



# PTCR Effect in BaTiO<sub>3</sub>: Structural Aspects and Grain Boundary Potentials

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**Abstract.** Extensive microstructural and structure-property studies on donor doped barium titanate have revealed that the PTCR phenomenon is strongly controlled by the density, number of grain boundaries available to conduction, domain orientation and grain boundary domain coherence. Structural heterogeneities lead to a wide range of grain boundary structures, potential barriers and, therefore, depletion widths. Conduction thus occurs primarily by percolation of electrons through favorably aligned domain pathways and low potential barrier grain boundaries. At the Curie point, the increase in the potential barriers along these pathways is likely to dominate the PTCR effect. To improve theoretical understanding a model needs to take heed of *local* values of parameters and also incorporate the fact that the bulk of the current flow is only through a certain percentage of grain boundaries. The specific structural factors that have led to an improved qualitative understanding of overall PTCR phenomenon are discussed.

**Keywords:** barium titanate, PTCR, grain boundary, semiconduction, domains

## 1. Introduction

The positive temperature coefficient of resistance (PTCR) behavior that is found in modified barium titanate is well known and is used in many industrial sensing, current protection and temperature control applications. In addition to the PTCR effect, barium titanate based materials also display pyroelectricity, piezoelectricity, ferroelectricity and polaron semiconduction among other useful properties, and as such barium titanate has been an extremely important system for the purposes of fundamental electroceramics research. The presence of these wide range of effects and their interdependence often makes this material difficult to analyze and less amenable to property control. Early investigation [1] showed that the PTCR effect occurs only in polycrystalline samples, and therefore, must be intimately linked with the properties of the grain boundaries. Thereafter, numerous investigators have researched the basic phenomena along with the chemistry, processing conditions and electrical properties of this material, resulting in several theories, the most important of which are attributed to Heywang [2], Jonker [3], Daniels and Wernicke [4], and Kulwicki and Purdes [5].

The PTCR effect is said to arise from the presence of a potential barrier at the grain boundaries; the barrier arising from the trapping of electrons (from ionized donors) by acceptor species at the grain boundary [2]. The barrier makes the grain boundary more resistive than the grain interior. Heywang [2] attributed the resistivity jump near the Curie point ( $T_c$ ) to the change in the grain boundary dielectric constant from  $\sim 10^4$  below  $T_c$  to  $\sim 10^2$  above  $T_c$ . Further analysis by Jonker [3] took into account the ferroelectric nature of barium titanate and explained that the spontaneous polarization ( $P_s$ ) below  $T_c$  can effectively cancel out the barrier potential in regions along the grain boundary, resulting in the low resistivities observed below  $T_c$ . These explanations have provided a starting point for analysis and modeling of PTCR behavior, but they do not accurately explain many aspects of the phenomena, primarily because of the simplicity of the formulation and the assumptions that are made to facilitate it. For instance, Daniels and Wernicke [4] showed that the assumption of a box shaped concentration profile of acceptor states on either side of the grain boundary is not accurate, since non-equilibrium conditions during high temperature treatments imply the existence of

diffusion *gradients*, rather than the sharp transition implied by this assumption. Another assumption was that the dielectric constant of the grain boundary was identical to that of the grain interiors. However, due to high electric fields in the grain boundary core, the actual grain boundary dielectric constants are estimated to be orders of magnitude lower than the bulk values [5].

Other very important factors that are generally left out of interpretations of the conduction process between grains are the lattice and domain structural relationships between and internally within each grain, generating internal stresses and defects that likewise modify and create potential barriers [6–12]. In this complex material, which is also very sensitive to manipulations in processing and chemistry, it is essential that a general understanding of the effects of different processing parameters be taken into account in the model. In order for explanations of a fundamental nature to be valid, a model must also be able to predict and account for observed microstructural features. Many studies have not paid strong attention to microstructural features, and typically only take into account the grain size of the material. Investigations of these aspects, though, have shown the vital significance of structural aspects on the PTCR effect. This paper is an attempt to bring to fore the full structural complexity of donor doped barium titanate, the processing conditions which induce it, and the properties which stem from it. An overall picture of the most relevant structural features and structure-property relationships are presented. These studies reveal that many different type heterogeneities and structural disruptions exist, resulting in a wide variety of grain boundary structures, which must correspond to a wide range of barrier potentials. In this context, the effect of grain boundary stress on barrier potentials, first suggested by Kulwicki and Purdes [5], takes on a renewed significance. Microstructural aspects, combined with previous theories, thus provide a more mature and more complete understanding of the overall phenomena. These aspects are discussed in detail.

## 2. Discussion

### 2.1. *Effect of Sintering, Grain Growth and Annealing*

Sintering causes coalescence of neighboring grains, increasing density and overall grain size. A donor dopant,

which is present as a uniformly precipitated second phase on the particles of a green body, is incorporated in the interior of the new larger grains, where it is distributed uniformly to minimize the free energy of the lattice. A large majority of PTCR barium titanate sintering is performed in the presence of a liquid phase, the amount of which can be modulated to produce a wide range of microstructures and properties. The liquid phase is deliberately created to increase sinterability by either/both of two methods: (1) changing the stoichiometry of the barium titanate batch, where greater Ti-excess produces greater amount of liquid phase, and; (2) by the addition of eutectic-lowering sintering aids like  $\text{TiO}_2$  and  $\text{SiO}_2$ . In the case of small changes to the stoichiometry of the batch ( $\text{Ba/Ti} \sim 0.998$  to  $1.004$ ), the liquid phase is most likely crystallized, since no evidence of a separate phase has been found in TEM observations [7]. However, if considerable change is made to the chemistry of the batch, especially if foreign ions like Si are added, a distinct second phase is precipitated at the grain boundaries. This second phase is non-ferroelectric and electrically insulating, thus effectively blocking off conduction through portions of the grain boundaries. Therefore, a distinction must be made when these two separate types of PTCR materials (single phase and two phase) are analyzed and compared. In the latter case, the effective conducting cross-section of the sample is reduced (the extent depends upon the amount of second phase), even though the grain size and density may be similar to materials not displaying a second phase.

The barium titanate system shows a very high sensitivity to even minute changes in chemistry. Small changes in stoichiometry and dopant concentrations can significantly change the microstructure from uniform grain sized to bi/multi-modal. Similar sensitivity is displayed with respect to sintering atmospheres, temperatures and time. The specific processes taking place during sintering are extremely complicated and most likely involve the formation of complex surface-states. The resultant microstructure can also be connected to minor variations in the amount, distribution and wetting behavior of the liquid phase, especially in the first few minutes of sintering. Experimental evidence shows that the donor dopant influences sintering mechanisms strongly, since donor doped materials show quite different microstructures compared to undoped materials prepared from the same powder batch [12]. This is further suggestive of the role played by complex surface conditions in influencing the quantity,

wettability and kinetics of generation of the liquid phase.

The density of the sintered compact is a very important measure of the magnitude of the PTCR effect. In experiment, densities varying between ~87% to >97% of theoretical are observed. Lower density is evidence that either: 1. Grain growth processes have dominated and prevented sintering from reaching a greater degree of completion; or, 2. Very little grain growth or sintering has occurred. From an electrical property point of view, for single phase materials, lower densities imply lesser amounts of grain to grain contact areas and less coherency between grains. The density is thus a measure of the number of grain-grain junctions available for conduction in single-phase materials. In the case of two phase materials, the number of conducting-grain to conducting-grain junctions can be greatly decreased by the presence of the insulating grain boundary phase, despite the fact that the material may show a high density overall. For the purpose of electrical conduction, therefore, two phase materials behave as single phase barium titanate with porosity.

The most significant implication of the above observations is that, whether the material is single phase or two phase, current can only flow through the *available* conducting-grain to conducting-grain contacts, a parameter whose magnitude depends strongly on sintering conditions, dopant chemistries and powder surface characteristics. (As will be discussed later, the actual situation is made more complicated by lattice mismatch strains and domain orientations, which result in some grain-grain junctions being less conducive to conduction than others.) It must be noted then that at  $T_c$  only the grain boundary barrier potentials along these active pathways need to increase for a resultant large increase in bulk resistivity. Experimental facts which point towards the importance of density (measure of number of current pathways in single phase material) on PTCR properties are: 1. *Low* room temperature resistivity ( $\rho_{RT}$ ) and a *nominal* PTCR effect ( $\sim 10^1$ ) has been observed from *small to moderate* grain size (3–8  $\mu\text{m}$ ) samples which had *high density* (>97%) [12]; 2. Kuwabara [13] has shown that extremely *high* PTCR effect materials can be fabricated from very *low* density compacts which also have *small* grain sizes (very little sintering and grain growth). The PTCR effect was found to maximize at an optimum density and decreased as density was increased further for his small grain size ( $\sim 1 \mu\text{m}$ ) samples.

Many studies have related the *grain size* to particular electrical properties. However, it is evident from the above that the number of conducting-grain to conducting-grain contacts is the most important parameter. Evidence suggests that, in general, *lower the number of conducting-grain to conducting-grain contacts, stronger the PTCR resistivity jump at  $T_c$* . Since the grain size and density of a sintered ceramic are interrelated, both parameters can serve as measures of the number of conducting-grain to conducting-grain contacts. However, density is a better measure in the case of single phase materials. Further, it is difficult to specify the combination of 'ideal' densities and grain sizes, again because these two parameters cannot for the most part be controlled independently, and data is not available from a wide enough range of density and grain size combinations.

