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The thermal sensitivity and dielectric properties of $SrTiO_3$-based ceramics

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Abstract

The thermal sensitivities of $SrTiO_3$-based ferroelectric ceramics and the dielectric properties have been investigated. Strontium–lead titanate ceramics with variable NTCR–PTCR composite effect were prepared by controlling Pb concentration of the grain boundaries. It was efficient for lowering the room temperature resistivity (ρ_{RT}) and weakening the negative temperature coefficient of resistance (NTCR) effect of (Sr, Pb)TiO_3 ceramics by adding a small amount of excess PbO. A transformation of thermal sensitivity from the positive temperature coefficient of resistance (PTCR) to NTCR–PTCR characteristics was also observed after a heating treatment process, showing the NTCR–PTCR composite effects of (Sr, Pb)TiO_3 semiconducting ceramics were closely related to the variation of Pb concentration at the grain boundaries. The conduction mechanism was proposed to reasonably explain the NTCR–PTCR composite effect of (Sr, Pb)TiO_3 semiconducting ceramics. $SrTiO_3$ ceramics capacitors were fabricated by using La_2O_3–CuO–PbO as dopants. It exhibited a high dielectric constant with stable temperature characteristics. It was found that PbO addition benefited to increasing the dielectric constant and CuO addition mainly segregated at the grain boundaries to form the isolation layers. The relationships between the microstructures and the dielectric properties of $SrTiO_3$–La_2O_3–CuO–PbO system were discussed.

Keywords: C. Dielectric properties; E. Thermistors; $SrTiO_3$-based ceramics; PTCR effect; NTCR effect

1. Introduction

Strontium titanate-based ceramics have been widely used to fabricate some electronic components, such as grain boundary layer capacitors (GBLC) [1], varistors [2], sensors [3], and so on. The Curie temperature (T_c) of pure $SrTiO_3$ is about 110 K, which can shift to the higher temperature by Ba^{2+} or Pb^{2+} substituting for Sr^{2+}. The composite perovskite structure materials, such as (Sr, Ba)TiO_3, (Sr, Pb)TiO_3 have been developed to fabricate some devices [4–6].

(Sr, Pb)TiO_3 ferroelectric ceramics have paid much attention since the composite thermal sensitivity was observed in 1988 [7]. This kind of semiconducting materials exhibits the negative temperature coefficient of resistance (NTCR) effect below the Curie temperature (T_c) and the positive temperature coefficient of resistance (PTCR) effect above T_c [8,9]. They have the potential to be utilized as the precise temperature controllers, the self-regulating heaters and the overflow protect devices etc. [10]. The research for improving the thermal sensitivity and revealing the conduction mechanism of (Sr, Pb)TiO_3 ceramics is still intriguing [11,12].

With the requirement of integration and miniaturization of instruments, it is necessary to fabricate the capacitors with high capacitance, high reliability and small size [13]. $SrTiO_3$ is paraelectric materials, which has potential advantage to prepare capacitors with high dielectric constant, and stable temperature characteristics based on $SrTiO_3$ ceramics.

As known, (Sr, Pb)TiO_3 semiconducting ceramics grain boundary layers capacitors (GBLC) with high dielectric constants are generally sintered in a reducing atmosphere [14,15]. But it is still difficult to obtain high dielectric constant $SrTiO_3$ ceramics by sintering in air. Therefore,

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it remains of interest to study the dielectric properties of $SrTiO_3$ materials in an oxidizing atmosphere.

In this paper, the ferroelectric (Sr,Pb)TiO_3 thermistors and paraelectric $SrTiO_3$ dielectric ceramics were prepared. The microstructures and electrical properties were investigated to find out the comparability between the both $SrTiO_3$-based ceramics mentioned above.

