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Particle sizes effects on electrical properties and densification of laminated $Ba_{1.002}La_{0.003}TiO_3$ ceramics

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Abstract

This paper investigated the influences of initial particle sizes on electrical properties and densification of laminated $Ba_{1.002}La_{0.003}TiO_3$ ceramics prepared by the reduction–reoxidation technique. $Ba_{1.002}La_{0.003}TiO_3$ powders with average size of ~820 nm and ~260 nm were prepared by the planet ball milling and the sand milling, respectively. For ceramic samples from ~260 nm particles, the inflection point where the densification rate begins to decrease occurs at a higher sintering temperature than that of ceramic samples from ~820 nm particles. An abnormal growth of grains is observed in ceramic samples from ~820 nm particles, which resists reoxidation. Samples from ~260 nm particles are prone to be globally reoxidized and exhibit a much greater change in grain boundary resistance and RT resistivity after reoxidation. A possible mechanism of the oxygen diffusion in the reoxidation process is proposed, which verifies that samples with smaller grains as well as lower density are easily oxidized to a deeper degree.

Keywords: Particle size; Reduction–reoxidation; PTCR; Densification

1. Introduction

The donor-doped $BaTiO_3$ fired in air can be semiconductive and the resistivity increases dramatically near the ferroelectric transition temperature T_C [1]. This behavior is usually referred as the positive temperature coefficient of resistivity (PTCR) effect. Nowadays chip PTC resistors with low room temperature (RT) resistance are required for many electrical applications. Many methods were adopted to reduce the RT resistivity of $BaTiO_3$ based PTCR ceramics [2–4]. However, there is limitation to reduce the RT resistivity. Therefore, structure innovation was taken to reduce the resistance of PTC resistors. Sasaki and Niimi proposed a laminated chip-type PTC resistor with parallelly connected ohmic inner electrodes, which exhibited low RT resistance [5,6]. The ceramics must be sintered in a reducing atmosphere to avoid oxidation of the inner electrodes and subsequently be annealed in air at a relatively low temperature to obtain the PTCR effect. This process is so called reduction–reoxidation of PTCR ceramics. However samples via the reduction–reoxidation process show a weaker PTCR effect than those sintered directly in air [7,8].

The PTCR effect is a grain-boundary related phenomenon [9] and affected by many factors. It was reported that small grain size, besides suitable porosity, was desirable for an excellent PTCR behavior [10]. And small grain size is requested in ceramic sheets to provide a sufficient withstanding voltage for devices [11]. Brutchey et al. prepared PTCR ceramics using $BaTiO_3$ nano-crystals (~6 nm) synthesized by sol–gel method, and the obtained PTCR effect was close to that of the samples prepared by solid state method [12]. Nevertheless, the RT resistivity was very large because of the super fine grains. Thus, suitable grain size is necessary for achieving both a good PTCR effect and a relatively low RT resistivity in the preparation of laminated PTC ceramics. Furthermore, it was reported by Zou et al. [13] that smaller sizes of initial $BaTiO_3$ particles would lead to smaller grain sizes at the same sintering temperature. In other words, the grain sizes of the samples

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could be adjusted by particle sizes of the initial $BaTiO_3$ powders. However, little attention has been paid to the effects of initial particle size of the $BaTiO_3$ on electrical properties and densification of laminated PTC ceramics prepared by the reduction–reoxidation process.

In this paper two initial $Ba_{1.002}La_{0.003}TiO_3$ (BLT) particles with sizes of ~260 and ~820 nm were used to prepare BLT ceramics through the reduction–reoxidation process. The electrical properties and densification of ceramics were investigated in detail. In addition, a possible mechanism of oxygen diffusion during the reoxidation process was proposed based on our results and other related reports [14]. This mechanism was applied to explain the electrical behaviors of ceramics.