Many PTCR materials are also subjected to a second heat treatment in the 1150–1250°C range for ~2–10 hrs after firing. The motivation is to enable defect segregation to the high-energy grain boundaries. Such a treatment increases the magnitude of the resistivity jump and also increases  $\rho_{RT}$ . As will be discussed in detail subsequently, the domain microstructure developed in these materials in the near grain boundary regions is distinctly more complex compared to non-annealed materials and the shape of the resistivity-temperature curve shows an initial sharp rise in the resistivity followed by a more gradual increase above  $T_c$  [6]. A permanent second resistivity transition, in the form of a 0.5–2.5 orders of magnitude decrease in  $\rho_{RT}$ , has also been discovered in the 450–650°C range [10, 11]. This is discussed in detail in Section 3.3.

## 2.2. Domain Evolution

Events occurring during high temperature treatments and during the process of cooling the sample to the paraelectric-ferroelectric transition have a profound effect on the domain structure evolved. Contrary to the case of dielectric barium titanate, optimally doped (minimum  $\rho_{RT}$ ) PTCR barium titanate materials ( $\sim 0.1$ – $0.25 \text{ mol\% } Y^{3+}$ ;  $\sim 0.1$ – $0.15 \text{ mol\% } La^{3+}$  or  $Nd^{3+}$ ) are characterized by *unidirectional domains* spanning the expanse of the entire grain, i.e., there is a texture to the domain structure within each grain [6]. This structural dependence on donor concentration, for undoped, optimally-doped and over-doped barium titanate, is shown in Fig. 1. The axis of texturing appears

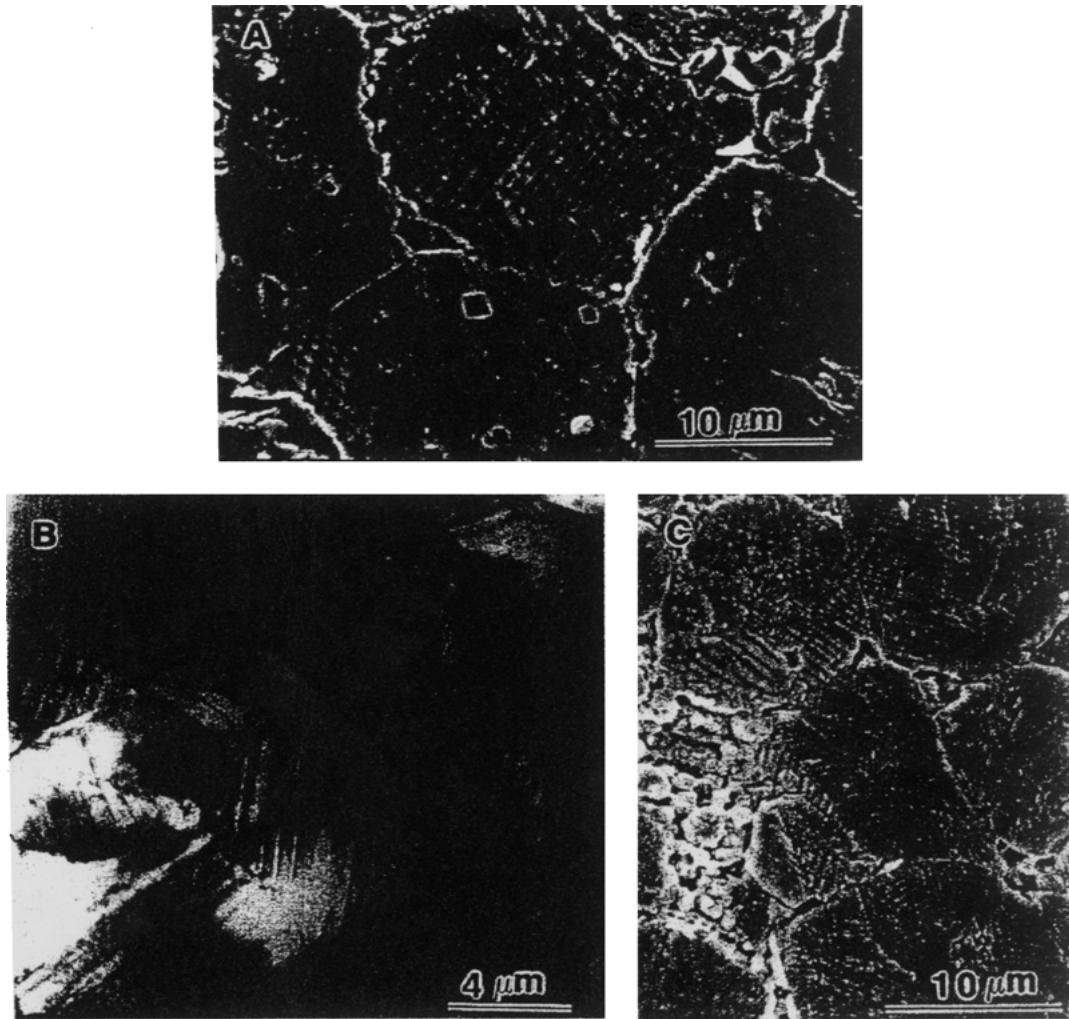


Fig. 1. (a) SEM micrograph of un-doped barium titanate showing random domain structure; (b) TEM micrograph of grains in optimally donor doped BaTiO<sub>3</sub> showing uniaxially aligned domains; and (c) SEM micrograph of over-doped barium titanate, also showing random domain structure.

to be random from grain to grain. Typical domain widths are  $0.1 \mu\text{m}$  to  $\sim 0.8 \mu\text{m}$ , the larger values seen in the case of donors creating less lattice strain (e.g., La<sup>3+</sup>). This type of domain structure, being unidirectional, shows a total lack of *a-c* type domain walls, and is somewhat reminiscent of very fine grain barium titanate (grain size  $\leq 1 \mu\text{m}$ ), where large internal stresses are believed to favor such a domain state. The texturing in donor doped barium titanate is however independent of grain size, being present in these type materials ranging in grain size from 3 to  $>50 \mu\text{m}$ . Figure 2 shows unidirectional domains in a smaller grain material and can be compared with Fig. 1(b). The texturing is seen

in the case of all types of donor dopants, despite the fact that their ionic radii vary [14]. It must be reiterated that only an *optimal* amount of donor produces this kind of microstructure; in the dielectric, under-doped and over-doped cases the domain orientations are, except for occasional isolated grains, quite random with several domain sets with different orientations and widths being visible (see Fig. 1(a) and (c)). In the optimally doped case in contrast, domain randomness is only observed in the near grain boundary regions of annealed samples [6, 7, 15] (this will be discussed in more detail later).

The above observations suggest that this type structure is due to the presence of an optimum concentration

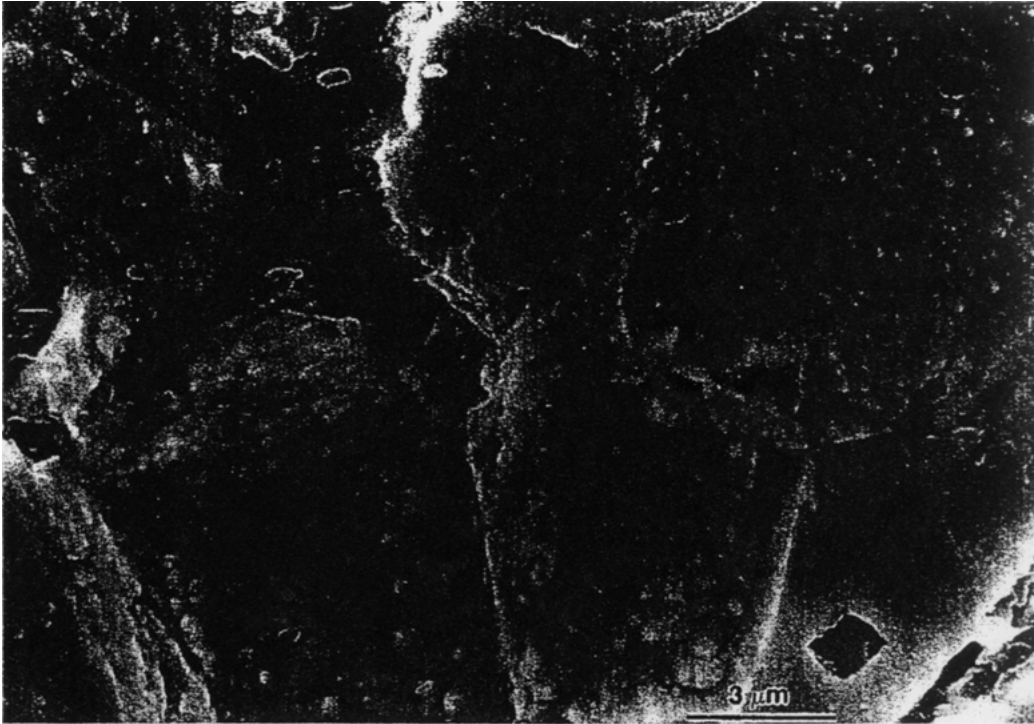


Fig. 2. SEM micrograph of etched sample of optimally doped, medium grained barium titanate, showing uniaxial domains. The domains seen here are 'c' domains (coming out of the plane of paper), compared to the 'a' domains seen in Fig. 1 (in the plane of paper). 'c' and 'a' domains are equivalent; differing only in viewing direction. This type uniaxial domain structure is seen in grain sizes varying between 3–50  $\mu\text{m}$ .

