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# POSITIVE TEMPERATURE COEFFICIENT RESISTANCE (PTCR) EFFECT OF BARIUM TITANATE BASED CERAMICS

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## ABSTRACT

Since the discovery of positive temperature coefficient resistance (PTCR) effect in donor doped barium titanate ceramics, there have been many investigations with the aim of developing new compositions having better PTCR properties. This paper presents the PTCR characteristics of the donor doped $BaTiO_3$ ceramic with different amounts of Mn concentrations and the nature of the current transport process. Y-doped barium titanate specimens having different Mn additions were prepared and the structural characterisation of the samples was studied using an X-Ray Diffractometer (XRD). The two-probe dc measurement technique was employed for electrical characterisation. In these samples PTCR regions were observed in the temperature range of 110°C to 230°C. In these PTCR regions, resistivity value of the samples was increased dramatically from $10^3$ Ω cm at 110°C to $10^9$ Ω cm at 240°C with a gradient of $10^4$ Ωcm°C$^{-1}$. Addition of Mn significantly enhanced the PTCR effect of the Y-doped $BaTiO_3$ ceramics. However, a large amount (more than 0.100 mol %) of Mn-addition increased the room temperature resistivity. This is probably due to the formation of non-conducting second phases at grain boundaries obstructing the conduction channels between the grains. The characteristics of current-voltage behaviour follows the modified classical model for donor doped $BaTiO_3$ ceramics.

## 1. INTRODUCTION

Barium titanate based ceramics are attractive materials because of their dielectric, semiconducting, ferroelectric and piezoelectric properties. These ceramics have a wide range of applications[1-5] such as electro-optic devices, multilayer capacitors, sound detectors, transducers and infra-red detectors. Furthermore, the donor doped barium titanate ($BaTiO_3$) ceramics show a Positive Temperature Coefficient Resistance (PTCR) effect, which is the change of dc resistivity by many orders of magnitude with temperature. As such, the donor doped based ceramics have many applications such as TV degausses, self-regulated heaters, thermal sensors, and current surge protectors[5-7].

Since the discovery of PTCR effect in donor doped barium titanate ceramics, there have been many investigations with the aim of developing new compositions having better PTCR properties and easy processing conditions. For practical applications of PTCR devices, some important factors such as magnitude of resistivity jump, room temperature resistivity, current -time dependence and breakdown voltage must meet the requirements for device designing[8]. The aim of this work is to improve the PTCR characteristics of Y-doped $BaTiO_3$ ceramics by adding Mn and also to understand the nature of the current transport process in these ceramics.

## 2. EXPERIMENTAL

Specimens with composition $(Ba_{0.997}Y_{0.003})TiO_3$ were prepared from $BaCO_3$ (99.9% purity; Hopkin & Williams Ltd.) $TiO_2$ (99.9 % purity; BDH chemicals Ltd.) and $Y_2O_3$ (99.99 % purity; Ventron Prooukte). Starting powders were ball milled for 20 hours with ethyl alcohol in a plastic bottle using $Al_2O_3$ balls (65 % of total weight) as a grinding media and then sieved (64 μm) and dried. In this study dry milling was also carried out but the X-ray analysis showed that the dry milling was not a satisfactory method in obtaining $BaTiO_3$. The mixed powder was calcined at $1150^0$C for 2 hours in an $Al_2O_3$ crucible using a box furnace. The calcined powder was then milled again for 30 hours, after addition of different amounts of Mn (0.025 to 0.125 mol %) and 4 mol % of $BaB_2O_4$. Afterwards, the mixed powder was moulded into pellets having thickness of 1 to 2 mm and diameter of 12 mm under a pressure of 80 to 100 MPa by using a hydraulic press. These green pellets were then placed on an $Al_2O_3$ plate and sintered at $1350^0$ C for 1 hour in air.

