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Acceptor compensation in (Sb, Y)-doped semiconducting $Ba_{1-x}Sr_xTiO_3$

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The characteristics of semiconducting $Ba_{1-x}Sr_xTiO_3$ samples with different doping procedures were studied. Complex impedance–measurements were used to separate the resistances of grains R_b, and grain boundaries as R_{gb}. It was shown that excess donors added after calcination diffused into the grain bulk more slowly and could be compensted on the grain boundary by acceptors, and thus samples with particularly low resistivity were obtained. Using an excess donor to compensate for the acceptor, a sample with room temperature resistivity of $\sim 200\,\Omega\,cm^{-1}$ and greater than 7.8 orders of jumping of resistance was obtained.

1. Introduction

The PTCR (positive temperature coefficient of resistance) characteristic is influenced greatly by dilute doping donors and acceptors in $BaTiO_3$ based ceramics. Previous investigations show that for various donors, there is an optimum doping content, D_m^0, at which the lowest resistivity is obtained in ceramics [1, 2]. These donors include trivalent ions that substitute for Ba in the lattice (i.e. La^{3+}, Sb^{3+}, Bi^{3+}, Y^{3+}, Nd^{3+}, etc.), and quinquevalent or sexavalent ions that replace the Ti site (i.e. Nb^{5+}, Ta^{5+}, Sb^{5+} and W^{6+} etc.). Donors are added generally before synthesis of the $BaTiO_3$ solid solution and the doping procedure is called once doping. If the donor doping content is greater than its D_m^0, the part other than D_m^0 is called the excess donor. On the other hand, acceptors (i.e. Mn, Fe, Cu, etc.) are added after the main crystal phase is compounded in order to make these ions rich on the grain boundary and near the surface of the grain body, which can promote the surface states of the acceptors [3, 4]. This doping after the main crystal phase is formed is called twice doping.

Many kinds of impurities have different distributions between the grain and the grain boundary. In yttrium-doped $BaTiO_3$ ceramics yttrium is only partly incorporated into grains as a result of rapid grain growth [5]. The rest of it remains in intergranular phases. Other kind of dopants, such as Li, Mg, Mn and Fe, can act as acceptors in $BaTiO_3$ based ceramics. Peng and coworkers have studied Mg–La and Mn–La codoping $BaTiO_3$ materials [6, 7]. Both Mg and Mn can compensate for donor-dopant La in the samples. But they have different mechanisms. Mg is incorporated into the body of the grain and Mn mainly exists in the grain boundary.

In our study, excess donors were added by once doping in some samples and twice doping in other samples. Comparisons between these two kinds of samples were made of the resistivity and PTC effects. By complex impedance analysis, the influence of the two doping styles of excess donor on compensation by an acceptor in the grain boundary was also studied.

2. Experimental procedure

Two basic compositions were prepared by mixing 0.5 mol % $Y(NO_3)_3 \cdot 6H_2O$ and 0.6 mol % $Y(NO_3)_3 \cdot 6H_2O$, respectively, with $Ba_{0.88}Sr_{0.12}TiO_3 +$ 1 mol % TiO_2. After calcination, different doses of $Mn(NO_3)_2$ (from 0 to 0.1 mol %) were added to the basic composition with 0.6 mol % $Y(NO_3)_3 \cdot 6H_2O$, and samples in series A were obtained. Some 0.1 mol % of $Y(NO_3)_3 \cdot 6H_2O$ and different doses of $Mn(NO_3)_2$ (from 0 to 0.14 mol %) were added to the basic composition with 0.5 mol % $Y(NO_3)_3 \cdot 6H_2O$ to obtain the series B samples. Different doses of $Mn(NO_3)_2$ (from 0 to 0.14 mol %) together with an equivalent total of Y and Sb from $Y(NO_3)_3 \cdot 6H_2O$ and Sb_2O_3 with various Sb : Y ratios were added to the basic composition with 0.5 mol % $Y(NO_3)_3 \cdot 6H_2O$ to obtain series C samples. All the samples were sintered 1350 °C for 1 h in air with 0.5 mol % $\frac{1}{3}Al_2O_3 \cdot \frac{3}{4}SiO_2 \cdot \frac{1}{4}TiO_2$ (AST) acting as a sintering aid. For electrical contact, the flat surfaces of the samples were coated with In–Ga alloy by rubbing. Direct current (d.c.) resistivity of these samples was measured at room temperature (r.t.) up to 250 °C using the two-probe method. The frequency dependence of impedance was determined by an impedance analyser (HP4192A). An Opton CSM 950 was used for microstructural analysis.

