Study on BaTiO$_3$ semiconducting ceramic materials with lower resistivity

S. L. Jiang · Q. Jiang · H. B. Zhang · S. P. Gong

Abstract In this paper, the semiconducting mechanism of BaTiO$_3$ semiconducting ceramics with ABO$_3$ perovskite structure was investigated. The PTCR characteristics of BaTiO$_3$ semiconducting ceramic with lower resistivity have been studied by substituting in A position via doping with single donor Sb$_2$O$_3$, composite substituting in A and B position via doping with double donor Y$_2$O$_3$+Nb$_2$O$_5$, and substituting in oxygen position via doping with CaF$_2$ or TiCl$_3$. The results obtained show that lower resistivity and good PTC effect of BaTiO$_3$ semiconducting ceramics with room temperature resistivity (ρ_{25}) of 6.08 Ω cm, temperature coefficient (α_T) of 12.21$\times$10^{-2} °C^{-1} and a lift–drag ratio (β) of 3.8$\times$10^4 can be achieved.

Keywords BaTiO$_3$ semiconducting · Ceramics · Lower resistivity · Composite substituting

1 Introduction

Semiconducting BaTiO$_3$ ceramic thermal resistor (PTCR) has been widely used. With the extensive use of current-limiting elements, the room temperature of existing current-limiting elements made by PTCR ceramic material is so high that they *cannot* meet the need for large current circuit application. Therefore, it is significant to research low resistivity PTCR thermal ceramic material. The present methods of preparing low resistivity PTCR ceramic
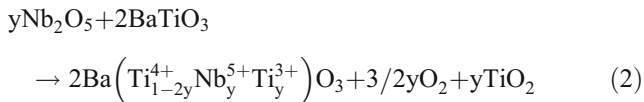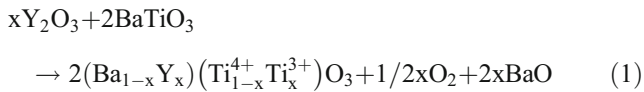
S. L. Jiang · Q. Jiang (✉) · H. B. Zhang · S. P. Gong
Department of Electronic Science and Technology,
Huazhong University of Science and Technology,
No. 1037 Luoyu Road,
Wuhan 430074, China
e-mail: erajohn163@163.com

material are [1–3]: Sb$_2$O$_3$ or La$_2$O$_3$ doping, Sb$_2$O$_3$+BN doping; A-, B-, O-positions mixed doping, metals and ceramics mixing, ceramics mixing of big and small grains. This article is aimed at ABO$_3$ *perovskite structure* which belongs to BaTiO$_3$ series, using Sb$_2$O$_3$ and Y$_2$O$_3$+Nb$_2$O$_5$, researching single doping Sb$_2$O$_3$ and double donor doping Y$_2$O$_3$+Nb$_2$O$_5$, the effect of double donor doping on property of resistance PTC ceramic material and O-position doping on low resistivity.

2 Experimental procedure

2.1 The effect of double donor doping on property of BaTiO$_3$ semiconducting ceramics

The raw materials in experiment are of all analytically pure. Samples were prepared by the conventional electronic ceramics technique. The nominal composition of materials is (Ba$_{0.90}$Ca$_{0.04}$Sr$_{0.06}$)Ti$_{1.01}$O$_3$+2.4 % SiO$_2$+x % (Sb$_2$O$_3$, Y$_2$O$_3$+Nb$_2$O$_5$), x=0.1–0.26. The resistance–temperature character is measured with ZWX-B R-T computational testing system made by Huazhong University of Science and Technology. Tables 1, 2 and 3 show sample grade of one-time doping Sb$_2$O$_3$, one-time doping Y$_2$O$_3$+Nb$_2$O$_5$, and tow times doping Y$_2$O$_3$+Nb$_2$O$_5$.

Figure 1 shows that the change of room temperature resistivity ρ_{25} presents U-shape curve with increase of Sb$_2$O$_3$ content, which is similar to other semiconducting elements such as Y$_2$O$_3$ and Nb$_2$O$_5$. As increasing Sb$_2$O$_3$ content, electron compensation converts to omission compensation, the restrained effect of donor on grain growth is strengthened at the same time [4]. Electric properties are obtained through appropriate technology as follows: ρ_{25}= 9.3 Ω cm, α_T=6.95$\times$10^{-2} °C^{-1}, β=3.37$\times$10^3. Table 4

Table 1 Grades of sample by doping Sb_2O_3.

Sample grade	S_{1-1}	S_{1-2}	S_{1-3}	S_{1-4}	S_{1-5}	S_{1-6}	S_{1-7}
$x(Sb_2O_3)$ (%)	0.10	0.12	0.14	0.16	0.18	0.22	0.26

Table 3 Grades of sample by double donor doping $Y_2O_3+Nb_2O_5$ with different doping methods.

