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Direct measurement of electrical and compositional inhomogeneities in PTC thermistors

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Abstract

Positive temperature coefficient (PTC) thermistors, based on donor doped barium titanate, show a large, reproducible increase in grain boundary resistance over a small temperature interval just above the Curie temperature (T_C). T_C can be increased by additions of lead, and reduced by adding strontium. In recent times thermistors have been prepared containing additions of both lead and strontium along with other dopants to modify device performance. However, the distribution of these dopants is rarely homogeneous, giving rise to local differences in the functional properties of these devices, which affect the overall behaviour. Electron microprobe analysis of a commercial thermistor disc has revealed a depletion of lead, together with calcium and strontium enrichment in a zone ~300 μm from the surface of the sintered pellet concurrent with a small decrease in grain size. Local resistance-temperature (*R–T*) measurements have also demonstrated that T_C is decreased and the pre-switching resistance increased in the near surface region.

Keywords: $BaTiO_3$; Electrical properties; Grain size; Local properties; Thermistor

1. Introduction

The functionality of PTC thermistors, based on donor doped $BaTiO_3$ ceramics is due to an anomalous increase in resistance on heating through the Curie temperature (T_C). T_C is approximately 130 °C in $BaTiO_3$ but suitable A-site doping with divalent cations allows it to be shifted to higher or lower temperature ranges, as illustrated in Fig. 1.[1] Recently, thermistors have been prepared with compensating additions of both lead and strontium.[2] Although it is the case that the effects of lead and strontium on T_C are in opposite directions, both are sometimes added to commercial compositions, where the lead enhances liquid phase sintering at lower temperatures and the strontium compensates the change in T_C caused by the lead addition. Calcium is also a common additive but does not greatly influence T_C, being mainly added for grain size control.[3]

The PTC effect in $BaTiO_3$ thermistors is generally accepted to be a grain boundary effect, with the grain interiors remaining conductive above T_C.[4,5] Several studies of the behaviour of individual grain boundaries have shown that the PTC effect is heterogeneous in nature, with the overall response of the pellet being dominated by a small number of highly resistive boundaries, whilst other boundaries show little or no PTC behaviour.[6–9] The observed differences in the magnitude of the PTC effect between grain boundaries are believed to be due to variations in the amount of segregating dopants at different interfaces, brought about by inhomogeneous processing or differences in grain boundary structure.[10]

In this study, compositional variations across a cross-section of a commercial PTC thermistor were characterised and correlated with local differences in *R–T* response, and microstructure.

2. Experimental

The thermistor samples used in this study were based on a commercial formulation of donor doped $BaTiO_3$, containing relatively high additions of lead, strontium and calcium. The samples were provided as disks 8 mm in diameter and 2 mm in thickness. A cross-section of each sample was prepared by sectioning a pellet across

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the diameter followed by polishing using 0.25 μm diamond paste.

Compositional analysis of the pellets was carried out using a Cameca SX100 Wavelength Dispersive Spectroscope (WDS) operating at 15 KeV beam energy and 20 nA beam current.

Local *R–T* characteristics were measured within a grid of 100 μm square electrodes, spaced 25 μm apart, which was deposited using a photolithographic process onto the polished cross section of the thermistor. An ohmic contact was obtained by using a dual layered electrode, with a titanium base layer covered by silver. Electrical contacts were made by micro-bonding 25 μm diameter gold wires to pairs of electrodes (Fig. 2). The sample was mounted in a tube furnace and connected through the lead out wires to a Keithley 487 picoammeter with internal voltage source (Fig. 3). This set up ensured an homogenous temperature distribution over the sample and allowed accurate local resistance measurements to be made from room temperature up to 300 °C.

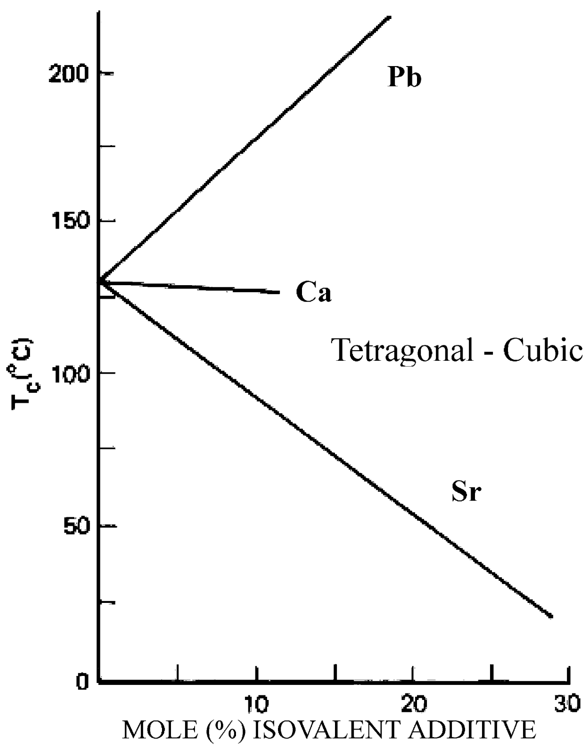

Fig. 1. Shift in Curie temperature and associated phase transformations as a function of dopant conentration (after Hill and Tuller[1]).

