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INFLUENCE OF REOXIDATION ON SILICA-CONTAINING BARIUM TITANATE CERAMICS FOR PTCR THERMISTORS PREPARED BY TAPE CASTING

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Silica-containing barium-rich $BaTiO_3$ ceramics for thermistors with a positive temperature coefficient of resistance are prepared by a tape-casting technique. The ceramics are sintered in a reducing atmosphere at low temperatures of 1175 - 1225°C. The influences of reoxidation are investigated after the reduced ceramics are reoxidized in air at 700 - 900°C. An anomalous correlation is illustrated between room temperature resistivity and reoxidation temperature. The anomaly results from the ferroelectricity rebuilding mechanism, which includes the spontaneous polarization theory and the ferroelectricity degradation caused by oxygen vacancies. The acceptor-state densities are estimated from the temperature-dependent resistivity. A critical temperature of 750 - 800°C is concluded for the grain boundary reoxidation.

INTRODUCTION

Donor-doped polycrystalline barium titanate ($BaTiO_3$) ceramics were first discovered to have positive temperature coefficient of resistance (PTCR) in the 1950s. This phenomenon was later ascribed to the permittivity loss of grain boundaries above the Curie point. In later decades, electronic components that the age requested fell into the tendency of miniaturization and integration. Therefore, laminated PTCR thermistors and their fabricating process of "reduction-reoxidation" were proposed to meet the demands of low room temperature (RT) resistance and a sufficiently high PTCR jump. The new techniques brought fresh investigations of $BaTiO_3$ ceramics. Niimi et al. proved that Ba-rich $BaTiO_3$ ceramics exhibit a more significant PTCR effect than those with Ti-rich composition [1]. The re-ported ceramics showed much lower PTCR jump of approximate 2 orders of magnitude compared to that of air-sintered pellets, which normally exhibited resistance jumps over four orders of magnitude.

The reoxidation process influenced the electrical properties of the ceramics by adsorption of oxygen on grains. Langhammer et al. divided the oxygen adsorption at different temperatures into three stages: (a) annihilation of surface oxygen vacancies (250 - 800°C), (b) oxidation of grain boundaries (800 - 1250°C and (c) oxidation of inner grain bulk (above 1250°C) [2]. The presence of defects in oxides is very important for electronic device applications, because they deter-mine the electrical properties [3]. For example, antisite defects were found responsible for the large bandgap enhancement in $SrTiO_3$ thin films [4]. In particular, the oxygen vacancies (V_O) play specific roles in ferroelectrics. Lee et al. reported that the ferroelectricity of the reduced $BaTiO_3$ was dependent on the degree of reduction [5]. The existence of V_O adds electrons to the otherwise empty Ti-3*d* band and causes a change in the orbital symmetry of Ti-3*d* electrons near the defects. Therefore, the Ti–O hybridization is strongly perturbed [6]. It was also predicted that the tendency of transition metal ion for off-center distortion in the oxygen octahedron is eliminated when its *d* shell becomes partially occupied [7]. Many results of the reoxidation effects have been reported. However, the present knowledge is still far from a full understanding of the reoxidation, which is a key process in the fabrication of laminated $BaTiO_3$ ceramics. Therefore, new studies are expected on this topic, on which the present work focuses.

In the present work, SiO_2-containing $BaTiO_3$ ceramics are fabricated by the tape-casting technique. Sinte-

ring was conducted at low temperatures of 1175 - 1225°C in a reducing atmosphere. The reduced ceramics were subsequently reoxidized in air. Influence of the reoxidation on RT resistivity and PTCR jump is discussed. An anomalous correlation between RT resistivity and reoxidation temperature was observed and discussed in connection with the spontaneous polarization theory as well as ferroelectricity degradation caused by V_O. The acceptor-state density at grain boundaries is estimated from the temperature-dependent resistivity.

