J Mater Sci (2007) 42:6696–6700
DOI 10.1007/s10853-007-1495-z

# Effects of oxygen partial pressure control on the microstructure and PTCR properties of Ho doped $BaTiO_3$

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Received: 14 June 2006 / Accepted: 2 January 2007 / Published online: 26 April 2007

**Abstract** Effects of oxygen partial pressure ($P_{O_2}$) control on the electrical properties and microstructural development of $(Ba_{1-x}Ho_x)_{0.997}TiO_3$ were studied. An oxidation condition ($P_{O_2} \sim 1.0$ atm) was maintained during the heating process, and then the specimen was sintered in a reducing atmosphere ($P_{O_2} < 10^{-9}$ atm) at 1350 °C, followed by the annealing process at 1000 °C and $P_{O_2} = 1$ atm. The switching temperature ($T_S$) from the oxidation atmosphere to the reducing condition was changed from 1100 to 1350 °C. A significant decrease in the room-temperature resisitivity ($\rho_{25}$) was observed as $T_S$ was increased. The temperature coefficient of resistance (TCR) was independent of the change in $T_S$, and closed pores decreased with increasing $T_S$.

## Introduction

Considerable attention has been paid to the electrical properties of $BaTiO_3$-based materials over the last several decades. One of the most important applications involves the positive temperature coefficient of resistivity (PTCR) behavior in the donor doped $BaTiO_3$ ceramics which exhibit an anomalous increase in the resistivity near the ferroelectric Curie temperature, $T_C$ [1–6]. This property has been proven useful in many temperature sensing applications, including temperature-regulated cooking appliances, automatic chokes in automobiles and self-regulating household heaters [7]. The decrease in room-temperature resistivity could broaden the applications of the semiconducting $BaTiO_3$ ceramics to electronic devices [8]. A number of reduction–reoxidation sintering methods have been investigated to achieve such a characteristic with a low resistance of grains and a high potential barrier at grain boundaries above the Curie point [9–10].

The PTCR effect can occur only in polycrystalline $BaTiO_3$ doped with small amount of donor. Donor additives are trivalent ions (e.g. $La^{3+}$, $Sb^{3+}$, $Ho^{3+}$) substituting on $Ba^{2+}$ sites, or pentavalent ions (e.g. $Nb^{5+}$, $Ta^{5+}$) substituting on $Ti^{4+}$ sites of the perovskite $ABO_3$ lattice [11–12]. Single crystals or acceptor doped $BaTiO_3$ do not exhibit PTCR behaviors. Thus, the nonlinear change in resistivity has been understood as a combination of ferroelectricity, semiconducting and grain boundary effects [6]. Sintering atmosphere is another factor which influences the PTCR effect. A low oxygen partial pressure is required during the sintering process and then the oxygen pressure should be increased to 1 atm to promote the grain boundary oxidation which is essential to the pronounced PTCR effect [13].

Numerous studies have been conducted to confirm the effects of processing conditions on the microstructure and electrical properties of donor doped $BaTiO_3$ [9–11, 14–17]. Al-Shahrani et al. [14] reported the effects of $Ho_2O_3$ addition on the DC resistivity, and identified the optimum $Ho_2O_3$ concentration for PTCR effects. Jeong et al. [11] studied the defect chemistry of Ho doped $BaTiO_3$ that $Ho_2O_3$ additions to $BaTiO_3$ up to 0.3 mol% were compensated by electrons under all oxygen partial pressures, exhibiting a low insulating resistance at room-temperature.

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The effect of cation nonstoichiometry (Ba/Ti ratio), on the microstructure and PTCR behaviors of $BaTiO_3$ ceramics was investigated by Lin et al. [15]. The relationship between relative density and PTCR effect of Sb doped $BaTiO_3$ confirmed that the smaller grain size of these materials, the larger was the PTCR effect as far as the ceramic bodies have relatively high bulk densities (≥90%) [16–17]. The sintering process without atmosphere controls left the residual pores trapped in large grains [9]. Those microstructures are unfavorable for applications such as thin film device and high withstand voltages. The effects of the oxygen atmosphere control on the densification of ceramic bodies revealed that the resistivities of the dense sample were lower by about one order than those of the porous samples [9–10]. It is thus required that the ceramic grain size, the oxygen pressure control and the cooling rate should be simultaneously controlled.