The structural characterisation of the samples was carried out using an X-ray Diffractrometer (XRD) with Cu-$K_\alpha$ radiation. The XRD measurements were carried out for powder samples as well as for sintered pellets. The two-probe dc measurement technique was employed for electrical characterization. To obtain an ohmic contact, different types of electrode materials such as graphite, silver, In/Ga and gold were applied on the sample and heat-treated before the electrical measurements. To make In/Ga paste, 24 wt. % of Indium (melting point $156.61^0$C) and 76 wt. % of Gallium (melting point $29.78^0$C) were mixed to form a liquid at room temperature. Once the electroding was completed, the pellet was sandwiched between two electrodes for the electrical measurements. The sample was kept in a furnace and the temperature of the sample was varied from room temperature to about $300^0$C. The electric field applied across the samples was maintained at a constant value (1 V/mm) during the experiment using a regulated DC power supply. The voltage across the sample and the respective current through the sample were measured using digital meters. Before taking each reading, the temperature was maintained at a constant value for several minutes to ensure that the sample was heated homogeneously. The resistance of the sample at different temperatures was calculated. The above procedure was repeated for five samples. Finally, the current-voltage measurements were made in order to investigate the nature of the current transport processes in donor doped barium titanate ceramics.

## 3. RESULTS AND DISCUSSION

### *3.1 XRD results*

The X-ray diffraction patterns of $BaTiO_3$ ceramic samples prepared by the dry milling route revealed the presence of $Ba_2TiO_4$, $BaTi_2O_7$ and unreacted $BaCO_3$ and $TiO_2$ [Fig.1(a)]. $Ba_2TiO_4$ is hydroscopic and therefore decomposes with swelling in moist air. As a result cracking or crazing of the ceramics was observed. Unreacted $BaCO_3$ and $TiO_2$ might be due to incomplete inter-diffusion of cations because of their large diffusion lengths. A schematic representation of reacting species in the dry milling route is shown in Fig.2. This incomplete inter-diffusion can be overcome by extensive milling. However, impurities such as alumina and silica can be introduced during the extensive milling process.

