Study of Reoxidation in Heavily La-doped Barium Titanate Ceramics

Yang Wenhu, Pu Yongping, Chen Xiaolong and Wang Jinfei
School of Materials Science and Engineering, Shaanxi University of Science and Technology, Xi’an 710021, China
E-mail:dellon9960@163.com ,06yangwenhu@sust.edu.cn

Abstract. The ceramic samples of (1-x)BaTiO$_3$+½xLa$_2$O$_3$+(2+x)mol%TiO$_2$ (0.003≤x≤0.15) were prepared by sintering in reducing atmosphere of H$_2$, subsequently reoxidized in air. The effect of heavily La dopant on the resistivity and microstructure of the reoxidized samples were investigated by means of scanning electron microscopy and electric properties testing. The results show that the critical concentration of La-doped samples increased obviously compared with the samples sintered in air. The grain size decreased with the increase of La-donor content. The positive temperature coefficient resistivity effect of the sample increased when a change reoxidizing temperature range of 600°C ~1200°C. The maximum of $\rho_{\text{max}}/\rho_{\text{min}}$ ratio was ~700 at the reoxidizing temperature of 1100°C when $x$=0.8mol%.

1. Introduction
Ferroelectric BaTiO$_3$ is one of the most important ceramic materials in electronics. It has been widely used in electronic devices, such as multiplayer capacitors (MLCC), sensors with positive temperature coefficients resistivity (PTCR), piezoelectric transducers, ferroelectric thin-film memories, etc. At room temperature, BaTiO$_3$ adopts a tetragonal perovskite structure and is a ferroelectric with high permittivity. It transforms to the cubic, paraelectric state at the Curie temperature ($T_c$=130°C). Undoped BaTiO$_3$ is electrically insulating, but the electrical resistance can be controlled effectively by doping in either barium or titanium site with proper donor impurity ions [1, 2], for example La$^{3+}$, Ce$^{3+}$ ions, etc.

Generally, the donor-doping barium titanate PTCR ceramics are prepared by a sintering reduced semiconducting barium titanate ceramics at the temperature range of 800°C ~1200°C. The grain boundary is partially oxidized under different oxygen partial pressure in cooling process, the samples show the PTCR effect [3]. The reason is that the oxygen ions escape from the lattice at high temperature in reducing atmospheres (H$_2$) and the donor partial substitution of A site ion, multiple ion occupation of A and/or B sites in ABO$_3$ compounds is expected to bring in changes in Curie temperature and other physical properties [4]. This kind of substitution can affect the lattice parameters, tetragonal distortion ($c/a$), polarization, ferroelectric transition and other characteristics of the samples. But the released oxygen partly enters into the sample when the samples are sintered in oxidizing atmosphere. The room temperature resistance is heavily sensitive to the degree of reoxidation, therefore, the research of reoxidation mechanism is very important to PTCR effect.

In this study, La-doped barium titanate ceramics sintered in H$_2$ with a range of concentration from 0.3mol% to 15.0mol% and reoxidized in air were investigated. The changes of the microstructure at a...
temperature range of 600°C ~1200°C were observed and the PTCR effect of samples was also reported.

2. Experimental
La-doped BaTiO$_3$ ceramics were prepared using conventional mixed-oxide technology according to the formulas of BaTiO$_3$+$\frac{1}{2}$La$_2$O$_3$+2.0mol%TiO$_2$($0 \leq x \leq 15.0\%$). The raw materials (BaTiO$_3$, TiO$_2$ and La$_2$O$_3$) with TiO$_2$-rich (2.0mol%) in order to promote sintering in the presence of liquid phase, were mixed and milled in water for 4h inside polyethylene jars using zirconia media, dried at 80°C. After being dried, the powders were granulated using poly-vinyl alcohol (PVA) binder and formed under uniaxial pressure of 100MPa, pressed into tablet (φ14mm×2mm). The disks were sintered in H$_2$ for 2h at 1350°C with a heating rate of 10K/min and a cooling rate of 5K/min. Subsequently, the sample reoxidized in air for 2h at a temperature range of 800°C ~1100°C. Fire-on silver was used as the electrode material for the measurement of electrical properties of the sintered samples. The nature surface microstructure was investigated by means of optical microscopy and scanning electron microscope. The temperature dependence of resistance was measured in a temperature-programmable furnace with a heating rate of 2°C/min from 20°C to 350°C.

