On its Conducting Mechanism of the Semiconducting Barium Titanate

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H. Hara, H. Kimura and Y. Mita*

Abstract

Semiconducting BaTiO₃ can be prepared by substituting small amounts of ions of highvalency for Ba or Ti ions. At higher concentrations the foreign ions are compensated by metal ion vacancies. Poly-crystalline samples prepared in air show an enormous increase in resistivity above the ferro-electric Curie point, monocrystalline samples prepared in Na₂CO₃ flux not show. According to this behaviour, Heywang model and other model previously proposed to explain the anomalous increase in resistivity. Theoretical treatment on the proposed Heywang model leads to an interpretation of the physical processes invalued and achieves good agreement with out experiment.

1. Introduction

Several models have been proposed[1-4] to explain the anomalous increase in resistivity that occurs in doped BaTiO₃ above the Curie point[5] but, discussion on this phenomenon, have not reached a final conduction. Sevral investigators recently have indicated that the resistivity anomaly may be due to barrier layers[6-9]. Then, we tried to explain these phenomenon to measure temperature dependence of electrical conductivity, Hall effect, dielectric constant of several-doped BaTiO₃ ceramics. These results compared with theoretical values.

2. Preparation of Samples

All the samples used in the experiments were prepared using the BaTi₃O powder obtained by thermal decomposition of Barium carbonate BaCO₃ $(1-X$ mol%), Titan dioxide (1 mol%), doped material of La₂O₃, Bi₂O₃, Ce₂O₃ $(X=0.1, 0.2, 0.3$ mol%) in air at 1100°C for 5 hrs. These powder was mixed with a water into Ball mill and was pressed into discs or square compacts under pressure of 750 kg/cm². These samples were fired in air atmosphere at 1400°C for about 1.5–2 hrs. in oben-type furnace. Both surfaces of these fired samples was contacted with Ni-metal plates, connected with lead wires.

3. Measurement of Hall effect, resistivity, dielectic constant

Hall effect was measured by ac method (1000 cps) using a Hall coefficient measuring Apparatus[10], these results are given in Fig. 1. the carrier concentration calculated from the Hall coefficient and on the Hall mobility from the electrical
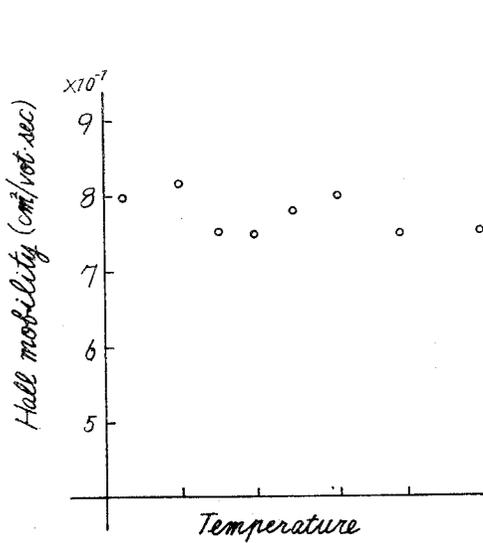

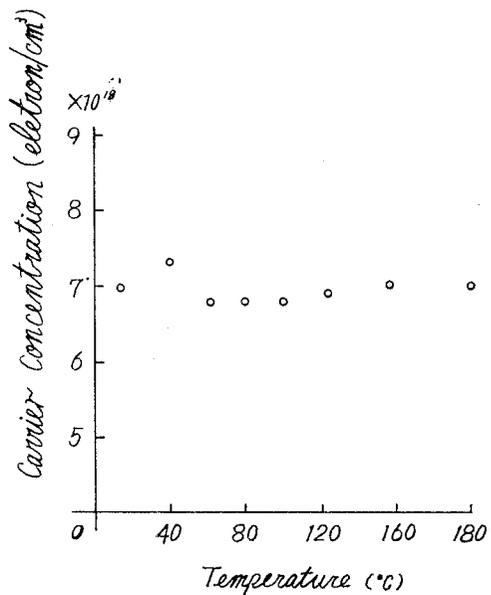* Waseda Univ.