2. Experimental

Commercially available high-purity $BaCO_3$, TiO_2, and La_2O_3 were used as starting materials, and they were weighed according to the following formula: $(Ba_{1.002}La_{0.003})TiO_3$. The weighted chemicals were mixed by ball milling (50 rpm, 50 h) in deionized water with ZrO_2 balls and then calcined at 1150 °C for 2 h in air after being dried. The calcined mixture was milled in deionized water with ZrO_2 balls again for 90 min by two different ball-milling processes: sand milling and conventional planet ball milling (350 rpm). The diameter of ZrO_2 balls in the sand milling was of ~0.5 mm, and the agitation speed was as fast as 2400 rpm. Then the dried particles were mixed with proportional alcohol and organic binder by ball milling (50 rpm) for 16 h to form slurries for tape casting, respectively. Then green sheets with thickness of 40 μm were obtained by tape casting. These sheets were stacked and pressed. And the final tapes were cut into 5.64 mm × 1.84 mm blocks. Then the green bodies were sintered in a reducing atmosphere (3 vol% H_2, 97 vol% N_2) at different temperatures between 1045 and 1170 °C for 2 h with the heating rate of 300 °C/h and cooling rate of 200 °C/h. The sintered BLT ceramics were reoxidized at 500, 600, and 700 °C for 1 h in air with the heating rate of 5 °C/min. The samples prepared from BLT particles achieved by sand milling and planet ball milling were labeled as BLTS and BLTP, respectively.

The density of the ceramic samples was measured by Archimedes method. The resistivity–temperature (R–T) characteristics were measured in a temperature range from RT to 250 °C (AWXB R–T Test System, Wuhan, China). Complex impedance spectroscopy (4294A, Agilent, USA) was used to estimate the grain-boundary and grain resistances. Scanning electron microscope (SEM, VEGA3, TESCAN, Brno, Czech Republic) was adopted to investigate the microstructure of the powders and the sintered samples. The average sizes of powders and grains in sintered samples were determined by the linear intercept method.

3. Results and discussions

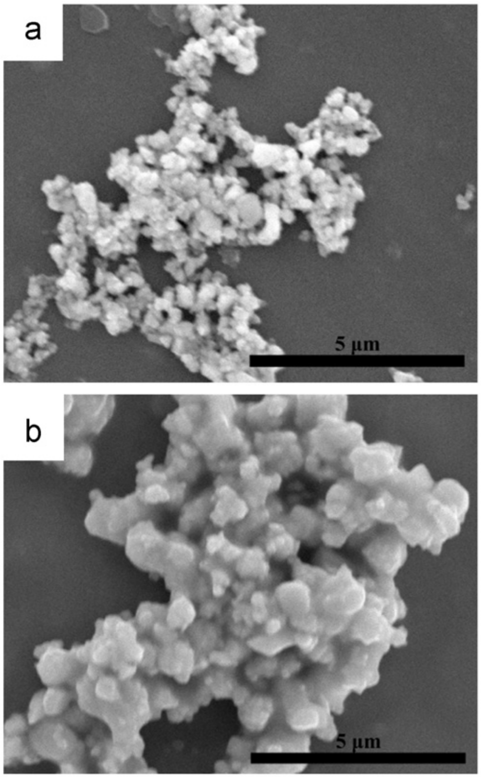

Fig. 1. Morphology of powders prepared by different milling processes: (a) sand milling and (b) planet ball milling.

Fig. 1 shows the SEM images of the sand milled and planet ball milled BLT particles. It is clear that the average size of the BLTS particles (~260 nm) is much smaller than that of the BLTP particles (~820 nm). And the two types of powders have a certain degree of aggregation.

Green tapes from BLTS and BLTP powders were prepared using the same tape casting process. The measured densities of the green compacts from BLTS and BLTP powders are 2.64 and 3.03 g/cm^3. With the same solid content (in mass), the slurry with finer particles will have a lower volume fraction value, and the strength of the sheets from the finer particles is higher than that from the coarser particles [15]. When the stacked sheets were subjected to the same pressure, the shrinkage rate of the BLTS green compact was smaller than that of the BLTP. So the density of the green compact from BLTS powders is smaller than that from BLTP powders.

Fig. 2 shows the relative density of BLTS and BLTP ceramic samples reduced at different temperatures. The densification curve of the BLTP samples shows a sigmoid shape. Similar results in ZnO ceramics were reported by Rahaman [16]. However, the curve of the BLTS samples reflects an incomplete sigmoid shape. For both BLTS and BLTP ceramics reduced at 1175 °C, the relative density is more than 0.90. Thus higher sintering temperature (> 1175 °C) was not carried out since higher sintering temperature and the corresponding higher density are not beneficial for the subsequent reoxidation process and recovery of PTCR effects [17]. For BLTP samples, the maximal densification rate is located in the relative density region of ~0.65–~0.80. When the relative density is more

