Journal of Electroceramics, 9, 173–177, 2002

The Variable Thermal Sensitivity of Strontium-Lead Titanate Semiconducting Ceramics

JINGCHANG ZHAO,* LONGTU LI, JIANQUAN QI & ZHILUN GUI

State Key Laboratory of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, People's Republic of China

Submitted August 29, 2002; Revised December 13, 2002; Accepted December 27, 2002

Abstract. Strontium-lead titanate semiconducting ceramics with low room temperature resistivity (ρ_{RT}) and variable NTCR-PTCR composite effects were fabricated at different sintering conditions. Both ρ_{RT} and the NTCR effect decreased at the higher heating rate or doping excess of PbO. After the heat-treatment at 950°C, the transformations from PTCR to NTCR-PTCR characteristics were observed in excess PbO-doped samples. According to the results, it is assumed that the lead vacancies (V''_{Pb}) in the grain boundary layers degenerate the conductivity of strontium-lead titanate semiconducting ceramics and the NTCR behaviors below the Curie temperature are ascribed to the electron detrapping of acceptor defects with increasing temperature.

Keywords: (Sr, Pb)TiO_3 materials, PTCR effect, NTCR effect

1. Introduction

Barium titanate is a ferroelectric material with the perovskite structure. In general, a small amount of dopant, such as trivalent cations Y^{3+}, Yb^{3+}, La^{3+} and pentavalent cations Nb^{5+}, Ta^{5+} are used to prepare semiconducting $BaTiO_3$ ceramics. These semiconducting ceramics may exhibit nonlinear electrical properties, including a positive temperature coefficient of resistance (PTCR) [1–3]. The Heywang model [4] is widely accepted to explain the PTCR effect in $BaTiO_3$ ceramics. The abrupt jump of resistivity above the Curie temperature (T_c) is proposed to originate from a barrier at the grain boundary, with the height of the barrier markedly increasing at the phase transition from the ferroelectric tetragonal to the cubic structure. Much research continues to be performed to improve the PTCR effect in $BaTiO_3$ materials and to develop electronic components based on the effect [5–7]. In order to enlarge the applicable temperature range of $BaTiO_3$-based PTCR systems, (Ba, Pb)TiO_3 and (Ba, Sr)TiO_3 solid solutions have been developed [8, 9].

*To whom all correspondence should be addressed. E-mail: zhaojingchang99@mails.tsinghua.edu.cn

Another perovskite system, (Sr, Pb)TiO_3 has received much attention since the NTCR-PTCR composite effect was observed in 1988 [10]. (Sr, Pb)TiO_3 semiconducting ceramics exhibit a negative temperature coefficient of resistivity (NTCR) below T_c and the PTCR effect above T_c. Furthermore, (Sr, Pb)TiO_3 is of interest because its sintering temperature is generally lower than that of the conventional $BaTiO_3$ PTCR materials [11]. (Sr, Pb)TiO_3 materials, therefore, have the potential to be utilized as components, such as precise temperature controllers, overflow protect devices etc. [12]. Wang et al. [13] first prepared (Sr, Pb)TiO_3 PTCR ceramics with a weak NTCR effect using oxalate coprecipitation synthesis and rapidly sintering technology (RST). The intensity of the NTCR effect below T_c could be changed by using different sintering conditions and ingredients. At present, (Sr, Pb)TiO_3 ceramics with the NTCR-PTCR composite effect were generally fabricated from glass/ceramic composing and the strong NTCR-PTCR composite effect was demonstrated to originate from the electrical behaviors of grain boundaries [14, 15]. However glass additions lead to high ρ_{RT} because the SiO_2 segregates in the grain boundaries. Therefore it remains of interest to decrease their ρ_{RT} and investigate the influence of the microstructure as well as defects on thermal sensitivity.

