The influence of calcination temperature on the PTCR effect in (Ba$_{x-0.002}$Sm$_{0.002}$) TiO$_3$ ceramics prepared by the reduction sintering-reoxidation method

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Abstract. We investigate the effect of calcination temperature on the positive temperature coefficient of resistivity (PTCR) characteristics in (Ba$_{x-0.002}$Sm$_{0.002}$)TiO$_3$ ceramics that were fired at 1250 °C for 30 min in a reducing atmosphere and reoxidized at 800 °C for 1 h in air. The results indicate that the room-temperature resistivity first decreased and then increased as calcination temperature increased from 1000 °C to 1200 °C. Moreover, the critical calcination temperature of 1150 °C is experimentally determined. The samples have a low room-temperature resistivity of 38.4 Ω·cm and exhibit a significant PTCR effect with a resistance jump of 2.1 orders of magnitude. Furthermore, the room-temperature resistivity of the S7 samples doped with a small amount of Mn(NO$_3$)$_2$ is much higher than that of the S3 specimens not doped with Mn(NO$_3$)$_2$ in our work.

1. Introduction

Barium titanate (BaTiO$_3$) is a ferroelectric material that becomes a semiconducting material and exhibits an anomalous increase in resistance at the Curie temperature when ions at the A or B site are replaced by small quantities of a trivalent donor (such as Y$^{3+}$, Sm$^{3+}$, etc.) or pentavalent impurities [1, 2]. The phenomenon is generally known as the positive temperature coefficient of resistivity (PTCR) effect, and has been explained by Heywang [3] and Jonker [4]. Nowadays, lowering resistance for PTCR ceramics has become a hot topic. However, it is difficult to obtain significantly lower room-temperature resistivity for BaTiO$_3$-based samples prepared using traditional methods. To further reduce the room-temperature resistance, samples with a laminated structure can be prepared using a reduction–reoxidation method [5–8]. Recently the influence of the sintering temperature on room-temperature resistivity was investigated by Chung [9]. Moreover, Zhou et al. [10] drew the conclusion that and the room-temperature was affected by the cooling rate too. Niimi et al. [11] found that PTCR characteristics were affected by the ion radius of a donor ion.

However, little attention has been paid to the effect of the calcination temperature on the electrical properties and the PTCR effect of (Ba$_{x-0.002}$Sm$_{0.002}$) TiO$_3$ ceramics, which are prepared through a reduction–reoxidation sintering process. As this is essential, we study the effect of the calcination temperature in the present paper. In addition, the influence of Mn(NO$_3$)$_2$ on the PTCR effect of the samples has been also analyzed.
2. Experimental Procedures
The starting materials were high-purity BaCO₃, TiO₂, Sm₂O₃, SiO₂, and Mn(NO₃)₂, and they were weighed according to the following formula: (Baₓ-Sm₀.₀₀₂)TiO₃ + 6 mol% SiO₂ (BST), where \( x = 1.018 \). In the experiment, the mixtures were mixed by wet ball milling for 4h (350 r/min) in deionized water using an agate ball in a polyurethane jar, and they were dried at 115 °C in a drying oven, then the powders were calcined at 1000, 1050, 1125, 1150, 1175, and 1200 °C for 2h in air, they is denoted by S₁, S₂, S₃, S₄, S₅, and S₆, respectively. The mixture which was doped small amount of Mn(NO₃)₂ was ground again through ball-milling for 4h. After drying and sieving, the calcined powder was ground again by wet ball milling for 4h in a polyurethane jar. Next, the dried powder was blended with dispersant, solvent, binder, and defoamer by ball milling for 18h in a nylon pot and cast into green sheets of 55-μm thickness by the doctor-blade method. These sheets were stacked with 15 MPa pressure at 50 °C to form a ceramic block. Then they were cut into rectangular blocks (4.7 mm × 3.2 mm × 0.8 mm). Subsequently, the binder was removed by heating at 330 °C in air. The blocks were subsequent fired in an aluminum tube at 1250 °C for 30 min in a reducing atmosphere (3 vol% H₂/N₂), with the heating and cooling rates being 200 °C/h, at a flow rate of 200 ml/min. The fired BST ceramics were reoxidized at 800 °C for 1h in air, and the surfaces were coated with In–Ga alloy (60:40) to form electrode. Resistance 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.

3. Results and Discussion
3.1. XRD analysis

Figure 1. XRD patterns of the BST powder calcined at various temperatures for two hours.