In this paper, the room-temperature resistivities and the PTCR effects of Ho-doped $BaTiO_3$ will be discussed in terms of switching temperature ($T_S$) of oxygen partial pressure ($P_{O_2}$) control and microstructural development.

## Experimental procedure

$(Ba_{1-x}Ho_x)_{0.997}TiO_3$ (Ba/Ti < 1) powders were prepared by the liquid-mix method developed by Pechini [18]. Holmium was added as weighted amounts of a solution of holmium chloride ($HoCl_3$) in deionized water. Each sample composition was prepared by polymerization and calcination of an organometallic solution containing precisely determined amounts of the metallic components, as described in the previous study [19]. The calcined powders were pulverized into fine particles. The powders were uniaxially pressed into disks of 4.98 mm in diameter and 0.8 mm in thickness at a pressure of 400 MPa.

In Fig. 1, an oxidation condition ($P_{O_2}$~1.0 atm) was maintained during the heating process in order to obtain a dense ceramics body [9]. And then the specimen was sintered in a reducing atmosphere ($P_{O_2} < 10^{-9}$ atm) at 1350 °C for 4 h in a mixture of 1.5% $H_2$-98.5% $N_2$. The switching temperature ($T_S$) from the oxidation atmosphere to the reducing condition was changed from 1100 to 1350 °C, followed by the annealing process at 1000 °C for 10 h and $P_{O_2}$ = 1atm. Gallium alloy electrodes (High Purity Chemistry, 75.5% Ga–24.5% In) with an ohmic contact to the PTCR ceramics were formed on the major surfaces of the sample disks.

The temperature dependence of resistance was measured by the 2-probe method in a temperature-programmable chamber, with a heating rate of 1 °C/min from 0 to 150 °C. The temperature coefficient of resistance (α) was calculated by the following equation,

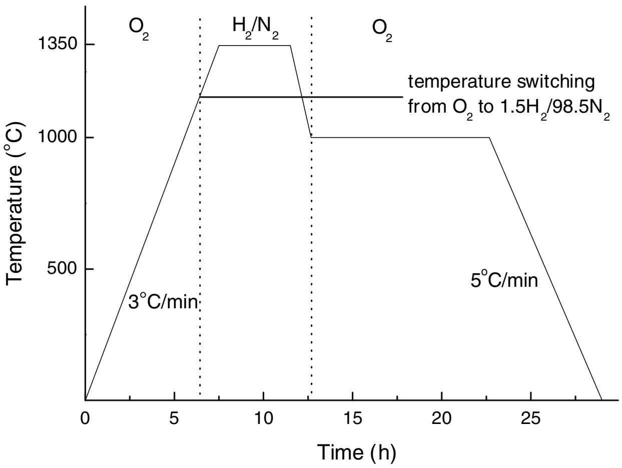


**Fig. 1** Sintering profile for reduction–reoxidation method

$$\alpha = [\ln(\rho_2/\rho_1)/(T_2 - T_1)] \times 100\,(\%/^oC),$$

where $\rho_1$ and $\rho_2$ are the resistivity corresponding to $T_1$ ($2 \times \rho_{25}$) and $T_2$ ($10 \times \rho_{25}$), respectively. Microstructures were investigated using a scanning electron microscope (SEM, Hitachi-S2150). For microstructure observation, sample surfaces were polished to 0.04 μm and chemical etching was performed for 40–50 s, using an etchant of $H_2O$, HCl and HF [20].

## Results and discussion

Electrical resistivities of $(Ba_{1-x}Ho_x)_{0.997}TiO_3$ (x = 0, 0.001~0.01) at room-temperature are shown in Fig. 2. The resistivity decreased with increasing Ho contents with the lowest resistance at 0.8 at% Ho, whereas an abrupt resistivity increase was observed with Ho > 0.8 at%, which is similar to the previous results of highly donor-doped $BaTiO_3$ ($La_2O_3$) sintered at a low oxygen partial pressure [20, 21]. The nominal composition, $(Ba_{1-x}Ho_x)_{0.997}TiO_3$ indicates that the Ba/Ti ratio (0.997) is supposed to force Ho ions to occupy Ba sites instead of Ti sites, where $Ho^{3+}$ ion is amphoteric and occupies both Ba and Ti sites depending on the Ba/Ti ratio. When $Ho^{3+}$ is substituted for $Ba^{2+}$ as a donor impurity, $Ho_2O_3$ has an extra oxygen compared with 2BaO and the released extra oxygen preferentially fills the oxygen vacancies accompanied by the background acceptor impurities normally included in $BaTiO_3$ [11]. At lower $P_{O_2}$, the excess oxygen contained in $Ho_2O_3$ is lost, and the donor ($Ho^{3+}$) impurities are compensated by electrons.