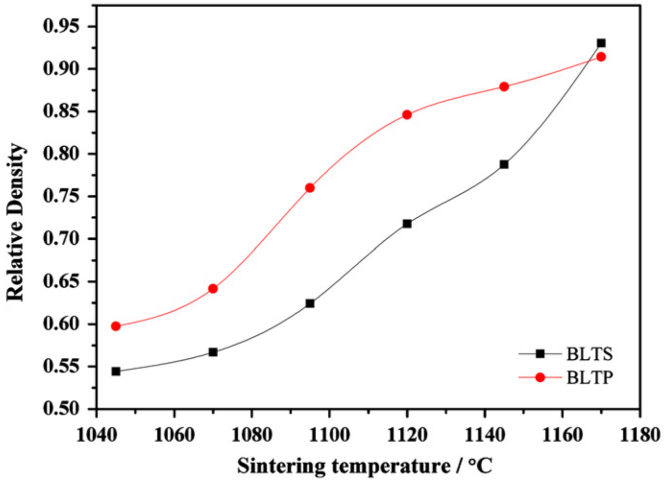

Fig. 2. Relative density of BLTS and BLTP ceramic samples reduced at different temperatures.

than ∼0.80 (corresponding to a sintering temperature of∼1110 °C), the densification rate begins to decrease. This observation is in a good agreement with the result reported by Rahaman [16]. But for the BLTS samples, the densification rate almost maintains a steady value in the sintering temperature range of 1070–1175 °C. It is supposed that for the BLTS samples the inflection point where the densification rate begins to decrease will move to a higher sintering temperature, probably due to their smaller initial particle size.

Fig. 3 shows the SEM images of samples reduced at different temperatures. It is demonstrated that smaller grains can be obtained from finer initial particles. The average grain sizes of the BLTP and BLTS samples reduced at 1145 °C are 1.6 μm (see Fig. 3(c)) and 630 nm (see Fig. 3(f)), respectively. The phenomenon is similar to the results of Brutchey et al. [12] and Zou et al. [13]. Abnormal growth is observed in the BLTP