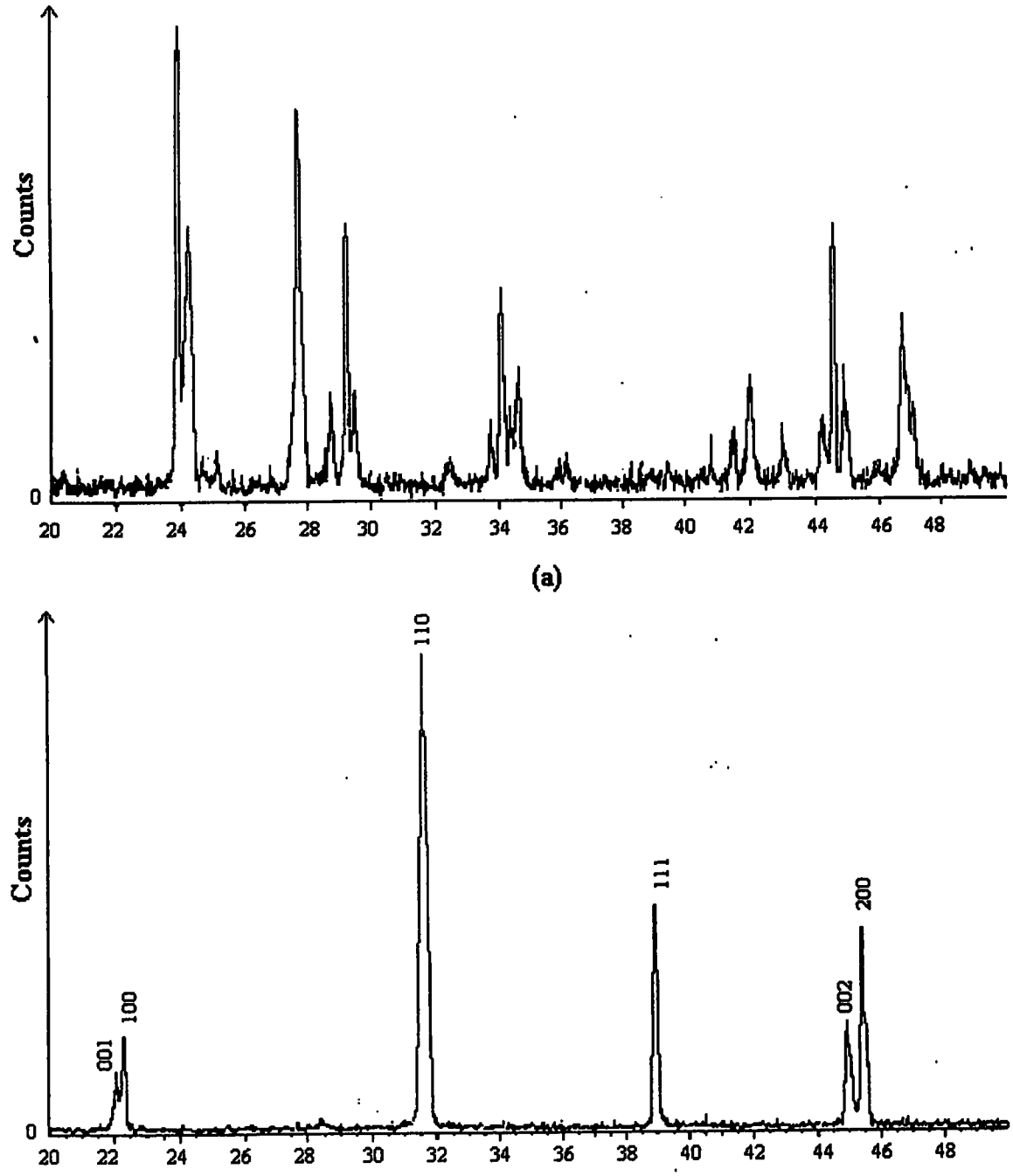


Fig. 1 Comparison of X - ray diffraction patterns of $BaTiO_3$ ceramics samples prepared by (a) the dry milling (b) the wet milling routes

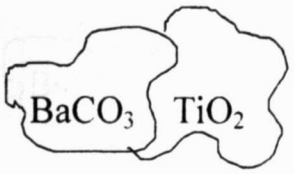


Fig. 2 A schematic representation of reacting species in dry milling route

The XRD patterns of $BaTiO_3$ ceramic samples prepared by the wet milling showed that there were no detectable unreacted impurities in the sample [Fig. 1(b)]. This is due to complete inter-diffusion by wet milling. A schematic representation of reacting species in the wet milling route is shown in Fig. 3. The structure of barium titanate was identified as perovskite $BaTiO_3$ [(Fig. 1(b)].

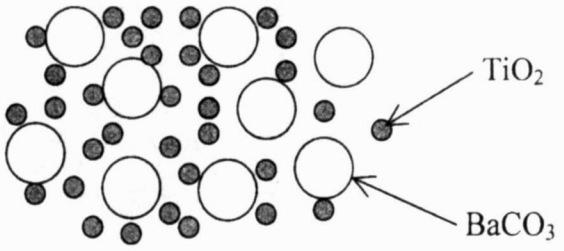


Fig. 3 A schematic representation of reacting species in the wet milling route

*3.2 Variation of Resistivity with Temperature*

Fig. 4 shows the resistivity-temperature characteristics of Y-doped barium titanate ceramics with low Mn concentrations (0.025 - 0.125 mol %). In general, PTCR regions were observed in the temperature range of 110 to 230 $^0$ C for these samples. The resistivities of samples were changed dramatically from $10^3$ Ω cm at $110^0$ C to $10^9$ Ωcm at $240^0$C. Since these materials are polycrystalline, a large number of acceptors can be present at the grain boundaries. This can create a potential barrier of height[9], $\phi = en_a/8\varepsilon N_d$, where e is the electronic charge, $N_d$ is the donor concentration per unit volume, ε is the dielectric constant of $BaTiO_3$ and $n_a$ is the number of ionised acceptor atoms. The temperature dependence of ε is given by Curie-Weiss law, above the ferroelectric transition temperature $T_c$, as $\varepsilon = C/(T-T_c)$. According to Heywang's model[9] (Fig. 5) the ionized acceptor density of states ($n_a$) at the grain boundaries can be written as $n_a = N_a\{1+\exp(\Delta E_a/kT)\}^{-1}$. Here $N_a$ is the total density of states of acceptors at the grain boundary and $\Delta E_a$ is the enrgy difference between Fermi level and the acceptor level (Fig. 5). Heywang[9] considered the grain boundaries as an n-type Schottky barrier with the acceptors sitting at the boundaries. Therefore, according to Heywang's model[9], the polycrystalline PTCR materials have a large number of acceptor states at the grain boundaries together with nearby ionized donor states giving rise to an electrical double layer, as shown in Fig. 5. As a consequence, conduction band electrons, moving up to a grain boundary from the interior of a grain, form a potential barrier.