$$Ho_2O_3 + 2TiO_2 \rightarrow 2Ho^{\bullet}_{Ba} + 2Ti_{Ti} + 6O_O + 1/2O_2 + 2e'. \tag{1}$$

The defect notation is suggested by Kröger and Vink [22]. The augmentation of conductivity with decreasing

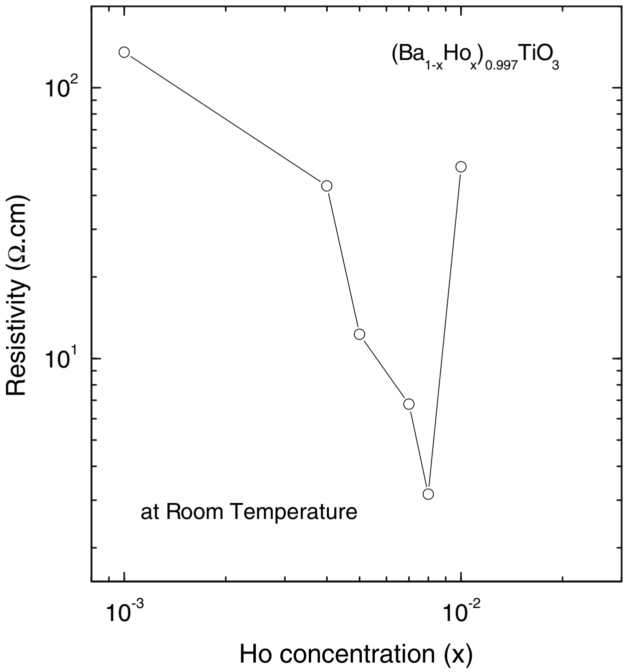


**Fig. 2** The room-temperature resistivity of Ho doped $BaTiO_3$

$P_{O_2}$ is also attributed to the reduction of oxygen in the $BaTiO_3$ lattice.

$$O_O \rightarrow 1/2O_2 + V_O^{\bullet\bullet} + 2e'. \tag{2}$$

At the low doping level of Ho (<0.8 at%), the electron compensation as written in Eqs. 1 and 2 contributes to the increase in charge carrier concentration, leading to the low resistivity at room-temperature. However, as the doping level is increased (>0.8 at%), there is an evident switch of the compensation mechanism from electrons ($e'$) to cation vacancies ($V''_{Ba}, V''''_{Ti}$). When $Ho^{3+}$ ions are substituted for $Ba^{2+}$, the possible compensation modes by cation vacancies may be written as follows:

$$Ho_2O_3 + 3TiO_2 \rightarrow 2Ho^{\bullet}_{Ba} + 3Ti_{Ti} + V''_{Ba} + 9O_O \tag{3}$$

$$2Ho_2O_3 + 3TiO_2 \rightarrow 4Ho^{\bullet}_{Ba} + 3Ti_{Ti} + V''''_{Ti} + 12O_O \tag{4}$$

$$3Ho_2O_3 + 6TiO_2 \rightarrow 6Ho^{\bullet}_{Ba} + 6Ti_{Ti} + V''_{Ba} + V''''_{Ti} + 21O_O \tag{5}$$

Equations 3 and 4 represent the compensation of donor ($Ho^{\bullet}_{Ba}$) impurities by Ba and Ti vacancies, respectively. The incorporation reaction in Eq. 5 could support the Schottky-type disorder which is more energetically favorable than a single type of vacancy formation at higher temperatures [11]. However, none of the above expressed incorporation modes has been confirmed to be exclusively predominant. At Ho > 0.8 at%, the compensation mode switching from electrons to cation vacancies in $(Ba_{1-x}Ho_x)_{0.997}TiO_3$ makes the material insulating. Thus, the resistivity behaviors with varying $Ho_2O_3$ contents are comparable with the incorporation modes of $Ho^{3+}$ ions into the Ba site, as described in Eqs. 1 and 3–5.

