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The PTCR effect in $BaTiO_3$ ceramics modified by donor dopant

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Abstract

The PTCR effect of $BaTiO_3$-based ceramics is influenced severely by either impurities or the process. The influence of Ce^{3+}, Sm^{3+} and Yb^{3+} on the PTCR effect was studied. In order to exclude other influential factors, the ceramics was only modified by donor dopant using high purity raw materials. It was found that, in each group of these donor doped samples, the RT resistance decreased with donor content in low doping level, after it reaches a minimum, and increases rapidly at high doping level; the PTCR effect decreased with donor content irrespective of the doping level.

Keywords: D. $BaTiO_3$; PTCR effect; Ce^{3+}, Sm^{3+}, Yb^{3+} dopants

1. Introduction

Donor doped $BaTiO_3$ semiconducting ceramics have positive temperature coefficient resistivity (PTCR) effect [1]. It was found that both trivalent ion (such as rare earth ion, Bi^{3+}, and Sb^{3+}) which replace the Ba site and pentavalent ion (such as Nb^{5+}, Ta^{5+}) which replace Ti site can act as donors. The PTCR effect of $BaTiO_3$ based ceramics can be influenced severely by either impurities or the process. Because the ceramics were often modified by not only one dopant, the relationship between the PTCR effect and donor content can be changed easily, and was not noticed by previous researchers. In this paper, we studied the PTCR effect in $BaTiO_3$ ceramics only modified by one kind of donor dopant to exclude other influential factors. Checking different kinds of donor doped samples resulted in the same rule that the PTCR effect decreased with the rising of donor content in the whole doping level.

2. Experiment

Using high purity $BaTiO_3$ and donor dopant as the starting raw materials, ceramics of composition $BaTiO_3 + x\%D(NO_3)_3$ with $x = 0$–0.6, were fabricated by conventional ball-milling, pressing and sintering techniques, where D is Yb, Sm and Ce respectively. After 24 h of ball milling, powders were dried and calcined at 1150 °C for 2 h. They were pressed into pellets 2 mm thick and 10 mm in diameter. The pellets were sintered in air at 1350 °C for 1 h. Both surfaces of samples were coated with In–Ga alloy electrodes. Then the temperature dependence of resistance of the samples was measured from room temperature up to 400 °C.

3. Results and discussion

The room temperature (RT) resistance of the samples as a function of donor content is shown in Fig. 1. The RT resistance decreased with the donor content in the low doping level, reached the minimum at a certain donor content, then increased rapidly with donor content in the high doping level. In the low doping level, the dopant replaces Ba-site

$$D_2O_3 \rightarrow 2D^{\bullet}_{Ba} + 2O^{\times}_{O} + \frac{1}{2}O_2(g) + 2e' \quad (1)$$

because the conductivity of the material is decided by

$$\sigma = ne\mu \quad (2)$$

where σ is conductivity (reciprocal of resistivity), n is free electron concentration and μ is mobility of electron. The neutrality condition can be simplified as

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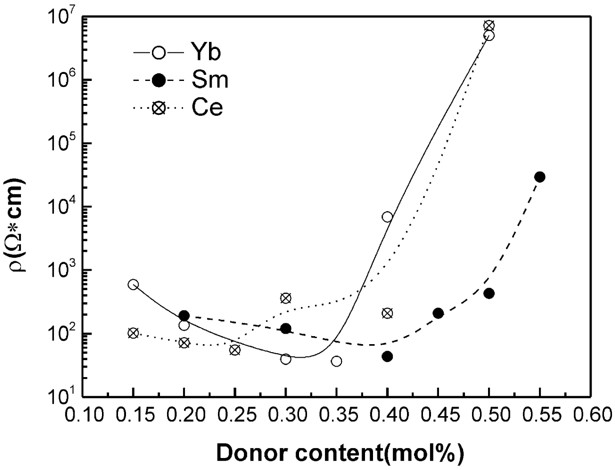

Fig. 1. Room temperature resistivity as a function of donor content.

$$[D^{\bullet}_{Ba}] = [e] \qquad (3)$$

the RT resistivity is decreasing with the rising of donor content. When donor content rises up to a certain value, the dopant can be compensated by cation vacancies

$$D_2O_3 \rightarrow 2D^{\bullet}_{Ba} + 3O^{\times}_{O} + V''_{Ba} \qquad (4)$$

or, the dopant can occupy Ti-site act as acceptor

$$D_2O_3 + 2e' \rightarrow 2D''_{Ti} + 3O^{\times}_{O} + V^{\times}_{O} \qquad (5)$$

thus, free electron concentrations decrease, and the resistivities of samples increase.