of the donor dopant. Therefore, the origin of this structural texturing must lie in the specific type of defects present (dopant defects and electronic compensating defects) and long range interactions between defect centers. This is a phenomenon where point defects are seen to strongly influence the martensitic type phase transformation and the resulting mesoscale structure. Such interactions are presently the subject of considerable research, and have recently been reviewed by Ren and Otsuka [16]. Such an observation in *n*-doped barium titanate thus raises many questions about domain nucleation and growth. Some of the important ones are: What is the mechanism by which this happens? Why does it happen only for donor (aliovalent) dopants? Why is this phenomenon relatively independent of the ionic radius of the donor? In the next few paragraphs, we present a tentative, qualitative, physical explanation:

In the case of a substitutional point defect created by an isovalent dopant such as Ca<sup>2+</sup> or Zr<sup>4+</sup>, the lattice strain field of the defect is spherically symmetric, and there is no compensating defect since charge

neutrality is maintained. In contrast, in the case of a donor dopant compensated by reduction of Ti<sup>4+</sup> to Ti<sup>3+</sup> (polaron compensation mechanism active in the optimum range [17–19]), the spherically symmetric strain field of the donor point defect is disrupted by the presence of the compensating defect: an extra electron on a neighboring titanium site (perovskite B-site). This extra electron on a neighboring Ti site generates a Jahn-Teller (ligand field) distortion [20], which disrupts the strain field of the donor atom in the neighboring unit cell, forming a spherically *asymmetric* defect-complex strain field. This type distortion field can be oriented in several spatially equivalent directions. Further, it is known that the Jahn-Teller distortion due to the compensating defect results in a finite tetragonality and *P<sub>s</sub>*, locally, *even in the paraelectric cubic phase* [20]. This type defect complex can, therefore, act as nucleation sites for the ferroelectric phase upon cooling through the Curie point [21].

A measure of the influence field of a defect is termed the *correlation radius* ( $r_c$ ) [21]. This parameter is temperature dependent, increasing as temperature

is lowered [21]. For a spherically asymmetric defect-complex field, a single parameter ( $r_c$ ) is not sufficient to describe the geometry of the defect field completely. Nevertheless, this concept can be utilized to explain the domain texturing. During the process of sintering of optimally donor doped barium titanate, donor atoms homogenize in the lattice in such a manner as to minimize the overlap of the strain and electric fields of each donor, i.e., to a first approximation it can be assumed that donor sites are separated by a minimum distance of  $2r_c$ . As the material is cooled from the sintering temperature,  $r_c$  increases, increasing the internal stress in the lattice. At temperatures still high enough for defect diffusion, donor atoms can easily redistribute to minimize this increasing internal stress. However, as the temperature is further lowered to values where defect diffusion is no longer enabled, donors cannot redistribute by diffusion and the internal stress starts increasing, becoming so large eventually as to cause *spontaneous alignment* of the spherically asymmetric defect fields to a lower stress state, in one or more spatially equivalent directions, since, as also described by Weertman and Weertman [22], uniformly distributed defects can alter the bulk stress of the system. Since donor diffusion is expected to cease at temperatures above  $125^\circ\text{C}$  ( $T_c$ ), the temperature range in which this alignment occurs is higher than the Curie point. When such a material is further cooled through the Curie point, these defect sites nucleate domains, and since the direction of the  $P_s$  in the nuclei are spatially aligned, the resulting domain structure also becomes spatially aligned.

In this type material the internal stress field of the donor dopant is the primary force dominating domain nucleation and growth over large distances, indeed over the entire grain. At places where other stresses and fields are stronger, for example, in the near-grain boundary regions in annealed samples where acceptor segregation occurs, they can overwhelm the donor related stress and become the primary influence.

This type defect alignment could not occur if the defect field were spherically symmetric, since in such a case a lower energy orientation would not exist. Therefore, isovalent dopants do not show this effect. Also, the distorted defect complex field is present no matter what the specific donor (as long as the compensation mechanism is electronic); thus this effect is seen in the case of all donors. Further, donor concentration has to be high enough so as to facilitate this type interaction (defect induced internal stress must dominate over other domain nucleation sources), and is the reason why the textured

domain structure is not seen in under-doped samples. In case of over-doped samples, the defect compensation mechanism switches to cation vacancy compensation [1, 23], and the Jahn-Teller distortion resulting from electronic compensation no longer exists.

The above analysis suggests that this type defect ordering should result in a monodomain state. However, a multi-domain state is still seen to be favored. TEM observations of these type domain structures [6] have revealed the presence of primarily *head-tail* type domain walls, suggesting that the criterion of minimization of extra internal electric fields [21] is fulfilled (domain walls are uncharged). The multi-domain state may simply be required to minimize the extra internal electric and elastic fields and the stress of the phase transformation, and/or be a manifestation of non-equilibrium cooling conditions. It is facilitated by the existence of more than one spatial orientation offering the lowest internal stress state, resulting in the uniaxially aligned *head-tail* type domain structure.

The above explanation is, obviously, tentative, and needs to be verified experimentally and theoretically. In summary, it can be said that though many different cooling, defect, and pore related stresses can pre-exist and influence domain formation in ferroelectric-ferroelastic materials, it is evident that in *optimally donor doped* barium titanate, the internal stress generated by donor doping dominates over large distances, indeed over the entire grain, and results in the unidirectional structure seen. Jonker [3] suggested that the presence of pre-existing charges on the grain boundary could influence domain growth in a manner so as to neutralize the effect of these charges. In the light of the above discussion it is suggested that donor induced internal stress is the primary influence in the interior of the grains; in the near grain boundary regions on the other hand, the total effect is likely a combination of all factors, with the strongest stress/field in any given region dominating domain formation.

### 3. Structural Influence on Conduction

#### 3.1. Grain Interior—Mobility Effects and Domain Walls

Conduction in these materials is ascribed to small polarons [17–19]. Motion occurs primarily by phonon assisted hopping—though band motion has also been suggested as a possible mechanism below  $T_c$  [18]—of

the excess electrons introduced by the donor dopant. Two structural aspects in the grain interiors are relevant to conduction and the PTCR effect, namely: (1) electron mobility along crystallographic axes; and, (2) the effect of domain walls. These are discussed sequentially.

*Mobility effects.* Berglund and Baer [24] have shown that anisotropy exists in the conductivities along the *a*- and *c*-axes in tetragonal barium titanate single domain crystals; the *c*-axis is more conductive than the *a*-axes in the tetragonal state. Electron mobility ( $\mu$ ) is 0.13 cm<sup>2</sup>/V · sec for *c*-axis and 1.2 cm<sup>2</sup>/V · sec for *a*-axis in the tetragonal phase, and 0.5 cm<sup>2</sup>/V · sec for the normalized value or for the cubic state [24]. The effect on the grain interior resistivity as a result of the phase transition can be evaluated using the following equation:

$$\rho_n = 1/n_o e\mu \quad (1)$$

where  $\rho_n$  is the grain interior resistivity;  $n_o \sim 2 \times 10^{19}$  cm<sup>-3</sup> (as determined from doping concentrations);  $e = 1.6 \times 10^{-19}$  C. Using the above mobility values, the resistivity in the cubic phase is 0.7 ohm-cm, and, the resistance along the *c*-axis in the tetragonal phase is 0.3 ohm-cm. Thus the theoretical grain interior resistivity is only affected by a *factor of*  $\sim 2$  between the two phases. The change in mobility within a grain, therefore, does not result in a significant change in resistivity at the phase transition temperature.

*Effect of domain walls.* The paraelectric-ferroelectric phase transition generates a volume strain in the ceramic, which is accommodated in the region of transition between domains (domain walls); the types of domains and their thickness thus reflect the amount of internal strain generated due to the phase transition. 90° domains are found dominant in ceramic barium titanate. Compared to 180° domains whose wall thickness is said to be  $\sim 1$  unit cell, 90° domain walls are said to be  $\sim 18 \pm 3$  unit cells wide [26]. Though experimental understanding of the structure of 90° domain walls is rudimentary as yet, theoretical arguments [25, 26] favor the possibility that unit cells within 90° domain walls have a gradual rotation of the polarization vector without a change in magnitude. Structurally, this represents a region of higher internal strain than the domain interiors; the elastic energy of 90° domain walls has been calculated to be of the order of magnitude of  $3 \times 10^3$

J/m<sup>2</sup> [26]. What effect does the structural disruption of a 90° domain wall have on conduction in the grain interior? Though data is lacking from single domain walls, the existence of piezoresistivity in bulk donor doped barium titanate [27, 28], and in thin bars containing a single grain boundary is known [29, 30]. Kuwabara et al. [29, 30] have attributed the piezoresistivity of single grain boundaries in the barium titanate bars to the change in the domain microstructure in the near grain boundary regions due to applied bending stress [30]; also significant is their result that some grain boundaries showed a differential negative piezoresistivity (DNR), whereas some showed almost no such effect, and others showed a positive piezoresistivity coefficient [30]. (Our observations of the near grain boundary structure (discussed in Section 3.2 and illustrated in Fig. 5) show variations in domain structures from region to region, and can possibly explain this result.) These facts further suggest that the structural disruption of the 90° domain wall presents a *higher resistivity path* (compared to domain interiors) to polaron conduction, and electrons within a particular domain prefer conducting pathways within the cylindrical geometry of the domain. If this hypothesis is true, conduction in the grain interiors in optimally doped samples can then be visualized to be primarily channeled parallel to the domains, with nominal conduction in the perpendicular directions. This is shown schematically in Fig. 3(a). Thus it is seen that the combined effect of unidirectional domains and higher resistance domain walls can cause an anisotropy in conduction within the grain interiors below  $T_c$ . (This anisotropy is in addition to that discussed above due to differential mobility along *c*- and *a*-axes of the tetragonal unit cell itself.) As a result of this, only certain preferentially aligned (with respect to the domain walls) grain boundaries can have a greater *incidence* of conducting electrons and can relate to a high probability of conduction (Fig. 3(b)). A percolation of electrons along mutually interacting uni-directional domain pathways and contacting grain boundaries creates the low  $\rho_{RT}$ 's found in these materials. It must be made clear that this type of domain mismatch (Fig. 3(b)) is *not the only factor* determining grain boundary resistance, but is merely another component (along with the electrical barrier potential, coherency stresses, porosity, etc.) contributing to the total effect, though the piezoelectric and ferroelastic effects imply that all these factors can be interrelated, as discussed in more detail in the Section 3.2.