Sample grade		YN_{2-1}	YN_{2-2}	YN_{2-3}	YN_{2-4}
Doping before	$x(Y_2O_3)$	0	0.05	0.10	0.02
presintering (%)	$x(Nb_2O_5)$	0	0.03	0.06	0.02
Doping after	$x(Y_2O_3)$	0.10	0.05	0	0.08
presintering (%)	$x(Nb_2O_5)$	0.06	0.03	0	0.04

shows electric properties of sample by doping $Y_2O_3+Nb_2O_5$ at one time.

It can be seen from Table 4 that double donor doping can further decrease room temperature resistivity ρ_{25} *when other electric properties are the same*. In structure of ABO_3-type perovskite, Y^{3+} and Nb^{5+} displace Ba^{2+} and Ti^{4+} which are in A and B positions, respectively. The questions are described as follows [4]:

$$xY_2O_3+2BaTiO_3$$
$$\rightarrow 2(Ba_{1-x}Y_x)(Ti^{4+}_{1-x}Ti^{3+}_x)O_3+1/2xO_2+2xBaO \quad (1)$$

$$yNb_2O_5+2BaTiO_3$$
$$\rightarrow 2Ba(Ti^{4+}_{1-2y}Nb^{5+}_yTi^{3+}_y)O_3+3/2yO_2+yTiO_2 \quad (2)$$

The semiconducting behaviors of double donor doping are indicated as follows:

$$2TiO_2+Y_2O_3 \rightarrow 2Ti_{Ti}+2Y^{\cdot}_{Ba}+6O^x_o+1/2O_2(g)+2e' \quad (3)$$

$$2BaO + Nb_2O_5$$
$$\rightarrow 2Ba_{Ba}+2Nb^{\cdot\cdot}_{Ti}+6O^x_o+1/2O_2(g)+2e' \quad (4)$$
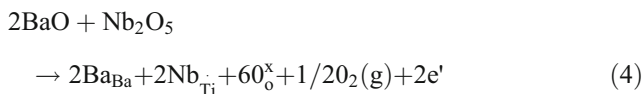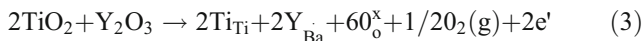
When the total donor doping concentration is low (0.16%, donor doping concentration in low resistivity PTC material should not be too high), Y^{3+} and Nb^{5+} displace Ba^{2+} and Ti^{4+} and become energy level in forbidden bands, respectively. According to Fermi energy statistic theory, ionized donor concentration $[D^0]$ is dependent on the chance rate of excess electrons occupying donor level, while excess electrons become donor level at Ba^{2+} and Ti^{4+} positions. The donor concentration $[D^0]$ is larger. From Eqs. 3, 4 and $\sigma = \sigma_\nu e^{-e\varphi 0/kT}(\sigma_\nu = n_0 e\mu)$, we know that σ_v is direct proportionable to n_0, that is to say ρ_{25} is inverse proportionable to $[D^0]$.

According to modified Heywang model by Jonker, grain boundary barrier region will be affected by ferroelectric polarization compensation and become lower below Curie temperature *with lower* room temperature resistance. Y^{3+} and Nb^{5+} displace Ba^{2+} and Ti^{4+} positions, respectively. Lattice structures have greater distortion than that by single donor doping. *Intensity of spontaneous polarization P_r below Curie temperature is strong under Ferroelectric tetragonal phase*. The space variation ratio of spontaneous polarization dP/dx is larger when the thickness of grain boundary barrier region is constant. From modified Passion Equation:

$$\frac{d^2\varphi}{dx^2} = \frac{1}{\varepsilon_0}\left(P, a - \frac{dP}{dx}\right) \quad (5)$$