Figure 3 shows bulk densities of $(Ba_{0.992}Ho_{0.008})_{0.997}TiO_3$ as a function of sintering temperature. The density increased stiffly up to 1200 °C and then leveled off, approaching to a density (~95% theoretical density). Figure 4 shows the microstructures of the samples sintered at various temperatures from 1100 to 1350 °C. The microstructure development is compatible with the bulk density at the corresponding temperature. The specimen sintered at 1100 °C included pores with open channels, whereas the specimens sintered at higher temperatures (>1200 °C) showed denser microstructures with negligibly small difference between them. Such a little difference in microstructures at >1200 °C is in good agreement with the slight increase in density shown in Fig. 3. As the temperature was increased to 1300 °C (Fig. 4c), most of pores diminished, resulting in few isolated pores left. This result would give a hint for the optimum switching temperature ($T_S$).

Figure 5 shows a typical PTCR effect of $(Ba_{0.992}Ho_{0.008})_{0.997}TiO_3$ at various switching temperatures ($T_S$). The switching temperature ($T_S$) from the oxidation atmosphere to the reducing condition was changed from 1100 to 1350 °C. The room-temperature resistivities are strongly dependent on the switching temperature ($T_S$). A significant decrease in the room-temperature resistivity ($\rho_{25}$) was observed as $T_S$ was raised. The specimen with $T_S$ = 1300 °C showed the lowest value of room-temperature resistivity. The room-temperature resistivity ranged from 2 to 11 Ω cm, depending on $T_S$. However, the temperature coefficient of resistance (α) was hardly dependent on the change in Ts.

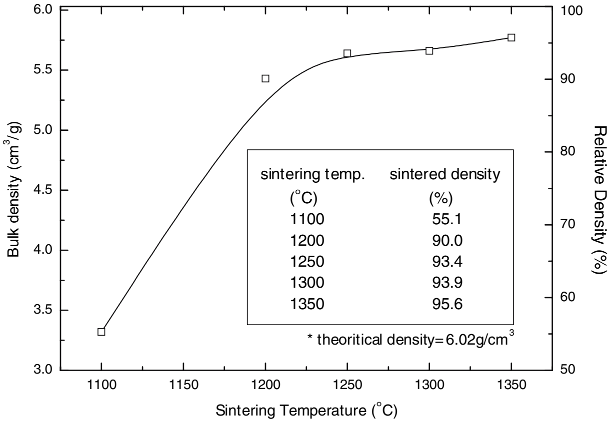
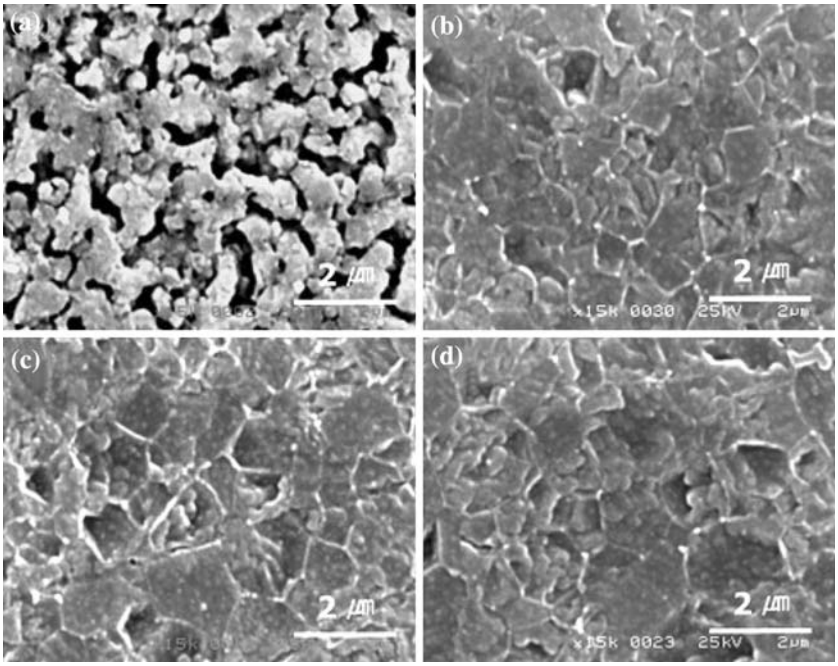