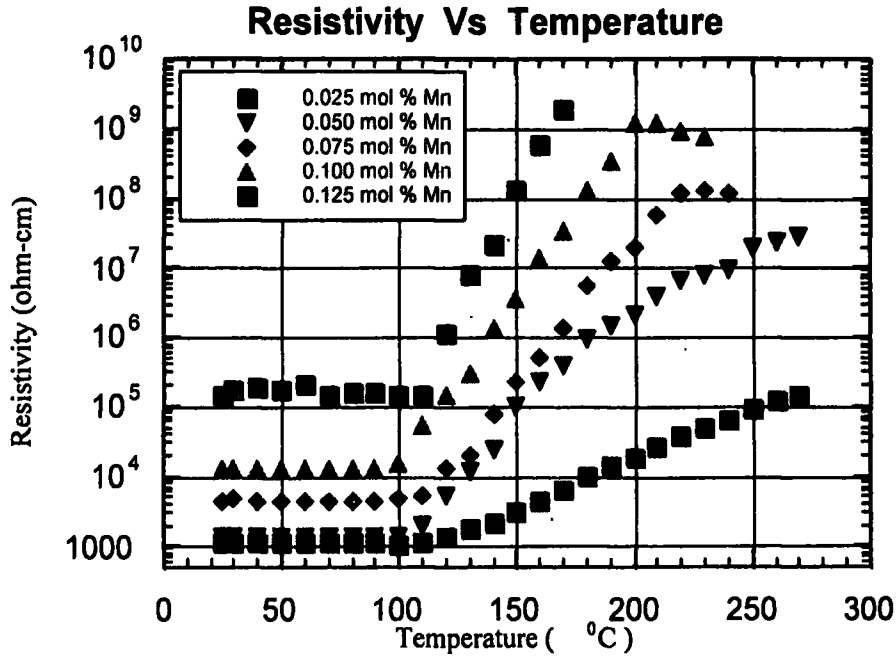


Fig. 4 Variation of resistivity with temperature of Y-doped $BaTiO_3$ ceramics having different Mn concentrations

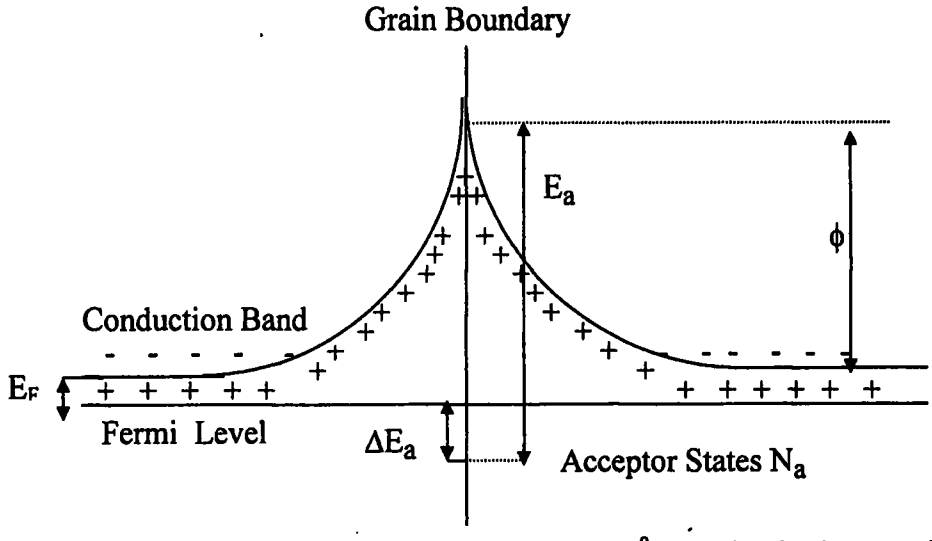


Fig. 5 A schematic energy diagram of Heywang's barrier model[9] for PTCR $BaTiO_3$ ceramics