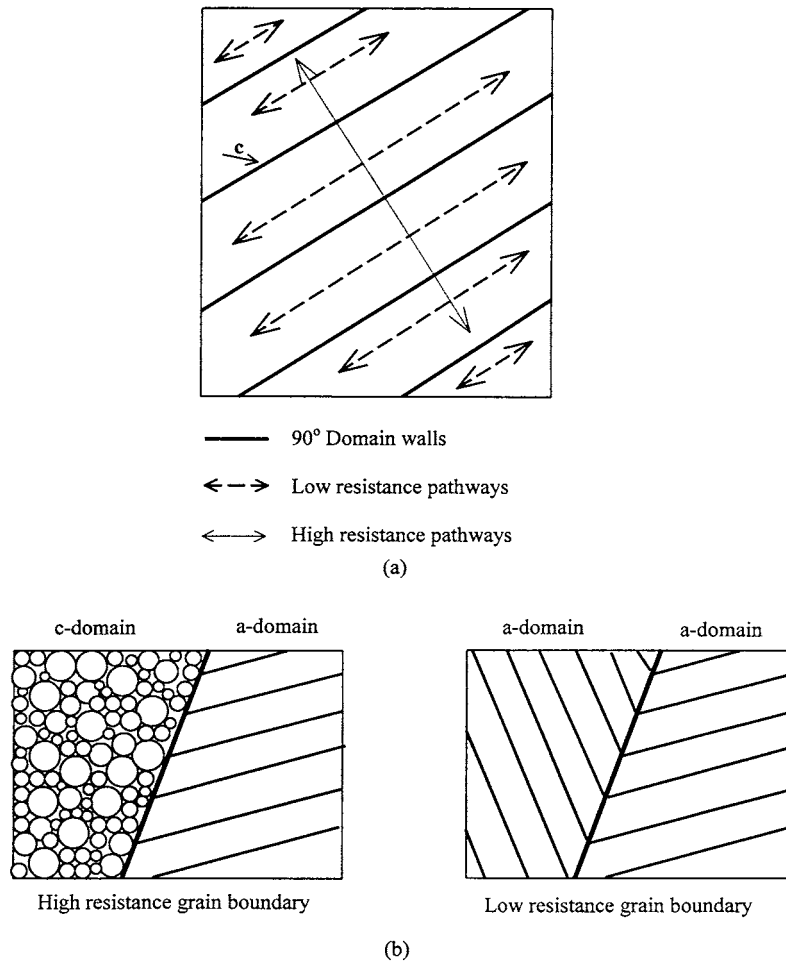


Fig. 3. Schematic showing the hypotheses suggested by structural observations that: (a) electrons are preferentially channeled along the domains and (b) grain boundaries corresponding to a-c and c-c domain walls have higher resistance than those corresponding to a-a domain walls. The contribution to grain boundary resistance due to a-c type domains is in addition to the resistance that is caused by the electrical barrier potential, coherence strains, porosity, etc., though the piezoelectric and ferroelastic ferroelectric effects imply that these factors are not independent.

**High lattice coherency and/or high density samples.**

A low  $\rho_{RT}$  with minimal PTCR effect (<1 order of magnitude) has been previously demonstrated, as given in Fig. 4 [9, 12]. These results are found in samples with high domain and lattice coherency across a large number (>70%) of grain boundaries [9] and also found in samples with a large amount of grain to grain contact area (density >97%) [12]. These materials were reproducible and repeatable upon temperature cycling to 300°C. With regard to the topic of this section, it can be said that though the grain boundary-domain orientation effects (Fig. 3(b)) are also present in these type materials, their effect is mitigated to a

large extent by the extremely large grain to grain contact areas present. Below  $T_c$ , even if a significant number of grain boundaries are blocked by unfavorably oriented domains, low  $\rho_{RT}$  is still facilitated by the large number of available favorably aligned conducting pathways. Above  $T_c$ , the number of grain boundaries which need to be cut off for a large increase in resistivity is significantly larger compared to normal PTCR samples, and the material shows only a weak PTCR jump.

Thus one can begin to understand the vital importance of structural aspects, and their combined effects, in determining conduction and PTCR behavior.



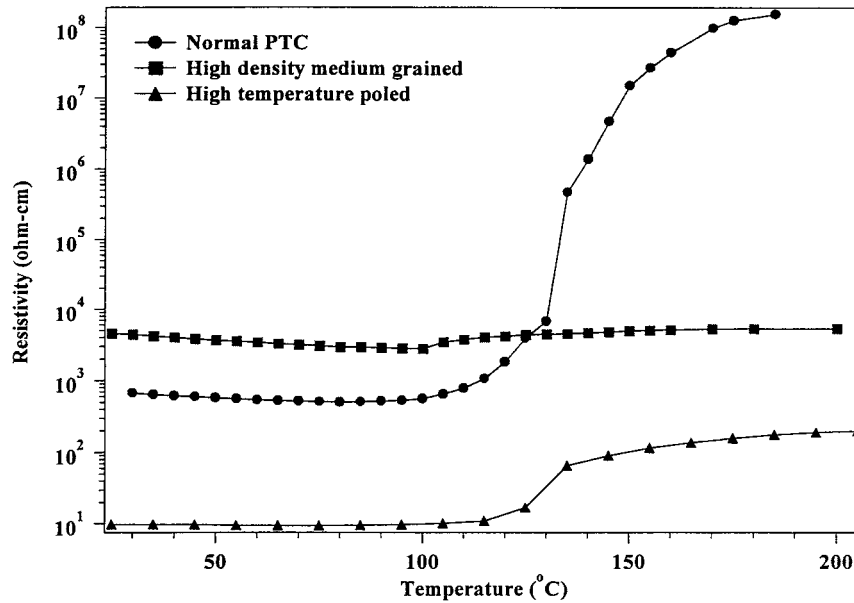


Fig. 4. Comparison of PTCR behavior of normal, high density, and high temperature poled ceramics [9]. The PTCR effect is severely reduced in the latter two cases, and semiconducting behavior is observed well above  $T_c$ .

Further, in the case of the high lattice coherence and high density samples discussed above, the domains are often seen to 'flow' across grain boundaries [9, 12], which seem to have a minimal effect on total resistivity between the two phases and the material behaves more as a single crystal. This leads us to a more detailed examination of the structural aspects relevant to the grain boundary.

### 3.2. Grain Boundary

SEM and TEM observations reveal that grain boundary structural conditions vary and are dependent on each grain to grain contact. Grain boundary potentials are dependent on a variety of different factors, the combination of which determines the magnitude in any given region. A number of different factors affect the grain boundary structure, as discussed below.

SEM and TEM of near grain boundary regions shows structural heterogeneity at the *micrometer* scale:

*Non-annealed samples.* In non-annealed samples, the domains develop without change up to the immediate grain boundary (Fig. 5(a)) [6, 7]. The PTCR effect is typically diffuse and of only a few orders of magnitude (Fig. 5(c)).

*Annealed samples.* Annealed samples (Fig. 5(b)) are described by a similar unidirectional domain structure throughout the grain interior, but with a disruption in the near grain boundary region where areas of fine domain patterns, changes in domain orientation and differences in the tetragonality of the unit cell occur randomly [6, 7, 23, 31]. These regions of domain disruption are seen to extend 1–2  $\mu\text{m}$  into the grains. The initial resistivity jump in these samples is typically sharp and significant, and is followed by a more gradual increase in resistivity beyond  $T_c$ . High temperature TEM has showed that upon heating these samples through  $T_c$ , the domain patterns in the highly stressed near-grain boundary regions disappear first, almost instantaneously, and is followed by a more gradual disappearance of the domain structure in the grain interiors, similar to non-annealed samples [6, 7]. The most significant consequence of this micrometer scale heterogeneity in domain structures is an increase in the electrical resistivity in these regions, caused by domain-domain misalignment (Section 3.1) and the piezoelectric and piezoresistive effects. The electrical behavior, shown in Fig. 5(c), can thus be said to mirror these microstructural changes.

HRTEM of the grain boundary core has also revealed structural heterogeneity at the *nanometer* scale [6, 7]:

*High disruption regions.* In some areas high lattice disruption with noticeable defects and incoherency is found, as shown in Fig. 6(a). These boundaries, whose percentage is higher in the case of annealed samples, show a regularly spaced defect along the immediate grain boundary, implying a specific type defect, regularly arranged to produce the lowest stress state [6, 7]. The periodicity of the barium and titanium ions are disrupted, a high strain is expected and cations and anions are displaced and missing to

relieve this elastic strain. These regions extend 1 to 10 nm into the grain [6, 7], and must correspond to high concentrations of acceptors and compensating defects.