It is obvious that space variance ratio of great spontaneous polarization P_r, total or partial countervails the effect of space charges, grain boundary barrier disappears or falls, which make ρ_{25} much lower. Table 5 shows room
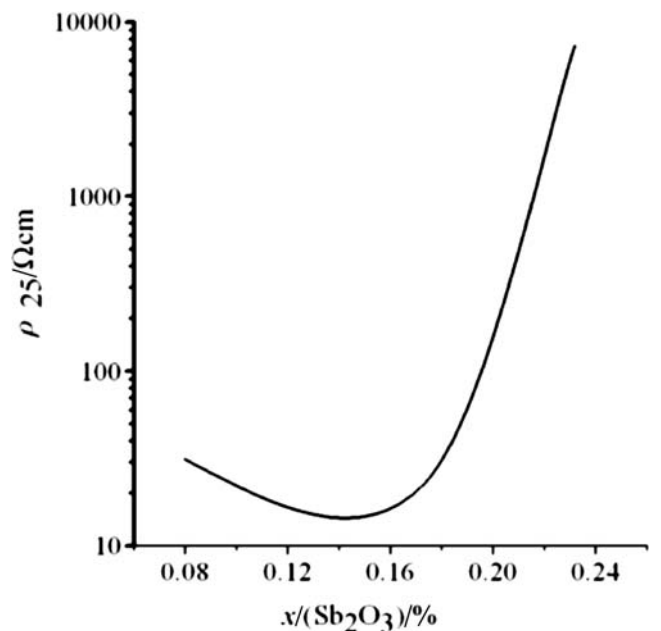
Table 2 Grades of sample by double donor doping $Y_2O_3+Nb_2O_5$.

Sample grade	YN_{1-1}	YN_{1-2}	YN_{1-3}
$x(Y_2O_3)$ (%)	0.10	0.08	0.12
$x(Nb_2O_5)$ (%)	0.06	0.08	0.04

Fig. 1 The relationship of the room temperature resistivity and Sb_2O_3 content of sample

Table 4 Electric properties of samples doped $Y_2O_3 + Nb_2O_5$ at one time.

Sample grade	ρ_{25} (Ω cm)	α_T (°C^{-1})	DT (°C)	β
YN$_{1-1}$	7.14	6.86	197.15	3.18×10^3
YN$_{1-2}$	8.3	5.76	195.14	2.93×10^3
YN$_{1-3}$	9.3	7.43	193.75	3.40×10^3

temperature resistance of sample by doping $Y_2O_3 + Nb_2O_5$ at two times.

From Table 5, we can see that room temperature resistivity ρ_{25} of YN$_{2-4}$ sample is the lowest. Through changing sintering technology, low resistivity PTC ceramics material can be obtained with $\rho_{25} = 4.49$ Ω cm, $\alpha_T = 6.04 \times 10^{-2}$ °C^{-1}, $\beta = 1.0 \times 10^3$, and $\Delta T = 199.5$.

According to Danniels' Ba vacancy diffusion model, the thickness of barrier region is determined by cool-down rate. The thicker *the* barrier region thickness is, the higher Ba vacancy concentration is, and the more difficult ferroelectric compensation is, so *the* higher the resistivity is below Curie temperature. Analysed from experiment result, the different in thickness of barrier region may be the different ways in semiconducting elements. Adding semiconducting elements before *presintering*, grain bulk become semiconducting homogeneously and sufficiently. The second time addition may cause the semiconducting degree of grain surface higher than that of grain bulks, which cause donor concentration in grain surface higher than that in sample by one-time semiconducting elements addition before preburing. According to Deniels modle, suppose donor on grain surface are all compasated by Ba vacancies, therefore the diffusion lengths of Ba vacancies on grain surface L_d are different under the two conditions. The grain boundary thickness of sample by adding semiconducting elements is thinner than that of one-time addition sample, which make grain boundary resistance much lower. Resistance of PTC semiconducting ceramic gives first place to resistance of grain boundary, so sample resistance at room temperature become lower; on the other hand, according to above discussion on modified Joker model, when barrier region thickness becomes thinner, it is possible that dP/dx will be further enhanced and the room temperature resistance will be *much* lower [5].
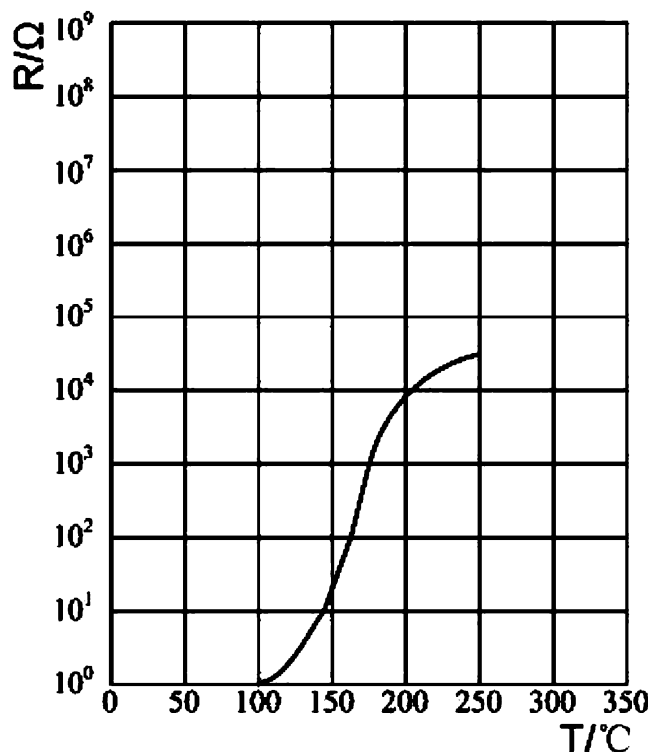

