

# The effect of processing variables on the mechanical and electrical properties of barium titanate positive-temperature-coefficient -of-resistance ceramics

## Part II *Sintering atmospheres*

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The effect of sintering atmospheres on the mechanical and electrical properties of four formulations of *n*-doped barium titanate PTCR ceramics has been investigated. Under sintering atmospheres with an oxygen partial pressure greater than 0.2 bar, it was found that the PTCR effect was unchanged up to a 100% oxygen atmosphere. Similarly mechanical strength, (measured by diametral compression and four-point bending of beams) and fracture toughness were little changed. However, at lower oxygen partial pressures, PTCR effects were reduced. The change in resistance was reduced from three orders of magnitude to one order of magnitude for one formulation. The corresponding strength and fracture toughness (measured by pure bending of small beams) were also significantly reduced from 83 MPa to 48 MPa and 1.0 MPa m<sup>1/2</sup> to 0.35 MPa m<sup>1/2</sup>, respectively.

### 1. Introduction

Part II of the main investigation considers specifically the effect of sintering atmosphere. This is one of the processing variables under which barium titanate PTCR ceramics are produced and its influence on the overall performance of the final component has been assessed. Improvements in the performance of these devices can include enhanced electrical properties and improved mechanical strengths, the latter of which potentially allow longer component lifetimes to be achieved.

Densification of the "green" sample is important both to permit the dopant to diffuse into the crystal lattice and to improve the mechanical strength of the component through the formation of a liquid phase. The action of sintering increases the density of a component by reducing the size of the pores initially present within the structure and brings about controlled grain growth. Normally a temperature of 85% of the material melting temperature is required and in many cases a liquid phase is used to fill the smaller pores.

Theories behind densification have been well documented [1] and mathematical definitions have been produced which explain the thermodynamic forces behind densification and grain growth. Experimental studies on barium titanate have concluded that there is an increase in densification at the onset of abnormal grain growth [2]. For doped materials, a minimum temperature is required to enable the dopant, in this case holmium, to replace some of the host barium in

the crystal lattice. Optimization of the entire sintering profile, including heating and cooling rates [3], has led to excellent PTCR characteristics. Kuwabara *et al.* [4] discovered that the best PTCR properties (steepest gradients and largest total resistivity change) were obtained with 20% porosity. However, in most engineering ceramics, porosity is rarely allowed to exceed 5%, due to the detrimental changes in mechanical strength which high porosity can yield.

Grain growth of barium titanate has been shown to increase to a maximum at 1240 °C where grains nominally 60 µm in diameter are produced, before decreasing to 10 µm by 1360 °C [5]. Additionally, studies by Kahn have indicated that grain size is not dependent on initial particle size and that grain growth could be limited by increasing dopant concentration [6]. This has the advantage of increasing the grain-boundary surface area, which is where the PTC effect is thought to originate. Lubitz has shown that limited grain growth can be accomplished by increasing the heating rate close to the maximum temperature. Changes in the time spent at this temperature (from 30 min to 50 h) had little effect on the grain size [7].

This part of the study is concerned with changes that result from sintering in both oxidizing and inert atmospheres. Emphasis has been placed on assessing changes in the mechanical properties of the material. Tensile strength was determined using both diametral compression and beam tests under three- and four-point loading. Fracture toughness was evaluated using miniature single-edge notched (SEN) beam

TABLE I Chemical compositions (mol%) of the mixes used in this investigation

Material	Mix 1	Mix 2	Mix 3	Mix 4
BaTiO <sub>3</sub>	99.0	—	80.2	80.2
BaCO <sub>3</sub>	—	49.5	—	—
TiO <sub>2</sub>	0.50	50.0	1.73	1.73
CaTiO <sub>3</sub>	—	—	13.9	13.9
Ho <sub>2</sub> O <sub>3</sub>	0.20	0.20	0.30	0.30
Si <sub>3</sub> N <sub>4</sub>	0.30	0.30	—	—
SiO <sub>2</sub>	—	—	0.70	0.70
Al <sub>2</sub> O <sub>3</sub>	—	—	0.40	0.40
MnCO <sub>3</sub>	—	—	0.10	0.10

specimens. Electrical characteristics have been limited to establishing resistance-temperature plots using techniques fully described elsewhere [8-10].

## 2. Materials and methods

### 2.1. Materials

The starting materials for this study were the same as those taken for the main experiments in Part I [10] of this investigation. They comprised of four formulations, summarized Table I, which, together with details of the sample preparation, have been described previously [9, 10].

For mixes 1, 3 and 4 barium titanate was obtained from TAM Chemicals as a high-purity grade (total impurities < 0.05% by mass). Mix 2 contained material prepared in the laboratory from barium carbonate and titanium dioxide.

