Influence of Reoxidation Time on Electrical Properties of Y$_2$O$_3$-doped BaTiO$_3$ Ceramics Sintered in a Reducing Atmosphere

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Abstract. The influence of the reoxidation time on electrical properties and the positive temperature coefficient of resistance (PTCR) effect in multilayer Y$_2$O$_3$-doped BaTiO$_3$ (BTO) ceramics were investigated. The BTO ceramics were sintered at 1160 °C–1270 °C for 2 h in a reducing atmosphere and then reoxidized at 500 °C–900 °C for 0 h–4 h. Results indicated that the room-temperature resistance of BTO ceramics reoxidized at 750 °C for 2 h decreased with the increasing of the sintering temperature. As the reoxidation time increased, the room-temperature resistance of the BTO samples slightly increased. In addition, the effect of the reoxidation time on the PTCR effect of the ceramics was also studied. The BTO ceramics had a low room-temperature resistance of 0.3 Ω and a resistance jump greater than 3.0 orders of magnitude.

1. Introduction
As is known, Barium titanate (BaTiO$_3$) is a ferroelectric material, which transforms from a tetragonal perovskite structure (ABO$_3$) at room temperature into a cubic structure at the Curie temperature (T$_c$) [1]. B site or A site of BaTiO$_3$ are replaced by trace amount of pentavalent impurities or trivalent donor becomes a semiconducting respectively, and exhibit an anomalous rise in resistivity at the T$_c$ [2, 3]. The phenomenon is known as the positive temperature coefficient of resistivity (PTCR) effect, which was explained by Heywang [4], and later modified by Jonker [5].

The low room-temperature resistance of the semiconducting BaTiO$_3$ based ceramics has been prepared by way of a reduction-reoxidation method [6, 7]. Moreover, in order to further reduce the resistance, the ceramics with a multilayer structure can be obtained [8-12]. Recently, Niimi et al. [11] found that the PTCR effect of samples is affected by the ion radius of the donor dopant. Chung et al. [13] reported that the sintering temperature could affect the room-temperature resistance of the specimens. Cheng et al. [14] indicated that the PTCR ceramics with 0.6 mol% Sm$^{3+}$ reoxidized at 750 °C for 3 h after sintering at 1200 °C for 30 min exhibited a significant resistivity jump. Yoon et al. [15] proposed that donor segregation could occur during the cooling process that follows heat treatment in air.

However, few studies have investigated the influence of reoxidation heat treatment on electrical properties and PTCR effect of multilayer Y$_2$O$_3$-doped BaTiO$_3$ Ceramics in a reducing atmosphere. Therefore, the PTCR characteristics of the samples with different reoxidation times in air were investigated in this paper.
2. Experimental Procedures

The starting materials were high-purity BaTiO(C₂O₄)₂·4H₂O (>99.5%), BaCO₃ (>99.8%), TiO₂ (>99.8%), and Y₂O₃ (>99.99%), and they were weighed according to the following formula: (Ba₁₋ₓYₓ)TiO₃ (BTO), where x is 0.4 mol%. In this experiment, the components were mixed by high energy ball milling for 60 minutes (2400 r/min) in deionized water using zirconia balls and then calcined at 1050 °C for two hours in air. After drying and sieving, the calcined powder was grinded again by wet ball milling for three hours in a polyurethane jar. After mixing, the dried powder was mixed with dispersant, defoamer, solvent, and binder by ball milling for 18 hours in a nylon pot and cast into green sheets of 55-μm thickness by the doctor-blade method. These sheets were laminated at 50 °C to form a ceramic block, which was applied to Ni inner electrodes, and then cut into rectangular blocks (3.6 mm × 1.8 mm × 1.4 mm). Subsequently, the binder was removed by heating at 330 °C in air. Sintering was conducted in an aluminum tube at 1160–1270 °C for two hours in a reducing atmosphere (3% H₂/N₂), with the heating and cooling rates being 200 °C/h. The schematic diagram of the cross section of the samples was shown in Scheme 1. The sintered BTO ceramics were re-oxidized at 750 °C in air for 0–4 hours, 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.