Fig. 2 *R–T* relations of samples doped with CaF_2

2.2 The effect of O- position doping on property of $BaTiO_3$ semiconducting ceramics

When researching semiconducting behaviors of $BaTiO_3$ semiconducting ceramics which belong to the structure of ABO_3 calcium ore, besides double donor doping at A-,B- positions, *low valence donor doping at O-positions* can also do according to semiconducting theory. Take $TiCl_3$, $BaCl_2$,
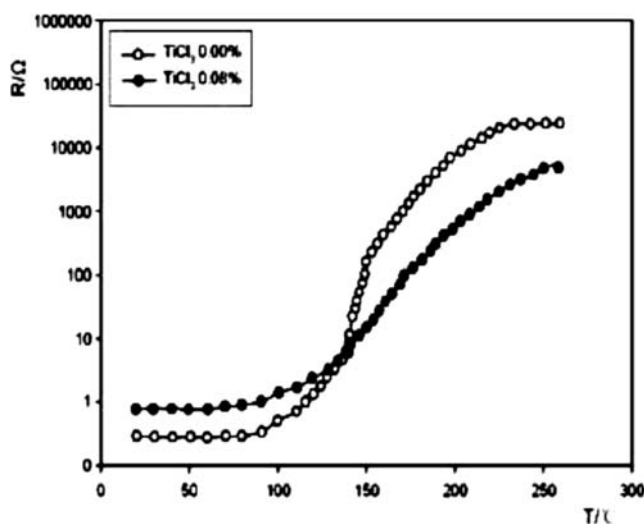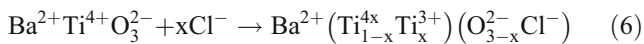
Table 5 Room temperature resistance of sample by doping $Y_2O_3 + Nb_2O_5$ at two times.

Sample grade	YN$_{2-1}$	YN$_{2-2}$	YN$_{2-3}$	YN$_{2-4}$
ρ_{25} (Ω cm)	226.6	6.9	7.4	6.7

Fig. 3 *R–T* relations of samples doped with different concentrations of $TiCl_3$

CaF$_2$ as doping materials, let part of O^{2-} be displaced by Cl$^-$ or F$^-$. The procedure is can be indicated as follows:

$$Ba^{2+}Ti^{4+}O_3^{2-}+xCl^- \rightarrow Ba^{2+}\left(Ti_{1-x}^{4x}Ti_x^{3+}\right)\left(O_{3-x}^{2-}Cl^-\right) \quad (6)$$

On the base of double donor doping above, through doping an amount of CaF$_2$, the dependence of sample resistance on room temperature are given by Fig. 2.

Figure 1 shows the electric properties as follows: ρ_{25}= 6.08 Ω cm, α_T=12.21×10^{-2} °C^{-1}, β=3.8×10^4. The properties of PTC elements made by this material have met the specification of "863." The situation is similar when doping TiCl$_3$, and the obvious result is that the R–T relations is obviously improved, and the resistivity is lower. The researching results are presented in Fig. 3.

3 Conclusions

(1) Through doping suitable Sb$_2$O$_3$ into semiconducting ceramic material (BaCaSr)TiO$_3$, grain will sufficiently become semiconducting, and in relatively complete doping extent the room temperature resistivity will be maintained relatively low ratio, ρ_{25}=9.3 Ω cm, a_T= 6.95×10^{-2} °C^{-1}, and b=3.37×10^3.

(2) Room temperature resistance of (BaCaSr)TiO$_3$ sample by double donor doping Y$_2$O$_3$+Nb$_2$O$_5$ can be further decreased, while a_T and b will fall slightly.

(3) Compared with one-time adding Y$_2$O$_3$+Nb$_2$O$_5$ before sintering, the resistivity by *double* addition before and after sintering can be much lower. Through appropriate technology, *the* sample property parameters can be obtained: ρ_{25}=4.49 Ω cm, a_T=6.04×10^{-2} °C^{-1}, and b=1.0×10^3.

(4) Through doping an amount of CaF$_2$ or TiCl$_3$ which displace oxygen position via, the R–T relations is obviously improved, and the resistivity is lower. Sample property parameters: ρ_{25}=6.08 Ω cm, a_T= 12.21×10^{-2} °C^{-1}, b=3.8×10^4 can be achieved.

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