It was observed that the PTCR jump becomes steeper (Fig. 4) with the increase of Mn content. This is likely to be due to an increase in acceptor type density of states at the grain boundaries. Presence of some of second phases and defects in grain boundaries might play a role of acceptors leading to enhance the PTCR effect. Large amounts (more than 0.100 mol %) of Mn addition, enhanced the PTCR slope. However, large additions of Mn increased the room temperature resistivity by about two orders of magnitude (Fig. 6). This is probably due to the formation of non-conducting second phases at grain boundaries obstructing the conduction channels between the grains and thereby increasing the resistivity of the specimen at room temperature. A similar observation has been reported by J. Lee and co-workers for B-added Y-doped $BaTiO_3$ ceramics[8].

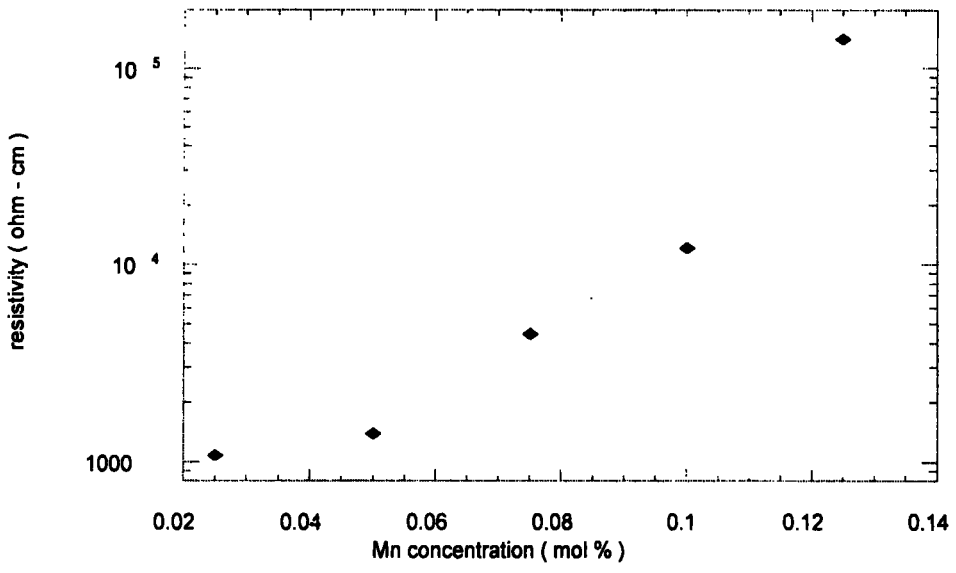


Fig. 6 Variation of room temperature resistivity of Y-doped $BaTiO_3$ ceramics with the concentration of Mn

*3.3 Ohmic Contact Behaviour*

For a good ohmic contact, the interfacial resistance and the resistance between the electrodes must be minimized as much as possible. The resistance between the electrodes can be minimized by choosing a suitable electrode material. When graphite paste was applied on the sample, the resistivity was in the order of $10^6$ Ωcm at room temperature. The high resistivity is due to lack of intimate bonding with the ceramic surface. When the air-drying silver paint was applied on the sample the resistivity value was reduced by about $10^5$ Ωcm. Therefore, the air-drying silver paste is useful for temporary electrodes. However, by applying In/Ga paste on the sample the resistivity value was reduced significantly ($10^3$ Ωcm). This may be due to the diffusion of atoms of the electrode material to form a continuous conductive layer on the surface of the ceramic. However, it was observed that the adhesion of electrode material on the surface of the sample was not satisfactory. This difficulty was overcome by roughening the surface using SiC paper. Finally, gold paste was applied, and it was observed that it enhances the ohmic contact similar to that of InGa electroding material. The gold electrode made a good contact to the surface of the sample. This is due to the formation of continuous conductive layer intimately bonded to the ceramic surface by sintering.