The aim of this study is to fabricate low ρ_{RT} (Sr, Pb)TiO_3 ceramics and investigate the influences of sintering conditions and PbO loss on the properties of Y-doped (Sr, Pb)TiO_3 thermistors.

2. Experimental

Analytical grade PbO, TiO_2, $Y(NO_3)_3$ and high purity $SrTiO_3$ (decomposed $SrTiO(C_2O_4)_2{\cdot}4H_2O$ at 1000°C for 4 h) were well mixed in stoichiometric ratios and then calcined at 800°C for 2 h to prepare 0.5 mol% Y-doped (Sr, Pb)TiO_3 powders. Then 0 mol%, 2 mol%, 4 mol%PbO were respectively added into the powders and mixed again. The powders were pressed into 10 mm diameter disks with about 1 mm thickness. The green pellets were stacked on an Al_2O_3 plane without packing powders and covered with a tightly fitted crucible. These disks were sintered at 1100°C for 0.5–1 h in air with a heating rate of 200–400°C/h and a cooling rate of 300°C/h to obtain $Pb_xSr_{1-x}TiO_3$ semiconducting ceramics ($x = 0.5, 0.6$), which were denoted as SPT50 and SPT60 ceramics, respectively.

The surfaces of the sintered ceramics were coated with In-Ga alloy and the resistivity-temperature characteristics were measured from room temperature up to 400°C with a DC resistivity-temperature measuring system. Subsequently, the In-Ga electrodes of 4 mol%PbO-doped samples were removed, the ceramics were heating-treated at 950°C for 4 h with a heating and cooling rate of 200°C/h, and their resistivity-temperature characteristics were measured again. Then, the above process was repeated again to obtain a further understanding of the influence of the heat-treatment on the thermal sensitivity. Simultaneously, Pb volatilization during the heat-treatment was evaluated by measuring the weight loss of 4 mol%PbO-doped SPT50 ceramics.

3. Results and Discussion

The resistivity-temperature curves of ceramics sintered at different heating rates are shown in Fig. 1. The semiconducting (Sr, Pb)TiO_3 ceramics exhibit strong PTCR effects at $T > T_c^*$ and variable NTCR effects at $T < T_c^*$. T_c^* is defined as the temperature corresponding to the twice minimum resistivity ($\rho_{\min}$) in the PTCR effect region. It can be seen that the resistivities jumped by 4.7–5.7 orders of magnitudes in the PTCR effect region. The maximum resistivity ($\rho_{\max}$) and positive temperature coefficients (α_{+30}) decrease at the higher heating rate, where α_{+30} is defined as the resistivity differential variability at $T_c^* + 30$°C. Below T_c, the resistivities drop with increasing temperature. ρ_{RT}, the negative temperature coefficients (α_{-50}) and the resistivity ratio ($\log \frac{\rho_{RT}}{\rho_{\min}}$) decrease at higher heating rate, where α_{-50}, is defined as the resistivity differential variability at $T_c^* - 50$°C.

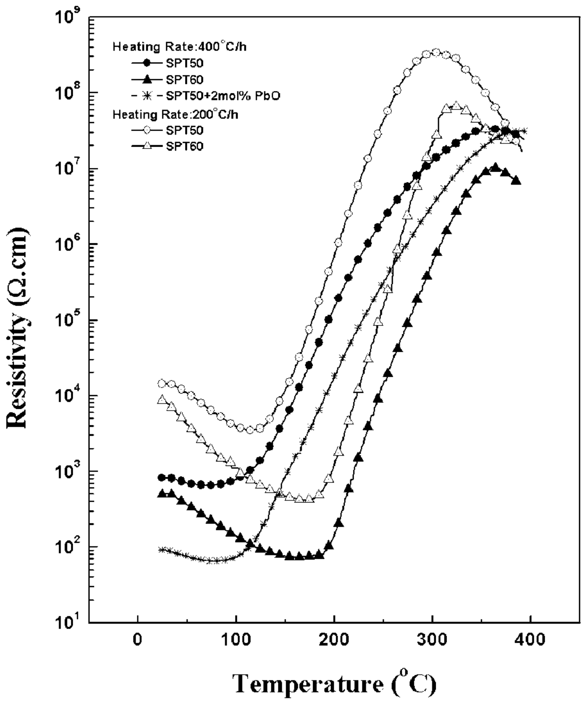

Fig. 1. Resistivity-temperature plots of Y-doped (Sr, Pb)TiO_3 ceramics.

