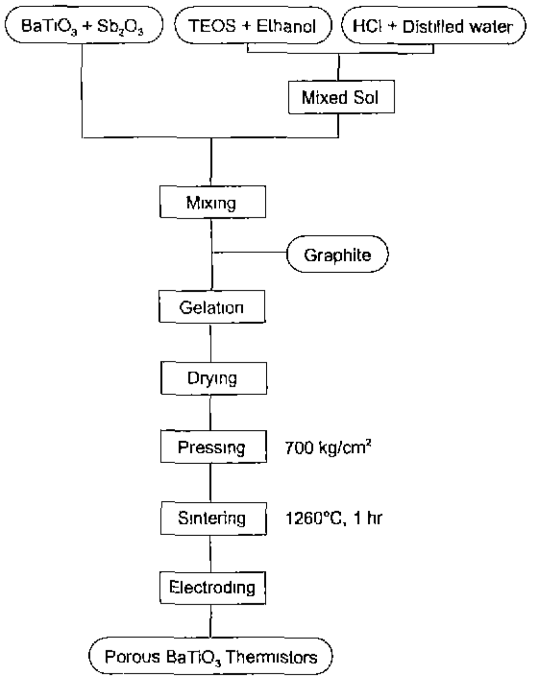

Fig. 1. Flow chart for the fabrication of porous $BaTiO_3$ thermistors.

III. Results and Discussion

The results of the density and porosity measurements of the samples sintered at 1260°C for 1 hour are shown in Fig. 2. The bulk density of no graphite-added sample was 5.12. In the case of 3 wt.% graphite-added sample, the density decreased to 4.95. As the graphite content increases to 5, 7, and 10 wt.%, respectively, the density decreased gradually to 4.76. On the other hand, the apparent porosity increased in the range of 9.1% to 16.2% with increasing graphite contents.

Figure 3 shows SEM photographs for the fracture surfaces of the sintered samples. It can be seen that the samples containing graphite have many pores and their pore sizes increased with the graphite contents. However, the grain size constantly maintained about 10 μm without regard to the graphite contents. These results are in keeping with the tendency of the density and porosity.

Complex impedance spectra for samples with various graphite content, measured at room temperature, are shown in Fig. 4. The real part (Z') and imaginary part (-Z") of the impedance were presented to identify the bulk (grain interior) resistance (i.e., the high-frequency intercept with Z'), the grain-boundary resistance (the diameter of low-frequency semicircle), and the role of porosity. Figure 4 shows that the bulk resistance was unchanged with increasing graphite contents, remaining constant at about 25 Ω and this phenomenon is in good agreement with previous result.[13] However, the grain-boundary resistance was increased from 12 Ω for the sample G3 to 65 Ω for the sample G10. As the graphite

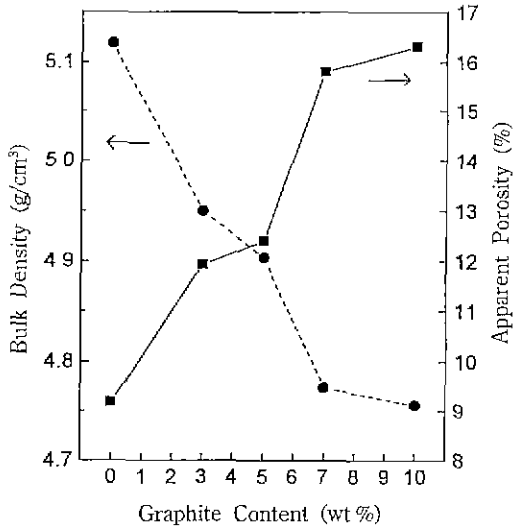

Fig. 2. Bulk density and apparent porosity of the 0.1 mol.% Sb_2O_3 and 0.25 wt.% SiO_2-doped $BaTiO_3$ thermistors as a function of graphite contents.

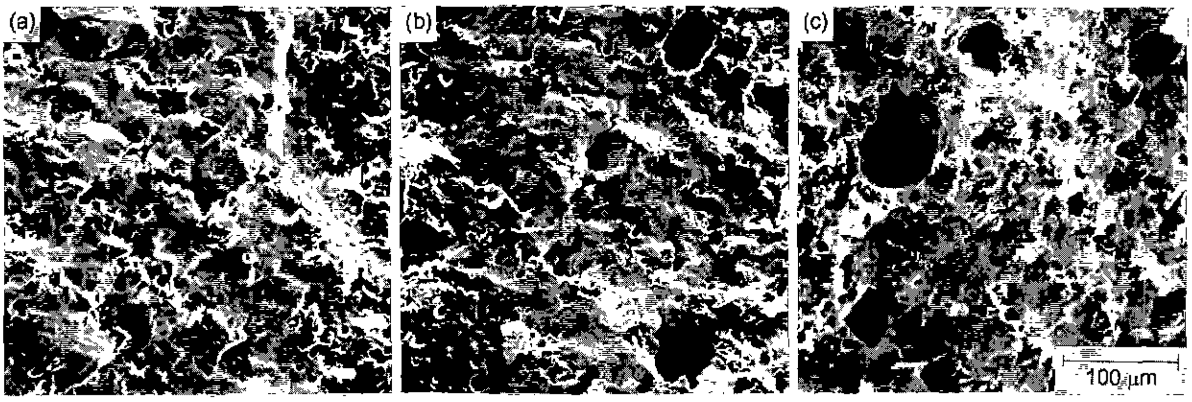

Fig. 3. Scanning electron micrographs for the fracture surfaces of the 0.1 mol.% Sb_2O_3 and 0.25 wt.%