Fig. 1. Hall mobility
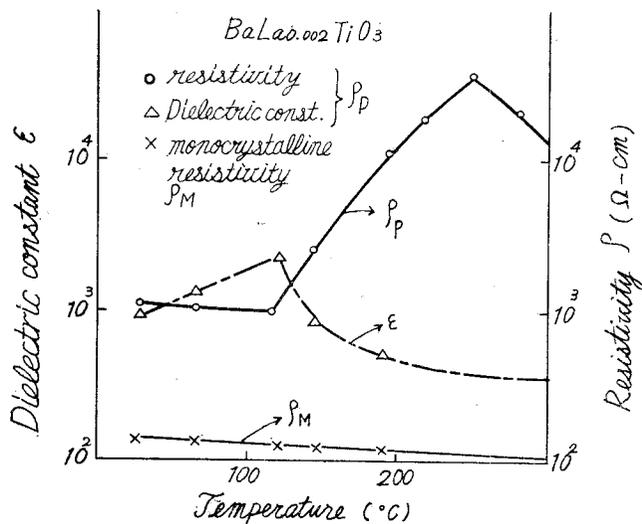

Fig. 2. Carrier mobility

Fig. 3. Ilustration dielectric constant and resistivity

conductivity are shown in Fig 2.

Resistivity and dielectic constant were shown about monocrystalline and poly-crystalline in Fig. 3 but as resistivity was influenced on voltage, we measured using small volutage. The dielectric constant was measured using Impeadance Bridge for 1 kc.

4. Theorectical treatment

From experimental results, anormaly resistivity show polycrystalline samples but not monocrystalline.   Then, for the potantial barrier, the resistivity anormaly can be treated quantitatively in Fig. 4 (A), (B).
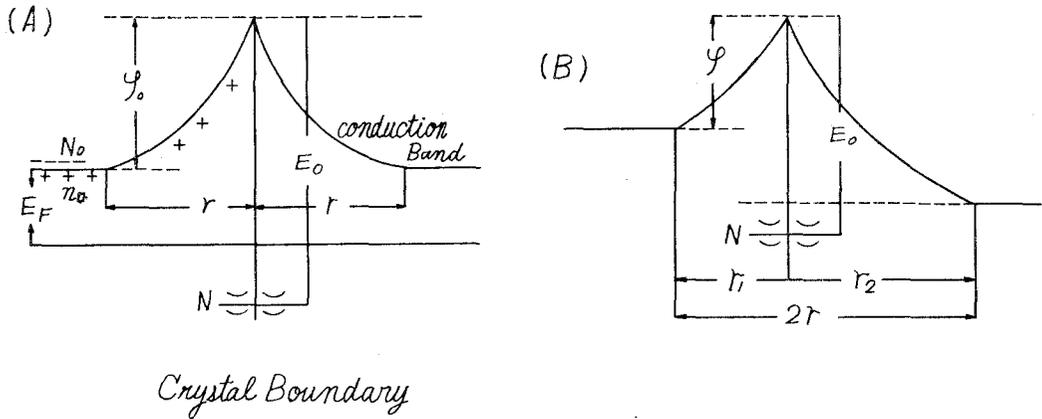

Fig. 4.   Barrier layer model of semiconducting BaTiO$_3$ (A) without external
voltage and (B) with external voltage

Notation

φ_0: Potential Barrier (eV)
E_0: Activation energy of the surface states (eV)
E_F: Fermi level (eV) r: The thickness sf Barrier layer (cm)
N: Density per cm^2 of each grain
n_D: Eelectron concentration in crystals ($\sim 10^{19}$ cm^{-3})
N_0: The number of Ti ions per cm^3

This statrts with the description of a boundary between the two n-type semi-conducting crystal with a number surface states in which electrons can be trapped. Such a contact can conveniently be described using the electron energy model.   In the volume of BaTiO$_3$ grains, electron donors n_D are embodied in the lattice which quantatatively dissociate above room temperature.   The electrons pass from the barrier layer at the grain surfaces to acceptor surfacc states.