3. Results and discussion

3.1. Room temperature resistivity

Donor-doped $BaTiO_3$ ceramics have the lowest r.t. resistivity at a certain donor content, D_m^0. When the

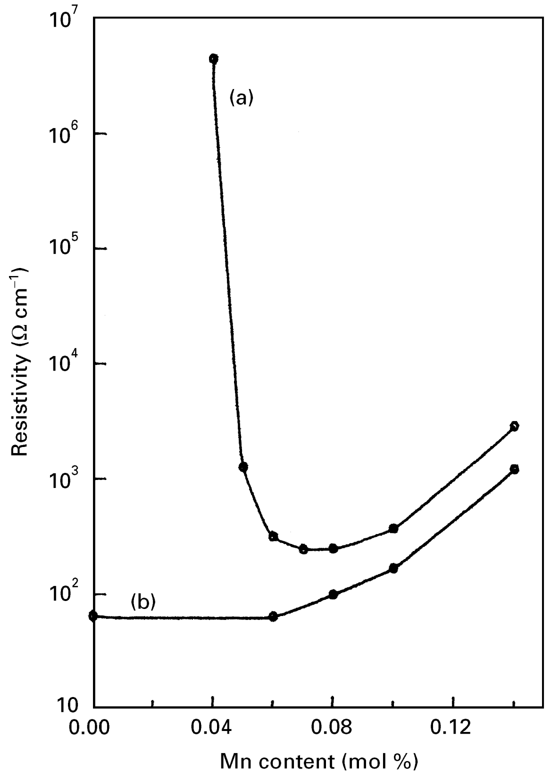

Figure 1 The relation between resistivity and acceptor content of the samples with different excess-donor doping types in series (a) A and (b) B.

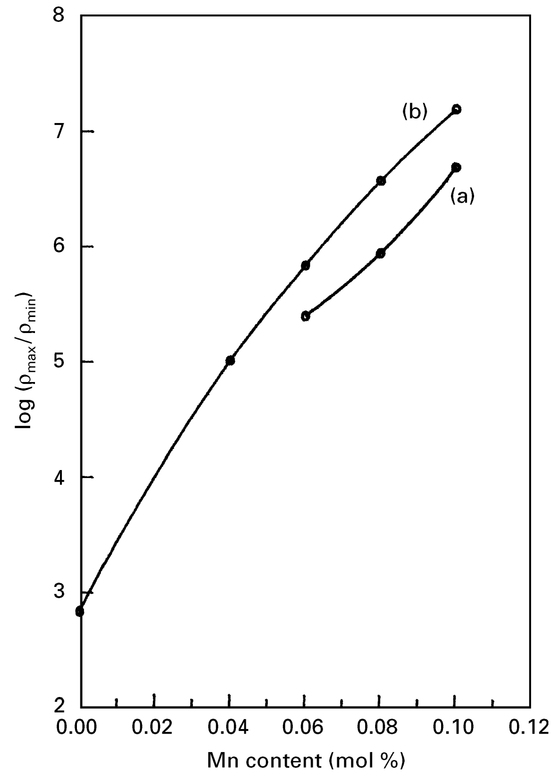

Figure 2 Relation between resistance jumping, ρ_{max}/ρ_{min}, and acceptor content of samples with different excess-donor doping types in series (a) A and (b) B.

donor's doping level was lower than its D_m^0, the r.t. resistivity decreased as the donor's doping level increased because the number of conducting electrons increased. This is expressed by the defect chemistry equation as [8]

$$Y_2O_3 \rightarrow 2Y^{\bullet}_{Ba} + 2e + 2O_O^{\times} + \tfrac{1}{2}O_2(g) \quad (1)$$

