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Electrical properties of Y- and Mn-doped $BaTiO_3$-based PTC ceramics

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Abstract

A series of nano-$Ba_{0.85-x}Y_xSr_{0.07}Ca_{0.08}Mn_yTi_{1-y}O_3$ ($0.7\% \le x \le 1.2\%$, $0\% \le y \le 0.06\%$) solid solutions have been synthesized by solid-state reaction at low temperature. The experiment of doping different content Y and Mn shows that the room-temperature resistance decreases by doping Y, and the resistance jump increases dramatically by doping Mn. The optimum donor level increases significantly with increasing acceptor level. The room-temperature resistance changes as a U-type curve with an increase of Mn additive concentration while the resistance jump is on the reverse. Meanwhile, the influence of sintering temperature and soaking time on property of PTC materials was discussed.

Keywords: Preparation; $BaTiO_3$; Donor and acceptor doping; Sintering conditions

1. Introduction

Solid-state reaction at low temperature is unique in synthetic chemistry, and it has been employed successfully in the synthesis of cluster compounds, coordination compounds, etc. [1]. Compared with synthetic techniques of solution phase and solid phase at high temperature, this method exhibits many advantages: no need for solvent, high productivity and selectivity, low energy consumption and simple reaction technology. Recently, this method has been established as effective in the synthesis of ultrafine particles of some metal oxides and insoluble salts in the laboratory [2–4]. In this paper, this new and simple method was employed to prepare nano-$BaTiO_3$ ceramic powder.

Barium titanate and its related compounds are ideal candidates for producing various PTC components due to their high-temperature coefficient of resistance. The addition of the trivalent (La^{3+}, Sb^{3+}, Y^{3+}) [5–8] or pentavalent (Nb^{5+}, Ta^{5+}) [9,10] donor dopants increases the room-temperature conductivity. On the other hand, as acceptor dopants, Mn^{2+} or Mn^{4+} ions are also usually added in PTC materials. The acceptors are expected to locate at the grain boundaries to enhance PTC effect [11,12]. The influence of sintering technique, donor Y, acceptor Mn, and their relationship on the performance of ceramics was discussed.

2. Experimental

A suitable amount of $TiCl_4$ was slowly added into the deionized water. The pH value of the solution was adjusted to 7–8 by ammonia, and H_2TiO_3 was formed. Then the chloride ion in H_2TiO_3 must be removed by washing and filtering. The pure H_2TiO_3 and calculated amount of $Ba(OH)_2\cdot 8H_2O$, $Sr(Ac)_2\cdot H_2O$, $Mn(Ac)_2\cdot 4H_2O$ and $Y(Ac)_3$ were mixed thoroughly in a mortar for 1 h at room temperature, then dried at 100 °C. The doped $BaTiO_3$ powder was obtained by drying and calcining for 1 h at 800 °C (the doped $BaTiO_3$ powder can be prepared at room temperature, and calcination at 800 °C made the doped acetate decompose completely). The sample was granulated with a suitable amount of chemical bond (8% PVA aqueous solution) and pressed into disks (15 mm × 15 mm × 2.5 mm) at a pressure of 8–10 MPa for 1 min. Then the disks were sintered at temperature ranging from 1290 to 1330 °C for 10–90 min and then furnace cooled. A kind of commercial ohmic paste (a mixture of 90% aluminum powder and 10% glass dust) was spread on two opposite side surfaces of the sintered samples (12 mm × 12 mm × 2 mm). Subsequently, the pastes were dried at 100 °C. These parts were thus baked at 640 °C for 10 min with a heating rate of 5 °C min^{-1}.

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The electrical resistance was measured as a function of temperature using a temperature-programmable furnace (ZWXB R-T test system, Wuhan, China) with a heating rate of 1 °C min^{-1} from room temperature to 230 °C. The microstructure and phase identification of the powder was analyzed by transmission electron microscopy (TEM JEM-100SX, Japan) and X-ray diffraction (Y-2000, Dandong, China), respectively.

3. Results and discussion

3.1. TEM analysis

The grain boundary plays a very important role in determining the PTC effect and therefore the grain size of samples need to be critically controlled. It requires the doped $BaTiO_3$ powder to have small particle size with a very narrow size distribution. The TEM photograph (Fig. 1) shows that the compounds are uniform, substantially spherical particles with an average particle size of 60 nm in diameter. The ceramic material sintered from nano-particles possesses better PTC effect since the PTC characteristics is an average effect of many grain boundaries.