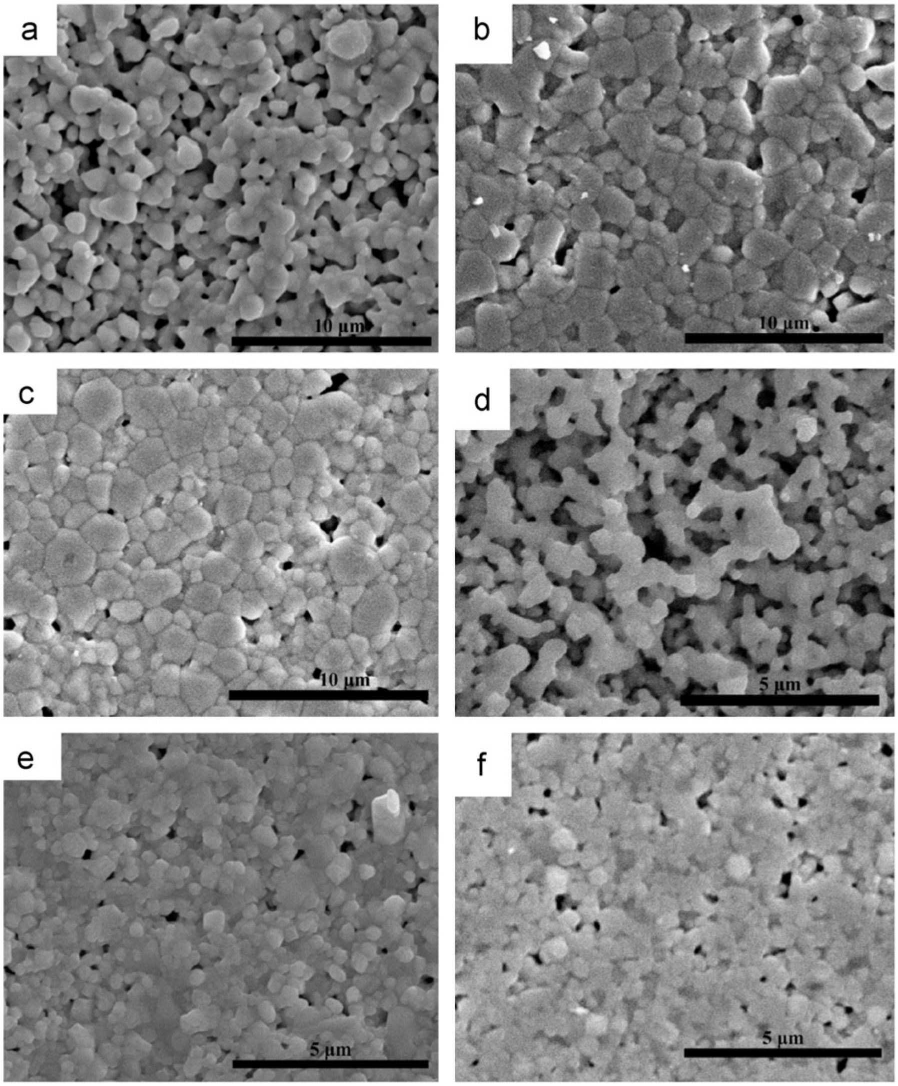

Fig. 3. Surface SEM images of BLTS and BLTP ceramic samples reduced at different temperatures: (a) BLTP, 1045 °C, (b) BLTP, 1095 °C, (c) BLTP, 1145 °C, (d) BLTS, 1045 °C, (e) BLTS, 1095 °C, and (f) BLTS, 1145 °C.

samples reduced at 1145 °C (see Fig. 3(c)) while not in the BLTS samples reduced at the same temperature (see Fig. 3(f)). According to Brook [18], when the pores are large and widely dispersed and the grain size is large as well, discontinuous grain growth is prone to take place. While this process is not easy to happen when the pores are large and the grain size is small. This is the reason why abnormal grain growth does not happen in the BLTS samples. Furthermore, for both BLTP and BLTS ceramic samples, the number and size of pores decrease with increasing sintering temperature, which is accordant with the results shown in Fig. 2.

Fig. 4 shows the R–T curves of BLTS and BLTP samples reduced at 1095 and 1145 °C and reoxidized in air at various temperatures for 1 h. It can be seen from Fig. 4(a) and (c) that the RT resistivities of the BLTS samples increase dramatically after the reduced samples being reoxidized. For example, the RT resistivities of BLTS samples reduced at 1095 °C without reoxidation and with reoxidation at 500, 700 °C are 97, 1.2×10^4, and $1.25 \times 10^6\ \Omega$ cm, respectively. This observation is in accordance with the results of Ured at al. [19]. In contrast, the changes in RT resistivity for BLTP samples are relatively small after reoxidation, as shown in Fig. 4(b) and (d). The PTCR jump of the BLTS samples reduced at 1095 °C increases when reoxidation temperature changes from 500 to 600 °C. However, it decreases when the temperature reaches 700 °C (Fig. 4(a)). The decrease of the PTCR effect may attribute to the huge RT resistivity. The resistivities of the BLTS samples reduced at 1145 °C are much smaller. Such abnormal decrease does not occur (Fig. 4(c)). In addition, the higher oxidation temperature leads to larger PTCR jump for the BLTP samples (Fig. 4(b) and (d)).

Fig. 5 is the impedance spectra of the BLTS and BLTP samples. Previous studies on impedance spectra of PTCR ceramics state that the left and right real axis intercepts of the arc stand for the grain bulk resistance and the sum of the grain bulk resistance and grain boundary resistance, respectively [20]. It can be seen that for both BLTS and BLTP samples the grain boundary resistance dominates the RT resistances. The grain-boundary resistance increases with the increase of the reoxidation temperature while the grain bulk resistance changes little. Moreover, the grain-boundary resistances of BLTS samples are much greater than those of BLTP samples. This is in agreement with the RT resistivity results shown in Fig. 4(a) and (b).

Based on above mentioned SEM, R–T curves, and impedance spectra results of BLTS and BLTP PTCR ceramic samples prepared by the reduction–reoxidation process, it is