EXPERIMENTAL

The ceramics were prepared by the tape-casting technique, the details of which were described before [8]. The composition of the ceramics was $Ba_{1.004}Y_{0.004}TiO_3$. Silica was added to promote liquid phase sintering and its effect could be found in the previous discussion [8], which illustrated the optimized silica doping amount in the present composition. Commercial analytical grade $BaCO_3$, TiO_2, Y_2O_3 and SiO_2 were used as starting materials, which were ball-milled in deionized water using ZrO_2 balls for 3 h. The mixture was dried and calcined at 1150°C for 2 h and the resultant powder was ball-milled, dried and mixed with organic solvents. The obtained slurry was tape-casted to prepare green ceramics, the dimension of which was 6 × 3.75 × 1.5 mm^3. Sintering was conducted in a reducing atmosphere (97 % N_2 – 3 % H_2) at 1175 - 1225°C for 0.5 h. Such obtained ceramics were named "reduced ceramics". Some of the reduced ceramics were reoxidized at 700 - 900°C in air. The ceramic surface morphology was examined by a scanning electron microscope (SEM, XL-30TMP, Philips, Netherlands). In-Ga electrodes were pasted for electronic characterization on both sides of the samples, the dimension of which was 5.52 × 3.44 × 1.4 mm^3. The ceramic resistivity and its temperature dependence were measured in the temperature range of 25 - 250°C. The PTCR jump was defined as the ratio of the electrical resistivity at 250°C (ρ_{250}) to the one at 25°C (ρ_{25}).

RESULTS

Morphology

Figure 1 shows the surface morphologies of $BaTiO_3$ ceramics before and after reoxidation at 900°C. The grains exhibit a roundish polyhedral shape, with pores among them. Figure 1 a1, b1 and c1 reveal the morphologies of the samples sintered at 1175, 1200 and 1225°C, respectively. After being reoxidized at 900°C, the grains and their structure are almost the same as before reoxidation, as shown in Figure 1 (a2, b2 and c2). That means the reoxidation effect on the ceramic surface morphologies is extremely limited since the reoxidation temperature is much lower than the sintering temperature. The composition of the $BaTiO_3$ ceramic has been confirmed by X-ray diffraction pattern in our previous work [8]. A pure perovskite phase of $BaTiO_3$ was observed without any evidence of another phase.

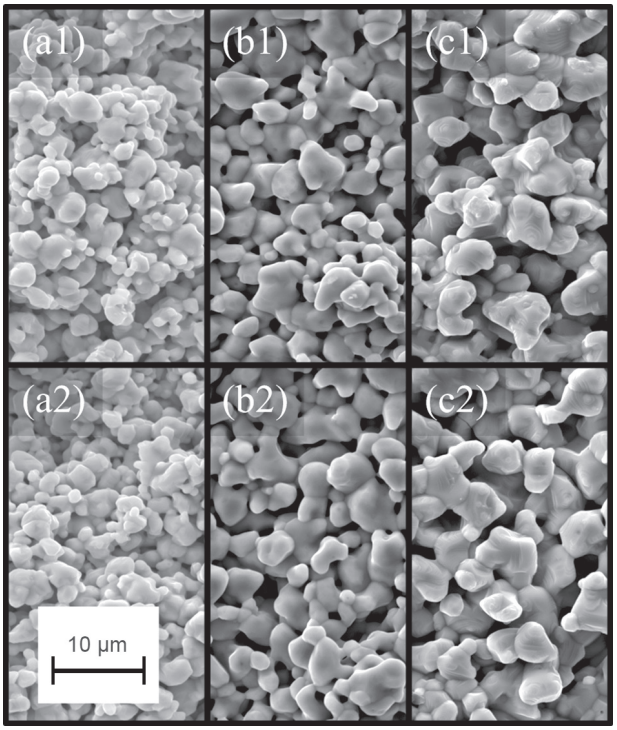

Figure 1. Surface morphologies of the $BaTiO_3$ ceramic samples sintered at 1175°C (a1), 1200°C (b1), 1225°C (c1) and their corresponding morphologies after reoxidation at 900°C (a2, b2, c2).

Electrical properties

The RT resistivity of ceramics is greatly influenced by the reoxidation. Figure 2 illustrates the dependence of RT resistivity on the reoxidation temperature of the samples sintered at 1175 - 1225°C. The resistivity curves first rise with increasing reoxidation temperature, reaching the maximum at 750°C and then turn to descend. After the stagnation points at 850°C, the resistivities make a slight lift at 900°C. The minimum resistivity of the reoxidized ceramics is obtained to be 28 Ω·cm, from the sample sintered and reoxidized at 1225 and 850°C, respectively.