3. Results and Discussion

3.1. Influence of sintering temperature on electrical properties

The room-temperature resistance of the BTO ceramics that are reoxidized at 750 °C for three hours in air after sintering at different temperatures (1160–1270 °C) for two hours in a reducing atmosphere is shown in Figure 1. From the Figure 1, we can see that the room-temperature resistance of the ceramics decreases with an increase in the firing temperature from 1160 °C to 1270 °C. This result indicates that the higher the sintering temperature is, the lower the room-temperature resistance. This is because the relative densities of the BTO samples obtained at different sintering temperatures are distinct. In general, the relative density of the specimens increases with the increasing of the sintering temperature because of an increase of the grain size and decreasing of the porosity. As a result, the ceramics obtained under a sintering temperature of 1270 °C have much higher densities than those obtained at 1160 °C.

![Figure 1. The room-temperature resistance of the BTO samples is as a function of the sintering temperature in the range of 1160–1270 °C.](image-url)
3.2. Influence of reoxidation time on electrical properties
The room-temperature resistance of the BTO ceramics reoxidized at 750 °C after sintering at different temperatures for 2 hours as a function of the reoxidation time is as shown in Figure 2. From the Figure 2, it is shown that the room-temperature resistance of the samples that were sintered at different temperatures all increases with the reoxidation time in the range from 0 min to 90 min, whereas the influence of the room-temperature resistance of the ceramics fired at 1160 °C on the reoxidation time is significantly faster than that of the specimens obtained at 1180 °C or 1210 °C. This is because that the relative density of the former is much lower than that of the latter. Thus, the grain-boundaries of the former are easy to be oxidized by the oxygen atoms in air. According to the following formula: \( V_{O}^{**} + \frac{1}{2}O_2 + 2e' \rightarrow O_{O} \), it is indicated that the content of free electrons in the ceramics will reduce with the increase of the reoxidation time. Therefore, its room-temperature resistance will increase. In addition, it is found that the room-temperature resistance of the ceramics reoxidized for 90 min is slightly higher than that of the samples reoxidized for 0 min.

![Figure 2](image)

**Figure 2.** The room-temperature resistance of the BTO ceramics reoxidized at 750 °C after sintering at different temperatures for 2 h as a function of the reoxidation time.

3.3. Influence of reoxidation time on PTCR effect

![Figure 3](image)

**Figure 3.** The temperature dependence of resistance of the BTO ceramics reoxidized at 750 °C for different times after sintering at 1180 °C for 2 h.

Figure 3 shows that the temperature dependence of resistance of the multilayer BTO ceramics reoxidized at 750 °C for the different times after firing 1180 °C for 2 h in a reducing atmosphere. From Figure 3, it is found that the room-temperature resistance of the samples slightly increases with
an increase in the reoxidation time of 0 to 4 h. Furthermore, the resistance jump increases with the increasing of the reoxidation time in the range from 0 to 2 h. In addition, we find that the multilayer BTO ceramics reoxidized at 750 °C for 2 h in air after sintering at 1180 °C for 2 h exhibit a significant PTCR effect with a resistance jump of 3.0 orders of magnitude, along with a low mean room-temperature resistance of 0.3 Ω. Furthermore, the resistance of the ceramics includes the resistance of both the grain boundaries and the grains. As the reoxidation time increases, the grain-boundaries resistance may also increase. According to Heywang-Jonker model [4-5], we can see that PTCR effect is an effect of the grain boundaries. Thus, the PTCR effect of the samples are reoxidized at 750 °C for 2 hours in air is better than that of the ceramics were reoxidized at 750 °C for 0 hour. In addition, the oxygen vacancies in BTO ceramics are occupied by oxygen atoms during the reoxidation process. The longer the reoxidation time, the lower the content of free electrons is, thus resulting in a bigger room-temperature resistance.

4. Conclusion
We investigated the influence of the reoxidation time on electrical properties and PTCR effect of multilayer BTO ceramics that reoxidized at 750 °C for 0–4 h in air after firing at 1160–1210 °C for 2 h in a reducing atmosphere. The results show that the room-temperature resistance decreases with the increase in the sintering temperature from 1160 °C to 1270 °C. Moreover, the room-temperature resistance of the samples slightly increases with the reoxidation time in the range of 0–90 min under different sintering temperatures. Furthermore, long reoxidation time results in high room-temperature resistance and PTCR effect. In addition, the multilayer BTO ceramics reoxidized at 750 °C for 2 h after sintering at 1180 °C for 2 h in a reducing atmosphere exhibit a resistance jump greater than 3.0 orders of magnitude, along with a low room-temperature resistance of 0.3 Ω.

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