2. Experimental

2.1. (Sr, Pb)TiO_3 thermistors ceramics

Analytical grade PbO, TiO_2, $La(NO_3)_3$ and high grade $SrTiO_3$ (decomposed $SrTiO(C_2O_4)_2 \cdot 4H_2O$ at 1000 °C for 4 h) were used as starting materials. The weighted powders were wet-milled in ethanol for 48 h in a plastic jar. After drying and sifting, the mixtures were calcined at 800 °C for 2 h to prepare 0.5 mol% La-doped $Sr_{1-x}Pb_xTiO_3$ powders ($x = 0.5, 0.6$). Furthermore, 2 mol% PbO powders were added to the $Sr_{0.5}Pb_{0.5}TiO_3$ powders and well mix again in order to compensate PbO loss. Above mixture powders were pressed into disks with 10 mm diameter and about 1 mm thickness. Then the green pellets were sintered at 1075–1200 °C for 1 h and cooled at the rate of 4 °C/min. The surfaces of samples were coated with In–Ga alloy and their resistivity-temperature characteristics were measured from room temperature up to 400 °C with a dc resistance–temperature measuring system.

2.2. $SrTiO_3$ dielectric ceramics

A small amount of PbO (<2 mol%) was added into high purity $SrTiO_3$ powders, the mixtures were wet-milled in ethanol for 48 h. After drying and sifting, the powders were calcined at 800 °C for 2 h. Subsequently, 0.25 mol% La_2O_3 and 1.0 mol% CuO were added into the calcined powders and well milled again. Then the drying powders were pressed into discs with about 1 mm thickness and 10 mm in diameter. Finally, the green pellets were sintered at 1280 °C in air for 2 h and cooled down.

The sintered ceramics were coated with silver electrodes. The dependence of dielectric properties on the temperature was measured by an impedance-frequency meter (HP4192A). The measuring temperature range is −60 to 150 °C, and the frequency is at 1 KHz. After ion-beam thinning, the sample's microstructure was investigated by a transmission electron microscope (Hitachi-800) associated with an energy dispersive analysis of X-ray (H-9100).

3. Results and discussion

3.1. Thermal sensitivity of (Sr, Pb)TiO_3 ceramics

Fig. 1 gives the resistivity (ρ)–temperature (T) plots of La-doped strontium–lead titanate semiconducting ceramics sintered at 1100 °C for 1 h. It shows that the sintered ceramics exhibit the strong NTCR–PTCR composite effects. At $T < T_c{}^*$, the ceramic resistivity dropped down with elevating the measuring temperature, showing a negative temperature coefficient of resistance (NTCR) effect. The values of $\log(\rho_{RT}/\rho_{min})$ are 0.533 (Sr/Pb = 1/1) and 1.15 (Sr/Pb = 2/3), respectively. At $T > T_c{}^*$, the ceramic resistivity jumped abruptly with the phase transformation from tetragonal to cubic, showing a typical positive temperature coefficient of resistance (PTCR) effect. The values of $\log(\rho_{max}/\rho_{min})$ are 5.45 (Sr/Pb = 1/1) and 4.54 (Sr/Pb = 2/3), respectively. Where $T_c{}^*$ is the switch point, which is defined as the temperature corresponding to the twice minimum resistivity (ρ_{min}) in the PTCR effect region.

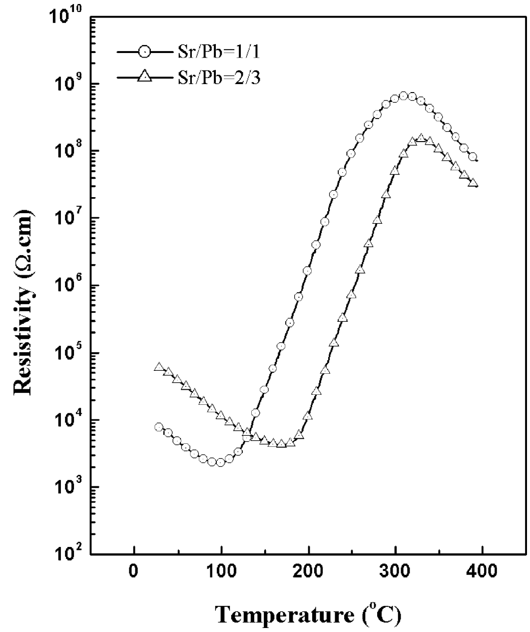

Fig. 1. Resistivity–temperature plots of 1100 °C-sintered (Sr, Pb)TiO_3 ceramics with Sr/Pb = 1/1, 2/3, respectively.