The influence of reoxidation temperature on the PTCR jump of the samples sintered at 1175 - 1225°C is shown in Figure 3. The ceramics acquire significant PTCR effects after the reoxidation. In the temperature range of 700 - 900°C, the PTCR jumps increase monotonously. The corresponding temperature-dependent resistivities of the samples sintered at 1200°CC with various reoxidation temperatures are shown in Figure 4. Furthermore, the increased sintering temperature not only reduces the RT resistivity, but also diminishes the PTCR jump of the ceramics.

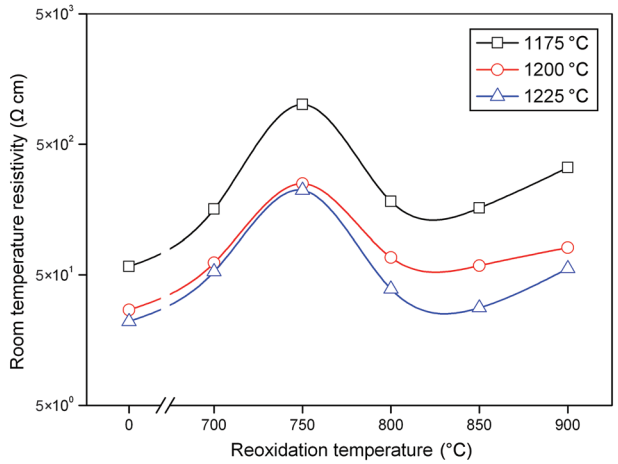

Figure 2. Dependence of room temperature resistivity on the reoxidation temperature of $BaTiO_3$ samples sintered at 1175, 1200 and 1225°C, respectively.

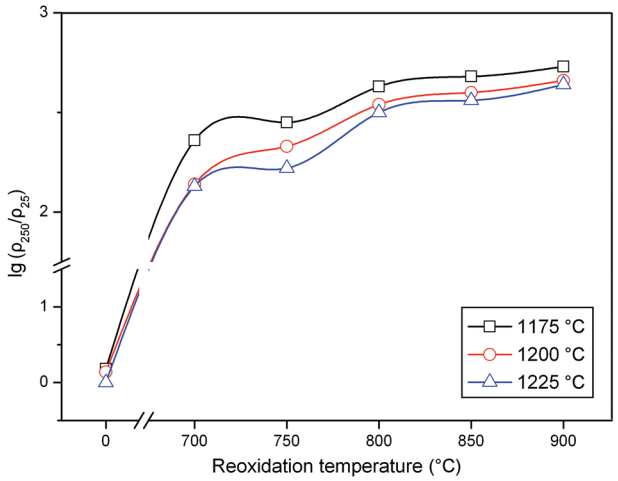

Figure 3. Relationship between PTCR jump and reoxidation temperature of the ceramic samples sintered at 1175 - 1225°C.

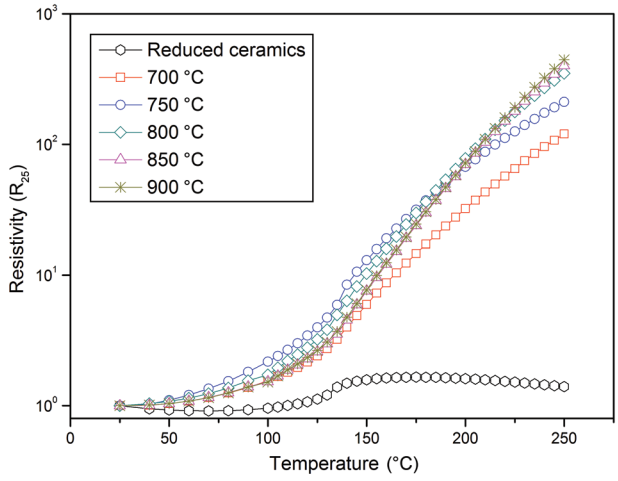

Figure 4. Temperature-dependent resistivity of the samples sintered at 1200°C and reoxidized at 700 - 900°C.