The temperature dependence of resistance of samples with different donor content is shown in Fig. 2.

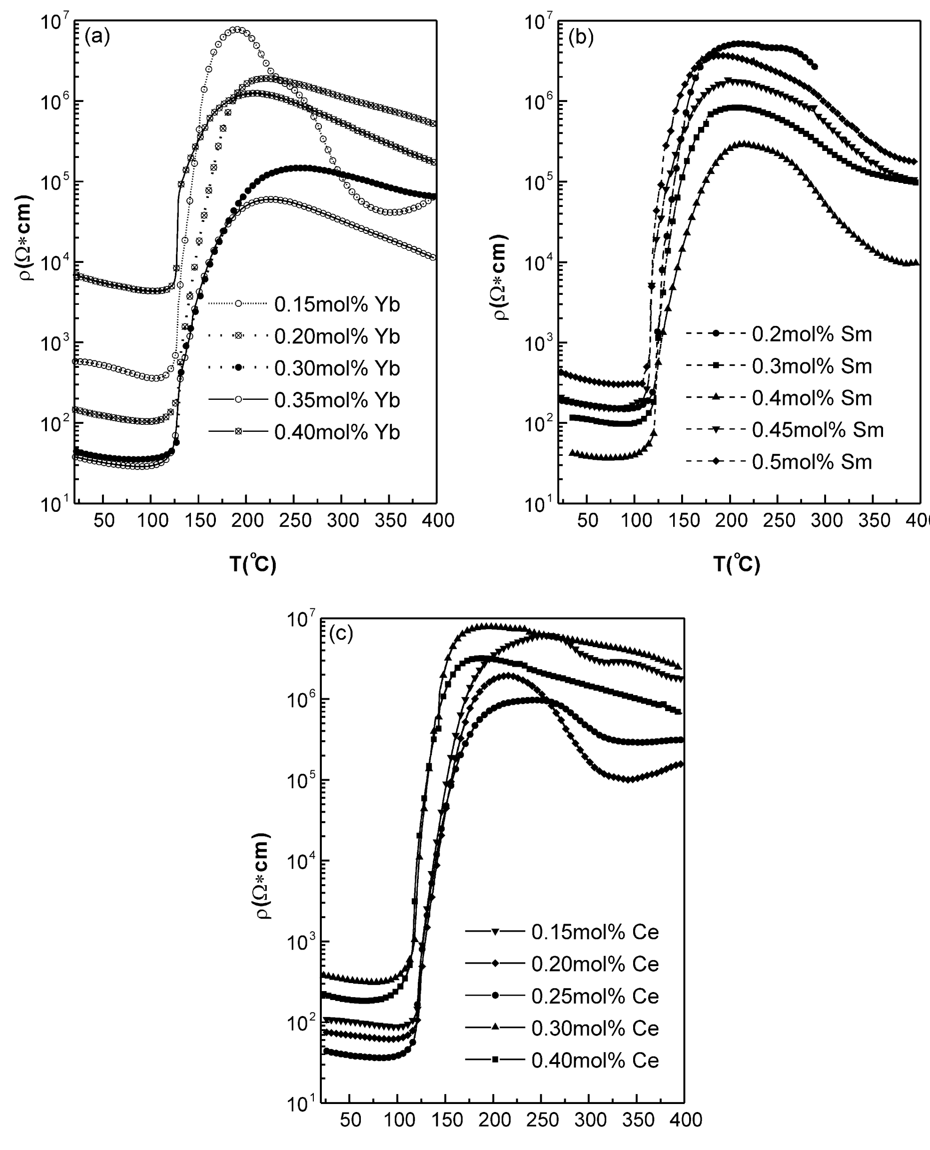

Fig. 2. Temperature dependence of resistivity: (a) Yb-doped samples; (b) Sm-doped samples; (c) Ce-doped samples.