It is well known that Pb volatilization during preparation of lead-based ceramics is generally inevitable. According to the above results, the electrical properties appear to be related to the variation of Pb concentration in the (Sr, Pb)TiO_3 materials because of PbO loss at the different heating rates. In order to investigate the influence of Pb loss on the properties of (Sr, Pb)TiO_3 semiconducting ceramics, excess PbO was added into the (Sr, Pb)TiO_3 powders to compensate for PbO loss during sintering. Figure 1 shows that the ρ_{RT} of SPT50 + 2 mol%PbO reduces to $7.1 \times 10^1\,\Omega \cdot$cm and its NTCR effect below T_c^* is relatively weak. The resistivity-temperature parameters corresponding to the samples in Fig. 1 are shown in Table 1.

Table 1. Resistivity-temperature parameters of Y-doped (Sr, Pb)TiO_3 ceramics at different heating rate.

Samples	Heating rate	ρ_{RT} ($\Omega\cdot$cm)	ρ_{min} ($\Omega\cdot$cm)	T_c^* (°C)	α_{-50} ($\%\cdot{}^\circ C^{-1}$)	α_{+30} ($\%\cdot{}^\circ C^{-1}$)	$\log(\rho_{RT}/\rho_{min})$	$\log(\rho_{max}/\rho_{min})$
SPT50	200°C/h	$1.4. \times 10^4$	$3.5. \times 10^3$	140	−2.11	9.9	0.60	4.99
SPT60	200°C/h	$8.6. \times 10^3$	$4.2. \times 10^2$	195	−1.69	13.1	1.31	5.20
SPT50	400°C/h	$8.2. \times 10^2$	$6.5. \times 10^2$	124	−0.15	6.1	0.10	4.71
SPT60	400°C/h	$5.0. \times 10^2$	$7.4. \times 10^1$	200	−0.85	12.0	0.83	5.15
SPT50 + 2 mol%PbO	400°C/h	$9.2. \times 10^1$	$6.6. \times 10^1$	120	−0.27	4.0	0.14	5.68