The mixture was dried, granulated and sieved to extract the granule size range of 90-500 μm. Pressing the powder into "green" pellets was achieved using a range of cylindrical dies. Samples 13 mm diameter and 2-3 mm thick were used for diametral compression testing, beam specimens being prepared from discs 40 mm diameter and 4 mm thick. Smaller pellets 5.1 mm diameter and 3 mm thick were used for the electrical measurements. A nominal green density of 55% theoretical was achieved using loads of 1.0, 8.0 and 0.2 ton for each size of die, resulting in compaction pressures of 78, 66 and 101 MPa, respectively.

The "green" pellets were sintered in a range of gaseous atmospheres in a tube furnace. The sintering profile was the same as that used in Part I of this investigation [10]. The binder was burnt off at 500 °C, this temperature being maintained for 60 min to ensure complete elimination of the binder. The temperature of the furnace was then raised to 1320 °C to allow the formation of the liquid phase and densification of the pellets. During this process contraction took place resulting in the pellets attaining typically 85% of their maximum theoretical density. The sintering atmospheres were primarily chosen to investigate the effect of increases in the oxidizing nature of the furnace conditions. A gas analyser was used to control the conditions which were maintained until the samples had cooled to below 300 °C. These conditions are summarized in Table II.

TABLE II Sintering atmospheres used in this investigation

Group	Atmosphere
1	100% nitrogen
2	80% nitrogen, 20% oxygen
3	60% nitrogen, 40% oxygen
4	40% nitrogen, 60% oxygen
5	20% nitrogen, 80% oxygen
6	100% Oxygen

### 2.2. Diametral testing

Sample preparation followed that described previously [10], making sure that the loading surfaces were parallel and free from large defects. With the 13 mm pellets some polishing was necessary. The larger faces of all of the pellets were ground flat, however, to enable accurate density measurements to be made using the mass/volume method which was used to assess the porosity of the pellets.

Concave loading anvils were used with radii of curvature of 6.25 mm. The diameter of the sintered pellets ranged from 10.5-11.2 mm and this combination resulted in a contact ratio of approximately 1.2. This value has previously been used successfully in obtaining accurate and repeatable results [8, 9, 10]. An Instron 1000 testing machine provided the loading through a 5 kN load cell at a speed of 2 mm min<sup>-1</sup>. An X-Y plotter was used to produce load-deflection curves from which the onset of cracking could be estimated. The specimens were examined after testing on the scanning electron microscope (Cambridge S600) to establish the point of crack initiation.

### 2.3. Four-point bend tests

Sectioning of the larger pellets using a rotating diamond coated saw of 0.75 mm width produced four beams from each disc. The faces of the beams were ground with 240 and 600 grit paper and then lapped with alumina paste. A cloth polishing wheel was used for finishing of the tensile surfaces. Four beams were used for each measurement of tensile strength.

The remaining four beams were notched to a depth of approximately 1.4 mm (40% of the depth) to enable fracture toughness to be evaluated. A Lloyd 6000R testing machine was used to apply four-point loading to these specimens at a rate of 2 mm min<sup>-1</sup>. Details of the testing arrangement have been described previously [10].

### 2.4. Electrical measurements

Measurement of the resistivity of the PTCR devices took place within an insulated thermal cabinet, controlled by microcomputer, which had capacity for nine samples. This system provided a steady temperature increase to the devices at a rate of 3 °C min<sup>-1</sup> and resistance was measured automatically after the temperature had been constant for 3 min. Four samples of each mix sintered in each atmosphere were examined and plots obtained from averaged measurements.

### 3. Results

#### 3.1. Mechanical properties

The as-fired porosities of all samples are shown in Fig. 1a–c. It can be seen that for the 13 mm diameter pellets there was an overall reduction in porosity with increasing oxygen partial pressure for all mixes. Mixes 3 and 4 showed similar porosity values, ranging from 16%–27%. Mixes 1 and 2 showed porosity values of 14% and 3%, respectively. The other pellets sizes, 39 and 5.1 mm diameters, showed similar levels of porosity, with lower values measured when the oxygen partial pressures during sintering were low.

Fig. 2 shows the values of strength obtained using both diametral compression and four-point bending. Those obtained from the beam tests were approximately double the values given by diametral compression. Mix 1 did not seem sensitive to sintering atmosphere and the values of 23 MPa (diametral compression) and 42 MPa (four-point bending) remained unaffected. Mix 2 showed small changes in strength with the highest values obtained at conditions close to atmospheric (70 MPa for diametral compression and 93 MPa for four-point bending). Mixes 3 and 4 showed similar values, mix 4 being slightly the stronger of the two, but these values were sensitive to sintering atmosphere with values from beam tests as low as 48 MPa at 0% oxygen to 83 MPa at 60% oxygen.