Fig. 2 gives the ρ–T plots of excess 2 mol% PbO-doped (Sr, Pb)TiO_3 ceramics sintered at 1075–1200 °C for 1 h. It can be seen that the samples sintered below 1100 °C only exhibit typical PTCR effect. The value of $\log(\rho_{RT}/\rho_{min})$ of 1100 °C-sintered sample decreased from 0.533 to 0.14 by doping 2 mol% PbO comparing with that in Fig. 1. With increasing the sintering temperature between 1100 and 1200 °C, the samples' ρ_{RT} and NTCR ($T < T_c$) regularly increase. A small amount of PbO additives lower the ρ_{RT} and weaken the NTCR effects of (Sr, Pb)TiO_3 ceramics. The ρ–T characteristics of (Sr, Pb)TiO_3 ceramics can be varied from NTCR–PTCR type to typical PTCR type by reducing PbO loss during sintering. The detail parameter of ρ–T characteristics are shown in Table 1, where α_{+30} and α_{-50} are defined as the resistivity differential variability at the temperature of $T_c^* + 30$ and $T_c^* - 50$, respectively. Meanwhile, the ρ_{RT} of 1075 °C-sintered sample is slightly higher than that of 1100 °C-sintered sample in Fig. 2. It can be explained that the residual PbO segregated on the grain boundaries to form an isolation layer, which increased the resistivity of (Sr, Pb)TiO_3 semiconducting ceramics.

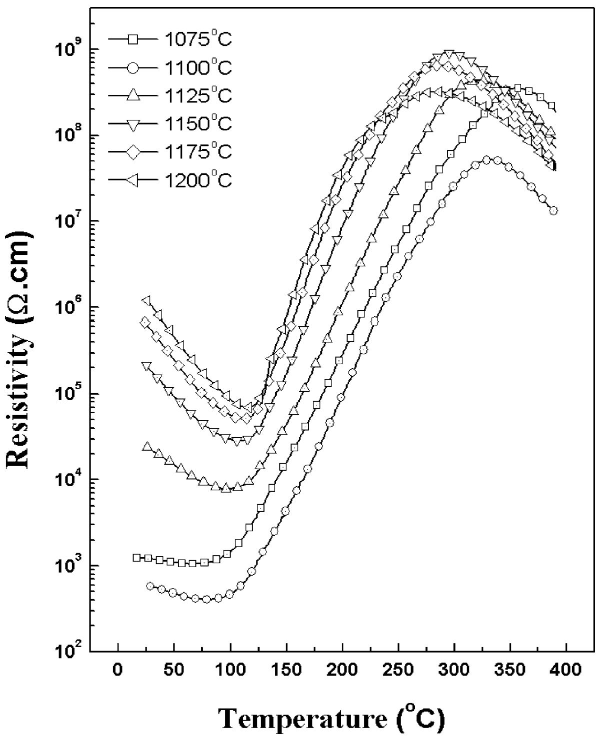

Fig. 2. Resistivity–temperature plots of 2 mol% PbO-doped $Sr_{0.5}Pb_{0.5}TiO_3$ ceramics sintered at 1075–1200 °C for 1 h.