*Coherent regions.* In some regions high lattice coherency is also seen, as shown in Fig. 6(b). The percentage of these is lower in annealed samples. These are related to low potential barriers and are suggestive of electron pathways [6, 7].

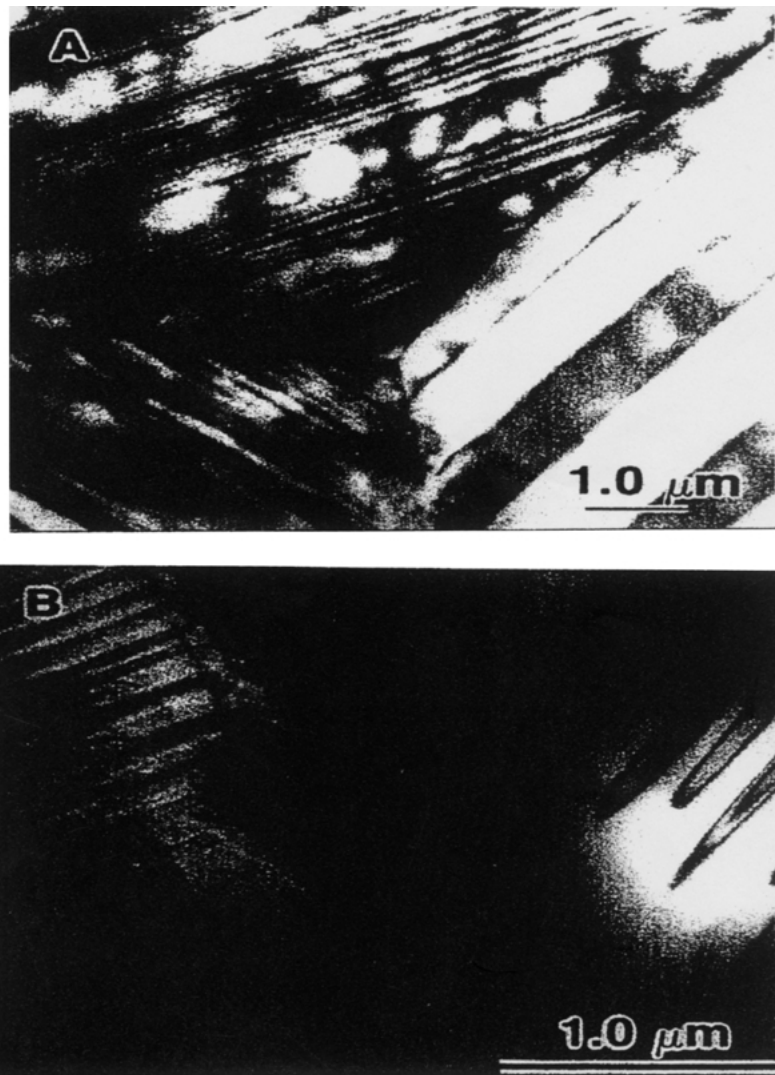


Fig. 5. Differences in microstructure and PTCR property of non-annealed and annealed materials: (a) TEM micrograph of *non-annealed* sample showing uniaxially aligned domains extending all the way to the grain boundary; (b) TEM micrograph of *annealed* sample showing domain disruption in near grain boundary regions; and (c) Comparison of PTCR behavior. Annealed samples display a sharper and larger resistivity jump at  $T_c$ .

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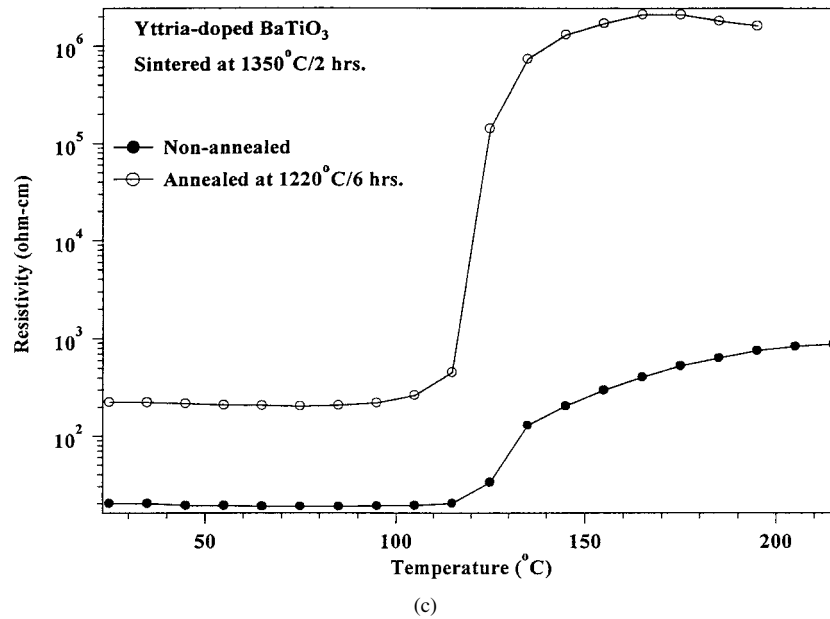


Fig. 5. (Continued).

The structural heterogeneities discussed above must imply *varying potential barrier strengths along the grain boundary*. This may be caused by a number of mechanisms, which are somewhat interdependent:

*Extent of sintering.* As discussed in Section 2.1, the extent to which sintering progresses during high temperature treatment determines the lattice coherence at places where two grains meet. Greater extent of sintering causes higher grain to grain contact areas and higher coherence/lower misfit strains. Vice-versa, if grain growth processes dominate and subdue sintering, lower contact areas, larger misfit strains, and a greater percentage of semi-coherent and incoherent grain boundaries are found. These effects are fundamental and present in all materials, ferroelectric or not, and are bound to modulate the grain boundary resistivity on their own. Further, *the interdependence of stress, electric fields and domain structure* in barium titanate means that the extent to which sintering progresses also influences grain boundary resistance in other ways, as discussed subsequently.

*Co-existence of a variety of acceptors.* There has been a long debate as to the exact nature of the grain boundary acceptor trap states. One study [32] indicates that several different types of acceptors (Ba-vacancies,

Ti-vacancies, Mn ions, adsorbed gases, etc.) can *co-exist*. This could result in varying strengths of the acceptor layer along the grain boundary, and is related to the nanometer scale heterogeneity.

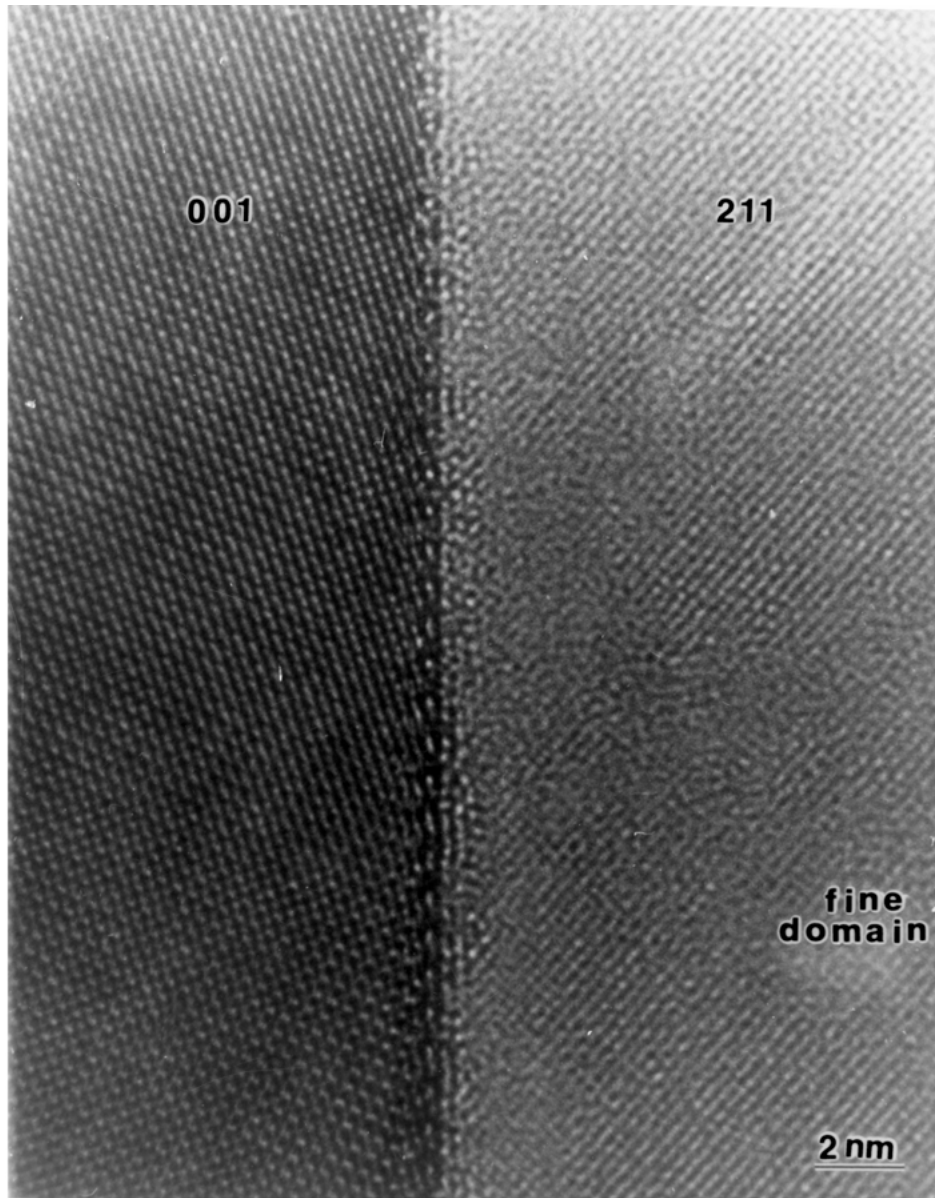
*Varying grain boundary energy.* Diffusion and segregation of acceptors and compensating defects to the near grain boundary regions play a significant role, especially in annealed samples [23, 31]. It is reasonable to expect that grain boundary and near grain boundary energy and diffusivities vary from region to region and, therefore, some heterogeneity in the distribution of these species is expected, especially since high temperature treatments are performed over a finite time and processes of homogenization may not be complete in many cases.