**Fig. 3** Bulk density of $(Ba_{0.992}Ho_{0.008})_{0.997}TiO_3$

**Fig. 4** Microstructures of $(Ba_{0.992}Ho_{0.008})_{0.997}TiO_3$ at various sintering temperatures for 4 h: (**a**) 1100, (**b**) 1250, (**c**) 1300, and (**d**) 1350 °C



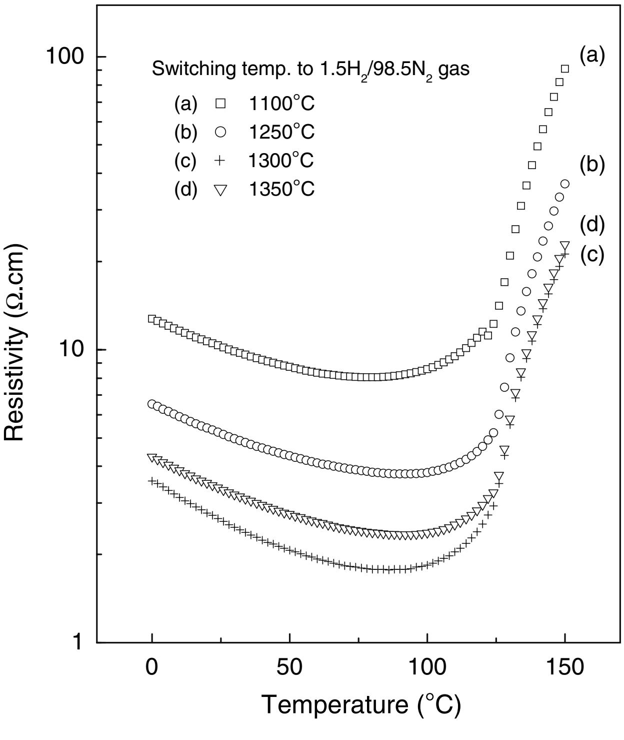


**Fig. 5** Resistivity versus Temperature curves of $(Ba_{0.992}Ho_{0.008})_{0.997}$-$TiO_3$ with various $1.5H_2$–$98.5N_2$ gas switching temperatures

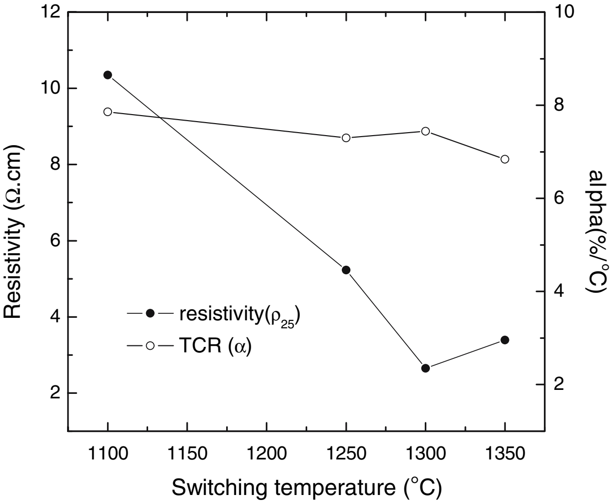


**Fig. 6** Room-temperature resistivity ($\rho_{25}$) and TCR (**a**) characteristics of $(Ba_{0.992}Ho_{0.008})_{0.997}TiO_3$ with various $1.5H_2$–$98.5N_2$ gas switching temperatures

Figure 6 summarizes the variation of the room-temperature resistivity ($\rho_{25}$) and temperature coefficient of resistance (α) as a function of switching temperature ($T_S$) from $O_2$ to $1.5H_2$–$98.5N_2$. The room-temperature resistivity ($\rho_{25}$) initially decreased as the switching temperature was increased and then rose up at $T_S$ = 1350 °C, whereas TCR (α) slightly decreased with increasing temperature. The experimental results demonstrate that the optimum switching temperature ($T_S$) could improve the PTCR properties, particularly lowering the room-temperature resistivity of the $BaTiO_3$ system with only a small change in the PTCR jump characteristics.

