Influence of Cooling Duration on the PTCR Effect of Sm$^{3+}$-doped BaTiO$_3$-based Ceramics Sintered in a Reducing Atmosphere

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Abstract. The influence of cooling duration on the electrical properties and the positive temperature coefficient of resistance (PTCR) characteristics of Sm-doped BaTiO$_3$ (BST) ceramics fired at 1200 °C for 30 min in a reducing atmosphere and deoxidized at 800 °C for 1 h were investigated. The cooling duration influenced the PTCR characteristics of the BST specimens. The room-temperature resistivity of the samples firstly reduced and then increased with the increase in the content of Sm$_2$O$_3$. A long cooling duration resulted in low resistivity of the BST ceramics. Meanwhile, the room-temperature resistivity of the BST ceramics decreased with an increase in cooling duration. Furthermore, the S2 samples exhibited a remarkable PTCR effect. The samples exhibited a resistance jump greater than 3.2 orders of magnitude and a low room-temperature resistivity of 228.4Ω·cm.

1. Introduction

It is well known that Barium titanate (BaTiO$_3$) is a ferroelectric material, which transforms from a tetragonal perovskite structure at room temperature into a Para electric structure at the curie temperature [1]. Ti site or Ba site of BaTiO$_3$ are substituted by small quantities of pentavalent impurities (Nb$^{5+}$, Ta$^{5+}$, etc.) or trivalent donor (Y$^{3+}$, Sm$^{3+}$, etc.) becomes a semiconducting, respectively. Moreover they have the positive temperature coefficient of resistivity (PTCR) effect [2, 3], the phenomenon was explained by Heywang [4] and Jonker [5].

Semiconducting BaTiO$_3$-based PTCR ceramics are sintered by traditional method, which have a high room-temperature resistance. However, it is difficult to further decrease the room-temperature resistivity of the samples, and being attributed to the own characteristics of BaTiO$_3$-based materials. In order to further reduce room-temperature resistance, multilayer PTCR ceramics are prepared [6–8] by way of a reduction–reoxidation method [9]. Niimi et al. [10] recently reported that the ion radius of the donor dopant affects the PTCR characteristic of samples. Zubair M.A. et al. [11] found that a reduction in room-temperature resistance can be due to increase cooling rate. Chen H.P. [12] also indicated that PTC effect could be enhanced by a slower cooling rate. In addition, several researchers have proposed theory of grain-boundary oxygen adsorption and diffusion [13–15].

However, few studies have investigated the influence of cooling duration on electrical properties and PTCR effect of BST ceramics in a reducing atmosphere. Therefore, the PTCR characteristics of
BaTiO₃-based ceramics with doping Sm₂O₃ sintered in a reducing atmosphere was investigated in this paper.

2. Experimental Procedures

The starting materials were high-purity BaCO₃, TiO₂, SiO₂, and Sm₂O₃, and they were weighed according to the following formula: \((\text{Ba}_{1.022-x}\text{Sm}_x\text{TiO}_3 + 0.007 \text{ mol SiO}_2\text{)}\) (BST). In this experiment, the components were mixed by wet ball milling for 4 h in deionized water using zirconia balls in a polyurethane jar and then calcined at 1150 °C for 2 h in air. After drying and sieving, the calcined powder was ground again by ball milling for 4 h. After mixing, the dried powder was mixed with dispersant, defoamer, solvent, and binder by ball milling for 18 h in a nylon pot and cast into green sheets of 55-μm thickness by the doctor-blade method. These sheets were stacked and laminated at 50 °C to form a ceramic block, which was cut into rectangular blocks (5.7 × 3.9 × 1 mm).

Subsequently, the binder was removed by heating at 280 °C in air. Sintering was conducted in an aluminum tube at 1200°C for 30 min in a reducing atmosphere (3% H₂/N₂), with the heating and cooling rates being 5 and 3 °C/min, respectively, at a flow rate of 200 cm³/min under a pressure of 1 atm. Three different cooling curves were used for our present experiment, as shown in Table 1. The sintered BST ceramics were deoxidized at 800 °C in air for 1 h, and the surfaces were rubbed with In–Ga alloy (60:40) to form electrodes. Resistance at room temperature was measured by a digital multimeter, and the temperature dependence of resistance was measured in a temperature-programmable furnace (ZWX-B, Huazhong University of Science and Technology, China) at a heating rate of 1.6 °C/min in the range of 25–250 °C.

Table 1. The various cooling curves during cooling.

| The temperature range (°C) | Samples and the cooling time (min) |
|----------------------------|----------------------------------|
| 1200→1150                  | 17 17 FC                         |
| 1150→1150                  | 30 0 0                            |
| 1150→800                   | 117 117 FC                       |
| 800→Rt.                    | FC FC FC                         |

†: Furnace Cooling

3. Results and Discussion

3.1. Influence of cooling duration on electrical properties

The dependence of the room-temperature resistivity of the BST based ceramics, deoxidized at 800 °C for 1 h after firing at 1200 °C for 30 min in a reducing atmosphere, on the dopant content is shown in Figure 1. From the figure, we can see that the room-temperature resistivity of the BST ceramics nearly decrease with increase in the concentration of doped Sm³⁺ for samples subjected to a long cooling time; however, it initially decreases and then increases as a function of the donor-doped content at a shot cooling time. It is indicated that the slower the cooling time, the smaller is the room-temperature resistivity of the specimens. Furthermore, the increase in resistance is attributed to the ionic compensation resulting from the formation of oxygen and cation vacancies. The decrease in resistance is generally due to the oxygen vacancies and the following electron compensation [16, 17]:

\[
O_2 → V_{O}^{\bullet \bullet} + \frac{1}{2}O_2 + 2e'
\]  
\[
\text{Sm}_2O_3 → 2\text{Sm}_{\beta d}^* + 2O_2 + \frac{1}{2}O_2 + 2e'
\]
Moreover, the content of oxygen vacancies are increasingly higher at slower cooling rates. Thus, the concentration of the electrons plays a dominant role. So the room-temperature resistivity of the BST based ceramics is much less than that of the same samples sintered in air.