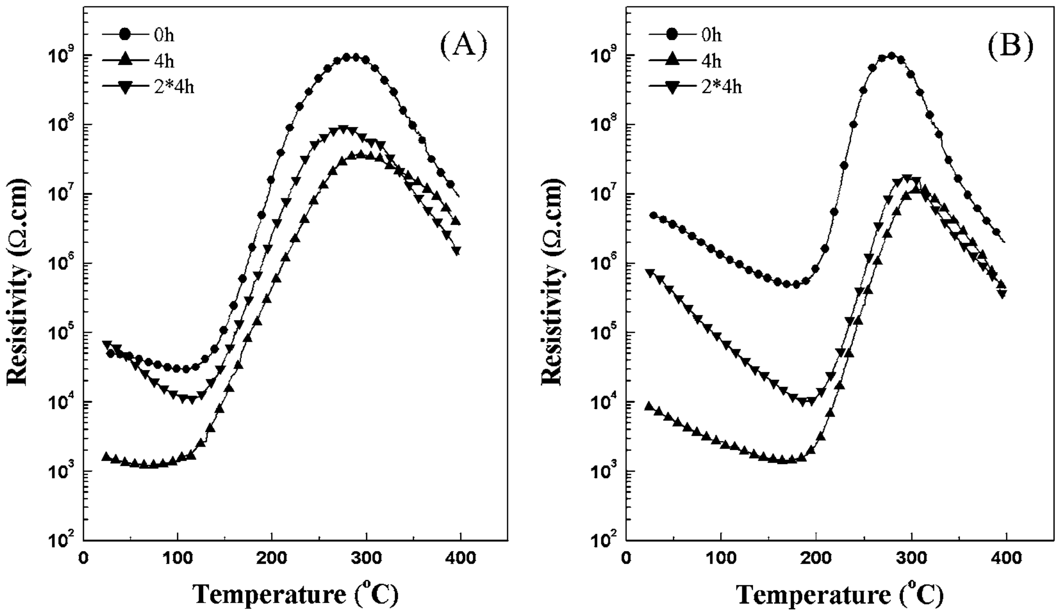

Fig. 2. Resistivity-temperature plots of (A) SPT50 + 4 mol%PbO and (B) SPT60 + 4 mol%PbO ceramics after the heat-treatment at 950°C for different time.

At the same sintering conditions (heating rate is 400°C/h), (Sr, Pb)TiO_3 semiconducting ceramics were also prepared by adding 4 mol%PbO and the sintered ceramics were heat-treated at 950°C. Figure 2 gives the corresponding $\rho - T$ characteristics: (A) SPT50 + 4 mol%PbO; (B) SPT60 + 4 mol%PbO. The corresponding resistivity-temperature parameters of the heat-treated samples are shown in Table 2. It can

Table 2. Resistivity-temperature parameters of 4 mol%PbO-doped (Sr, Pb)TiO_3 semiconducting ceramics after the heat-treatment at 950°C for different time.

Samples	Heat-treatment	ρ_{RT} ($\Omega\cdot$cm)	ρ_{min} ($\Omega\cdot$cm)	T_c^* (°C)	α_{-50} ($\%\cdot{}^\circ C^{-1}$)	α_{+30} ($\%\cdot{}^\circ C^{-1}$)	$\log(\rho_{RT}/\rho_{min})$	$\log(\rho_{max}/\rho_{min})$
SPT50 +	0 h	5.0×10^4	2.9×10^4	139	−0.69	8.30	0.23	4.50
4 mol%PbO	4 h	1.6×10^3	1.2×10^3	123	−0.05	8.00	0.11	4.48
	2 × 4 h	7.0×10^4	1.1×10^4	139	−2.81	7.76	0.80	3.90
SPT60 +	0 h	5.0×10^6	4.9×10^5	202	−0.98	12.98	1.01	3.30
4 mol%PbO	4 h	8.4×10^3	1.4×10^3	202	−0.66	12.22	0.77	3.91
	2 × 4 h	7.4×10^5	1.0×10^4	212	−2.98	10.00	1.86	3.23

be seen that ρ_{RT} (without heat-treatment) is high and the resistivity ratios (log $\frac{\rho_{RT}}{\rho_{min}}$) below T_c are small. After the first heat-treatment at 950°C for 4 h, a weight loss of about 1.2 wt% was found in SPT50 + 4 mol%PbO ceramics. The $\rho - T$ characteristics in Fig. 2 show that ρ_{RT} decreases and the NTCR effects below T_c remain weak. However, after the second heat-treatment at 950°C for 4 h, the weight loss of sample was only 0.1 wt% and the obvious changes in thermal sensitivity were observed. ρ_{RT} increased and the NTCR effects became stronger, especially the $\rho - T$ characteristics of SPT50 + 4 mol%PbO ceramics changed from the PTCR to the NTCR-PTCR type. According to the results, it confirms that the NTCR effect of strontium-lead titanate semiconducting ceramics is closely related to the variation of Pb concentration in the materials.