Fracture toughness values measured from the notched beams are shown in Fig. 3. The values were consistent with previous measurements on pure barium titanate dielectric materials [11]. Mix 1 showed the lowest values, ranging from 0.6–0.75 MPa  $m^{1/2}$  with the lowest values at 0% oxygen. Mix 2 was slightly tougher with a similar dependence on atmosphere. Mixes 3 and 4 showed similar characteristics with very low values at 0% oxygen (0.35 MPa  $m^{1/2}$  for mix 3) which rose to values of 1.0 MPa  $m^{1/2}$  at oxygen

partial pressures of greater than 0.20. Mix 4 consistently showed values 30% higher than mix 3.

#### 3.2. Electrical characteristics

The resistance temperature plots for the four mixes are shown in Fig. 4. These were all sintered in flowing air. Mix 1 showed the largest resistance change of over three decades, with a switching temperature of 145 °C. Mix 2 showed the smallest resistivity change as well as the shallowest gradient, with a switching temperature at about 150 °C. As expected, mixes 3 and 4 showed very similar characteristics, with mix 4 exhibiting a slightly larger PTCR effect. Switching temperatures were higher than for the other mixes at 180 °C.

The electrical characteristics following sintering in 100% nitrogen are presented in Figs 5 and 6. Fig. 5 shows the response of the samples directly after firing and Fig. 6 shows that of similar samples following annealing in air at 1100 °C for 120 min. All of the samples showed greatly improved PTCR effects following annealing. Mix 4 showed the steepest gradient and a resistivity change of almost 3 orders of magnitude. Mix 3 was similar and both materials showed switching temperatures of 180 °C. Prior to annealing, the switching temperature was lower at 165 °C. Mix 1, following annealing, showed a similar resistivity change to the group sintered in air, but a shallower gradient. Figs 7–10 show the  $R$ – $T$  plots obtained at oxygen partial pressures higher than 0.2 bar. The results were similar to the samples sintered in air. Mix 1 exhibited a small decrease in switching temperature at high ( $\geq 0.8$  bar) oxygen partial pressures. Mix 2 exhibited its largest resistivity change of 2 orders of magnitude in a 100% oxygen atmosphere, but mixes 3 and 4 showed little change.

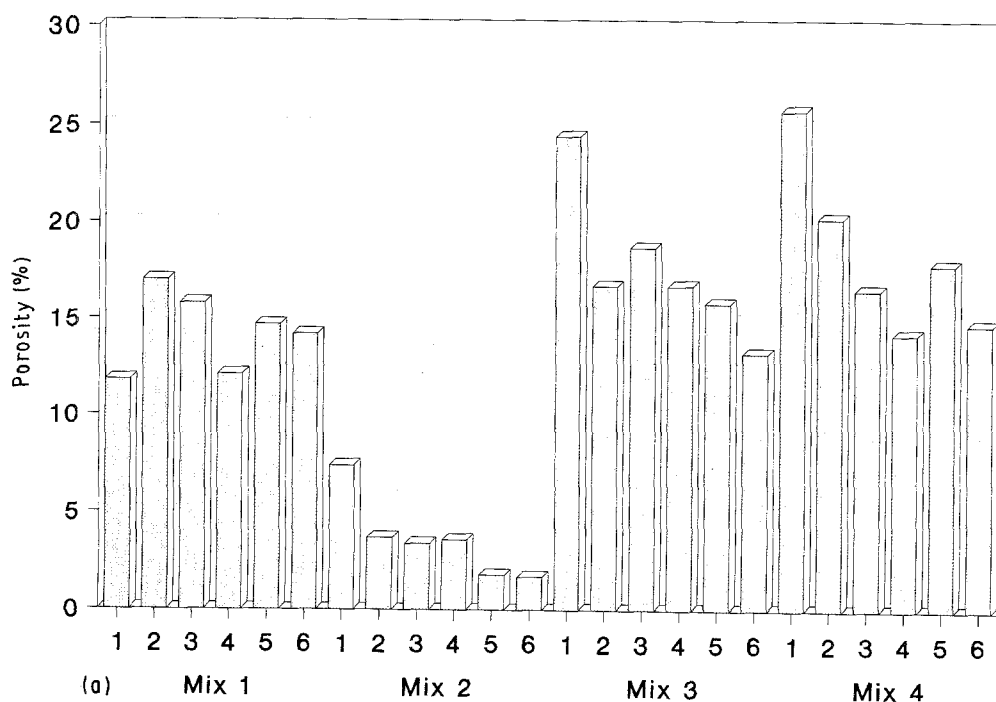


Figure 1 (a) Porosity levels of (a) 13 mm, (b) 39 mm, and (c) 5.1 mm diameter barium titanate samples sintered under the atmospheric conditions described in Table II.