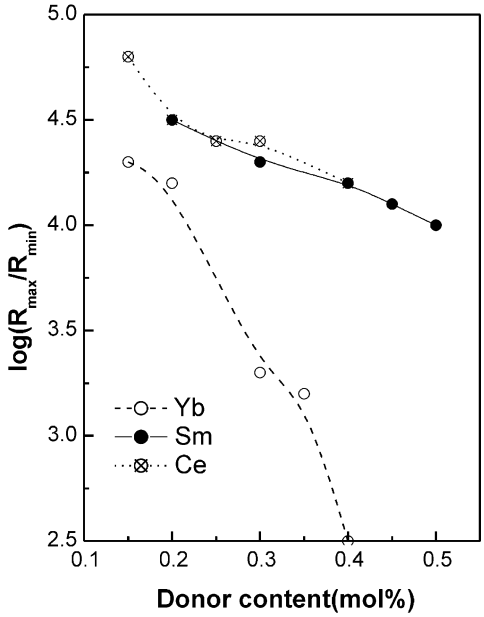

Fig. 3. Relationship between the resistance jumping and donor content.

According to these results, the relationship between the resistance jumping and donor content is illustrated as Fig. 3. It is clear that the resistance jumping is decreasing with donor content in Fig. 3. When the pure $BaTiO_3$ is sintered in air, the following defect reaction can occur [2]

$$\frac{1}{2}O_2(g) \rightarrow O_O^\times + V_{Ba}^\times \tag{6}$$

Because of the high oxygen pressure at grain boundary when samples are sintered in air, this reaction prefers to happen at the grain boundary rather than in the grain lattice. The neutral barium vacancy may be ionized by the electron that was introduced by the donor dopant

$$V_{Ba}^\times + 2e' \rightarrow V_{Ba}'' \tag{7}$$

or

$$D_2O_3 + V_{Ba}^\times \rightarrow 2D_{Ba}^\bullet + V_{Ba}'' + 2O_O^\times + \frac{1}{2}O_2(g) \tag{8}$$

In pure donor doped $BaTiO_3$ ceramics, the capturing of a free electron by neutral barium vacancy at the grain boundary during ferroelectric phase transition would respond for the PTCR effect [3–4]. So the PTCR effect is determined by the concentration of neutral barium vacancy of the sample at low temperature. From (7) and (8), with the rising of the donor content, the concentration of neutral barium vacancy is decreasing. The barium vacancy, which the excess donor introduced in the starting materials, can not promote the PTCR effect because they are an ionized-vacancy as (4); they cannot capture free electrons any longer. As shown as (8), high oxygen pressure can prevent the neutral barium vacancy from ionizing. At the same time, it can promote the production of neutral barium vacancy as (6). The relation between the PTCR effect and donor content may be changed by other impurities, but in the case of only being modified by donor dopant, the PTCR effect decreased with the donor content.

4. Conclusion

The RT resistance of $BaTiO_3$ ceramics only modified by donor dopant, decreased with donor content in the low doping level, after it reaches a minimum, it increases rapidly with donor content in the high doping level. The PTCR effect decreases with donor content in the whole doping level. The decrease of neutral barium vacancy would be responsible for this result.

References

[1] P.W. Haayman, R.W. Dam, H.A. Klasens, Method of Producing a Semiconding Materials. German Pat. No. 929,350, 23, June 1955.
[2] J. Daniels, R. Wernicke, Defect chemistry and electrical conductivity of doped barium titanate ceramics, Philips Res., Rep 31 (5) (1976) 544–559.
[3] J.Q. Qi, W.P. Chen, Y.J. Wu, et al, Improvement of the PTCR effect in $Ba_{1-x}Sr_xTiO_3$ semiconducting ceramics by doping of Bi_2O_3 vapor during sintering, J. Am. Ceram. Soc. 81 (2) (1998) 437–438.
[4] T.R.N. Kutty, P. Murugaraj, N.S. Gajbhiye, EPR evidence for activation for trap centers in PTCR $BaTiO_3$ ceramics, Mater. Res. Bull. 20 (5) (1985) 565–574.