*3.4 Nature of the Current Transport Process in PTCR Ceramics*

The current-voltage measurements have been made on donor doped $BaTiO_3$ ceramics in order to investigate the nature of the current transport processes. As discussed earlier according to Heywang model[9], the potential barrier was assumed to be a Schottky barrier as shown in Fig. 7. When the external potential is applied, the barrier height reduces and the current is due to thermionic emission.

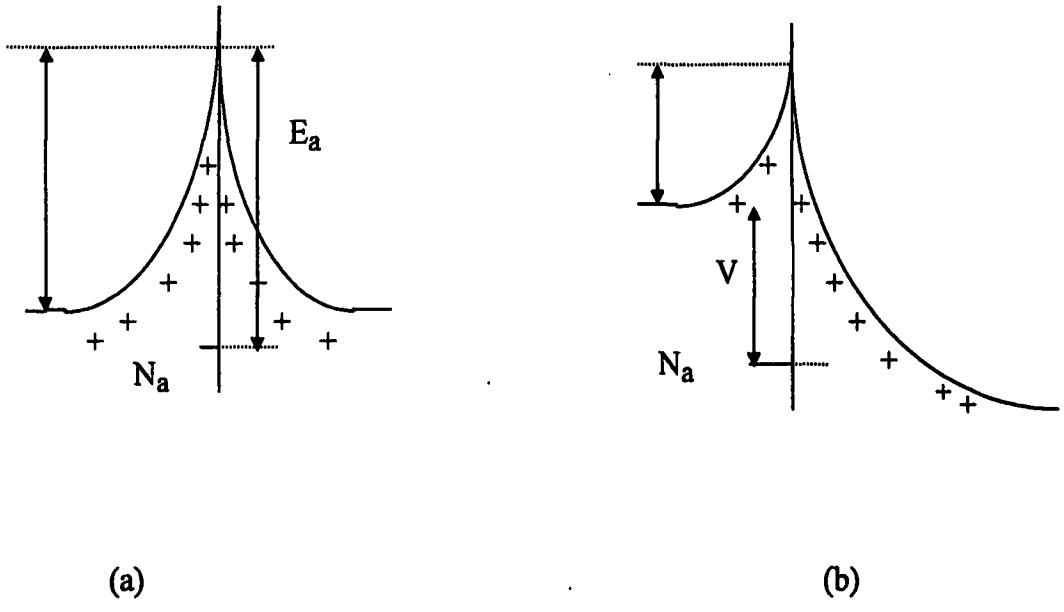


Fig. 7 Heywang's barrier model in PTCR $BaTiO_3$ ceramics;
(a) without an external voltage and (b) with an external voltage, V