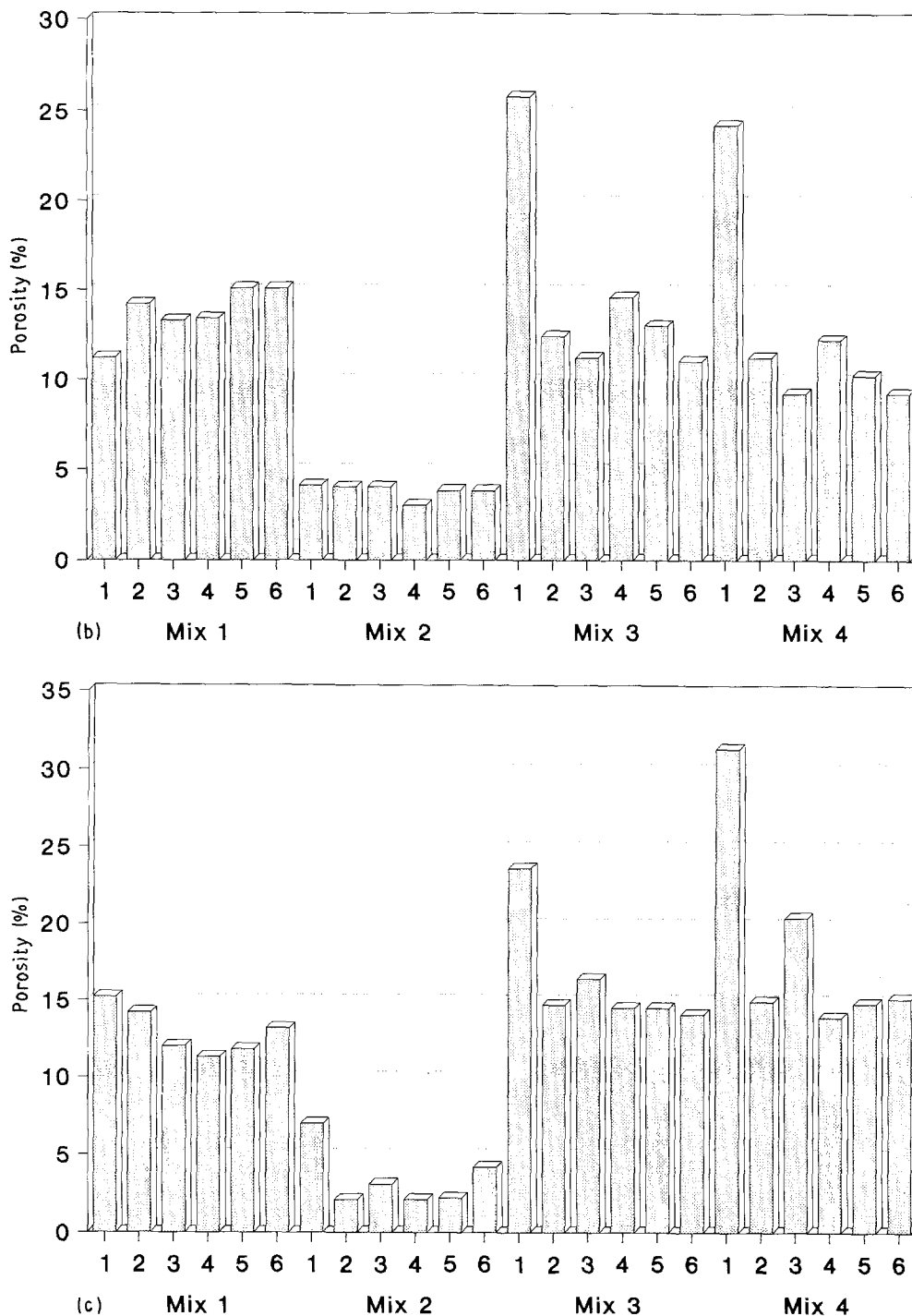


Figure 1 Porosity levels of (a) 13 mm, (b) 39 mm, and (c) 5.1 mm diameter barium titanate samples sintered under the atmospheric conditions described in Table II.

In addition, the properties of samples fired in the production and laboratory furnaces as well as vacuum-sintered material were recorded (Fig. 11). The laboratory furnace (tube design) produced the best results, with the vacuum-sintered samples showing no PTCR effect at all.