When the doping level is greater than D_m^0, the dopant can be compensated by cation vacancy as follows

$$Y_2O_3 \rightarrow 2Y^{\bullet}_{Ba} + V''_{Ba} + 3O_O^{\times} \quad (2)$$

or

$$2Y_2O_3 + 3TiO_2 \rightarrow 4Y^{\bullet}_{Ba} + 3Ti_{Ti}^{\times} + V''''_{Ti} + 12O_O^{\times} \quad (3)$$

and this makes the materials insulating. When the acceptor content is below 0.07 mol %, the resistivity versus acceptor content in series A samples exhibits a greater difference compared with samples in series B. Compensation in the cation vacancy is the main mechanism occurring with higher donor concentration and lower acceptor concentration, below 0.02 mol %, and thus insulating samples in series A are obtained. The r.t. resistivities of samples in series A decreases rapidly as the acceptor content increases, and reaches their lowest values as the acceptor content reaches 0.07 mol %. This implies that the acceptor has the best compensation effect at this content. While the r.t. resistivities of samples in series B vary slightly with acceptor content in a wide range from 0 to 0.07 mol %, the donor added after calcination remains mainly on the grain boundaries or in the intergranular phases. In samples of both the A and B series the r.t. resistivities increase with acceptor contents over 0.07 mol %, while in the series B samples resistivities increase more slowly (Fig. 1).

According to the processes of preparation, it is clear that the different doping styles of the excess donors have different influences on the r.t. resistivity and on the compensation effect of the acceptors.

Under a given acceptor content, the r.t. resistivities of C series samples only varied slightly with Sb:Y ratio. So acceptor compensation of the two different excess donors had a similar influence on r.t. resistivity.

3.2. PTCR effect

Resistivity jumping of donor-doped $BaTiO_3$ ceramics could be increased considerably by doping of some 3d (orbital) elements, including Mn, Fe and Cu; whereas this is not the case for the other 3d (orbital) ions [9]. In our study, all jumping of resistance of samples increased with acceptor content, and greater improvement of resistance jumping was acquired in series B than in series A samples (Fig. 2).

In series C, the result is similar to that in series B. This implies that excess donors added after calcination can compensate with the acceptor more thoroughly on the grain boundary, and compensation on the grain boundary will not damage the jumping of resistivity and the temperature coefficient. So this method is good for determining the PTCR characteristics of the materials. In series C, different from the r.t. resistivity, the jumping of resistance varies considerably with Sb:Y ratio. The greatest jumping is obtained when Sb:Y = 2:1 (Fig. 3). In this condition,

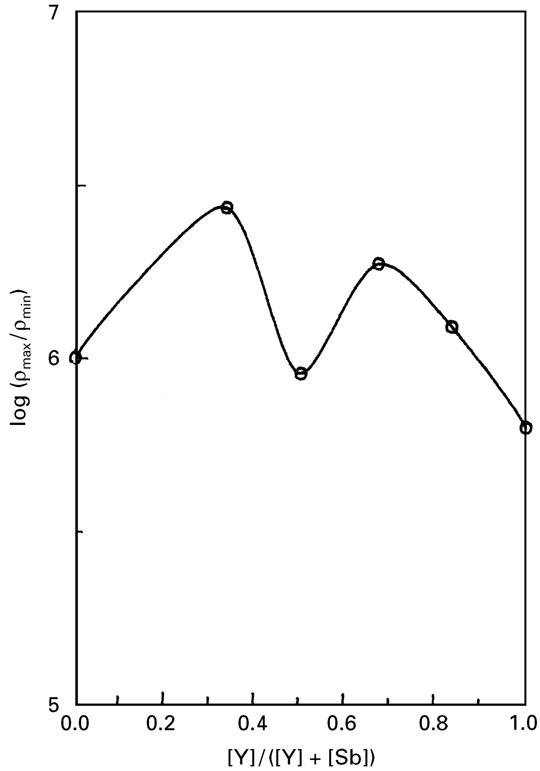

Figure 3 Influence of Y : Sb ratio of excess donors on the resistance jumping, ρ_{max}/ρ_{min} of samples in series C.

