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Investigation of surface acceptor state density and resistivity jump of ytterbium-doped (Ba, Sr)TiO_3 materials

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The acceptor state density was calculated by a new method based on Heywang Model. By using the plot of natural logarithm of resistivity versus $1/\varepsilon_{app}T$, the acceptor state density of Yb-doped $BaTiO_3$ was calculated. The doping effects of Yb and Mn were also investigated. Yb doped after preheating can decrease the acceptor state density and resistivity jump; Mn doped after preheating may increase the acceptor state density and resistivity jump.

1. Introduction

The 'Positive Temperature Coefficient of Resistivity' (PTCR) effect in $BaTiO_3$ ceramics commonly refers to the anomalous increase in resistivity near the Curie temperature (T_c). Since its discovery, several models have been proposed [1–3]. Most recent investigations of PTCR materials aim at improving PTCR properties by doping different acceptors (i.e., Mn, Fe, Cu etc.) and donors (i.e., Y, Nb, Sb etc.) [4, 5]. Many researchers have calculated acceptor state density (N_s), Fermi level (E_f), and the energy gap between the conduction band and the electron trap energy (E_s) to explain the PTCR effect. However, most methods are either infeasible or complex in calculation.

Previous research by Mi Qing *et al*. has proved that Yb-doped $BaTiO_3$ material exhibits excellent electrical properties [6]. In this paper, a new method was proposed to calculate the surface acceptor state density (N_s) of Yb-doped $BaTiO_3$ material.

2. Theory

The most widely accepted model to explain PTCR effect is Heywang Model which describes the resistance-temperature behavior based on a double Schottky barrier. This barrier is caused by deep acceptor states trapped at the surface of grains. The height of the barrier, ϕ, at the grain boundaries is described as:

$$\phi = eN_s^2/2\varepsilon_0\varepsilon_r N_d \tag{1}$$

where N_s is the acceptor state density; N_d is the charge carrier density; T is the temperature; ε_0 is the permittivity in free space, and ε_r is the relative permittivity of the grain boundary region.

Thus the resistivity R is given by:

$$R = R_0 \exp(e\phi/KT) \tag{2}$$

where R_0 is a constant, K is the Boltzmann constant, and e is the electron charge.

According to the Curie-Weiss Law:

$$\varepsilon_r = C/(T - T_c) \tag{3}$$

where C is the Curie-Weiss constant, T is the temperature, and T_c is the Curie Temperature. Above the Curie point, the resistivity increases quickly because of the variation of ε_r. Thus, PTCR effect directly relates to grain boundary. From Equation 1, N_s, N_d, and ε_r can greatly affect the height of the barrier.

From dielectric theory, as derived by Wernicke, [7] ε_{app} is given by:

$$\varepsilon_{app} = \varepsilon_r(d/2b) \tag{4}$$

where d is the average grain size and b is $N_s/(2N_d)$, the barrier width. With the assumption that each of the samples can be regarded as a capacitor, ε_{app} can be derived from the following equation:

$$\varepsilon_{app} = Ft/\varepsilon_0 S \tag{5}$$

where F is the electric capacity, t is the thickness of the sample, ε_0 is the permittivity in free space, and S is the area of the electrode. From Equation 1, 2 and 4, we have

$$R(T) = R_0 \exp\left(e^2 N_s d/4\varepsilon_0\varepsilon_{app}KT\right) \tag{6}$$

or

$$\ln R(T) = \ln R_0 + e^2 N_s d/4\varepsilon_0\varepsilon_{app}KT \tag{7}$$

N_s can be calculated from the slope of the natural logarithm of the resistivity versus $1/\varepsilon_{app}T$ as follows:

$$N_s = 4\varepsilon_0 Kg/e^2 d \tag{8}$$

where g is the slope of the line. In Equation 8, d can be obtained by messuring the average diameter of the grains in SEM photos.