3. Results and Discussion
The room temperature resistivity of La-doped BaTiO$_3$ ceramics sintered in air and H$_2$ as a function of dopant concentration is shown in Fig.1. From the figure, it is found that the resistivity decreased with the increase of La-doped concentration when $x \leq 0.3$mol%, subsequently increased rapidly with the increase donor content. The concentration ($x=0.3$mol%) was regarded as critical concentration. The resistivity drop was generally attributed to the electron compensation of the substituted cation via donor-doping.

The subsequent rise in resistivity for dopant concentration $x>0.3$mol% is attributed to a change in doping mechanism to ionic compensation via creation of cation vacancy. But the critical concentration increased up to 0.8mol% when the sample was sintered in H$_2$. It is found that the critical concentration closely depended on sintering atmosphere.

![Figure 1](image_url)

**Figure 1.** The room-temperature resistivity as a function of La-dopant concentration for BaTiO$_3$ ceramics sintered in air and H$_2$ at 1350°C.

3.1. Microstructures
Fig.2 shows SEM photographs of La-doped samples sintered at 1350°C in atmosphere of H$_2$. It is indicated that the grain size of the sample rapidly decreased with increasing La concentration from 0.3 mol% to 15.0 mol%.
Figure 2. SEM micrograph of La-doped ceramics sintered at 1350°C in atmosphere of H2

In Fig.2 (a) and (b), the grain size is ~30 μm, however it is decreased with the La doping concentration increasing from 0.3mol% to 15mol%. There must be given two condition in the process of grain growth, one is liquid phase intervened and the other is BaTiO3 grains must be dissolved [5]. In present work, the excess amount of TiO2 present in the samples, which caused the formation of the reactive liquid phase during sintering. When the samples were sintered in 1350°C, the liquid phases Ba6Ti17O40 was formed [6]. BaTiO3 grains highly dissolved in the liquid phases, which enhanced the mass transport, promoted the small grain growth rapidly at low La-doped concentration. By comparison, the La3+-donor prevented grain growth, which was related to the oxygen partial pressure of the sintering atmosphere. According to the thermodynamic model, it can be expressed by the following format (1) [7]:

\[ \lg p(O_2) = \frac{A}{x_c} + B \]  

where, \( p(O_2) \) is the oxygen partial pressure, \( A \) is the stored surface energy at the phase boundary, \( x_c \) is the critical donor concentration, and \( B \) is the free energy of oxygen released during anomalous grain growth. The critical concentration is highly related to the oxygen partial pressure while \( A \) and \( B \) were constant.

3.2. Grain Boundary Reoxidation
The original La-doped samples were black. After reoxidation at different temperature in air, the color of the samples turned to light blue gradually. It is known that the dark color of BaTiO3 ceramics is related to the presence of Ti3+. Oxygen uptaking occurred at outer and inner surface of the samples during the reoxidation process, oxygen diffused along with the grain boundary on the grain surface toward the center of the grains, which was related with the La-doped concentration by the format (2).

\[ [V_{O}^{\delta}] = [La_{m_\delta}]^n \]  

It is shown that the concentration of oxygen vacancies \( [V_{O}^{\delta}] \) decreased with the increase of \( [La_{m_\delta}] \), while \( n \) was between 0.5 and 1 in a range of heating temperature 600°C ~1000°C. Thus, the reduced samples with heavily La-doped concentration were easily oxidized at low reoxidation temperature (800 ~1200°C).
In order to get the detailed knowledge about the thermodynamics and the kinetics of the several steps of the reoxidation process, Langhammer et al [8] measured the oxygen exchange between the 1.5mol% La-doped samples and sintered atmosphere by the oxygen coulometry in \( P(O_2)=260 \text{Pa} \). It was found that the amount of oxygen adsorbed by the grain boundaries increased with the increase in temperature (800 ~1200°C), during the transformation from the reduced phase to oxidized phase.

3.3. PTCR effect

The resistivity dependence of reoxidizing temperature for the same samples is shown in Fig.3, there is obviously change on resistivity under the reoxidized temperature 1100°C, but it is find that the sample insulated when \( x=15.0 \text{ mol\%} \) at the reoxidizing temperature 600°C, as well as \( x=2.0\text{mol\%} \) or \( 6.0\text{mol\%} \) at 1200°C. The change of resistivity (when \( x=0.8\text{mol\%} \)) and the value of \( \rho_{\text{max}} / \rho_{\text{min}} \) ratio of samples with different reoxidizing temperature are illustrated in Fig.4 and table1. It is shown that the maximum value of \( \rho_{\text{max}} / \rho_{\text{min}} \) ratio was ~700 at the reoxidizing temperature of 1100°C. Combined with the microstructure shown in Fig.2, it is concluded that the small uniform grain size formed while samples were sintering in strong reducing atmosphere, given La-doped content over the critical concentration. It is easily reoxidized in the air. The acceptor ion appeared on grain boundary surface in the grain boundary reoxidizing process, which led to the PTCR effect [9].