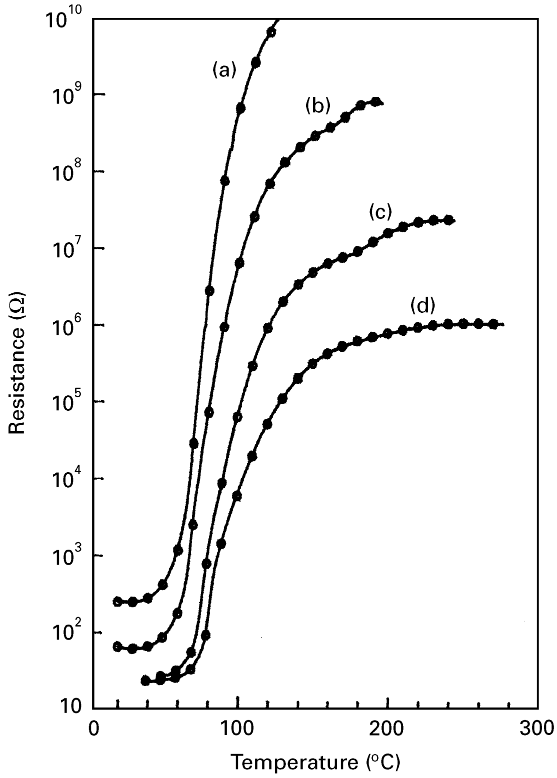

Figure 4 The resistance–temperature characteristics of the samples twice doped by Sb and Y excess donors (Sb : Y = 1 : 2) in series C at Mn concentrations of (a) 0.12 mol %, (b) 0.09 mol %, (c) 0.06 mol %, and (d) 0.05 mol %.

the higher the concentration of dopants, the greater jumping of resistance and the higher temperature coefficient gained (Fig. 4).

When the total excess donor concentration, which was equal to that of the acceptor, reached 0.12 mol %, over 7.8 orders of jumping of resistivity and 200 $\Omega\,cm^{-1}$ of r.t. resistivity were obtained. The properties of this material were better than given in previous reports using a conventional solid method. As shown in the scanning electron microscope (SEM) photograph (Fig. 5), this material has a dense structure as well.

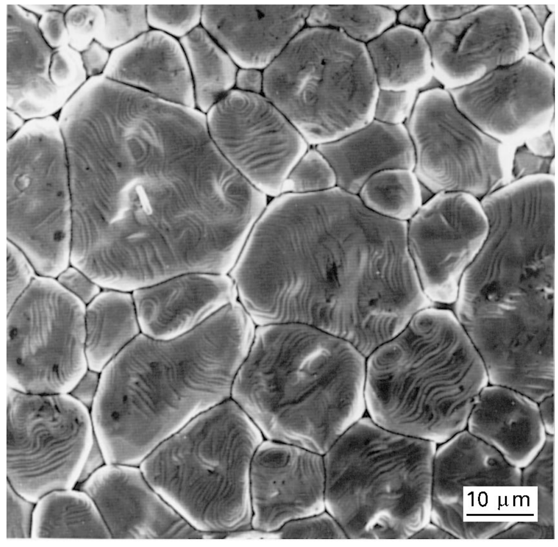

Figure 5 Microstructure of the sample in series C twice doped by 0.08 mol % Sb and 0.04 mol % Y excess donors and by a 0.12 mol % Mn acceptor.

3.3. Complex impedance

Complex plane impedance analysis is a very efficient way of determining the resistances of grains and grain boundaries [10–12]. Maiti and Basu applied complex-plane impedance analysis successfully to study the grain boundary barriers in semiconducting $BaTiO_3$ for development of PTC thermistors [13]. For electrical contact, an In–Ga alloy electrode was chosen as it forms a good ohmic contact with semiconducting $BaTiO_3$. According to many authors, the grain bulk phenomenon can be represented by a pure resistance, R_b [14]. The resistances of the bulk grain, R_b, and grain boundary, R_{gb}, were derived, respectively, from the low- and high-frequency resistance intercepts of Z'. The grain boundary capacitance, C_{gb}, was found from the maximum value of Z''. Impedance diagrams of samples in series A and B are given for different manganese contents in Fig. 6a–c and d, e respectively. An optimum circle was fitted by the method of least squares, and the relative factors were all bigger than 0.997.

