Effects of Ca substitution on room temperature resistivity of donor-doped barium titanate based PTCR ceramics

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Barium titanate based semiconducting ceramics were synthesized using Ca²⁺ and La³⁺ as dopants, TiO₂, SiO₂ and MnO as sintering aids, and various firing process. The Ca²⁺ contained ceramics without impurity phases, sintered in reducing atmosphere and subsequent annealing in air, showed both the PTCR (Positive Temperature Coefficient of Resistivity) behavior and low room temperature resistivity $\rho_{RT}$ $2.2$ $\Omega$ cm. Based on knowledge of ionization energy and bond disassociation energy, it was cleared that Ca substitution plays an important role in lowering the $\rho_{RT}$ value in the ceramics.

Key-words: Barium titanate, Positive temperature coefficient of resistivity, Semiconducting ceramics, Ca substitution, Room temperature resistivity

1. Introduction

Materials with a positive temperature coefficient of resistivity (PTCR) property exhibit an anomalous increase in their electrical resistance when heated above a certain temperature. They are widely used as numerous electrical and electronic applications, for example as thermal sensors, resettable fuses against current overload and self-regulating heater elements. Recently, due to demands of miniaturization of the electrical devices or reduction of the energy consumption, PTCR materials with lower electrical resistivity at room temperature $\rho_{RT}$ have been strongly required. Both barium titanate based semiconducting ceramics and polymer composites have been applied to the PTCR devices. The polymer composites show lower $\rho_{RT}$ values than barium titanate based semiconducting ceramics, but their electrical properties easily deteriorate due to poor mechanical or thermal stability. Even if the devices are used under applying high current and power, the electrical properties must be stable. Therefore, barium titanate based semiconducting ceramics with low $\rho_{RT}$ value are undoubtedly desired.

Slightly donor doped barium titanate with ions such as La³⁺, Y³⁺ and Nb⁵⁺ indicates semiconducting and PTCR behavior. Electrical properties of barium titanate based semiconducting ceramics vary drastically with compositions including sintering additives and processing parameters. It was reported that an isovalent substitution of Ba²⁺, for example Ca²⁺, Sr²⁺ and Pb²⁺ substitution, is effective to lower $\rho_{RT}$ values. However, the mechanism has not been cleared. Use of sintering aids such as TiO₂ and SiO₂ is also effective to give low $\rho_{RT}$ to the ceramics. Acceptor additives such as MnO are important to improve PTCR behaviors namely resistivity jump properties in barium titanate based semiconducting ceramics. The PTCR ceramics sintered in reducing atmosphere show very small or no PTCR behavior but have low resistivity at room temperature. It was also reported that the ceramics possess PTCR properties after post annealing in air. Recently, it has been reported that the solid solution of bismuth sodium titanate and barium titanate can be semiconductive by adding CaO. Therefore, we expected that Ca²⁺ substitution effectively reduce $\rho_{RT}$ value in barium titanate based ceramics.

In this study, we have mainly investigated the influence of Ca²⁺ substitution for Ba³⁺ on electrical properties in barium titanate based semiconducting ceramics.

2. Experimental procedure

Samples were synthesized by solid state reactions. Commercially available high purity BaCO₃, TiO₂, CaCO₃, SiO₂ powder and the nitrate of lanthanum and manganese were used as starting materials and weighed as following formula:

$$\text{Ba}_{0.998-\delta}\text{Ca}_{\delta}\text{La}_{0.002}\text{Ti}_x\text{O}_{3+y} + 0.02\text{SiO}_2 + 0.0004\text{MnO} \quad (1)$$

When $x$ is the amount of Ca²⁺ substitution for Ba²⁺ ($x = 0, 0.02, 0.05, 0.08, 0.13, 0.23, 0.33$) and $y$ is the amount of titanium ion ($y = 1.000, 1.002, 1.005, 1.010$). Weighed raw materials were mixed by ball milling for 15 h in ethanol with ZrO₂ balls (3 mm in diameter) and calcined at 1150°C for 2 h in air. The calcined powder was mixed again by ball milling for 15 h in 0.1% ammonia water with poly (vinyl acetate) as a binder with ZrO₂ balls (3 mm in diameter). Mixed powder was dried and granulated. Granules were pressed into pellets of 13 mm in diameter. Green bodies were sintered at 1320°C for 2 h in air. Green bodies with composition of $x = 0$, $y = 1.002$ and $x = 0.13$, $y = 1.002$ were also sintered at 1320°C for 2 h in reducing atmosphere with an oxygen partial pressure of $5 \times 10^{-12}$ MPa. The ceramics were then post annealed at 1100°C for 2 h in air. The heating and cooling rates in all the sintering processes were $5°C/min$.