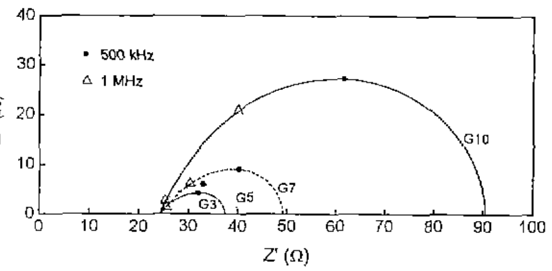

Fig. 4. Complex impedance spectra of 0.1 mol.% Sb_2O_3 and 0.25 wt.% SiO_2-doped $BaTiO_3$ thermistors with various graphite contents.

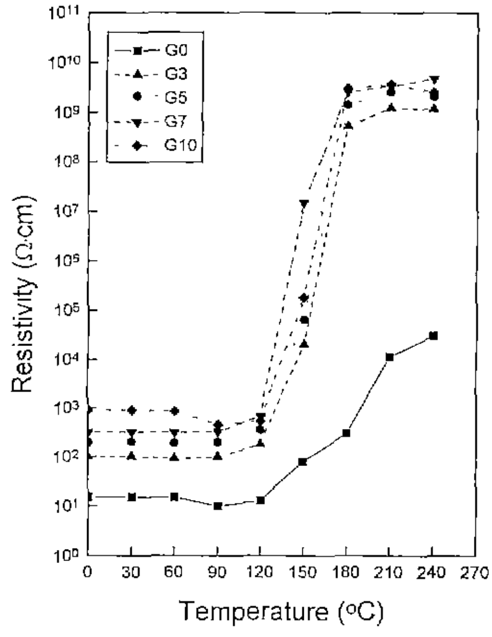

Fig. 5. Resistivity versus temperature characteristics of 0.1 mol.% Sb_2O_3 and 0.25 wt.% SiO_2-doped $BaTiO_3$ thermistors with various graphite contents.

content increases, the low-frequency semicircle was enlarged by the porosity while maintaining its shape. The change of the grain-boundary resistance by porosity is similar to the result of Brailsford and Hohnke.[14] In summary, the porous samples fabricated in the present study maintained a constant level of the bulk resistance whereas their grain-boundary resistances varied with porosity. The pores did not affect the bulk resistance and affected the grain-boundary resistance.

The PTCR characteristics of the samples are shown in Table 1 and Fig. 5. The magnitude of PTCR effect can be expressed as $\frac{\rho_{max}}{\rho}$, where ρ_{max} is the maximum resistivity attained above T_c and ρ is the minimum resistivity below T_c. In the case of graphite-added samples compared to the sample without graphite, the magnitude of PTCR effect markedly increased from 3 orders to 7 orders. It is assumed that this phenomenon is due to the decrease of mobility and concentration of carrier (electron) associated with the decrease of contact area of grain boundaries in the porous body. These results are in good agreement with Kuwabara's report[11] for porous $BaTiO_3$ ceramics. The PTCR characteristics of the porous $BaTiO_3$ thermistors using graphite obtained in the present study is also similar to those of the Mn-doped $BaTiO_3$.[9]

IV. Summary

In the present study, the porous $BaTiO_3$ thermistors were newly fabricated using graphite powders. The basic composition of $BaTiO_3$ thermistors was the 0.1 mol.% Sb_2O_3 and 0.25 wt.% SiO_2-doped $BaTiO_3$. As increasing graphite contents (0, 3, 5, 7, and 10 wt.%, respectively), the bulk density was decreased from 5.12 to 4.76 and the apparent density was increased from 9.1% to 16.2%. The increase of these porosity was also confirmed by SEM photographs of the fracture surfaces.

Complex impedance spectra conducted at room temperature showed that the bulk (grain interior) resistance was constant value of about 25 Ω regardless of graphite contents. The grain-boundary resistance was increased from 12 Ω to 65 Ω for graphite addition of 3 wt.% to 10 wt.%. Accordingly, it was confirmed that the pores affect only grain-boundary resistance and affect also PTCR effects.

The PTCR characteristics were evaluated by resistivity versus temperature plot. The magnitude of PTCR effect (ρ_{max}/ρ) markedly increased from 3 orders to 7 orders by only graphite addition without any acceptor dopant such as Mn, Cr, Fe, Cr, etc.

Acknowledgement

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