From these fittings, the resistances of grains, R_b and grain boundaries, R_{gb} of series A and B are obtained and are shown versus variance of manganese content in Fig. 7.

For the samples in series A, grain resistances decreased as the manganese content increased, and in the range of our doping, the resistances did not reach the lowest values possible. On the contrary, grain boundary resistance reached its minimum value at a content of 0.07 mol %. Twice-doped manganese

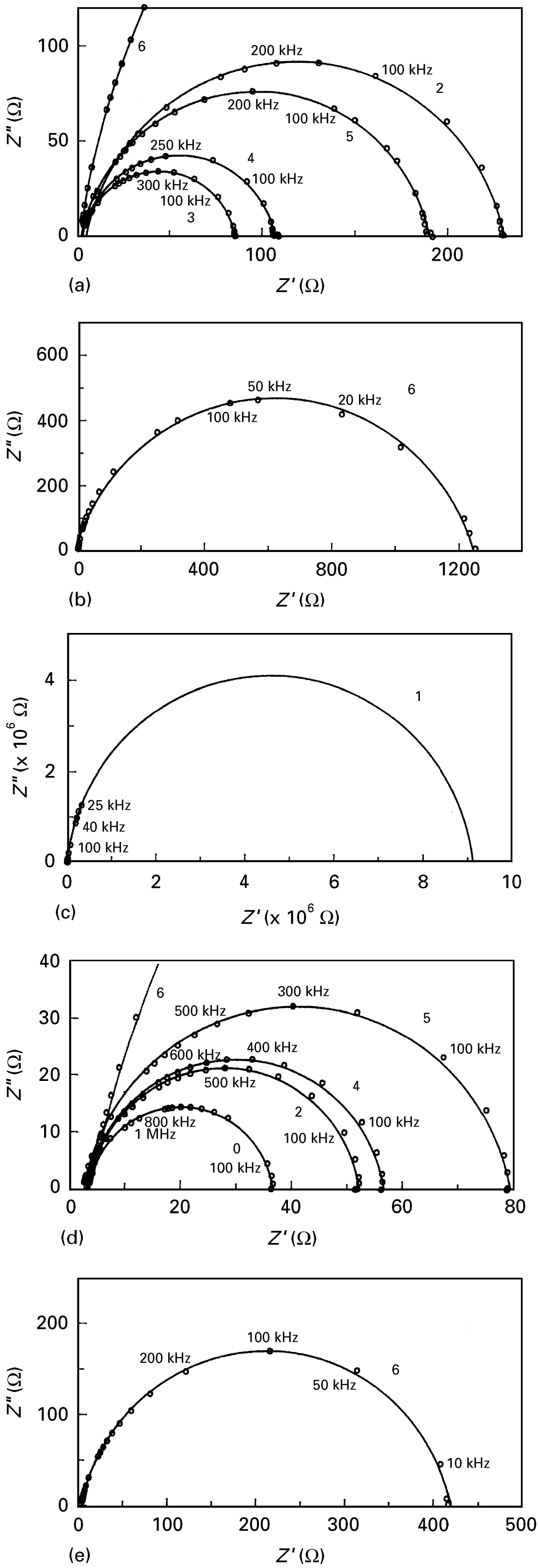

Figure 6 Impedance diagrams of samples in a–c series A, and d–e series B with different Mn contents. The Mn contents of samples 0–6 were 0.00, 0.04, 0.06, 0.07, 0.08, 0.10 and 0.14 mol %, respectively.

diffused into the bulk slowly, and excess donors were not completely compensated until the manganese content increased to 0.14 mol % as a result of the greater