## 4. Discussion

### 4.1. Mechanical properties

The levels of porosity of the fired pellets were largely dependent on the partial pressure of oxygen present in the sintering atmosphere. This was most noticeable at low pressures where oxidation was not taking place. In all of the tests the binder was burnt off in air so that

the effect of residual hydrocarbons within the matrix may be ruled out. It is possible that the liquid-phase components melt at a higher temperature in a non-oxidizing atmosphere and this may lead to only partial production of the liquid phase material and increased levels of porosity due to the open pore network being maintained. It was also noted that the grains of material following sintering in nitrogen appeared more spherical, which could lead to a reduction in their packing efficiency.

Oxygen is clearly very important in the thermodynamics of grain growth and densification. As expected, different sized pellets, which were subjected to differing pressing pressures, showed only small variations in porosity. It was shown in Part I [10], that

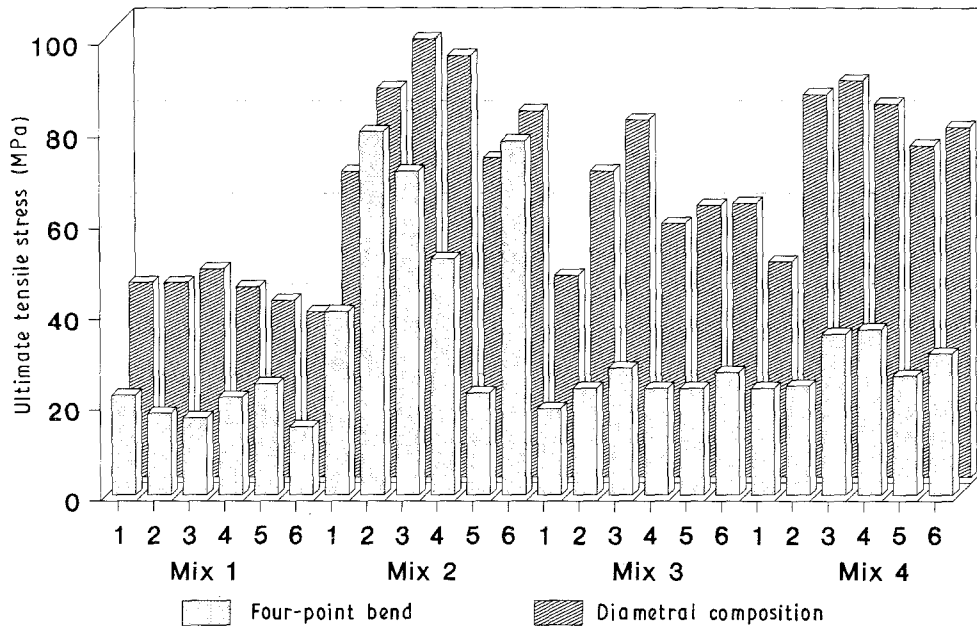


Figure 2 Diametral compressive and four-point bend strengths of samples sintered under the atmospheric conditions described in Table II.

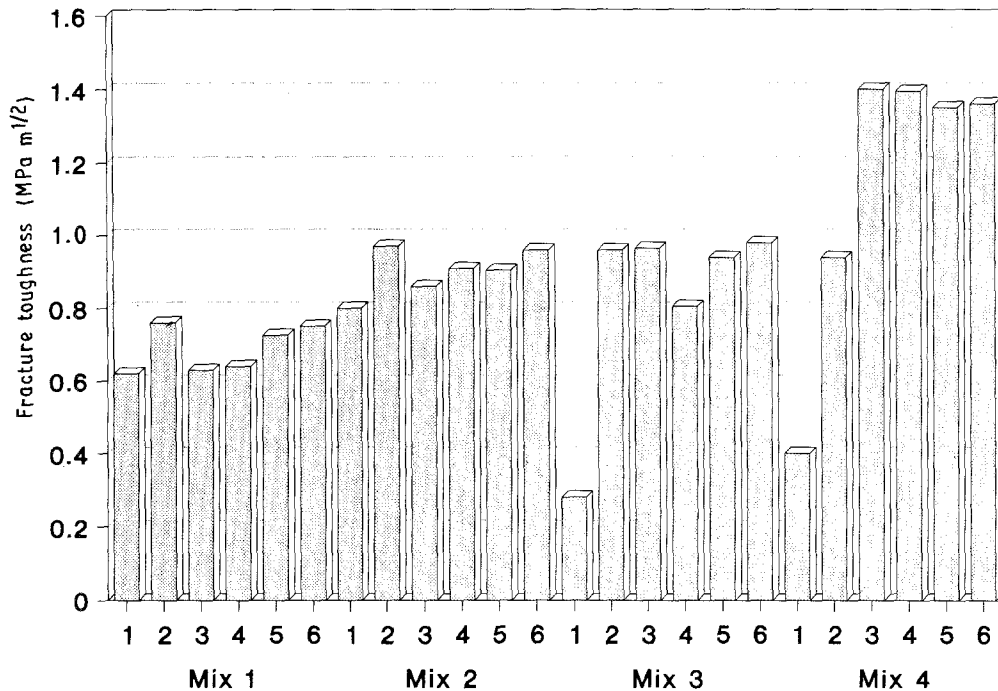


Figure 3 Fracture toughness values of samples sintered under the atmospheric conditions described in Table II.

very high compaction pressures were required to produce significant changes in fired porosities. It was also noted that the smaller pellets, which had a larger ratio of thickness to diameter, showed the greatest distortion following sintering and required substantial polishing prior to density and electrical measurements. This was attributed to the differing pressures developed by the die on the powder during compaction.