The crystalline phases of sintered ceramics were analyzed and identified by the powder X-ray diffraction (XRD) technique. In order to calculate the lattice parameters, Si powder was added as an internal standard. The microstructures of the ceramics were analyzed by scanning electron microscopy (SEM). The ceramic surfaces of as-fired samples were observed. The electrical resistance of sintered ceramics was measured by the two-terminal method with In-Ga liquid alloy counter electrodes for a temper-
3. Results and discussion

XRD patterns of the ceramics with composition of $y = 1.002$ sintered in air are shown in Fig. 1(a). Ceramics with $\text{Ba}^{2+}$ replaced by a little $\text{Ca}^{2+}$ of the range from $x = 0$ to $x = 0.13$ were composed of the barium titanate single phase. On the other hand, highly replaced by $\text{Ca}^{2+}$ of range from $x = 0.23$ to $x = 0.33$ samples include calcium titanate phase as an impurity. We confirmed no deference in XRD patterns between the ceramics sintered on various conditions, namely sintered in air, sintered in reducing atmosphere and post annealed in air after sintering in reducing atmosphere. Figure 1(b) shows the lattice parameters and the tetragonality ($c/a$) of these samples. As the amount of $\text{Ca}^{2+}$ substitution for $\text{Ba}^{2+}$ increased, the lattice parameters $a$ and $c$ decreased and the tetragonality slightly increased.

Figure 2 shows grain size change against the composition $x$ of $\text{Ba}_{0.998-x}\text{Ca}_x\text{La}_{0.002}\text{Ti}_{1.002}\text{O}_3$ ceramics sintered at 1320°C for 2 h in air. The average grain size of the ceramics with $x = 0$ had approximately 20 $\mu$m. The average grain size of ceramics with composition of $x = 0.33$ and $y = 1.002$ was approximately 5 $\mu$m. It was found that the substitution of $\text{Ca}^{2+}$ for $\text{Ba}^{2+}$ inhibited the grain growth.

Figure 3 shows grain sizes changes against the composition $y$ of $\text{Ba}_{0.998-x}\text{Ca}_x\text{La}_{0.002}\text{Ti}_{1.002}\text{O}_3$ ceramics with $x = 0$ and 0.13 sintered at 1320°C for 2 h in air. When the ceramics contained no Ca, the average grain size decreased with increasing the amount of $\text{Ti}^{4+}$. On the other hand, in the ceramics with the composition of $x = 0.13$, the average grain sizes are substantially constant at 10 $\mu$m without depending on the amount of $\text{Ti}^{4+}$.

Figure 4 shows the $\rho_{\text{RT}}$ value of each ceramics sintered in air. In the ceramics with the composition of the range from $x = 0$ to 0.13, which were composed of the barium titanate single phase, the $\rho_{\text{RT}}$ value decreased with increasing the amount of $\text{Ca}^{2+}$. On the other hand, when calcium titanate phase appeared (when $x$ is more than 0.23), the $\rho_{\text{RT}}$ value increased with increasing the amount of $\text{Ca}^{2+}$. The lowest $\rho_{\text{RT}}$ with 4.3 $\Omega\text{cm}$ among the ceramics sintered in air was obtained in the ceramics with composition of $x = 0.13$ and $y = 1.002$. In most of PTCR ceramics, the grain boundary has higher electrical resistivity than the grain inside. Therefore, the ceramics with larger grain size (less grain boundary density) should show lower $\rho_{\text{RT}}$ value. However, in the ceramics with the compositions of $x$ in the range from $x = 0$ to 0.13 and $y = 1.002$, the $\rho_{\text{RT}}$ value decreased with the increase of the amount of $\text{Ca}^{2+}$ although the grain size decreased, that is, the grain boundary density increased. Therefore, it was concluded that $\text{Ca}^{2+}$ substitution is an important part in the lowering $\rho_{\text{RT}}$ in...
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Fig. 3. Grain sizes changes against the composition \( y \) of \( \text{Ba}_{0.998-x}\text{Ca}_x\text{La}_{0.002}\text{Ti}_3\text{O}_{4.5} \) ceramics with \( x = 0 \) and 0.13. These ceramics were sintered at 1320°C for 2 h in air.

Fig. 4. Room temperature resistivity \( \rho_{RT} \) of \( \text{Ba}_{0.998-x}\text{Ca}_x\text{La}_{0.002}\text{Ti}_3\text{O}_{4.5} \) ceramics sintered at 1320°C for 2 h in air.

Fig. 5. Temperature dependence of the electrical resistivity of \( \text{Ba}_{0.998-x}\text{Ca}_x\text{La}_{0.002}\text{Ti}_3\text{O}_{4.5} \) ceramics sintered (a) at 1320°C for 2 h in air, (b) at 1320°C for 2h in reducing atmosphere with the oxygen partial pressure of 5 \( \times \) 10^{-12} MPa and (c) post annealed at 1100°C for 2 h in air after sintering under the condition (b). The dashed lines correspond to \( x = 0 \) and the solid lines correspond to \( x = 0.13 \).

4. Conclusions

In this study, the barium titanate based semiconducting ceramics with both the PTCR behavior and low \( \rho_{RT} \) value were synthesized. It was found that Ca\(^{2+} \) substitution for Ba\(^{2+} \) was effective in lowering the electrical resistivity at room temperature. This observation was well explained by the difference in both ionization energy and bond dissociation energy between Ca\(^{2+} \) and Ba\(^{2+} \). Moreover, the Ca contained ceramics sintered in reducing atmosphere were less influenced by post annealing in air, that is, re-oxidation process, compared with the ceramics without Ca substitution. In this study, we clarified the role of Ca\(^{2+} \) substitution for Ba\(^{2+} \) playing in the electrical resistivity.

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