The reduced ceramics show a moderate PTCR effect, which means that the resistivity jump at the depletion layer in the grain is rather small. Generally, acceptors on the grain surface seize the free electrons in the grain, leaving the depletion layer, in which there is a Schottky potential barrier as a function of the permittivity. However, for the reduced ceramics, there is a great amount of V_O that compensates the acceptors. Therefore, a moderate PTCR effect is observed. After reoxidation, the V_O disappears and leaves the depletion layer to the acceptors. Consequently, the reoxidized ceramics show their PTCR effect when the temperature is higher than the Curie's point, above which the permittivity of the ceramic follows Curie-Weiss law. Similarly, the addition of Y may have a negative effect on the PTCR jump, as reported by Niimi et al [9]. They proved that some of the reduced ceramics may have a PTCR effect when donor additives other than Y were introduced, provided that the Ba/Ti ratio was above 1.02. The PTCR was also found in reduction-sintered $SrTiO_3$ ceramics with V_O, which would be responsible for the resistivity jump [3]. However, this phenomenon was proved to be associated with the Ba/Ti ratio of $BaTiO_3$ ceramics. Only a high Ba/Ti ratio is able to stimulate the PTCR effect of the reduced ceramics. Thus, no PTCR jump is observed in the present reduced Y-doped $BaTiO_3$ ceramics with their relatively low Ba/Ti ratio.

Estimate of donor and acceptor-state densities

According to research by Lee at al., two types of donors exist in the present n-type ceramics sintered in the reducing atmosphere [10]. One of them is yttrium and the other is the oxygen vacancy. It has been demonstrated that the resistivity of bulk grains is hardly influenced by reoxidation at a temperature below 1250°C [2]. Thus, the donor density (N_d) can be calculated to be 4.57×10^{17} cm^{-3}, from the corresponding RT resistivity (ρ_{RT}) of the reduced sample by $N_d = 1/\rho_{RT} q \mu$. Here, μ is the electron mobility in $BaTiO_3$ and was estimated to be 0.5 $cm^2 \cdot V^{-1} \cdot s^{-1}$ [11].

The estimate of acceptor-state density (N_S) is completed by using Hybrechts's method [11], which is based on the linear relationship between $\ln\rho$ and T^{-1} of the $BaTiO_3$ ceramics. If S is the slope of the linear function, N_S can be estimated according to Equation 1, provided that N_d is known.

$$S = -\frac{\partial \ln \rho}{\partial (T^{-1})} = \frac{q^2 \theta N_S^2}{8 k \varepsilon_0 C N_d}. \quad (1)$$

where k, q, ε_0 and T are the Boltzmann constant, the elementary charge, the permittivity of vacuum space and temperature, respectively. C and θ represent the Curie constant ($C = 1.5 \times 10^5$ K) and the extrapolated Curie-Weiss temperature ($\theta = 383$ K) [11].

Figure 5 plots the temperature-dependent resistivity

of the ceramic sintered at 1200°C and reoxidized at various temperatures in the range 700 - 900 °C in the coordinates of $\ln \rho \cdot \text{vs} \cdot T^{-1}$. The slopes ($S$) are acquired from the linear fitting functions used to calculate N_S. The inset of Figure 5 shows the influence of reoxidation temperature on the N_S values, which are within the range of 2.1 - 2.5 × 10^{13} cm^{-2}. N_S increases all along in the range of 700 - 900°C, meaning that the oxygen adsorption on the reduced grains is enhanced by increasing reoxidation temperature.

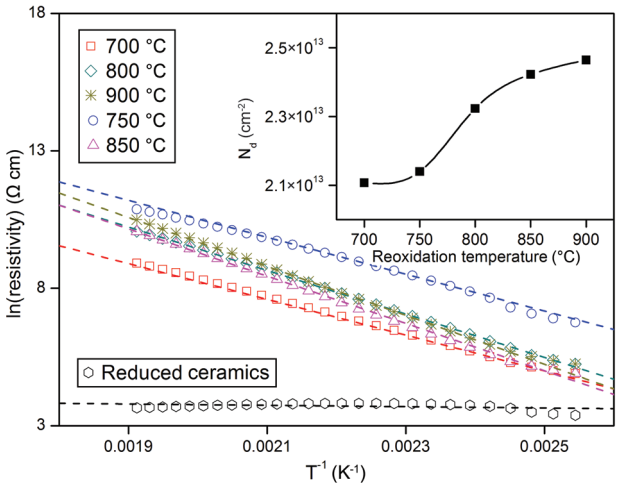

Figure 5. Plots of $\ln \rho$ vs T^{-1} of the ceramics sintered at 1200°C and reoxidized at 700 - 900°C and the estimated acceptor-state density (NS) in the inset.