Above results show that the thermal sensitivity of (Sr, Pb)TiO_3 ceramics is obviously affected by the variation of PbO concentration at different sintering conditions. PbO additives forms a concentration gradient between the grain boundary and the grain interior during sintering, which decreases the transfer of Pb^{2+} ions and prevents the formation of the Pb-deficient grain boundary layers. Certainly, the residual PbO at the grain boundaries also increase the ceramic resistivity because formed the isolation layers. In our previous study, a heat-treatment at 950 °C was employed to wipe out the residual PbO, so a transformation from PTCR to NTCR–PTCR characteristics was observed in 4 mol% PbO-doped (Sr, Pb)TiO_3 ceramics [16]. In addition, overmuch Pb volatilization also results in the formation of cationic vacancies, sample exhibits the high ρ_{RT} and strong NTCR effect ($T < T_c$*) with increasing the sintering temperature. Therefore, it is important for preparing low ρ_{RT} (Sr, Pb)TiO_3 ceramics by controlling Pb concentration at the grain boundaries suitably, and the NTCR effect ($T < T_c$*) is related to the PbO loss.

3.2. Conduction mechanism of (Sr, Pb)TiO_3 thermistors

According to above results, the electrical conduction of La-doped (Sr, Pb)TiO_3 ceramics is closely related to the variation of Pb content in the materials. Pb volatilization is beneficial to the substitution of Pb^{2+} positions by La^{3+} ions, which can be described as following:

$$Sr_{1-x}Pb_xTiO_3 + yLaO_{3/2} \rightarrow (Sr_{1-x}Pb_{x-y}La_y) \times (Ti_{1-x}{}^{4+}Ti_x{}^{3+})O_3 + yPbO + \tfrac{1}{4}yO_2 \uparrow \quad (1)$$

Eq. (1) showed that the substitution of Pb^{2+} positions by La^{3+} ions produces the redundant charges in $Sr_{1-x}Pb_xTiO_3$ lattices. The non-equivalent charges can be compensated by a way of forming Ti^{3+} ions, which will increase the charge carrier density and improve the electrical conduction of (Sr, Pb)TiO_3 ceramics. Meanwhile, overmuch PbO loss also resulted in the formation of Pb^{2+} vacancies (V''_{Pb}), which can also compensate the redundant charges produced by donor defects ($La_{Pb}{}^{\bullet}$). The later compensation can be approximately described as following:

$$Sr_{1-x}Pb_xTiO_3 + yLaO_{3/2} \rightarrow Sr_{1-x}Pb_{x-(3/2)y}O_{1-(3/2)y} \times La_{Pb}{}^{\bullet} + \tfrac{3}{2}yPbO + \tfrac{1}{2}yV''_{Pb} + \tfrac{3}{2}yO_O \quad (2)$$

$$V''_{Pb} + 2La_{Pb}{}^{\bullet} \leftrightarrow (V''_{Pb}\,2La_{Pb}{}^{\bullet}) \quad (3)$$

It can be seen that Pb volatilization plays a key role for prepare strontium–lead titanate semiconducting ceramics. Small amount of PbO loss from lattices benefits to lowering the room temperature resistivity because the Pb^{2+} vacancies will be easily occupied by rare-earth ions, such as Y^{3+}, La^{3+}, and so on. However, overmuch Pb^{2+} vacancies also degenerate the electrical conduction of strontium–lead titanate ceramics by forming defect composition ($V''_{Pb}\,2La_{Pb}{}^{\bullet}$). Therefore, controlling Pb volatilization or supplying suitable PbO are key processes for preparing low resistivity (Sr, Pb)TiO_3 ceramics. In addition, the NTCR effect of (Sr, Pb)TiO_3 ceramics became strong at

Table 1
Resistivity–temperature parameters of 2 mol% PbO-doped $Sr_{0.5}Pb_{0.5}TiO_3$ ceramics sintered at 1075–1200 °C for 1 h