*Dependence of boundary potential on boundary curvature.* Scholl [33] has developed theoretical arguments, the thesis of which is that grain boundary potentials are dependent on the curvature of the boundary. According to this work, the grain boundary triple junctions, points of maximum curvature, should display the lowest potential barrier.

*Variation of normal component of  $P_s$ .* The spontaneous polarization ( $P_s$ ) alignment alters the already

existing potential barrier, probably with different magnitudes at different locations along the grain boundary [3]. Two grains which have ferroelectric axes that intersect at an angle have normal components of the polarization that are not equal and the continuity condition is

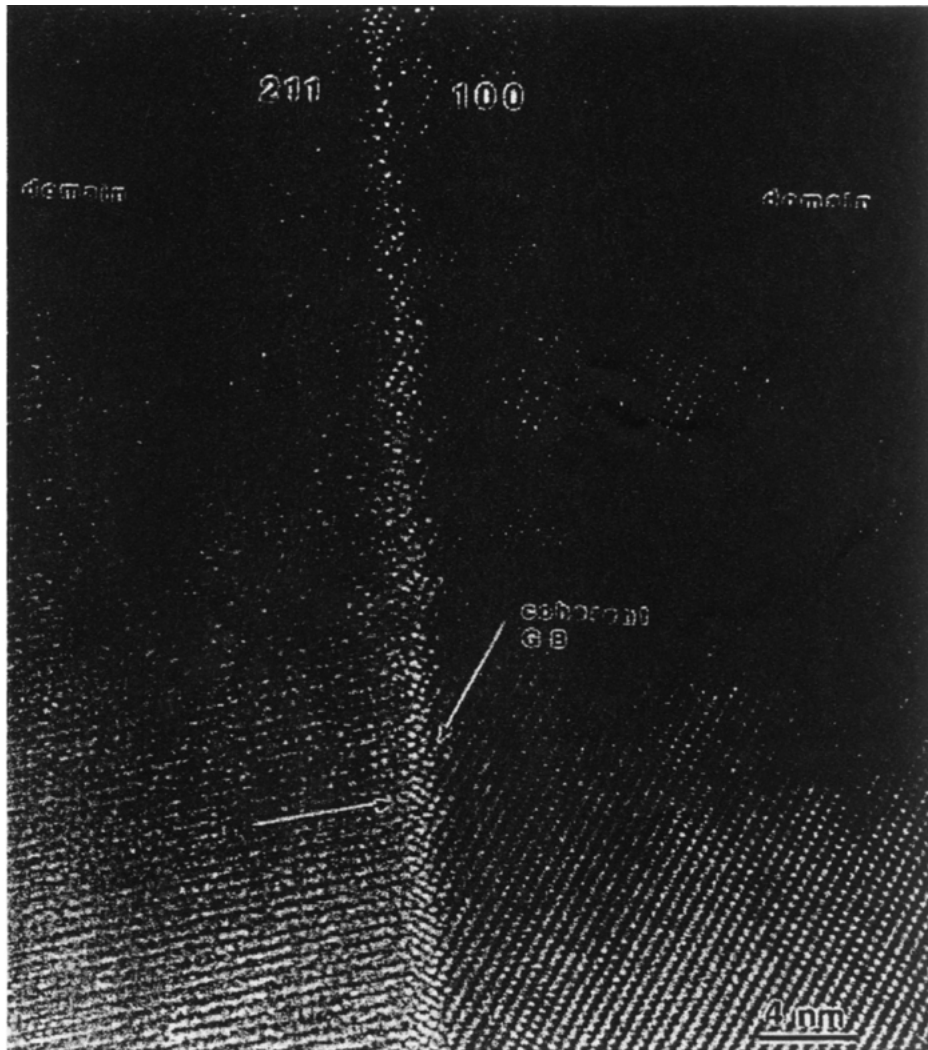
not satisfied. If there are no free charges to compensate the polarization charges produced by the difference between the normal components, the crystal is distorted at the contact zone. If there are free charges, they accumulate on the surface and prevent the distortion from



(a)

*Fig. 6.* HRTEM micrographs of grain boundary core and near grain boundary regions. (a) Image showing high lattice disruption and (b) Image showing high lattice coherency. The percentage of coherent regions is lower in annealed samples. Simultaneous existence of these type regions in the same sample suggests a range of barrier potentials in the same sample [6, 7].

*(Continued on next page.)*



(b)

Fig. 6. (Continued).

occurring [20]. This is also related to domain to domain coherent grain boundaries, where low distortion is found.

*Stress effects on potential barrier and varying internal stress.* This aspect was first considered by Kulwicki and co-workers [5]. The piezoelectric effect links the internal stress to the electrical potential barrier and depending on the sense of the stress, it can either decrease or augment the barrier potential locally. Further proof of stress effects on barrier potential comes from the work of Capurso et al. [27, 28], and Kuwabara

et al. who have observed strong piezoresistivity in thin bars of barium titanate [29, 30], some of which had only one grain boundary. Our structural studies also reveal variations in the tetragonality along the grain boundary and even regions where the lattice is cubic (no domains) [6, 7], making it evident that the internal stress state varies from region to region. Along with linear piezoelectricity and piezoresistivity, the presence of heterogeneous stress also invokes second-order piezoelectricity. These effects are not independent of, but are intimately linked with the ones discussed in the previous paragraphs, viz., incomplete

sintering, heterogeneous distribution of acceptors, and variation in  $P_s$ , and also strongly influence the domain structure in the grain boundaries (micrometer scale heterogeneity).

Consideration of the range of grain boundary structures observed physically, both at the micrometer and at the nanometer scales, and other factors discussed above must lead to the conclusion that in any given sample a *range of effective grain boundary potentials* exist. The consequences of this heterogeneity on the theoretical understanding of the PTCR effect will be discussed in Section 4.

### 3.3. *Second Transition*

It has recently been discovered that heating non-annealed samples to 450–650°C causes a sharp drop in the resistivity [10, 11]. The effect is shown in Fig. 7 for typical samples. This only occurs once, the first time that a sample is heated to this temperature range after cooling to below  $T_c$  from sintering temperature. A sample subjected to this heat treatment displays a  $10^{0.5}$ – $10^{2.5}$  times lower  $\rho_{RT}$  henceforth and the PTCR jump is significantly enhanced as a result (Fig. 7(b)). No gross microstructural changes are observed to occur concurrently. This effect is nearly instantaneous; samples inserted in the furnace at 600°C and removed within 5 minutes display it. The possibility of oxygen diffusion and/or electrodes in causing this behavior has been ruled out [11]. Instead it is believed that this effect is mechanical in nature, caused by the relaxation of mechanical strains in the near grain boundary regions. When the sample is cooled from the sintering temperature, domains grow for the first time. Domain growth possibly exerts stress on grain boundary structures, which results in distortion and increase in grain boundary resistivity. As the sample is reheated above  $T_c$ , domains disappear at  $\sim 125$ – $130^\circ\text{C}$ , but the strain relaxes only at a much higher temperature, 450–650°C as observed. Relaxation of these strains results in the decrease in grain boundary resistivity (Fig. 7(a)). This implies that the strain displays a ‘memory effect’ with respect to the domain structures, i.e., even in the absence of the domains, relaxation of the strain occurs so as to minimize re-occurrence the next time domains appear. It is interesting that this phenomenon only occurs once and subsequent cycling to the heat treatment temperature does not cause any further appreciable change in resistivity. The specific nature of this deformation,

whether elastic, anelastic or plastic, is not clear yet, but has been tentatively ascribed to the re-orientation of oxygen vacancy dipoles in the near grain boundary region [11]. Annealed samples also show the second transition, but the magnitude of  $\rho_{RT}$  drop is much less compared to non-annealed samples.