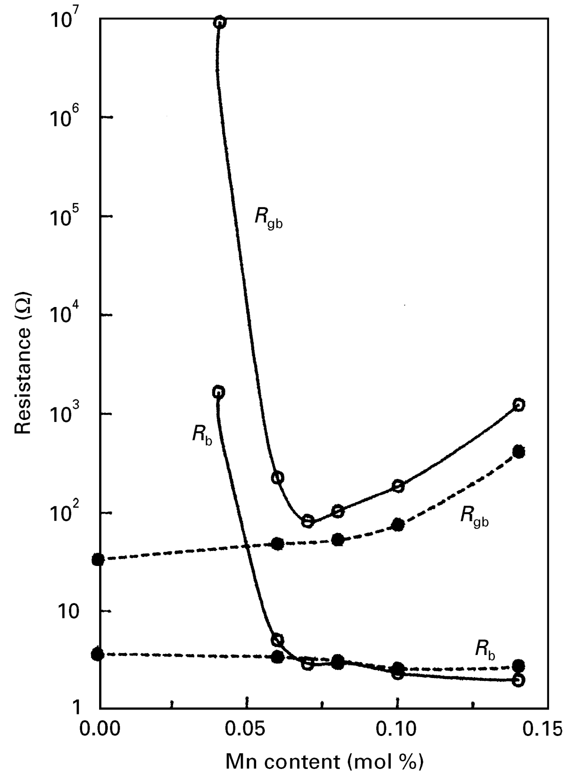

Figure 7 Relation between Mn content and grain bulk resistance R_b, grain boundary resistance, R_{gb}, derived from the impedance diagrams of series A (○) and B (●) samples.

part of it remaining on the grain boundary. Then, a manganese content of 0.07 mol % could compensate excess grain boundary donors completely.

The grain resistance of series B reached its lowest value when the manganese content was 0.1 mol %, but grain boundary resistance increased with manganese content. Under the sintering temperature, twice-doped Y and Mn could diffuse into the bulk at the same time; yttrium doped after calcination might remain in the intergranuler phase(s) partly. Yttrium diffused to the grain and grain boundary more slowly because of an oxidizing sintering atmosphere

$$Y_2O_3 + Mn_2O_3 \rightarrow 2Y_{Ba}^{\cdot} + 2Mn'_{Ti} + 6O_O^{\times} \quad (4)$$

thus, the oxidizing atmosphere slowed down the diffusion of yttrium. On the contrary, Mn^{3+} dissolved on the grain boundary more quickly than in the bulk of the grain in an oxidizing atmosphere

$$Mn_2O_3 \rightarrow 2Mn'_{Ti} + V_O^{\cdot\cdot} + 3O_O^{\times} \quad (5)$$

Furthermore, manganese was apt to be doubly ionizing in the $BaTiO_3$ solution. In yttrium and manganese codoped samples, diffusion of these dopants into the bulk of the grain was promoted by reaction of

$$Y_2O_3 + Mn_2O_3 \rightarrow 2Y_{Ba}^{\cdot} + 2Mn'_{Ti} + 6O_O^{\times} \quad (6)$$

then, twice-doped donors and acceptors could diffuse into the grain bulk and be compensated there; the others could be compensated on the grain boundary and moderate the r.t. resistivity of the samples.

From Fig. 7, in the samples of both series A and B, the grain boundary resistances increased with manganese content, except in a few samples of series A of which the Mn content was very low and compensation of the cation vacancy occurred as described in Equations 2 and 3. The grain resistances of those semiconducting samples both of series A and B only changed slightly with Mn content. So manganese can influence grain boundary resistance more than the resistance of the grain bulk.

4. Conclusions

Excess donors that were added after calcination can be more thoroughly compensated by an acceptor on the grain boundary, and good PTCR characteristics of the material can be obtained. Complex impedance analysis shows that manganese could influence the grain boundary resistance more than the resistance of the grain bulk.

When the excess donors were from a binary Sb and Y system, under a given acceptor content, the Sb:Y ratio had little influence on the r.t. resistivity but could influence the jumping of resistance considerably. The greatest jumping of resistance could be obtained at a certain Sb:Y ratio.

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