Chang et al. [16] proposed that annealed $Sr_{0.4}Pb_{0.6}TiO_3$ materials contain homogeneous grains and Pb-deficient grain boundary layers, but there are no adequate evidences to support their opinion. In this paper, the heating rate and excess PbO significantly affect the room temperature resistivity and thermal sensitivity of Y-doped (Sr, Pb)TiO_3 ceramics. It can be assumed that PbO loss results in the formation of lead vacancies (V''_{Pb}) during sintering in air because the oxygen atoms will revert to the (Sr, Pb)TiO_3 lattices during the cooling stage. Therefore, a small amount of PbO can compensate the PbO loss during the sintering, which is beneficial in stabilizing Pb/Ti ratio in the sintered samples. Certainly, the residual PbO segregated at the grain boundaries also increased their resistivities, so the decrease of ρ_{RT} was observed after the first heat-treatment at 950°C for 4 h in this work.

Y-doped (Sr, Pb)TiO_3 ceramics are n-type semiconductors. PbO loss is beneficial for the substitution of the Pb^{2+} positions by Y^{3+} ions in (Sr, Pb)TiO_3, which form donor defects $Y^{\bullet}_{Pb}$. The non-equilibrium charges can be compensated by the valence change of the octahedral Ti^{4+} ions. One can visualize electrical conduction originating from the hopping of electrons between Ti sites in (Sr, Pb)TiO_3. The process can be described as following:

$$Ti^{4+} + e' \leftrightarrow Ti^{3+} \tag{1}$$

As acceptor states, lead vacancies (V''_{Pb}) cause electron trapping in the grain boundary layers, which can be carried out through the defect complex with $Y^{\bullet}_{Pb}$ as following:

$$V''_{Pb} + 2Y^{\bullet}_{Pb} \leftrightarrow (V''_{Pb} \cdot 2Y^{\bullet}_{Pb})^{\times} \tag{2}$$

The above defect complexes $(V''_{Pb} \cdot 2Y^{\bullet}_{Pb})^{\times}$ compensate the residual charges of the defect $Y^{\bullet}_{Pb}$, which decreases the carrier charge density by restraining neighboring Ti^{4+} ions from changing their valences. Therefore, (Sr, Pb)TiO_3 ceramics prepared at lower heating rate or heat-treated at 950°C for a long time exhibited the higher room temperature resistivity in our experiments.

According to the results of EPR for $BaTiO_3$, Hari et al. [6] proposed that the neutral barium vacancies ($V^{\times}_{Ba}$) present in the tetragonal and orthorhombic phases change into singly ionized barium vacancies (V'_{Ba}) and the PTCR effect is related to charge trapping at the acceptor states having higher concentration in the region of the grain boundary layer. Below the Curie temperature, (Sr, Pb)TiO_3 ceramics, at low heating rate, exhibit strong NTCR behaviors. A small amount of PbO addition decreases ρ_{RT} and the negative temperature coefficient. It can be estimated that lead vacancies are significant contributors to the NTCR effects. Furthermore, the NTCR characteristic should be originated from the increase of carrier charges, which would not only depend on the thermal activation with the increasing temperature. Therefore, we suppose that V''_{Pb} in defect complexes $(V''_{Pb} \cdot 2Y^{\bullet}_{Pb})^{\times}$ may release their trapped electrons to form singly ionized lead vacancies (V'_{Pb}) and neutral lead vacancies ($V^{\times}_{Pb}$) with increasing temperature, which is a fundamental cause of the strong NTCR effects of (Sr, Pb)TiO_3 semiconducting ceramics below the Curie temperature:

$$(V''_{Pb} \cdot 2Y^{\bullet}_{Pb})^{\times} \leftrightarrow (V'_{Pb} \cdot Y^{\bullet}_{Pb})^{\times} + Y^{\bullet}_{Pb} + e' \tag{3}$$

$$(V'_{Pb} \cdot Y^{\bullet}_{Pb})^{\times} \leftrightarrow V^{\times}_{Pb} + Y^{\bullet}_{Pb} + e' \tag{4}$$

These reversible processes provide more electrons to participate in conduction below T_c, so the resistivity of (Sr, Pb)TiO_3 ceramics drops with increasing temperature. From the above points of view, lead vacancies in (Sr, Pb)TiO_3 ceramics exhibit the reverse effect by decreasing ρ_{RT} and enhancing the NTCR effect. High performance (Sr, Pb)TiO_3 ceramics with low room temperature resistivity and strong NTCR-PTCR composite effect can be prepared by suitably controlling the formation of lead vacancies.