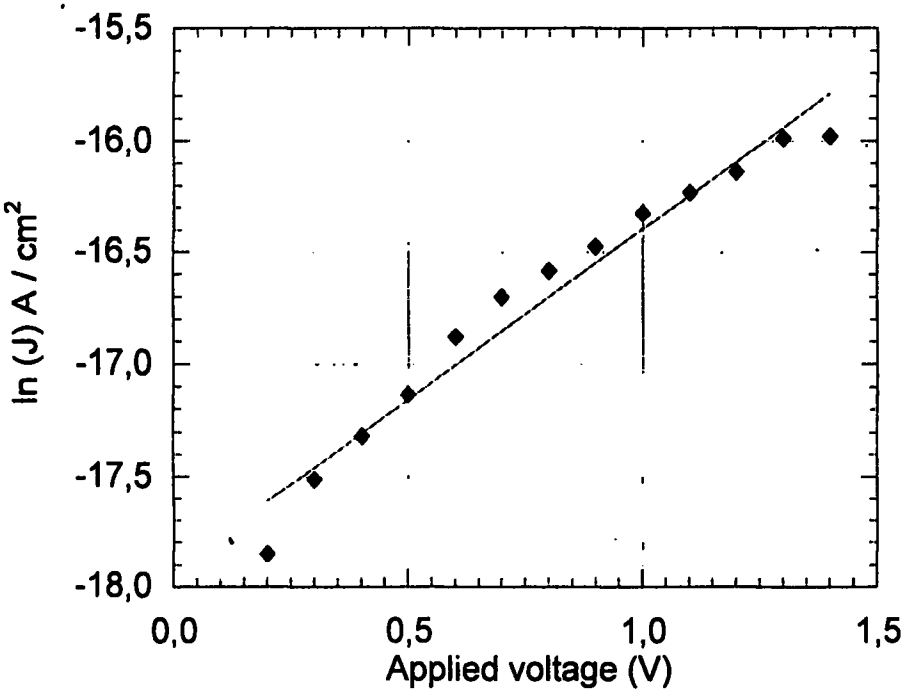


Fig. 8 ln (J) vs V for a Y-doped $BaTiO_3$ sample having 0.1 mol % Mn. This composition showed the best PTCR effect

According to Heywang model[9], the relationship between the current density J, and the applied voltage V, is approximately given by, ln (J) $\propto$ V. Fig. 8 shows the characteristic of the current-voltage curve, plotted according to Heywang model for the sample( 0.1 mol % Mn addition) which showed the best PTCR effect. It can be seen that there is no complete point to point agreement between the experimental data and the mathematical relationship. The non-linear behaviour of the current density with voltage may be due to the attractive force exerted by the acceptors at the grain boundaries on the positive charge at the space charge region.

This attractive force is called the image force and the work done by the image force is called the image potential. The image potential greatly influences the shape of the Schottky potential barrier. Instead of a sharp potential barrier such as a Scottky potential barrier, Zhang and Cao[10] considered the potential barrier due the image force to be a smoothly changing potential. The corresponding energy diagram is shown in Fig. 9.

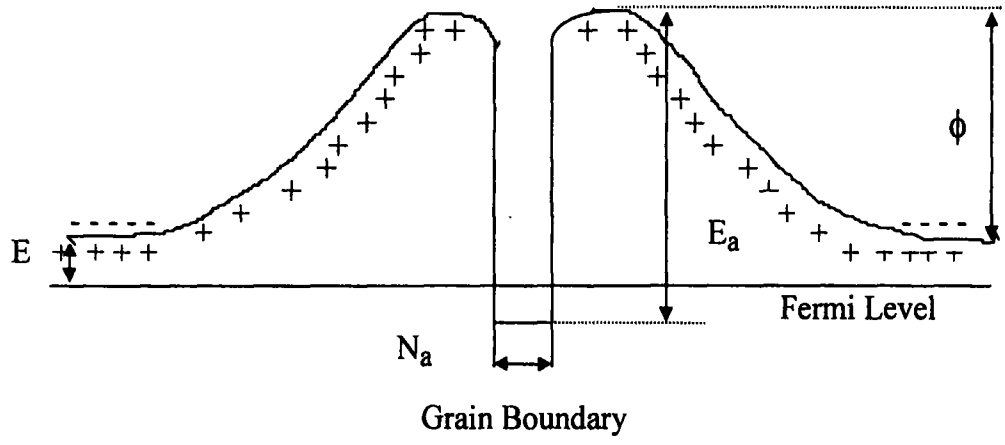


Fig. 9 A schematic energy diagram of modified Heywang's barrier model for PTCR $BaTiO_3$ ceramics

When a voltage is applied on the double Schottky barrier as shown in Fig. 10 the barrier height $\phi_1$ is reduced and $\phi_2$ is increased. The result is easy migration of carriers from $\phi_1$ to $\phi_2$, rather than $\phi_2$ to $\phi_1$ . This gives rise to a non-linear variation of the current density, with the applied voltage. Zhang and Cao[10] further showed that, the variation of the current density with the applied voltage is given by, $\ln (J) \propto V^{1/2}$. It is evident from Fig. 11, that the prepared Mn containing Y-doped $BaTiO_3$ ceramic, closely obeys this modified Heywang model suggested by Zhang and Cao[10].