The porosity levels of samples sintered from each mix were very different, with mix 2 consistently showing much lower porosities than the other samples. It was noted in the first part of this investigation that the

samples which attained the highest fired densities, showed similar shrinkage levels in both the axial and radial directions [10]. The time spent above a certain temperature during sintering also appears to be important in the densification, suggested by the lower porosities of samples produced under commercial conditions.

The tensile strengths of mixes 3 and 4 were the most susceptible to the effects of sintering atmosphere. Very low strength values were noted in pure nitrogen atmospheres and the strength doubled as the partial pressure of oxygen in the furnace was increased to 0.6 bar.

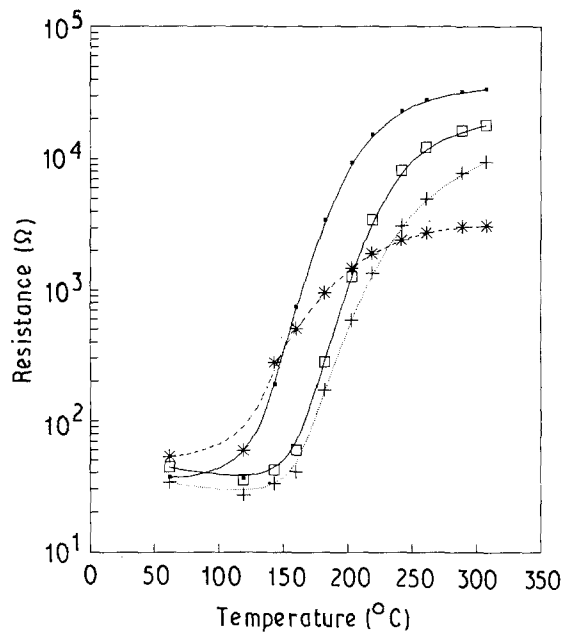


Figure 4 Resistance-temperature plots for mixes 1-4 sintered in flowing air. Mix: (●) 1, (\*) 2, (+) 3, (□) 4.

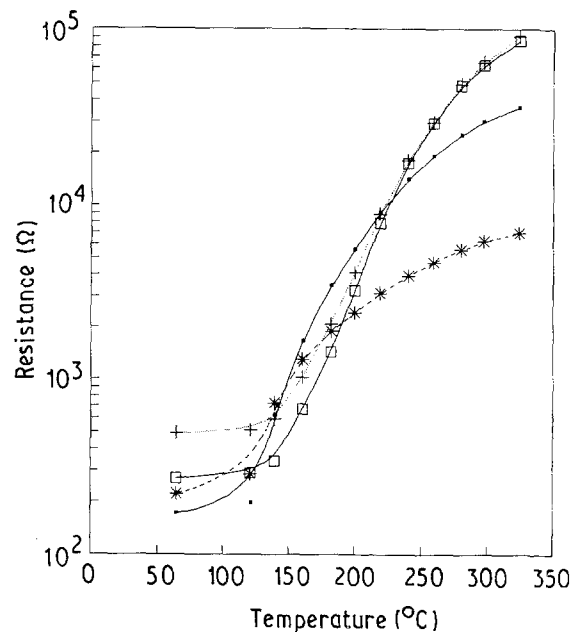


Figure 6 Resistance-temperature plots for mixes 1-4 sintered in 100% nitrogen followed by annealing in air. Mix: (●) 1, (\*) 2, (+) 3, (□) 4.

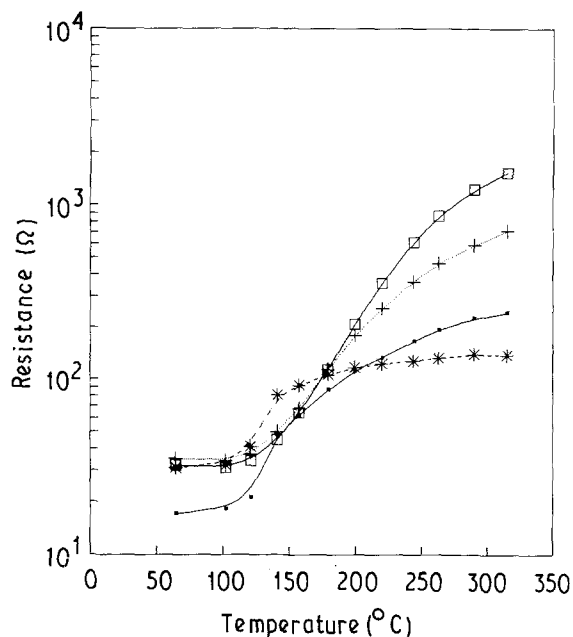


Figure 5 Resistance-temperature plots for mixes 1-4 sintered in 100% nitrogen. Mix: (●) 1, (\*) 2, (+) 3, (□) 4.