On the other hand, the phase transformation of (Sr, Pb)TiO_3 ceramics also results in the variation of trapping of the electrons at the acceptor states, e.g. $V_{Pb}^{\times}$, V_{Pb}', in the grain boundary layer regions, which will affect the PTCR effect above the Curie temperature.

4. Conclusions

Strontium-lead titanate semiconducting ceramics were fabricated at different heating rates. The sintered ceramics exhibit low room temperature resistivity and weak NTCR behaviors at higher heating rate or by doping with 2 mol%PbO. Meanwhile, the transformation from PTCR to NTCR-PTCR characteristics was observed in 4 mol%PbO-doped samples after heat-treatment at 950°C. It shows that the PbO loss is important in affecting the electrical conduction of (Sr, Pb)TiO_3 ceramics. High performance (Sr, Pb)TiO_3 ceramics with low room temperature resistivity and strong NTCR-PTCR composite effect can be prepared by suitably controlling the PbO concentration on the grain boundaries.

According to the results, it is estimated that the defect complexes $(V_{Pb}'' \cdot 2Y_{Pb}^{\bullet})^{\times}$ would decrease the conduction of strontium-lead titanate semiconducting ceramics and the electron detrapping of lead vacancies with increasing temperature result in the strong NTCR effect below the Curie temperature.

References

1. O. Saburi, *J. Am. Ceram. Soc.*, **44**(3), 54 (1961).
2. O.I. V'yunov and A.G. Belous, *J. Eur. Ceram. Soc.*, **19**, 935 (1999).
3. E. Brzozowski, M.S. Castro, *Ceramics International*, **26**, 265 (2000).
4. W. Heywang, *Solid State Electronics*, **44**(3), 51 (1961),
5. E. Andrich, *Electron. Appl.*, **26**(3), 123 (1965).
6. N.S. Hari, P. Padmini, and T.R.N. Kutty, *J. Mater. Sci. Mater. in Electronics*, **8**, 15 (1997).
7. T.R.N. Kutty and N.S. Hari, *Mater. Lett.*, **34**, 43 (1998).
8. Liang-Fu Chen and Tseung-Yuen Tseng, *IEEE Trans. Part A*, **19**(3), 423 (1996).
9. Feng Zhang, Zhongtai Zhang, Qing Mi et al., *J. Mater. Sci.*, **34**, 5051 (1999).
10. Y. Hamata, H. Takuchi, and K. Zomura, Jpn. Patent No. 63-280401, 1988.
11. D.J. Wang, J. Qiu, Y.C. Guo et al., *J. Mater. Res.*, **14**(1), 120 (1999).
12. Chengkuo Lee, I-Nan Lin, and Chen-Ti Hu, *J. Am. Ceram. Soc.*, **77**(5), 1340 (1994).
13. D.J. Wang, Z.L. Gui, and L.T. Li, *J. Mater. Sci. in Electronics*, **8**, 271 (1997).
14. Yuh-Yih Lu and Tseung-Yuen Tseng, *Materials Chemistry and Physics*, **53**, 132 (1998).
15. D.J. Wang, J. Qiu, Z.L. Gui, and L.T. Li, *J. Mater. Res.*, **14**(7), 2993 (1999).
16. H.Y. Chang, K.S. Liu, C.T. Hu et al., *Jpn., J. Appl. Phys.*, **35**, 656 (1996).