![Graphs of resistivity vs. temperature for different La concentrations and reoxidizing temperatures]
Figure 4. Temperature dependence of resistivity for reoxidized BaTiO$_3$ samples doped with La concentrations of 0.8mol% (sintered under reducing conditions and reoxidized in air for 2h at different temperature)

Table 1. Value of $\rho_{\text{max}}/\rho_{\text{min}}$ ratio of samples with reoxidizing temperature

| La-doped concentration | Reoxidizing temperature / °C | 800 | 900 | 1000 | 1100 |
|------------------------|-----------------------------|-----|-----|------|------|
| 0.3mol%                |                             | 8   | 55  | 198  | 100  |
| 0.6mol%                |                             | 8   | 18  | 105  | 396  |
| 0.8mol%                |                             | 4   | 18  | 79   | 662  |
| 2.0mol%                |                             | 5   | 5   | 5    | 2    |
| 6.0mol%                |                             | 3   | 3   | 3    | 5    |

4. Conclusions
The La-doped concentration and the sintering atmosphere heavily affect the microstructure and resistivity of the BaTiO$_3$ ceramics. Combined with the sample sintered in air, the critical concentration was highly improved up to 0.8mol% when ceramic samples were sintered in H$_2$. Meanwhile, the grain size decreased with the increase of La$^{3+}$ donor content. It is shown that the critical concentration closely depended on sintering atmosphere. When the sample was reoxidizing in air at temperature range of 800°C ~1200°C, it is obviously found the PTCR effect exist in some samples. This is related to the donor concentration, oxygen partial pressure and the reoxidation temperature. However, when the La-doped concentration is up to 9mol%, the sample insulated after annealed in air at 600°C. Thus, the reduced samples with heavily La-doped concentration were easily oxidized at low temperature. In the process of reoxidizing, the oxygen diffused along with the grain boundary on the grain surface toward the center of the grains or the released oxygen partly entered into the sample, which resulted in a strong PTCR effect.

References
[1] Hector Beltran, Eloisa Cordoncillo, and Purificacion Escribano. Insulating Properties of Lanthanum-Doped BaTiO$_3$ Ceramics Prepared by Low-Temperature Synthesis. J. Am. Ceram. Soc., 87 [11] 2132–2134 (2004)
[2] Finlay D. Morrison, Derek C. Sinclair, and Anthony R. West. Doping mechanisms and electrical properties of La-doped BaTiO$_3$. International Journal of Inorganic Materials, 3 1205–1210(2001)
[3] Darko Makovec and Miha Drofenik. Microstructural Changes during the Reduction/Reoxidation Process in Donor-Doped BaTiO$_3$ Ceramics. J. Am. Ceram. Soc., 83
[10] 2593–2599 (2000)

[4] Makoto Kuwabara and Hiroyuki Matsuda. Shift of the Curie Point of Barium Titanate Ceramics with
Sintering Temperature. J. Am. Ceram. Soc., 80 [10] 2590–2596 (1997)

[5] Finlay D. Morrison, Derek C. Sinclair, and Anthony R. West. Characterization of Lanthanum-
Doped Barium Titanate Ceramics Using Impedance Spectroscopy. J. Am. Ceram. Soc., 84 [3] 531–538 (2001)

[6] Finlay D. Morrison, Derek C. Sinclair, and Anthony R. West. An Alternative Explanation for
the Origin of the Resistivity Anomaly in La-Doped BaTiO3. J. Am. Ceram. Soc., 84 [2] 474–476 (2001)

[7] Katsuro Hayashi, Takahisa Yamamoto, Yuichi Ikuhara, and Taketo Sakuma. Formation of
Potential Barrier Related to Grain-Boundary Character in Semiconducting Barium Titanate. J.
Am. Ceram. Soc., 83 [11] 2684–2688 (2000)

[8] Hans Theo Langhammera, Darko Makovec, and Yongping Pu et al. Grain boundary reoxidation
of donor-doped barium titanate ceramics. Journal of the European Ceramic Society, 26[11] 2899–2907 (2006)

[9] Pu Yongping, Chen Shoutian, and Langham Mer HT. Grain Boundary Reoxidation of Barium
Titanate Ceramic Doped with Lanthanum. Journal of the Chinese Ceramic Society, 33[10]1237-1242 (2005)