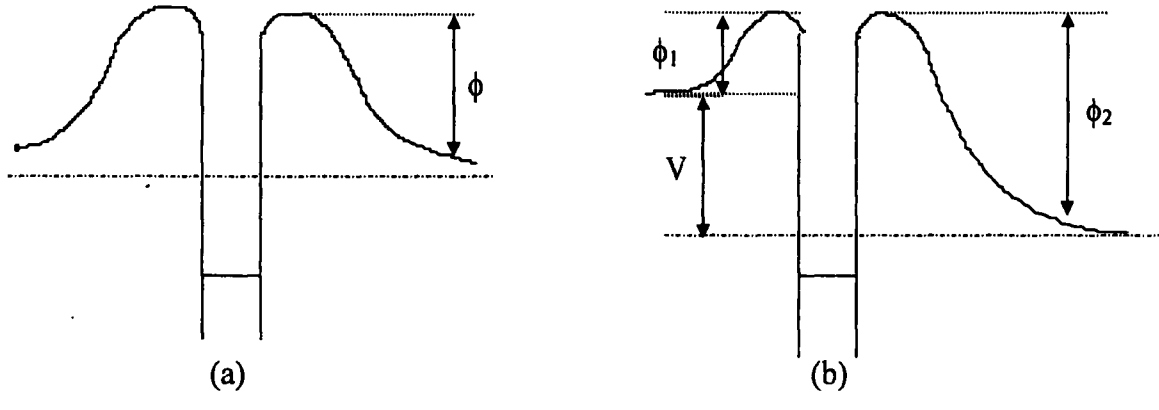


Fig. 10 Modified Heywang model in Y - doped $BaTiO_3$ ceramics ; (a) without an external voltage (b) with an external voltage

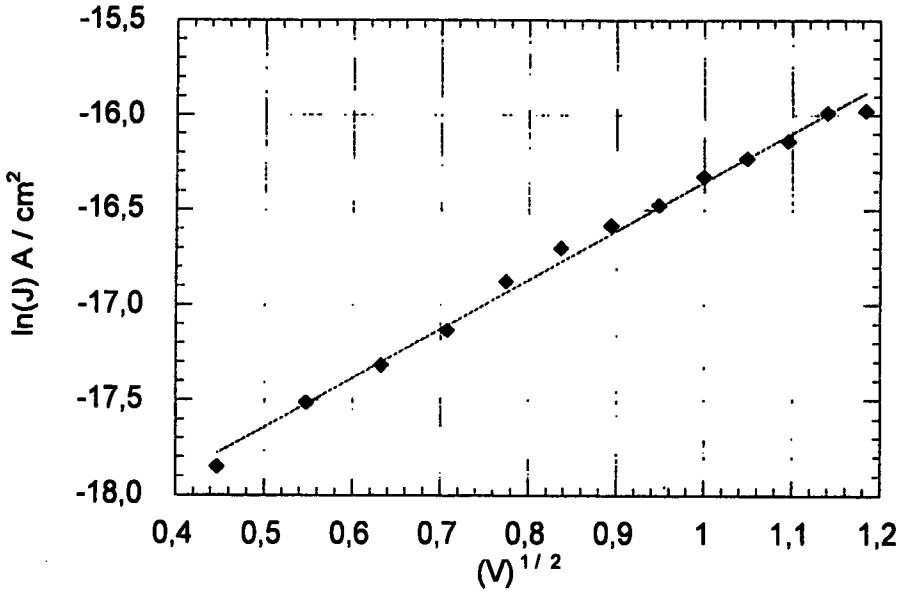


Fig. 11 ln ( J ) vs $V^{1/2}$, for a Y- doped $BaTiO_3$ sample having 0.1 mol % Mn. This composition showed the best PTCR effect

## 4. CONCLUSION

This study reveals that a small addition of Mn significantly enhances the PTCR effect of Y-doped $BaTiO_3$ ceramics. However, addition of large amounts (more than 0.100 mol %) of Mn gives rise to a significant increase of the room temperature resistivity. Formation of non-conducting second phases at grain boundaries obstructing the conducting channels between the grains could be responsible for this behaviour. Furthermore, this study shows that the characteristics of current-voltage do not follow the Heywang model. However, a modified Heywang model proposed by Zhang and Cao gives a better agreement with the experimental observations. This study also reveals that the In-Ga and Gold pastes are good electroding materials for these ceramics.

## ACKNOWLEDGMENTS

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