	Samples					
	1	2	3	4	5	6
Sintering temperature (°C)	1075	1100	1125	1150	1175	1200
ρ_{RT} (Ω cm)	1.22×10^3	5.53×10^2	2.39×10^4	2.06×10^5	6.33×10^5	1.19×10^6
ρ_{min} (Ω cm)	1.04×10^3	4.02×10^2	7.83×10^3	2.85×10^4	5.11×10^4	6.94×10^4
$\log(\rho_{max}/\rho_{min})$	5.53	5.11	4.74	4.50	4.10	3.66
$\alpha_{+30}/10^{-2}$ (°C^{-1})	6.83	7.15	7.42	8.30	8.55	9.83
$\log(\rho_{RT}/\rho_{min})$	0.07	0.14	0.48	0.86	1.09	1.23
$\alpha_{-50}/10^{-2}$ (°C^{-1})	−0.16	−0.55	−1.79	−2.40	−2.87	−2.93

a higher sintering temperature or after a heat-treatment at 950 °C. The thermal sensitivity of strontium–lead titanate ceramics can change between typical PTCR effect and NTCR–PTCR effect characteristics by controlling PbO loss suitably. Therefore, it is estimated that the NTCR effect of (Sr, Pb)TiO_3 ceramics would not only depend on the thermal activation with elevating the measuring temperature. The formation of Pb^{2+} vacancies at the grain boundary layer is the main cause of NTCR effect ($T < T_c$*). It is assumed that Pb^{2+} vacancies in defect complexes $(V''_{Pb}\,2La_{Pb}^{\bullet})^{\times}$ may release their trapped electrons to gradually form singly ionized lead vacancies (V'_{Pb}) and neutral lead vacancies ($V^{\times}_{Pb}$) with elevating the measuring temperature, which is a fundamental cause of the strong NTCR effects of (Sr, Pb)TiO_3 semiconducting ceramics at $T < T_c$*. The conduction mechanism can be described as following:

$$(V''_{Pb}\,2La_{Pb}^{\bullet})^{\times} \leftrightarrow (V'_{Pb}\,La_{Pb}^{\bullet})^{\times} + La_{Pb}^{\bullet} + e' \quad (4)$$

$$(V'_{Pb}\,La_{Pb}^{\bullet})^{\times} \leftrightarrow V^{\times}_{Pb} + La_{Pb}^{\bullet} + e' \quad (5)$$

Eqs. (2)–(5) show that Pb^{2+} vacancies in (Sr, Pb)TiO_3 ceramics have the converse effect on lowering ρ_{RT} and enhancing NTCR effect.

4. Dielectric properties of $SrTiO_3$ ceramics

The investigation of (Sr, Pb)TiO_3 semiconducting ceramics showed that Pb volatilization benefit to the substitution Pb^{2+} positions by La^{3+} ions, and the compensation to the redundant charges by changing valence of Ti^{4+} will lower the ceramic resistivity. According to above discussion, it is suggested that partial Sr^{2+} positions in strontium titanate could be replaced by Pb^{2+} ions, it would be helpful to the substitution of Pb^{2+} positions by rare-earth ions because Pb^{2+} ions are easy to leave the lattice during the sintering, the process can be described as Eqs. (6) and (7) mentioned below:

$$SrTiO_3 + x\,PbO \rightarrow Sr_{1-x}Pb_xTiO_3 + x\,SrO \quad (6)$$

$$Sr_{1-x}Pb_xTiO_3 + y\,LaO_{3/2} \rightarrow Sr_{1-x}Pb_{x-y}La_y \times (Ti_{1-y}{}^{4+}\,Ti_y{}^{3+})O_3 + y\,PbO + \tfrac{1}{4}O_2 \uparrow \quad (7)$$

The investigations of microstructure and electrical properties confirmed that $SrTiO_3$ GBLCs are comprised of the conducting grains and the isolated grain boundaries. Therefore, it is important for fabricating $SrTiO_3$-based capacitors to lower the resistivity of the grains and realize the isolation of grain boundaries. In our experiments, $SrTiO_3$ powders doped with a small amount of PbO were calcined at 800 °C in order to replace partial Sr positions of strontium titanate by Pb^{2+} ion. Subsequently, the doped La^{3+} ions substituted the Pb positions again during sintering. Thus, the donor defects $La_{Pb}^{\bullet}$ will increase the grains' conductivity of $SrTiO_3$-based ceramics, which benefits to increase the ceramic dielectric constant. Meanwhile, CuO was added to form the isolated grain boundaries and to lower the sintering temperature.