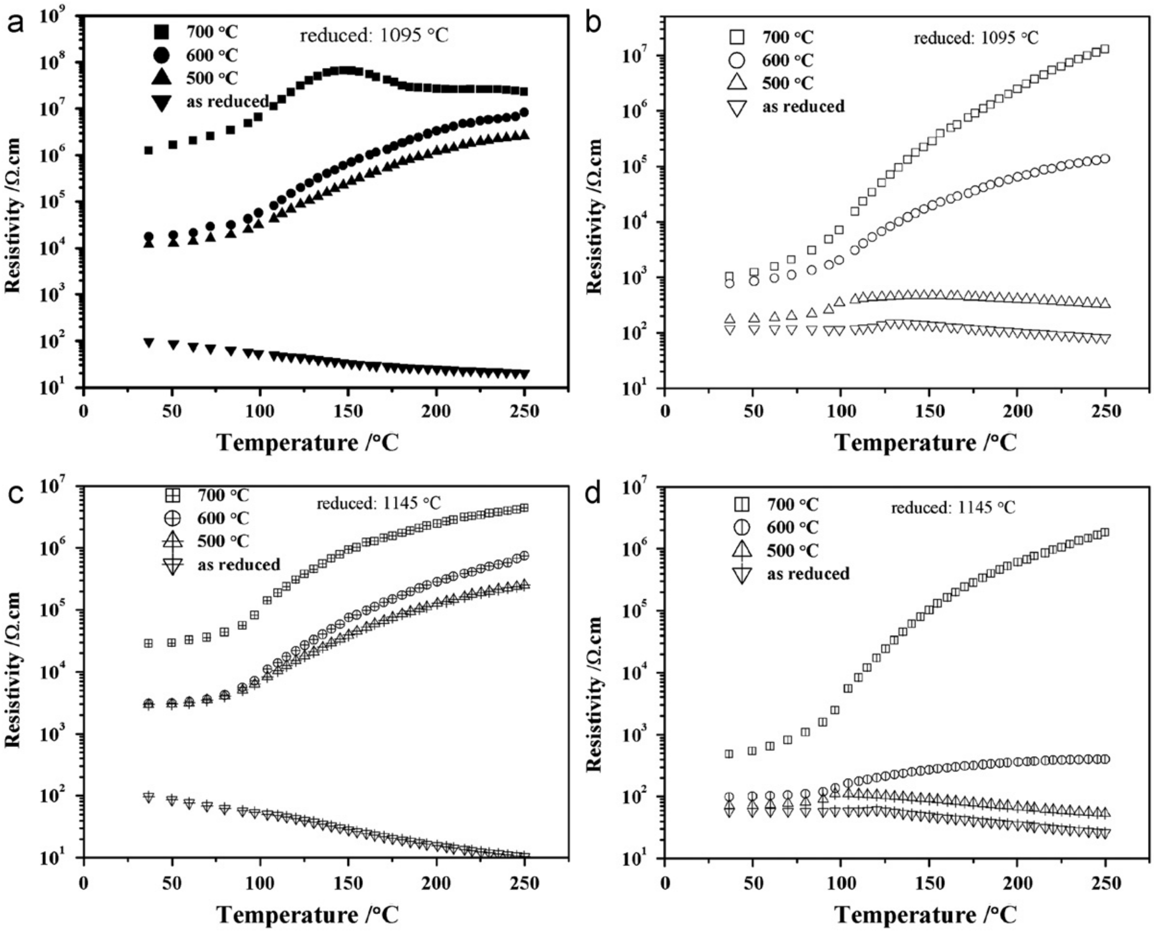

Fig. 4. Temperature dependence of the resistivity of as-reduced samples and the samples reoxidized at different temperatures for 1 h. (a) BLTS samples reduced at 1095 °C, (b) BLTP samples reduced at 1095 °C, (c) BLTS samples reduced at 1145 °C, (d) BLTP samples reduced at 1145 °C.

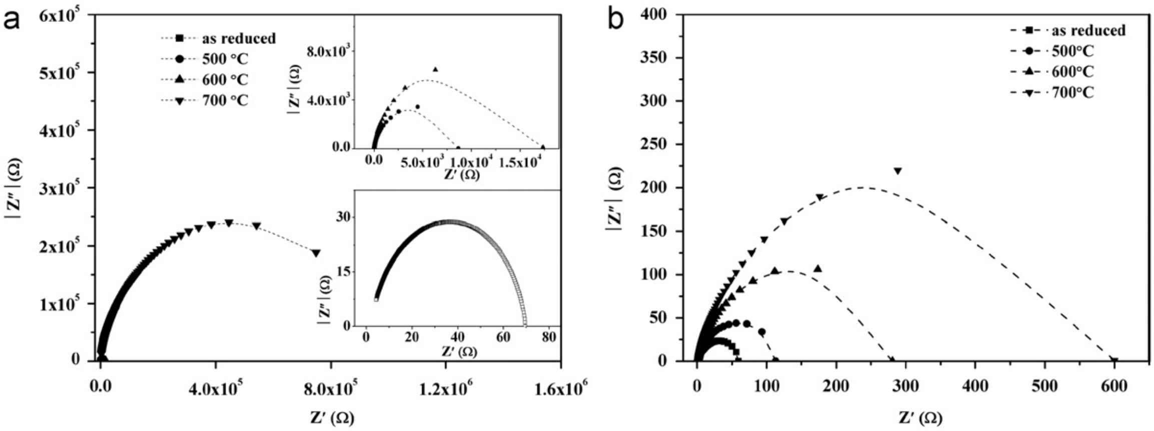

Fig. 5. Complex-plane impedance of samples reduced at 1095 °C and reoxidized at different temperatures (500–700 °C). (a) BLTS samples, (b) BLTP samples.

concluded that BLTS samples with smaller grains exhibited greater RT resistivities than BLTP samples. In order to explain this phenomenon, a possible mechanism of oxygen diffusion is put forward as follows.