DISCUSSION

It is commonly accepted that reoxidation can enhance the RT resistivity of the reduced ceramics, on which oxygen is adsorbed in the thermal treatment. However, as shown in Figure 2, an anomalous performance of RT resistivity is observed when the reoxidation temperature is within the range of 750 - 800°C, where a sharp decrease in RT resistivity is found. A similar phenomenon is found in Ba-excessive $BaTiO_3$ ceramics with BN addition produced via different fabricating routes in our previous work. A tentative explanation has been proposed by combining spontaneous polarization theory and ferroelectricity degradation caused by oxygen vacancies [12]. The degraded depletion layer at grain boundaries can rebuild its ferroelectricity after oxygen defects are eliminated. Therefore, the ceramic resistivity reveals an expected rising trend before the peak at 750°C, followed by a decrease due to the rebuilding ferroelectrical compensation.

Furthermore, the foregoing explanation of ferroelectricity rebuilding mechanism can be supported by the interpretation of Huybrechts et al. [11], which focuses on the relationship between the RT resistivity and N_S. The proposition demonstrates that the RT resistivity depends very strongly upon the N_S, if no ferroelectrical compensation occurs at grain boundaries. A relatively small influence of RT resistivity on N_S means that the acceptors are partially compensated. Otherwise, the compensation in Jonker's theory [13] will result in the independence of resistivity on N_S. Figure 6 gives out the plots of RT resistivity against N_S. The plots can be divided into two parts. The first part that shows an increasing trend comprises the reduced ceramics and the ones reoxidized at 700 and 750°C, as fitted by curve (a). The strong dependence of RT resistivity on N_S indicates that the acceptors are not compensated at all. Nevertheless, the second part derived from the ceramics reoxidized at 800 - 900°C exhibits much less variation, as fitted by curve (b). It means that acceptors are completely or partially compensated by the spontaneous polarization charges under the ferroelectricity compensation mechanism, which disappears in the reduced ceramics and is rebuild after the reoxidation in a temperature higher than 750°C. There would be a critical temperature between 750 and 800°C, above which the aerial oxygen is able to diffuse into the grains significantly in the reoxidation process to rebuild the ferroelectricity of the $BaTiO_3$ ceramics. The result is in good agreement with that of Langhammer et al. [2].

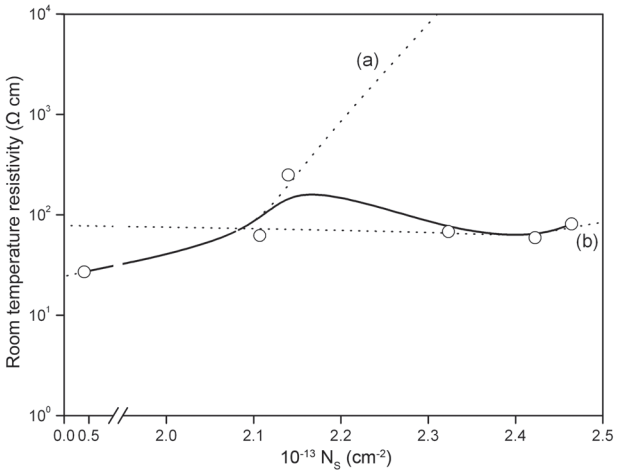

Figure 6. Room temperature resistivity as a function of the acceptor-state density (NS) of the ceramic sintered at 1200°C.

CONCLUSIONS

Y-doped $BaTiO_3$ ceramics with silica addition were prepared by the tape-casting and reduction/reoxidation process. The influences of reduction-sintering and reoxidation temperatures on ceramic characteristics have been discussed. The RT resistivity shows an anomalous trend against reoxidation temperature. This correlation is ascribed to the rebuilding of spontaneous polarization

after the V_O annihilation of the ferroelectric $BaTiO_3$ ceramics in the reoxidation process. The estimated N_S of samples reoxidized at various temperatures is correlated with RT resistivity, resulting in a critical temperature between 750 - 800°C, above which the reduced grain boundary region starts to oxidize in the reoxidation.

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