![Figure 1](image1.png)

**Figure 1.** The room-temperature resistivity is as a function of the dopant concentration at different cooling methods.

### 3.2. Influence of the donor-doped content on PTCR effect

The temperature dependence of resistivity of the BST ceramics that is S2 samples as functions of the different Sm$^{3+}$-doped concentration of 0.2 mol% – 0.8 mol% are as shown in Figure 2. It is shown that the room-temperature resistivity of the ceramics that are deoxidized at 800 °C for 1 h after firing at 1200 °C for 30 min initially reduces and then increases with an increase in the dopant content from 0.2 mol% to 0.8 mol%. While, the critical donor-doped content for the S2 samples is 0.4 mol%. Moreover, the S2 ceramics doped Sm$^{3+}$ of 0.4 mol% exhibit a significant PTCR effect, with a resistivity jump of 3.2 orders of magnitude, along with a low mean room-temperature resistivity of 228.4 Ω·cm. However, although the resistivity jump of the 0.2 mol% Sm$^{3+}$-doped BST ceramics is exhibited by 3.4 orders of magnitude, the room-temperature resistivity is slightly higher than that of the specimen with doping Sm$^{3+}$ of 0.4 mol%. According to Heywang-Jonker model [4, 5], the PTC effect is the grain-boundaries effect, and a better PTCR effect may be attributed to the higher height of the potential Schottky barrier.

![Figure 2](image2.png)

**Figure 2.** The temperature dependence of resistivity of the BST ceramics is as a function of the different Sm-doped contents.

### 3.3. Influence of cooling process on PTCR characteristics

The electrical properties and PTCR effect of the 0.4 mol% Sm-doped BST based ceramics for various cooling duration are as shown in Table 2. The ceramics are cooled at different cooling process after sintering at 1200 °C for 30 min in a reducing atmosphere and then deoxidized at 800 °C for 1 h. The cooling curves and their corresponding times are shown in Table 1. From the Table 2, we can see that...
the room-temperature resistivity of the S1, S2, and S3 samples are 115.8, 228.4, and 44056.6 Ω-cm, respectively. Moreover, they show a remarkable PTCR effect with a resistance-jumping ratio of 3.0, 3.2, and 3.3, respectively. Furthermore, the temperature coefficient ($\alpha_T$) of the BST ceramics is also observed, whereas $\alpha_T$ is the following formula: $\alpha_T = \left[ \frac{\ln R_{T_{c+25^\circ C}} - \ln R_{T_{c+10^\circ C}}}{10^\circ C} \right] \times 100\%$, where $T_c$ is the Curie temperature, $R_{T_{c+25^\circ C}}$ is the resistance of the samples at a temperature of $T_c+25^\circ C$, and so does $R_{T_{c+10^\circ C}}$. On comparing the experimental results, the room-temperature resistivity of the S1 samples is found to be the lowest. This is because the content of oxygen vacancies in S1 specimens is the highest. According to Eq. (1), it is found that the longer the cooling duration, the higher is the concentration of electrons in the samples, thus resulting in a smaller room-temperature resistivity. This result indicates that the electrical properties of the BST samples are closely related to the cooling duration. In addition, we can see that the $\alpha_T$ is more than that of both S2 and S3 ceramics in Table 2. It is shown that the S1 samples are very sensitive to the temperature change. Therefore, we found that the S1 samples can exhibit significant PTCR characteristics.

### Table 2. The PTCR characteristics of the BST ceramics with doping Sm3+ of 0.4 mol% for the different cooling duration.

| Sample | $\rho$ (Ω-cm) | $\text{Lg}(R_{\text{max}}/R_{\text{min}})$ | $\alpha_T$ (%) |
|--------|---------------|---------------------------------|--------------|
| S1     | 115.8         | 3.0                             | 2.9          |
| S2     | 228.4         | 3.2                             | 3.0          |
| S3     | 44056.6       | 3.3                             | 2.4          |

### 4. Conclusion

We investigated the influence of cooling duration on the PTCR characteristics and electrical properties of BST ceramics deoxidized at 800 °C for 1 h after firing at 1200 °C for 30 min in a reducing atmosphere. The room-temperature resistivity firstly decreased and then increased with of the increasing of the content of Sm$_2$O$_3$. Long cooling duration resulted in low room-temperature resistivity of the BST samples. Furthermore, the resistivity of the grain boundaries of the samples decreased with the increase in cooling duration. Lastly, the S2 samples deoxidized at 800 °C for 1 h after sintering at 1200 °C for 30 min in a reducing atmosphere exhibited a resistance jump greater than 3.2 orders of magnitude and a low RT resistivity of 228.4 Ω-cm.

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