In a number of n_S electrons are trapped in the surface states (density N per cm^2 of each grain) at a distance E_0 below the conduction level (or narrow band), we find on both sides a deplation layer with an effective thickness r.   If the normal electron concentration in the crystals is n_D ($\sim 10^{19}$ cm^{-13}), the relation between surface charge and deplation layer thickness is

$$2rn_D = n_S \tag{1}$$

Because of the positive space charge of the non-compensated ionised donors a level curvature appers, with a surface potential with respect to the bulk of the crystals, then, for surface charges, from Poisson's equation

$$\Delta\phi = -\frac{\rho}{\varepsilon_0 \varepsilon} \tag{2}$$

(2) equatin's solution

$$\phi = \frac{e^2 n_S^2}{8\varepsilon_0 \varepsilon n_D} \tag{3}$$

the occupied state of this barrier layer is

$$n_S = \frac{N}{1 + \exp(\phi_0 - E_F - E_0)/KT} \tag{4}$$

with Fermi level

$$E_F = KT \ln\frac{n_D}{N_0} \tag{5}$$

and $N_0 = 1 \sim 2 \times 10^{22}$ cm^{-3} (the number of Ti ions per cm^3), from equations (1), (4) and (5) can be known

$$n_S = \frac{N}{N_0/n_D \{1 + \exp(\phi_0 - E_0)/KT\}} \tag{6}$$

from equation (6)

$$\phi_0 = \frac{e^2}{2\varepsilon_0 \varepsilon n_D} \frac{N^2}{(N_0/n_D)\{1 + \exp(\phi_0 - E_0)/KT\}} \tag{7}$$

If all donor electrons are completely dissociate, conductivity of grains become

$$\sigma_V = e\mu n_D \tag{8}$$

μ : Molibity

Between grain boundary, untill height of potencial Barrier becomes plain, dielectric constant is very large, then electron carriers contributing to conduction required to surmount the barrier layer with thermo energy i. e., the height of the potencial barrier are presented by following equation

$$\sigma_C = \sigma_V \exp(-\phi_0/KT) \tag{9}$$

Increasing temperature, σ_V is little influence of temperature, conductivity is proptional to ϕ_0/KT

$$\ln \sigma_C = -\frac{\phi_0}{KT} = -\frac{e^2 N^2}{2C\varepsilon_0 n_D K}\left(1 - \frac{\theta}{T}\right) \Big/ \left[\frac{N_0}{n_D}\{1 + \exp(\phi_0 - E_0)/KT\}\right]^2 \tag{10}$$

ϕ_0 is depend to dielectric constant i. e. above curie point.

Dielectric constant is large, its value is shown by following equation

$$\varepsilon = \frac{C}{T - \theta} \tag{11}$$

ε : Dielectric constant

θ : Curie temperature

C : 1.2×10^5

or $\sigma_C = \dfrac{1}{\rho_C}$ ρ_C : resistivity

equation (9) is varying

$$\rho_C = \rho_V \exp(\phi_0/KT) \tag{12}$$

the potential barriers at the various temperature can be compared (Table 1).

Table 1. Potential barrier in barrier layer

Temp. (°C)	ϕ_0 (eV)
200	0.6~0.8
20	0.08
−20	0.03

The increase in resistivity with decreasing temperatures is not caused by the height of potential barriers as is the case at high temparature but rather is due to a deplation of free charge carriers such as may be expected to occur in any semiconductor at low temperatures when the log of the resistivity in this range is plotted versus $1/T$, straight lines result with an activationenergy E_A of 0.1, 0.14 eV (at the low temperature between $-100°C$ and $20°C$). then, equation (12) now yields for the region below Curie point with the known relation

$$\rho_V \simeq \rho_0 \exp(E_D/2KT) \tag{13}$$

E_D : Donor activation energy.