3. Experimental

A mixture of 82 mol % $BaTiO_3$, 18 mol % $SrCO_3$, 18.25 mol % TiO_2 and 0.25 mol % $Yb(NO_3)_3$ of reagent grade was mixed by wet milling for 20 h. After preheated at 1050 °C for 2 h in air, different amount of $Yb(NO_3)_3$ and/or $Mn(NO_3)_2$ was added into the initial compositions. In series A, Yb25-Ybx, only $Yb(NO_3)_3$ was added after preheating, where x was the content of Yb added after preheating. In series B, Yb25-Mnx, only $Mn(NO_3)_2$ was added after preheating. In series C, YbMnab, Yb and Mn were added at different ratios of a/b after preheating. All the powders were then ball milled again for 12 h. After mixed with 10 wt % aqueous PVA solution and seived, the powder was pressed into disks with diameter of 10 mm and approximately 1.5 mm in thickness. All the samples were sintered at 1340 °C in air for 30 min and furnace-cooled to room temperature.

To measure the resistance-temperature characteristics, samples were electroded with In-Ga alloy. HP4192A LF impedance analyzer was used to measure the complex impedance. The R-T curve was measured from room temperature to 250 °C by using self-assembled apparatus. SEM (Hitachi S-450) was used to analyze the microstructure.

4. Results and discussion

4.1. A.C. resistivity of PTCR materials

Yb doped (Ba, Sr)TiO_3 is not only a kind of ferroelectric materials, but also a dielectric material. As the frequency (f) varies, the electric capacity, resistivity and the relative dielectric constant of PTCR materials also change. Liang-Fu Chen proved that when $f > 1$ KHz, the value of electric capacity changed little [8]. In Fig. 1, the A.C. resistivity is greatly affected by f above T_c. When f goes up, the resistivity and PTC effect will decrease. It is mainly because that at high frequency, the polarization can not match the change of f above T_c. Thus, at the grain boundaries, the domains of different grains have different orientations and compensate with each other. When $f \to \infty$, the resistance of the samples at grain boundary is equal to R_b, which is far less than $R_b + R_{gb}$. In Fig. 1, it also can be found that when frequency is greater than 10 KHz, the decrement of resistivity is relatively low. Thus, the Frequency of 20 KHz was selected as experiment frequency.

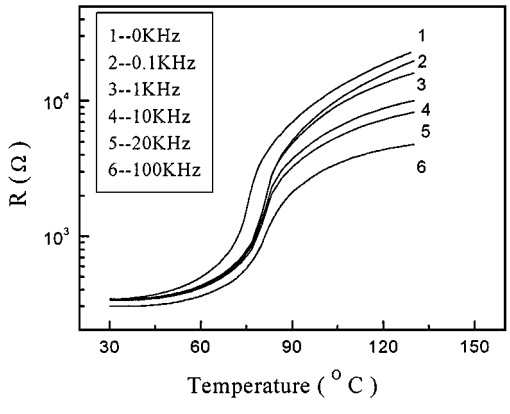

Figure 1 PTC effect of different frequencies.

4.2. N_s

By measuring the diameters of grains in Fig. 2 and calculating the average diameter, the value of N_s was obtained. Fig. 3 shows linear fit figures of the natural logarithm of the resistance versus $1/\varepsilon_{app}T$ of Yb25-Yb8 at different frequencies. The resistance and the slope decrease, when frequency increases. The results of linear fit is shown in Table I. Every relative coefficient is greater than 0.99.

TABLE I Results of linear fit

Frequency (KHz)	Slope ($\times 10^7$)	Acceptor state density N_s ($\times 10^{17}/m^2$)	Relative coefficient
5	1.58	1.59	0.9973
10	1.28	1.29	0.9964
15	1.16	1.17	0.9963
20	1.09	1.10	0.9959
25	1.05	1.06	0.9957

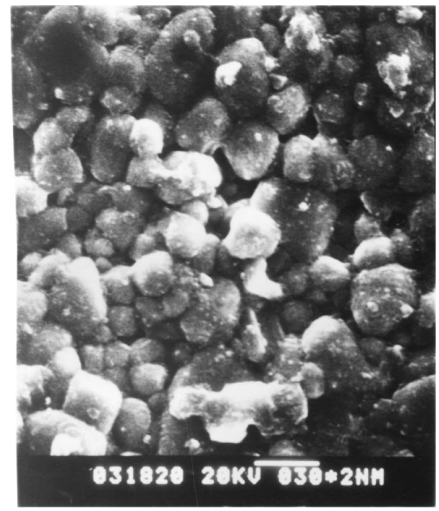

Figure 2 SEM of Yb25-Yb8.