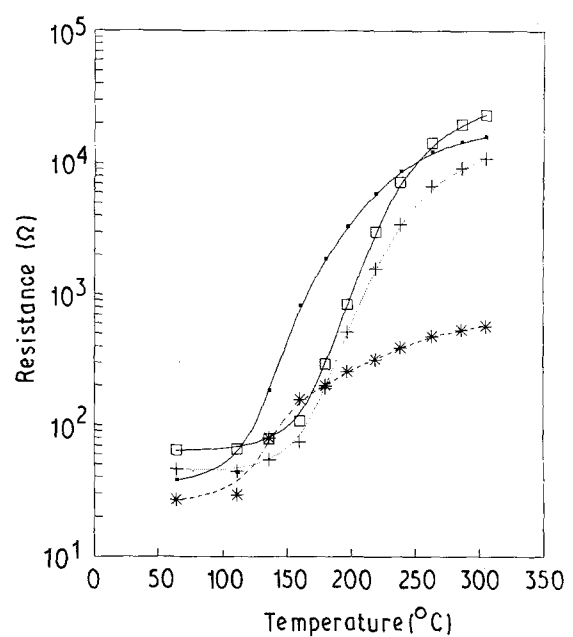


Figure 7 Resistance-temperature plots for mixes 1-4 sintered in 60% nitrogen and 40% oxygen. Mix: (●) 1, (\*) 2, (+) 3, (□) 4.

It is possible that the lead and calcium titanates, present only in these two formulations, require an oxidizing atmosphere to displace the barium in the lattice. Under unfavourable conditions this could lead to a non-homogeneous material, in which cracking could be induced from stress concentrators within the structure. It was noted that the fracture toughness values for these two materials sintered in nitrogen were also very low. The tensile strength and fracture toughness of the other materials were affected by the reducing atmosphere but as has been suggested, this could be due to the lack of available liquid-phase

material, leading to a more porous and therefore weaker structure.

#### 4.2. Electrical properties

A less-oxidizing atmosphere subdued the PTCR effect substantially which may be attributed to the inability of holmium to diffuse into the barium titanate lattice under these conditions. However, annealing in air allowed the diffusion to take place and hence produced a material which exhibited very similar PTCR properties to that sintered in air. The use of higher

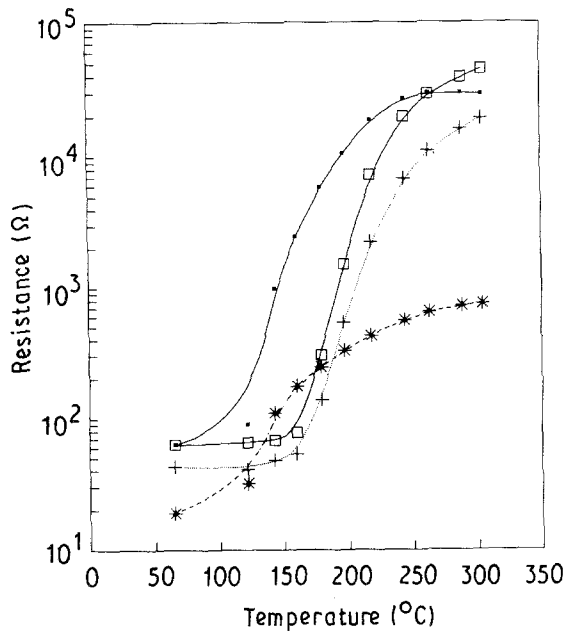


Figure 8 Resistance-temperature plots for mixes 1-4 sintered in 40% nitrogen and 60% oxygen. Mix: (●) 1, (\*) 2, (+) 3, (□) 4.