The dielectric constant-temperature characteristics of 1280 °C-sintered $SrTiO_3$ ceramics doped La_2O_3–CuO–PbO is shown in Fig. 3. The dielectric constant at room temperature (ϵ_{25}) is about 7702 and the minimum dielectric

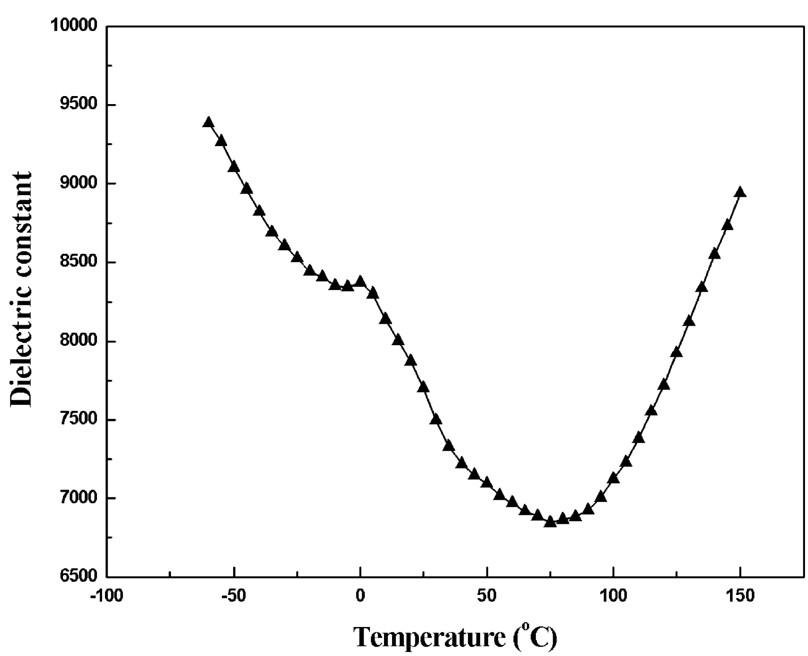

Fig. 3. Dielectric constant–temperature characteristics of 1280 °C–2 h sintered $SrTiO_3$ ceramcis doping with La_2O_3–CuO–PbO.