Figure 1 shows the XRD patterns for the BST powder calcined by firing at 1000 °C–1200 °C for two hours in air. Note that the BST powder has a two-level structure. The BST powder for the ceramic at 1000 °C has a pseudocubic structure. In addition, a small quantity of BaCO₃ can be observed. At temperatures above 1125 °C, a tetragonal structure is formed along with a structure with reflections (002) and (200), as shown in Fig. 1. However, the structure of the samples calcined at 1000 °C is not split into two reflections. Therefore, it does not have a tetragonal structure.

3.2. Influence of the calcination temperature on the electrical properties
The room-temperature resistivity of the BST ceramics as a function of the calcination temperature (1000 °C–1200 °C) is shown in Fig. 2; note that the ceramics were reoxidized at 800 °C for 1h in air
after sintering at 1250 °C for 30 min in a reducing atmosphere. The room-temperature resistivity of the different specimens first decreases and then increases with the calcination temperature. The results show that the corresponding calcination temperature of the minimum resistivity is approximately 1150 °C, and its room-temperature resistivity is 38.4 Ω·cm. The decrease in resistivity is generally attributed to the inadequacy of the solid-state reaction. Thus, it is difficult to completely form a principal crystalline phase. This can be confirmed by the data from Fig. 1. Therefore, the electron density of the ceramics increases as the calcination temperature increases from 1000 °C to 1150 °C. The increase in resistivity may be due to the crystallite sizes of the calcinated samples; the mean crystallite sizes ($d_{\text{BT}}$) of the BST ceramics increases with increasing calcination temperature [12, 13]. Moreover, it is difficult to obtain a low room-temperature resistivity for the samples that were calcinated at high temperatures. Therefore, the room-temperature resistivity of the S6 ceramics is higher than that of the S4 samples.

![Figure 2](image)

**Figure 2.** Dependence of the room-temperature resistivity of the BST ceramics reoxidated at 800 °C after sintering at 1250 °C for 30 min on the different calcinated temperature.

3.3. *Effect of the calcinated temperature on PTCR effect*

![Figure 3](image)

**Figure 3.** The temperature dependence of resistivity of the BST ceramics with different calcinated temperatures reoxidized at 800 °C for 1 h after firing at 1250 °C for 30 min.

Figure 3 shows the temperature dependence of resistivity for the BST samples shown in Fig. 2; note that these samples were reoxidized at 800 °C for 1 h in air after firing at 1250 °C for 30 min in a
reducing atmosphere. From the figure, the S1 ceramics calcined at 1000 °C exhibit significant PTCR characteristics, with a resistivity jump of 3.2 orders of magnitude and a high room-temperature resistivity of $1.8 \times 10^3 \, \Omega \cdot \text{cm}$. Although the resistivity jump of the above samples is the highest, their room-temperature resistivity is also very high. However, the S4 samples calcined at 1150 °C have a low room-temperature resistivity of 38.4 $\Omega \cdot \text{cm}$, along with a weak PTCR effect, with a resistivity jump ($Lg(R_{max}/R_{min})$) of 2.1 orders of magnitude. This may be due to the lower height of the Schottky barrier.

### 3.4. Influence of PTCR effect on the acceptor dopant

![Figure 4. The temperature dependence of resistivity of the S3 and S7 samples with different Mn$^{2+}$ content.](image)

Figure 4 shows the temperature dependence of resistivity in the S3 and S7 samples for different Mn$^{2+}$ content reoxidized at 800 °C for 1 h in air after sintering at 1250 °C for 30 min in a reducing atmosphere. Note that the S7 ceramics were doped with a small quantity of Mn(NO$_3$)$_2$ (0.05 mol%), but the S3 samples were not doped with Mn(NO$_3$)$_2$. From Fig. 4, we can obviously see that the room-temperature resistivity of the S7 specimens is much higher than that of the S3 ceramics. Moreover, the former has a higher resistivity jump—2.8 orders of magnitude—than that of the latter. Mn(NO$_3$)$_2$ acts as an acceptor, so it can not only raise the sample resistivity, but also improve their PTCR effect.

### 4. Conclusion

The influence of the calcinated temperature on the PTCR effect of (Ba$_{x}$-0.002Sm$_{0.002}$) TiO$_3$ ceramics reoxidized at 800 °C for 1 h in air after sintering at 1250 °C for 30 min in a reducing atmosphere was investigated in this work. The results indicated that the room temperature resistivity first reduces and then increases as the calcination temperature increases from 1000 °C to 1200 °C. Moreover, the critical calcination temperature (i.e., 1150 °C) was determined in our experiment. The room-temperature resistivity and the resistance jump of the S3 samples are 38.4 $\Omega \cdot \text{cm}$ and 2.1 orders of magnitude, respectively. Furthermore, the experimental results signify that a small amount of Mn(NO$_3$)$_2$ can improve the PTCR effect in the S7 samples.

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