3.2. XRD analysis

As shown in Fig. 2, the doped $BaTiO_3$ solid solution powder has the same XRD pattern as pure $BaTiO_3$ phase and both of them belong to the cubic system. The peaks shift a little towards higher angle owing to doping some additives whose ionic radii are smaller than Ba^{2+}. It can also be proved that the doped acetate decomposed completely at 800 °C because there is no other impure peak.

3.3. Influence of Y and Mn concentration

The tetragonal-to-cubic phase transformation temperature of semiconducting $BaTiO_3$ (T_c) can be shifted significantly by the substitution of structurally compatible divalent cations (Sr, Ca) as isovalent dopants for barium in the pervoskite lattice. Combined introduction of calcium and strontium into the barium sublattice makes an additional effect on the grain size, makes the T_c (Curie temperature) point shift towards lower temperature and improves its breakdown voltage. The concentration of Sr (7 mol%) and Ca (8 mol%) were employed in this research [13–15]. We put emphasis on the concentration of donor Y and acceptor Mn, their relationship, and sintering conditions on performance of PTC materials.

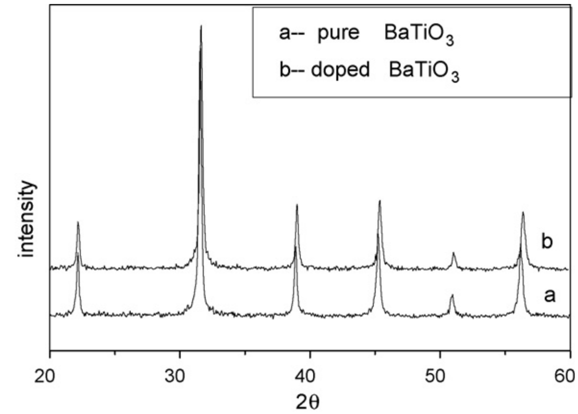

Fig. 2. XRD patterns of the sample.

As we know, the pure $BaTiO_3$ is an insulator, and its room-temperature resistance is 10^{10} to 10^{12} Ω [16]. At first, the resistance at room temperature should be reduced by doping semiconducting additives. The semiconducting $BaTiO_3$ is formed at a very low donor dopant concentration and sufficiently high conductivity of the sample (at room temperature) is achieved only within a narrow concentration range. A single dopant Y of 0.1–0.8 mol% was introduced in place Ba site to reduce the resistance. The room-temperature resistance (R_{25}) changes as a U-type curve with the increase of Y additive concentration (Fig. 3). The minimum resistivity at room temperature of 16 Ω cm can be achieved when the dopant concentration is 0.7 mol%.

Doping by Y could effectively make the room-temperature resistance decrease, but the PTC resistance jump could not reach a high level (Fig. 4). Among the different acceptor dopants used to improve the PTC characteristics, addition of Mn^{2+} is known to have the most pronounced effect [17].

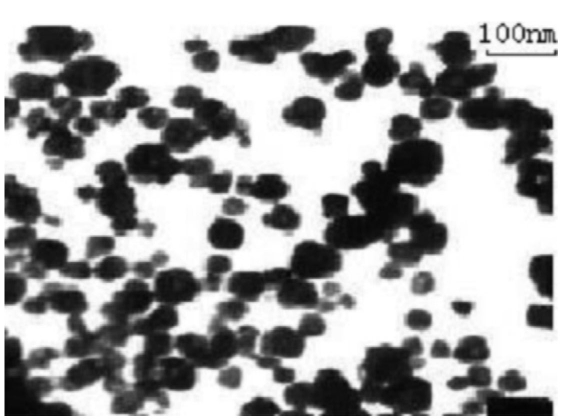

Fig. 1. TEM photograph of the sample.

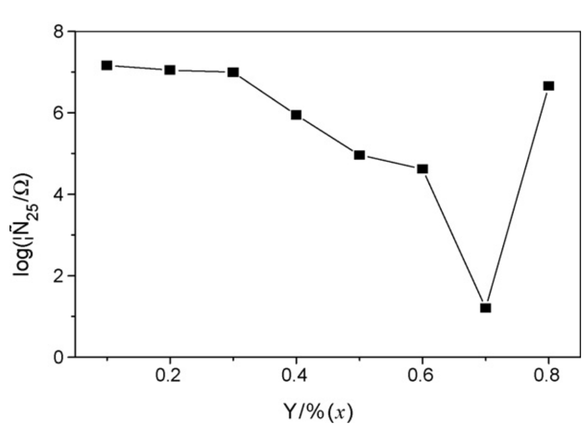

Fig. 3. Variations of room-temperature resistivity with different donor content.