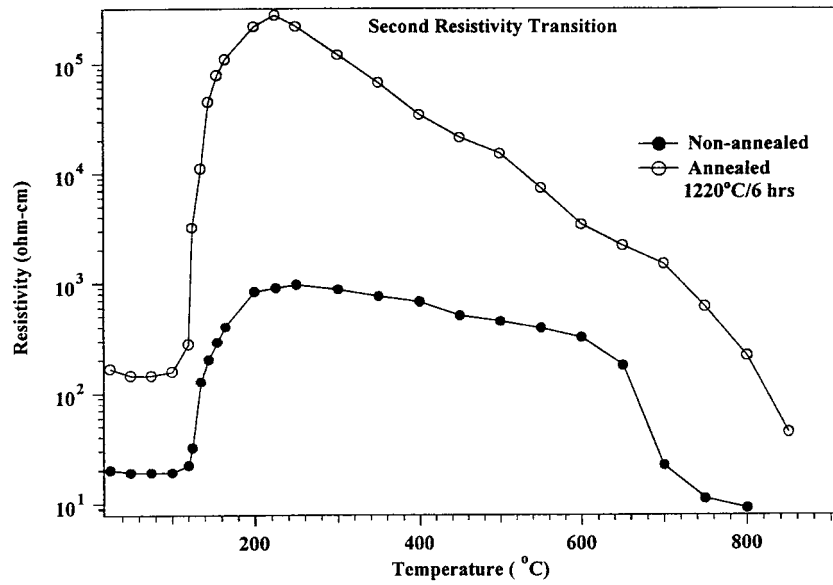
### 3.4. *Microstructural Dependence of Voltage Sensitivity*

The voltage dependence of the PTCR effect is well known and has been discussed in literature [34]. Typically, resistivities above  $T_c$  are lowered by 1–2 orders of magnitude when the applied field is increased to the order of magnitude of  $\sim 100$  V/mm. However, the specific microstructure of the device has been found to affect this voltage sensitivity [35]. The presence of a grain boundary insulating second phase has the most significant effect.

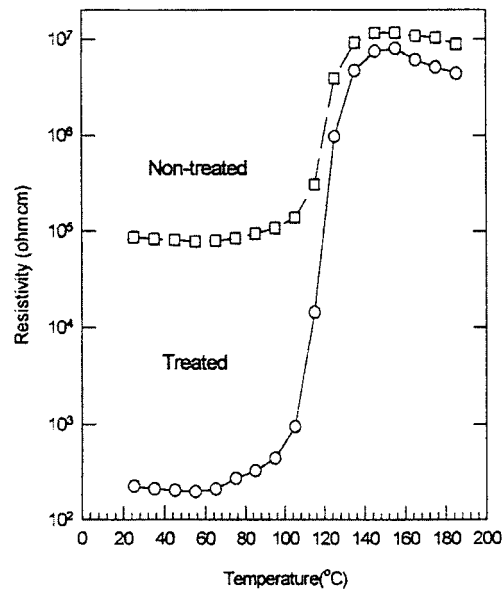
*Insulating second phase samples.* In these two phase materials the  $\rho_{RT}$  is relatively insensitive to the voltage but the high temperature resistivity is significantly decreased, as shown in Fig. 8(a).

*Single phase samples.* In the absence of a second phase, the high temperature resistivity is affected along with a corresponding large decrease in  $\rho_{RT}$ . Figure 8(b) shows the behavior observed from high-density ( $>97\%$ ), medium grain size (3–8  $\mu\text{m}$ ) single phase samples. As seen,  $\rho_{RT}$  suffers a large decrease in resistivity (unlike two phase samples) as applied field is increased to  $\sim 10^2$  V/cm, and the PTCR effect, which is minimal to begin with, is almost completely subdued, resulting in low resistance from RT to  $>200^\circ\text{C}$ .

The differences between two phase and single phase samples can be tentatively attributed physically to the presence of the insulating second phase, and the varying amounts of grain to grain contact areas and number of conducting pathways available. In the case of the two phase materials, the insulating second phase severely decreases the number of available conducting pathways. Thus, current flow is expected to be dominant through a lesser number of pathways (as compared to single phase samples). As the applied voltage is increased, local electric fields increase, increasing the current flow through the existing pathways, but the mechanism(s) responsible for non-linear current generation seem to be activated only at higher temperatures, resulting in the applied voltage-induced resistivity drop



(a)



(b)

Fig. 7. (a) A second resistivity transition occurs in the 450–650°C range and (b) A permanent decrease in  $\rho_{RT}$  is seen as a result of this second transition, and the magnitude of the PTCR jump is enhanced. The samples shown in (a) and (b) are not the same, but are typical of the trend observed.

occurring primarily above  $T_c$ , as seen in Fig. 8(a). In contrast, in the case of single phase samples, many pathways of slightly varying resistance can be present (as discussed previously, a range of barrier potentials is expected). In these samples, the mechanism(s) responsible for non-linear current generation seem to

be equally active at all temperatures, thus resulting in voltage-induced resistivity decrease at all temperatures (see Fig. 8(b)) [35].

Thus it is seen that though both type samples show voltage sensitivity, the nature and extent of the non-linearity is microstructure dependent. (In the case of

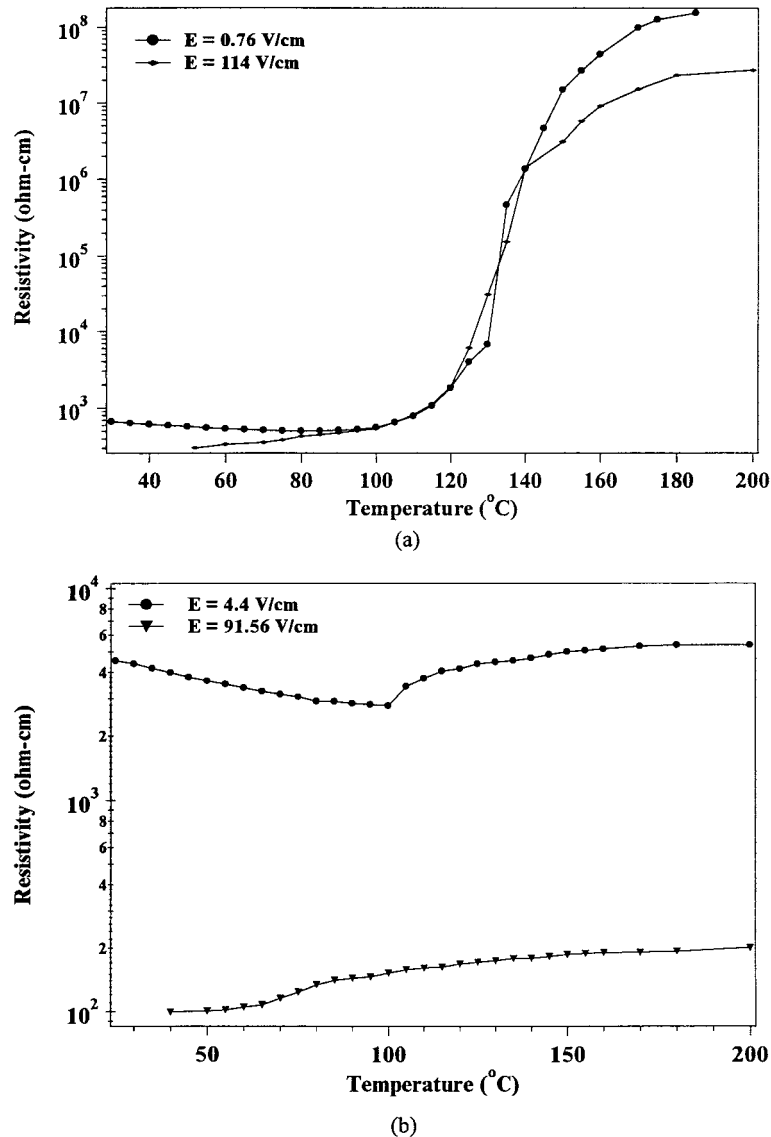


Fig. 8. (a) Voltage sensitivity typical of two phase (insulating grain boundary phase) material and (b) voltage sensitivity typical of high density (>97%), medium grain size (refer Fig. 2) material. The behavior of moderate density ( $\sim$ 90%) single-phase samples is intermediate to these.

medium density ( $\sim$ 90%) single phase samples, behavior that is in between the two extremes discussed here is observed [35].) In literature, several possible mechanism(s) responsible for the voltage sensitivity have been suggested [34, 36, 37]. Further analysis of the microstructural differences between two- and single-phase samples, and their different voltage sensitivities is thus likely to provide more insight into the specific mechanism(s) responsible for non-linear I-V behavior in these materials.

Based on the structural aspects presented so far, the differences in PTCR behavior among different microstructures can be hypothesized: The resistivity change of any grain boundary at  $T_c$  comes from, we believe, Jonker's theory (disappearance of  $P_s$ ). However, the observations presented in this paper suggest that the barrier potential varies from region to region. A high density single phase sample, which has a higher percentage of grain boundaries where the barrier is minimal/non-existent to begin with will not



experience a large increase in bulk resistivity at  $T_c$ . In two phase samples on the other hand, the number of higher conductivity paths are few, and the higher resistance paths are very high resistance (because of the insulating grain boundary phase). Therefore, as  $T_c$  is crossed, only the few conducting paths have to switch-off (i.e., the  $P_s$  change in only a small number of grain boundary regions determines the PTCR jump); PTCR jump is usually  $>10^5$  (see Fig. 4, normal sample). In contrast, in single phase high density samples, many low/negligibly small potential barrier grain boundaries exist. Below  $T_c$ , conduction occurs primarily through these grain boundaries where the barrier potential is minimal and also through boundaries where the barrier is strong but is canceled by the  $P_s$  most effectively. Above  $T_c$ , the latter junctions become highly resistive, but the low potential barrier boundaries suffer minimal change in resistivity, and since the percentage of these type boundaries is high, the PTCR effect is typically observed to be  $<10^1$  (see Fig. 4, high density sample). In single phase moderate density ( $\sim 90\%$ ) samples, the PTCR effect is in-between these two extremes ( $\sim 10^3 - 10^4$ ) [35].