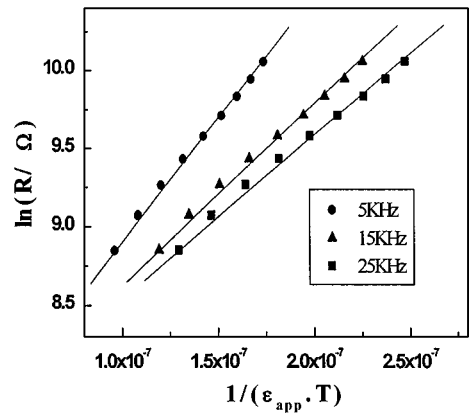

Figure 3 Plot of the natural logarithm of the resistivity versus $1/\varepsilon_{app}T$ of Yb25-Yb8 at different frequencies.

It also can be found that the width of barrier calculated out in this method ranges from 1 to 10 nm, 1/100–1/1000 to the size of grains. Z. A. Netamo obtained the same results by SEM. Compared with other research results, this method of calculating N_s is correct and feasible [9, 10].

4.3. Effects of different doping elements to N_s

It is easy to discover that N_s has same tendency to resistivity jump in Figs 4–6. Above T_c, the barrier at grain boundary rises and causes the increment of resistivity. In Equation 1, $\phi \propto N_s^2$. So the resistivity jump has close relationship with N_s. Previous research has proved that after the main crystal phase is formed, ions which are added after preheating, mainly concentrates on the grain boundary [11]. For sample Yb25-Ybx, most Yb added after preheating concentrates at grain boundary with the reaction:

$$Yb_2O_3 + 3TiO_2 \rightarrow 2Yb_{Ba}^{\cdot} + V_{Ba}'' + 3Ti_{Ti}^{\times} + 9O_o^{\times} \quad (9)$$

A great deal of V_{Ba}'' which can reduce the acceptor state concentration is produced. When the content of V_{Ba}'' rises up in grain boundary, the diameter of grain, resistivity jump and N_s decrease as shown in Fig. 4.

Previous research has proved that Mn can increase both the resistivity at room temperature and the resistivity jump [10]. For sample Yb25-Mnx, when Mn increases, N_s and resistivity increase as shown in Fig. 7. The defect chemistry equation is:

$$MnO + BaO \rightarrow Mn_{Ti}'' + Ba_{Ba}^{\times} + 2O_o^{\times} + V_o^{\cdot\cdot} \quad (10)$$

Both of Mn^{2+} and $V_o^{\cdot\cdot}$ can increase N_s. Thus, the resistivity jump increases. At room temperature, when Mn exceeds a critical value, the amount of acceptors exceeds the compensation limit of spontaneous polarization, then the extra acceptors can not be compensated at all. Therefore the room-temperature resistivity increases.

To obtain better properties such as low room temperature resistivity and large resistivity jump, different proportions of Yb and Mn was added. The results are shown in Fig. 6. When Yb : Mn = 1 : 3 or Yb : Mn = 1 : 1, the introduction of acceptor can not compensates the effect of donor to the materials. Thus relatively less V_{Ba}'' appears. N_s and resistivity jump increase when the contend of Mn increases. When Yb : Mn = 2 : 1, relatively more V_{Ba}'' is produced. Until Mn is greater than 0.08 mol %, the effect of Mn is greater than that of Yb. A sample of this series with room-temperature resistivity less than 40 Ω cm^{-1} and greater than 5.5 orders of resistivity jump was obtained. Fixing the content of Mn, the effect of Yb can be observed clearly in Fig. 7.

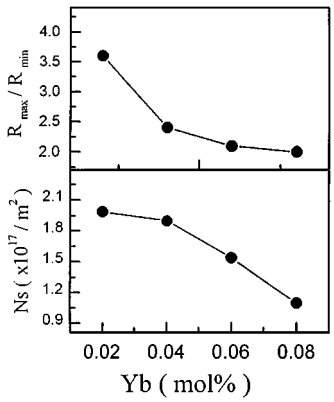

Figure 4 Resistivity jump and N_s of Yb25-Ybx.