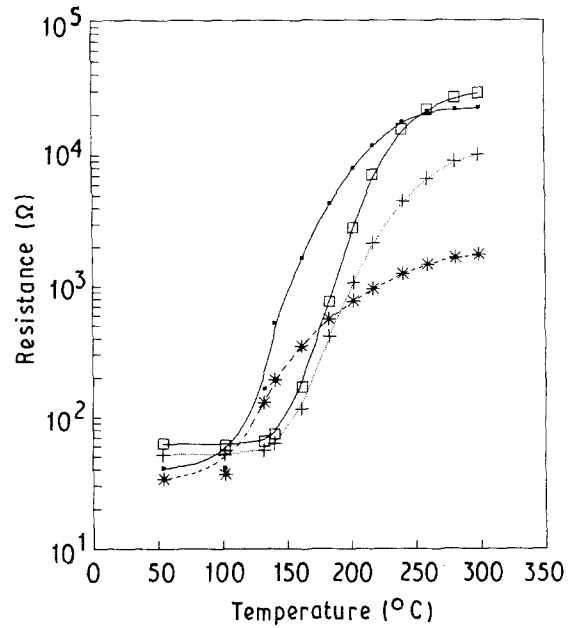


Figure 10 Resistance-temperature plots for mixes 1-4 sintered in 100% oxygen. Mix: (●) 1, (\*) 2, (+) 3, (□) 4.

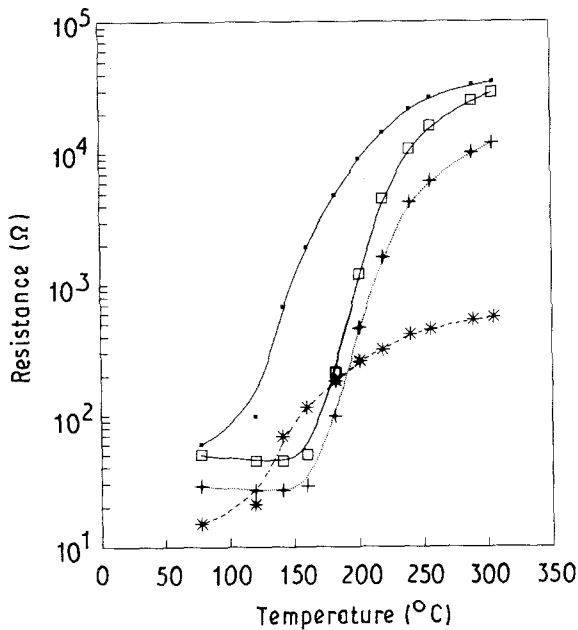


Figure 9 Resistance-temperature plots for mixes 1-4 sintered in 20% nitrogen and 80% oxygen. Mix: (●) 1, (\*) 2, (+) 3, (□) 4.

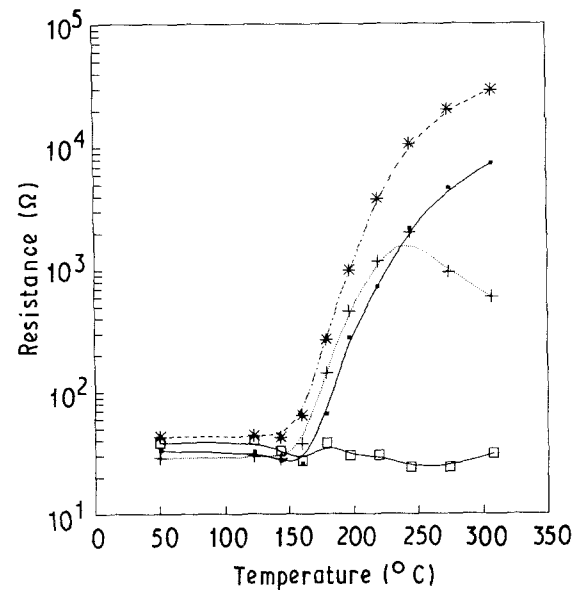


Figure 11 Resistance-temperature plots for mixes 3 and 4 sintered under the conditions indicated. Mix: (●) 4, Elmwood; (\*) 4, Durham; (+) 3, Durham; (□) 4, vacuum.

partial pressures of oxygen produced no advantageous changes in the PTCR effect. This indicates that an air atmosphere is sufficiently oxidising to allow full diffusion of the additives into the matrix.

## 5. Conclusion

An air atmosphere produces favourable sintering conditions for the production of barium titanate PTCR devices. A more oxidizing atmosphere produces only limited advantages – a small but significant increase in strength. For a commercial process it is important to monitor sintering atmosphere to ensure

that the oxygen content does not fall substantially below 20%. At partial pressures below 0.2 bar, extremely poor electrical and mechanical properties were obtained.

## Acknowledgements

The provision of a SERC studentship for one of us (J.M.B.) is gratefully acknowledged. The authors also thank Dr H. M. Al-Allak and other colleagues from the Applied Physics Division of the School and Mr P. D. Thompson, Elmwood Sensors Ltd, for many stimulating discussions.

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*Received 29 September  
and accepted 21 October 1992*