#### 4. Theoretical Aspects—The Need for Modeling

In light of these structural aspects, the question now arises whether the existing theory is able to quantitatively account for and relate these structural effects to experimentally measured resistivities. Heywang's [2] well known equations have been the basis for many theories of the PTCR effect.

$$\rho = A \exp(\phi/kT) \quad (2)$$

$$\phi = e^2 n_s^2 / 8 \epsilon_r \epsilon_o n_o \quad (3)$$

where  $\phi$  is the value of the potential barrier;  $A$  is the proportionality constant with same units as  $\rho$ ;  $n_o$  is the concentration of charged species in the depletion layer, and  $n_s$  is the concentration of surface acceptor states. In this model, the sudden change in the dielectric constant at  $T_c$  is considered to cause the change in resistivity. Jonker [3] modified the model by taking into account the spontaneous polarization below  $T_c$ :

$$\phi = (e^2 n_s^2 - \Delta P_n^2) / 8 \epsilon_r \epsilon_o n_o \quad (4)$$

This model states that the normal component of the spontaneous polarization ( $\Delta P_n$ ) at the end of alternate  $90^\circ$  domains across a grain boundary could compensate the surface states and depletion layer and decrease/eliminate  $\phi$  in regions. Kulwicki and Purdes [5] also considered the piezoelectric effect, which generates additional charges ( $\Delta P_z$ ) due to the stresses at the grain boundary and further lowers  $\phi$  in some regions:

$$\phi = (e^2 n_s^2 - [\Delta P_n^2 + \Delta P_z^2]) / 8 \epsilon_r \epsilon_o n_o \quad (5)$$

It is obvious that these equations utilize unique values of the parameters and result in unique values of  $\phi$  and  $\rho$ . Though these equations may provide a good qualitative picture, in the face of the structural heterogeneity observed and the wide ranges of values of parameters that it implies, it is evident that a simple calculation using only unique values of parameters is not sufficient for a quantitative understanding, as it will only involve 'global averages'. Since conduction occurs preferentially through selected pathways and the change of  $\phi$  along these pathways dominates the PTCR effect, such global averages are inadequate to facilitate the theoretical understanding of why the magnitude of PTCR effect changes from sample to sample. Moreover, these equations do not factor in the effect of density (number of grain boundaries blocked to conduction by porosity and/or second phase). Instead, an improved theoretical attempt needs to incorporate variations in these parameters in a statistical manner and simulate the case of a polycrystalline sample with a controlled amount of grain to grain contact area. The equations and assumed values of parameters used by Heywang and subsequent researchers can be used as the starting points for such an analysis, although certain problems exist with regard to the value of the dielectric constant used in these, as discussed next.

Consideration must be given to the dielectric constant values ( $\sim 10^4$  below and  $\sim 10^2$  beyond  $T_c$ ) used in analyses of the potential barrier and resultant PTCR effect. Two factors, as to the validity of these dielectric constants, must be taken into consideration: (1) In this semiconducting material, this is not a true dielectric constant, but is actually a Maxwell-Wagner type polarization which is significantly altered by frequency, as shown in Fig. 9. The reported dielectric constants of  $10^4 - 10^5$  are obtained at frequencies of 20–30 kHz as shown [1, 38, 39]. Changes in the values above and below  $T_c$  are also shown to be highly dependent upon frequency, as the dielectric constants obtained above  $T_c$

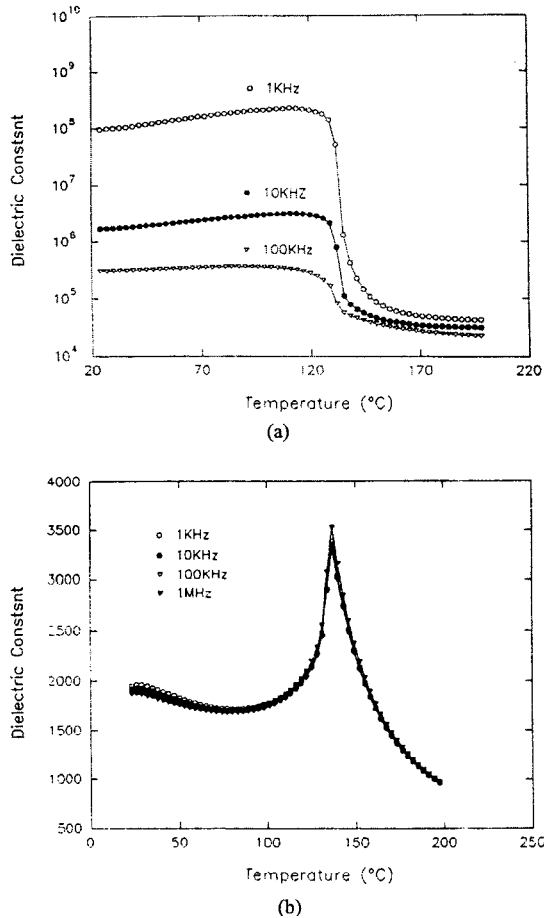


Fig. 9. Dielectric constant versus temperature plots: (a) Optimally doped (0.24 mol%  $Y_2O_3$ ) semiconducting sample, showing the frequency dependence of  $\epsilon_r$ , suggesting a Maxwell-Wagner type polarization mechanism and (b) in comparison, in the case of an overdoped insulating sample (0.5 mol%  $Y_2O_3$ )  $\epsilon_r$  is independent of frequency in the range measured.

do not vary greatly with frequency; (2) These dielectric constants are also *low field* values of the *bulk* material. In the grain boundary core, a high field of  $\sim 10^7$  V/m is expected. In ferroelectric  $BaTiO_3$ , the high field dielectric constant is significantly lower than the low field value; theoretically it has been determined to be  $\sim 300$  at  $100^\circ C$  [5]. This temperature is slightly less than, but near to  $T_c$ , relating to a maximum.

### 5. Improved Understanding Through Structural Observations

Structural observations discussed in this paper have resulted in an improved understanding of the overall

effect, and these can now be employed for better control of device properties. The most important additions to known phenomena are summarized:

- The amount of grain to grain contact area is important. In single phase samples, the density is a measure of this. In the case of samples with added second phase forming compounds, a material with high density but few conducting-grain to conducting-grain junctions may still result. The amount of grain to grain contact areas generated is a sensitive function of the chemistry and processing conditions.
- Optimally doped PTCR materials show a distinct texture to the domain pattern within each grain. The optimal range of dopant concentrations for the occurrence of this type structure coincides with the optimal range for obtaining lowest  $\rho_{RT}$ 's and highest resistivity jumps. The textured domain pattern can generate an anisotropy in grain interior conductivity due to the presence of high resistance domain walls.
- Not all regions of the grain boundary have the same resistivity. This may arise out of a number of effects as discussed.
- Given the above constraints, conduction takes place in a tortuous manner through the solid, favoring the paths of least resistance. The change in resistance of these paths at  $T_c$  is likely to primarily determine PTCR behavior.
- Depending upon chemistry and processing conditions, high domain alignment across grain boundaries and a high density (large number of conducting-grain to conducting-grain contacts) can be obtained. The PTCR effect is sharply quenched in these cases. In these materials the grain boundaries offer minimal disruption to charge flow and the material behaves more as a single crystal.
- The typical electrical behavior of annealed materials can be explained by microstructural observations as related to a sudden release of internal strain in the near grain boundary regions at  $T_c$ . Also, a second transition in resistivity is seen the first time a sample is heated to  $450-650^\circ C$ . This results in a permanent 0.5–2.5 order of magnitude drop in  $\rho_{RT}$ . The effect has been attributed to the relaxation of mechanical strains in the near grain boundary regions. These facts make it evident that the piezoelectric and piezoresistive effects, suggested by Kulwicki et al., play a strong role in determining the resistivity.
- The voltage sensitivity of these materials is microstructure sensitive. The presence of a grain

boundary insulating phase is the most critical parameter. In these materials,  $\rho_{RT}$  is relatively insensitive to the applied voltage. In materials that do not have a second phase, resistivities at all temperatures are lowered significantly with increasing applied fields.

- Considerations of structural factors can possibly explain variability in results obtained among different studies and even among materials which have been processed “identically”. It is recommended that an approach incorporating microstructural observations be adopted when analyzing these materials. Certain themes occur consistently in the microstructure, making it relatively easy to co-relate to both processing and electrical properties.
- The microstructural observation based hypotheses presented in this paper need to be further verified experimentally and theoretically. A better theoretical understanding will be facilitated by mathematical simulations which utilize statistical variations in the values of relevant parameters and also control the number of available conducting pathways.

## Conclusions

Extensive microstructure-property studies on PTCR barium titanate ceramics have revealed that these materials are far more complex than suggested by the original models proposed several decades ago. The most significant microstructure-property aspects have been discussed in detail. It is seen that the PTCR properties are strongly controlled by the density, grain to grain contact areas, domain alignment, and structural heterogeneities present in the grain boundaries. The existing theoretical framework is unable to account for these aspects in a quantitatively satisfactory manner. Limitations in the assumptions of the original models, and the clear need for mathematical simulation to enhance the theoretical understanding of these materials, have been discussed. Microstructural observations have enabled a more mature understanding of this complicated material in which a host of effects interact.

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