According to the general equation

$$\rho_V \simeq \rho_0 \exp(E_D/2KT + \phi_0/KT) \tag{14}$$

If ϕ_0 is given as an approximation by

$$\phi_0 = \phi_0^{(0)} + \phi_0^{(1)} T \tag{15}$$

where $\phi_0^{(0)}$ is estimated by equation (3) and below the Fermi level, $n_S = N$, therefore

$$N/\sqrt{n_D} = 3 \times 10^4 \, \text{cm}^{-1/2} \tag{16}$$

from equation (16) and $n_D \doteqdot 10 \, \text{cm}^{-3}$

$$N \simeq 1 \times 10^{14} \, \text{cm}^{-2} \tag{17}$$

$\varepsilon \simeq 10^4$ (experimental value at $-20°C$)

$e \simeq 1.6 \times 10^{-19}$ Coulomb $\left(\text{Vaccum diele. const.} = 8.85 \times 10^{-21} \dfrac{\text{Coulomb}^2}{\text{dyne cm}^2} \right)$

$\phi_0^{(0)} \simeq 0.03$ eV (Boltzman const. $K = 1.38 \times 10^{-16}$ erg/deg)

at the low temperature, the donor activation energy yields

$$E_D = 2(E_A - \phi_0^{(0)}) \simeq 0.15 \text{ eV}$$

at the region of low temperature, its resistivity can be shown by equation (13), at the region between room temperature and curie point, its resistivity can be shown by equation (14), such as the case, $\phi_0 \lesssim 0.1$ eV.

At the region above the curie point, its resistivity can be shown by equation (12), such as the case, $\phi_0 = 0.5 - 0.6$ eV. By blocking the region, explainning, the theoretical curve agrees well with the one obtained by our experiment. Fig 5 presents this relation. It was this agreement that provided to use the barrier-layer model to explain the resistivity anomaly.
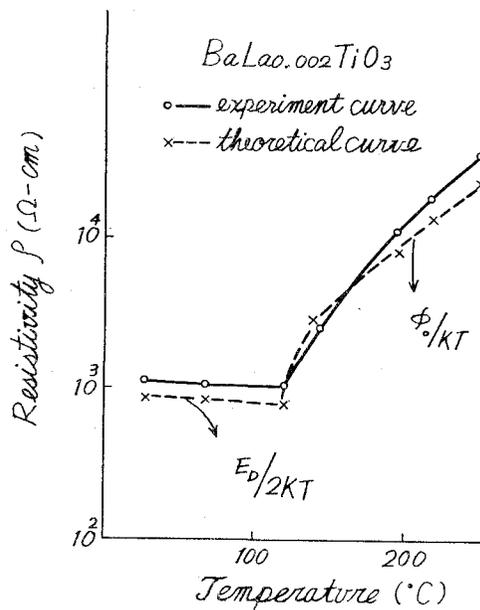

Fig. 5. Experiment and theoretical curve on the
resistivity of $BaLa_{0.002}TiO_3$

5. Conclusion

In spite of the faithful depiction of all the physical details obtained with the aid of the model of barrier layer at the crystal boundaries, it should be emphasized that the surface states have been introduced only phenomenologically and that very little knowledge exists as to their nature. Only the density and activation energy of the surface states are known. Theoretically, such states are conceivable in the inner surfaces of single crystal, it has not as yet been possible to confirm any resistivity anomaly by investigations on singlecrystal specimens. This seems to justify the assumption that the chemical conditions at the grain surfaces may have an important bearing on the surface states. This aussumption is also surported by the follwoing facts:

(1)   The resistivity anormaly can be decreased progresively by treating the specimen in a slightly reductive atmosphere.

(2)   Specimens that have interfaces with a very high La_2O_3 content (more than 0.4 mol%) exhibit a resistivity anormaly of quite another charactor with an increase of these : this may be explained by a charge in the surface states[11]

This two features are mentioned only to show that many qestions concerning the nature and mechanism of surface states are still unanswered and that their solution should be quantatitively solved.

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