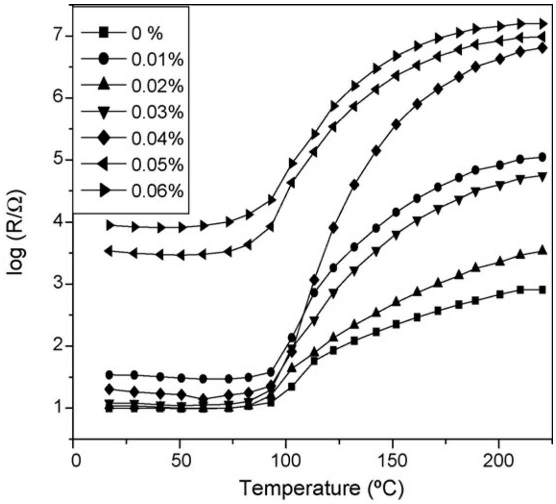

Fig. 4. *R–T* curves of the samples with different acceptor content.

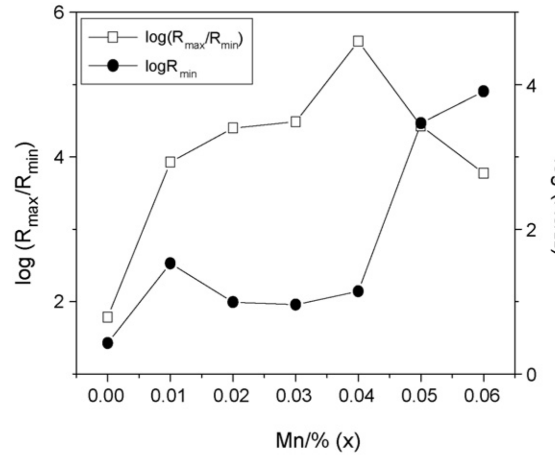

Fig. 5. Room-temperature resistance and resistance jump of Mn-doped samples.

Therefore, acceptor Mn was also introduced in this research. A systematic study was taken up in this investigation on the effect of concentration of Y and Mn. The excellent PTC ceramic materials have been obtained by adjusting Y (0.7–1.2%) and Mn (0.01–0.06%) concentration. Fig. 4 shows the comparison of PTCR characteristics with (0.01–0.06%) and without doping acceptor Mn. It can be seen that the samples with Y and Mn dopant all exhibit the PTC effect. The samples with Mn content (0–0.04%) show a blue color and are semiconducting, but the magnitude of the resistivity jump changed with the acceptor content. It indicates that there are improvements in both steepness and jump order with addition of the acceptor Mn. Keeping the acceptor ion concentration fixed, the donor ion concentration has been varied so as to get the appropriate combination corresponding to minimum resistivity. The resulting Y content and R_{25} are listed in Table 1. It can be noted that the acceptor concentration has a much stronger influence on the resistance minimum of doped $BaTiO_3$. Thus, the optimum donor level increases significantly with increasing acceptor level; the minimum of resistance value changes as the U-type curve with an increase of Mn additive concentration.

According to the data from these *R–T* curves, the relationship between the R_{25}, resistance jump and acceptor content (with according Y content) is illustrated in Fig. 5. Fig. 5 shows the variations of the R_{25} and resistance jump with different content of acceptor Mn. It can be seen that the sample without doping Mn reaches the lowest R_{25} (2.6 Ω). The R_{25} is 13.9 Ω, and the ratio of log (R_{max}/R_{min}) is near 6 when the content of Y and Mn are 1 mol% and 0.04 mol%, respectively. The room-temperature resistance (R_{25}) varies as the U-type curve with an increase of Mn additive, and the resistance increases rapidly when the content of Mn is beyond 0.04%. The probable reason is that less O_2 in the grain boundary is consumed when the concentration of Mn, which exists in grain boundary, is low. Then, the cavities produced from Mn quench extra free electrons in crystal grain and make the effective electron concentration reduced. Subsequently, the conductivity of grain is improved as a result of producing free electrons from Y. The production of oxygen vacancy enhances the concentration of cationic vacancies in the grain boundary, and the resistivity decreased [18].