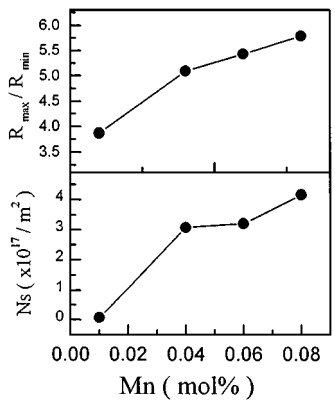

Figure 5 Resistivity jump and N_s of Yb25-Mnx.

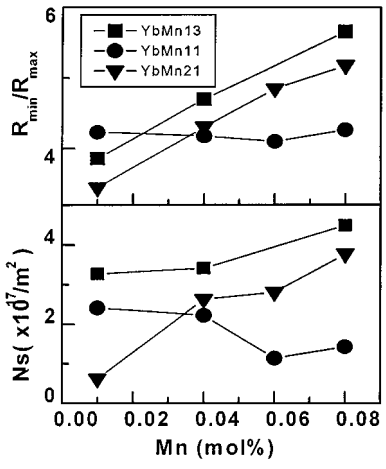

Figure 6 Resistivity jump and N_s of YbMnab.

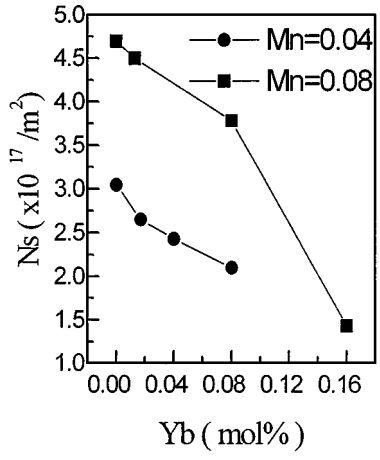

Figure 7 N_s when Mn = 0.04 mol % and Mn = 0.08 mol %.

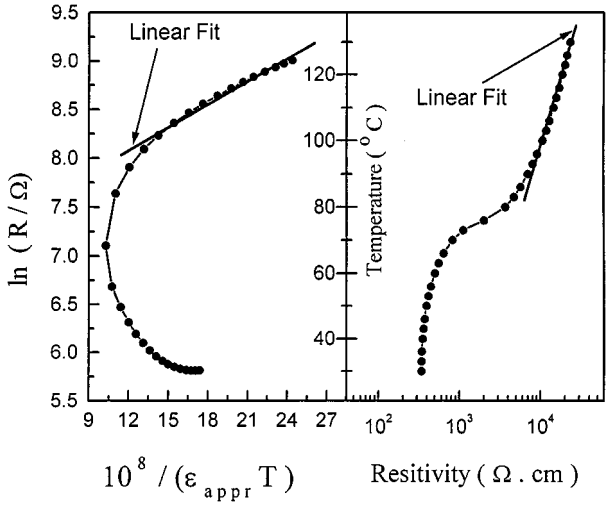

Figure 8 Explanation of PTC effect.

4.4. Explanation

The right part of Fig. 8 is a measured PTCR effect curve. And the left part obtained by calculation matches the right part. In the part above Curie temperature, both figures are quite similar. In this part, each of them can be fit by a line. It is mainly because that the calculation used in this paper is based on Heywang Model. When below the Curie temperature, PTCR effect can be explained by Jonker Model.

To explain the low resistivity below T_c, Jonker proposed a model based on the ferroelectric behavior of tetregonal $BaTiO_3$. He suggested that the barrier is partly or completely compensated by the difference of the normal component of spontaneous polarization between two adjacent grains. With the modification by Jonker, Heywang model is called as Heywang-Jonker Model. It means that the method used here can only explain the PTCR effect above T_c.

5. Conclusion

A feasible method based on Heywang Model has been developed to calculate N_s. It can be applied above T_c.

N_s can be represented by resistivity jump in quality.

V''_{Ba} that concentrates at the grain boundary can reduce N_s and resistivity jump. On the contrary, $V^{\cdot\cdot}_{o}$ that concentrates at the grain boundary can increase N_s and resistivity.

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