Hasegawa et al. used O^{18} as tracer to examine the diffusion behavior of O_2 in the donor doped barium titanate dense ceramics sintered in air and Eq. (1) was used to calculate the depth profile of the tracer [7,21]:

$$(C-C_0)/(C_s-C_0)=\exp(x/2\sqrt{Dt}) \tag{1}$$

where C is O^{18} ion concentration at depth x from the sample surface, C_0 is the background intensity, C_s is the surface concentration of O^{18}, D is the diffusion coefficient, and t is the diffusion annealing time. It was found that the PTCR effect was proportional to the C_0, and the value of the C_0 is determined by the penetrated O_2 into the grain boundary. C_0 will increase with decreasing grain sizes and increasing reoxidation temperature since samples with smaller grains had more grain boundaries and the diffusion velocity of O_2 is quicker at higher reoxidation temperatures [7].

The diffusion behavior of O_2 in the reoxidation stage in this paper is different from that in dense ceramics mentioned above. Ceramics obtained by the reduction–reoxidation process are usually porous, and it is proposed that the diffusion process of the O_2 in the porous ceramics consists of three steps: diffusion of O_2 into pores, diffusion of O ion produced by chemisorbed oxygen into the grain boundary with a diffusion coefficient D_g, and subsequently into the grain bulk with a diffusion coefficient D_v. Grain boundary is oxidized quickly and O ion concentration in grain boundary reaches saturation value C_0 since D_g may be much larger than D_v for porous materials [6]. An approximate description of the depth profile of the O ion in the single grain bulk can be expressed by Eq. (1) just using D_v to replace D. Eq. (2) can be derived from Eq. (1)

$$\partial C'/\partial C'_s=\exp(x'/2\sqrt{D_v t})\geq 0 \tag{2}$$

where $C'_s=C_0$, namely the O ion concentration in the grain boundary. C' is the O ion concentration diffusing into the grain bulk at the depth x', which measures the depth from the surface of grain boundary. C'_0 is the background intensity of a single grain bulk, and $C'_0 < C'_s$.

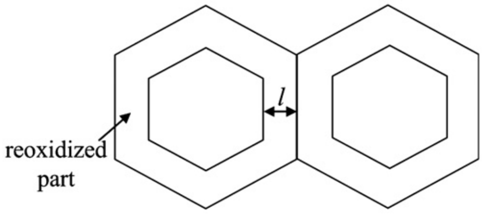

Fig. 6. Schematic drawing of the reoxidation process of the grains.

Compared with BLTP samples, BLTS samples have a lower relative density and a smaller grain size when the sintering temperature is lower than 1175 °C. So the value of C0 for BLTS samples is much larger than that of BLTP samples processed at the same oxidation temperature. For a single grain bulk, D_v is independent of the grain size [7]. Therefore it can be derived from Eq. (2) that BLTS samples have a larger C' at the same depth x' and annealing time t. In other words, BLTS samples have a larger O ion diffusion distance l (See Fig. 6). This means that BLTS samples with smaller grains are prone to be oxidized to a deeper degree and therefore have a much greater change in grain boundary resistance after reoxidation.

4. Conclusions

The densification and electrical properties of $Ba_{1.002}La_{0.003}TiO_3$ ceramics prepared by the reduction–reoxidation process with different initial particle sizes were investigated. The inflection point in the densification curve of BLTS samples prepared from smaller initial powders moves to a higher sintering temperature than that of the BLTP samples. The grains of the BLTP ceramic samples which resist reoxidation show an abnormal growth because of the large and widely dispersed pores and large initial powder particles. The BLTP samples reduced at 1095 °C have an excellent PTCR effect (~4.15 orders of magnitude) after reoxidized at 700 °C. However, the BLTS samples are prone to global reoxidation and exhibit a much greater change in grain boundary resistance and RT resistivity after reoxidation. A possible mechanism of oxygen diffusion is presented, which verifies that samples with smaller grains as well as lower density are easy to be oxidized to a deeper degree.

Acknowledgments

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