The microstructures of $(Ba_{0.992}Ho_{0.008})_{0.997}TiO_3$ processed with $P_{O_2}$ control at various switching temperatures ($T_S$) are shown in Fig. 7. When the furnace atmosphere was switched at 1100 °C, the specimen included numerous small pores trapped in large grains, whereas the samples with switching temperatures of 1250–1350 °C had few

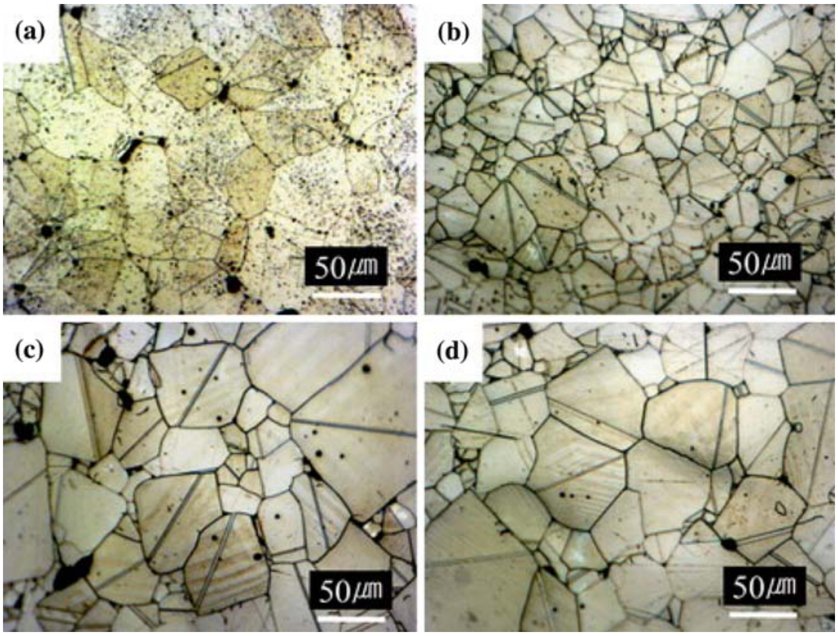


**Fig. 7** Microstructure of $(Ba_{0.992}Ho_{0.008})_{0.997}TiO_3$ with various $1.5H_2$–$98.5N_2$ gas switching temperatures: (**a**) 1100, (**b**) 1250, (**c**) 1300, and (**d**) 1350 °C

pores within grains and exhibited minor pores normally occurring in sintered ceramic bodies. It should be noted that the closed pores within grains diminished in numbers with increasing $T_S$. These results are in good agreement with the PTCR property profiles shown in Figs. 5 and 6. Pores are open at 1100 °C, as shown in Fig. 4 and filled with nitrogen. Such pores are too sluggish to diffuse out through the further sintering processes because the diffusion rate of nitrogen is significantly low in oxide materials, pores remaining trapped in the ceramic body. This result leads to the increase in resistivity. Above $T_S$ = 1250 °C, all pores are mostly closed and filled with oxygen before switching to the nitrogen gas atmosphere. Oxygen in the pores diffuses easily out of the ceramic body in the progress of densification, where the diffusion rate of oxygen is much greater than that of nitrogen in oxide ceramics.

## Conclusions

Room-temperature electrical resistivities decreased with increasing Ho contents and the lowest resistance with 0.8 at% Ho. At Ho > 0.8 at%, the compensation mode switched from electrons to cation vacancies. The bulk density of Ho-doped $BaTiO_3$ gradually increased above 1250 °C, and the relative densities were about 95% of the theoretical density. Upon increasing the switching temperature to 1300 °C, almost all pores gradually diminished in number with few closed pores. The specimen with switching at 1300 °C exhibited the lowest room-temperature resistivity, with the temperature coefficient of resistance ($\alpha$) value of 7.4%/°C. The experimental results demonstrate that the optimum switching temperature ($T_S$) could improve the PTCR properties, particularly lowering the room-temperature resistivity of the $BaTiO_3$ system with only a small change in the PTCR jump characteristics.

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