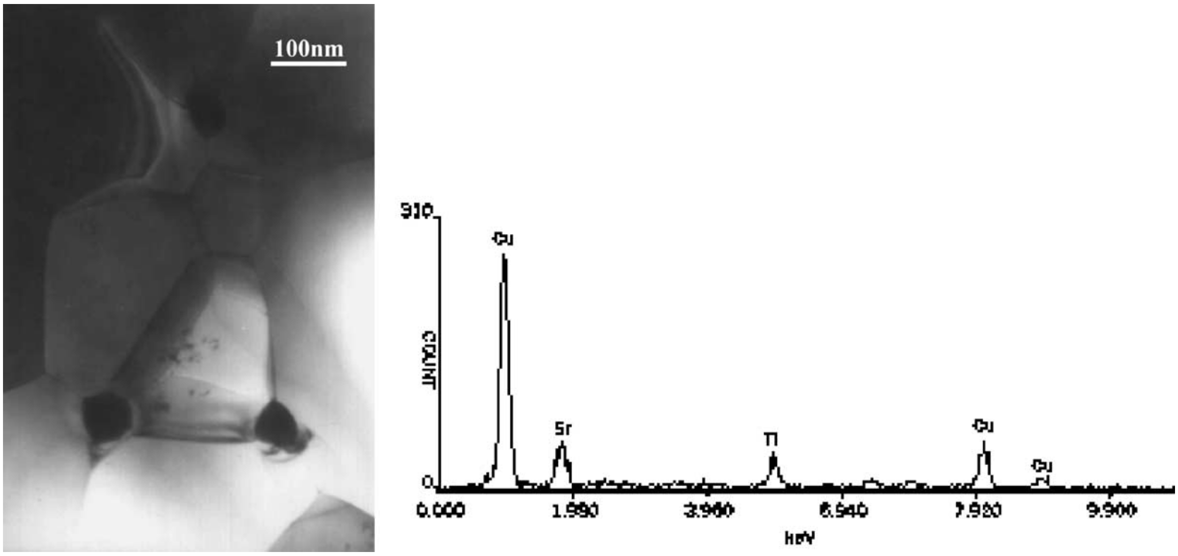

Fig. 4. TEM micrograph of $SrTiO_3$ ceramic doped with La_2O_3–CuO–PbO and EDS spectrum of the grain junctions.

constant is about 6843 at 75 °C. In the temperature range of −40 to 145 °C, the change of the ceramic dielectric constant is within ±15% comparing with the value at 25 °C. Through the modification of impurity, it is possible to prepare high dielectric constant $SrTiO_3$ ceramics, whose dielectric constant-temperature characteristic could meet the EIA X7R specification.

TEM micrography of 1280 °C–2 h sintered $SrTiO_3$ ceramics are shown in Fig. 4. There is no electrical domain can be observed in the grains and some impurities segregate on the grain junctions. The analysis of EDS confirms that the impurity in Fig. 4 is mainly comprised of CuO, showing CuO additives segregated on the grain boundaries to form isolation layers. This microstructure is similar to that of traditional $SrTiO_3$-based GBLCs sintered in a reducing atmosphere [17]. As to (Sr, Pb)TiO_3 thermistors (Sr/Pb < 1/1), they are ferroelectric materials with tetragonal structure at room temperature, so an obvious electrical domain with 90 and 180° distribution were observed in our previous study.

The conventional $SrTiO_3$ GBLCs were fabricated in a reducing atmosphere. The study of defect chemistry showed that the formation of oxygen vacancies is the main cause to obtain n-type $SrTiO_3$ semiconducting ceramics sintered in a low oxygen pressure. However, it is difficult to obtain the high dielectric constant $SrTiO_3$ ceramics sintered in air because the oxygen atoms will fill into the anionic vacancies. Therefore, the substitution of Sr positions by donors is a significant approach to produce electron compensation in an oxidizing atmosphere. Above results shows that PbO additives played a key role to prepare high dielectric constant $SrTiO_3$ ceramics in our experiments. The volatilizable Pb positions in $SrTiO_3$ materials can be substituted by rare-earth ions to form donor defect, which is helpful to obtain high dielectric constant $SrTiO_3$ ceramics.

5. Conclusions

Ferroelectric (Sr, Pb)TiO_3 semiconducting ceramics with variable NTCR–PTCR effect were fabricated. It was found that the ρ_{RT} and the NTCR effect ($T < T_c$) are related to variation of Pb^{2+} concentration at the grain boundaries. The ρ–T characteristics of (Sr, Pb)TiO_3 ceramics can be varied from typical PTCR effect to NTCR–PTCR composite effect by controlling PbO loss during sintering. Pb volatilization produces more Pb^{2+} vacancies, which will increase the resistivity and enhance the NTCR effect. It is estimated that the defect complexes $(V''_{Pb}\,2Y_{Pb}^{\bullet})^{\times}$ would decrease the conduction of strontium–lead titanate semiconducting ceramics, and the electron-detrapping of lead vacancies with the elevating temperature results in the strong NTCR effect below the Curie temperature.

Paraelectric $SrTiO_3$ ceramics were fabricated by doping La_2O_3–CuO–PbO system. The sample exhibit a high dielectric constant ($\varepsilon_{25} = 7702$) with stable temperature characteristics ($\Delta C/C(-40\,\text{to}\,145\,^{\circ}\text{C}) < \pm 15\%$). It was found that CuO addition mainly segregated on the grain boundaries to form the isolation layers. According to defect chemistry, it is estimated that the volatilizable Pb positions in $SrTiO_3$ could be substituted by rare-earth ions in an oxidizing atmosphere, which obviously increased the ceramic dielectric constant.

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