Table 1
The optimum Y content and R_{25} of Mn-doped samples

	Mn (mol%)					
	0.01	0.02	0.03	0.04	0.05	0.06
Y (mol%)	0.7	0.8	0.8	1.0	1.1	1.2
R_{25} (Ω)	33.8	9.84	9.13	13.92	2934	8095

It is also evident from Fig. 5 that the resistance jump increases with the increase of Mn content, and reaches the maximum value at acertain donor content and then decreases. The optimum value of the acceptor concentration is 0.4% (mol) while the R_{max}/R_{min} is 5.6. For PTC materials, the resistance jump near the Curie temperature is related to the grain-boundary barrier, and higher grain-boundary barrier leads to

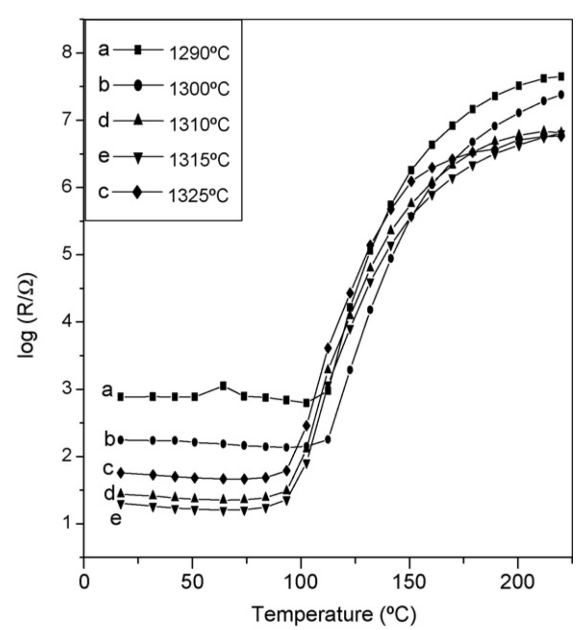

Fig. 6. *R–T* curves of same sample sintered at different temperature.

Table 2
R_{25} of sample sintered at 1315 °C with different soaking time

t (min)	R_{25} (Ω)
10	4064
20	13.9
30	21.1
60	136.5
90	240.9

larger resistance jump [11]. The grain-boundary potential barrier as well as PTC effect improves by doping an increasing content of Mn. The PTC effect, however, reduces with doping at high level because the excessive acceptor Mn enriches the grain boundary, produces negative surface charge, and engenders a depth of positive space charge layer to keep neutral electrical charge. Taking into account both the low R_{25} and better PTC effect, the composition of the sample doped with 1.0 mol% Y and 0.04% Mn, whose room-temperature resistance is 13.9 Ω, ratio of log (R_{max}/R_{min}) is 5.6 and temperature coefficient of resistance α is 21.9%/°C, exhibits the optimal electrical property. The sample of this composition was chosen for further investigation.

3.4. Sintering conditions

Sintering temperature (T_s) is a very important factor in the process of sintering ceramics. In order to reduce the R_{25} of the ceramics and increase the resistance jump, the disks were sintered at various different temperatures (1290–1330 °C) with different soaking time (10–60 min). The temperature dependence of the resistance of the samples sintered at different T_s is shown in Fig. 6. It can be seen from Fig. 6 that the optimal sintering temperature of sample (Y 1.0%, Mn 0.04%) is 1315 °C because the ceramics sintered at this temperature exhibit lowest R_{25} and maximum resistance jump.

Moreover, it is crucial to choose an optimal soaking time. It can be concluded that soaking time is very important to R_{25} of the materials. The Ba^{2+} of the $BaTiO_3$ ceramics were substituted by semiconducting ions more effectively with sintering for an appropriate soaking time, and it is beneficial to make the ceramics semiconducting. Table 2 lists the resistance of sample with same composition and T_s for different soaking time. We can see from Table 2 that the resistance generally increases with an increase of soaking time, and the optimum soaking time is 20 min. The resistance with 10 min is abnormally high possibly because the ceramics could not be formed and great deals of pores exist in ceramics sintered for a very short time.

4. Conclusions

A series of nano-$Ba_{0.85-x}Y_xSr_{0.07}Ca_{0.08}Mn_yTi_{1-y}O_3$ ($0.7\% \leq x \leq 1.2\%$, $0 \leq y \leq 0.06\%$) solid solutions have been synthesized by solid-state reaction at low temperature. The PTC ceramic materials whose room-temperature resistance is 13.9 Ω, ratio of log (R_{max}/R_{min}) is 5.6 and temperature coefficient of resistance α is 21.9%/°C was prepared through the optimal concentration of Y, Mn and optimum sintering conditions.

Because of the donor and acceptor compensation, the optimum donor level increases significantly with increasing acceptor level. The room-temperature resistance changes as the U-type curve with an increase of Mn additive concentration while the resistance jump is on the reverse. Sintering conditions are very important factors to PTC resistance materials. The R_{25} of material increases with an increase of the soaking time, and the optimal T_s and soaking time are 1315 °C and 20 min.

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