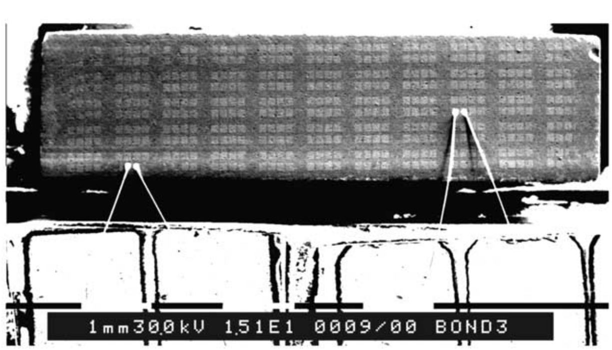

Fig. 2. Specimen configuration for local *R–T* measurements.

3. Results and discussion

A backscattered electron image of the polished surface of the sample is shown in Fig. 4, in which the extensive twinning gives rise to channelling contrast. Also visible are the edges of the electrodes used for the local *R–T* measurements at the extreme left and right hand sides of the image.

Compositional line-scan data, collected along the path indicated in the inset of Fig. 5, showing the variations in

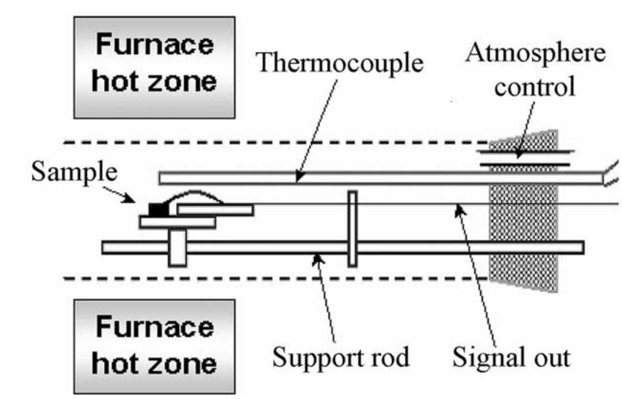

Fig. 3. Furnace based local *R–T* measurement rig.

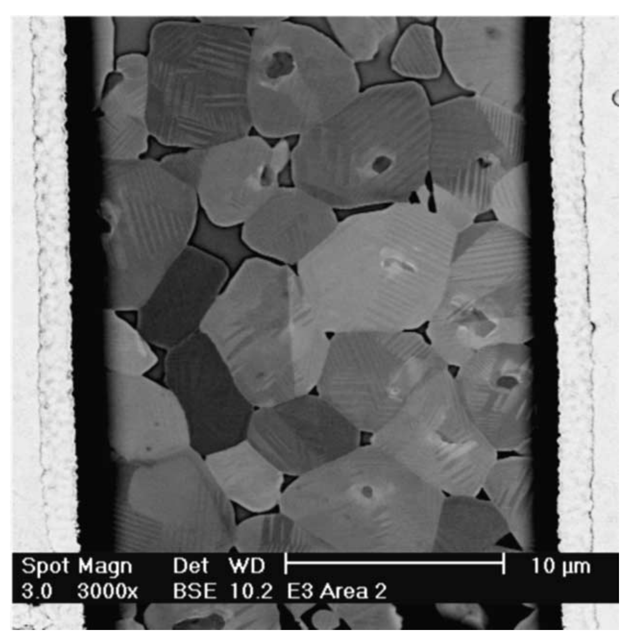

Fig. 4. Backscattered electron image of inter-electrode sample area showing extensive twinning.

lead, strontium, calcium and barium concentrations between the central and surface regions of the thermistor disk sample are presented in Fig. 5. Lead loss due to volatilization from the sample during sintering results in a surface zone approximately 300 μm thick, which is depleted in lead. The surface loss of lead is predominately compensated by barium with some enrichment in strontium and calcium. DSC studies have indicated that this lead volatilisation initiates at 1150 °C during sintering and becomes more rapid as the sintering temperature is increased.

Grain size measurements were carried out in the central and near-surface regions of the sintered pellet. It was found that the mean grain size decreased from 4.0 μm in the centre to 3.7 μm at the surface. This variation is attributed to a small grain refining effect due to increased Ca levels in the depletion zone. [3,11]

Comparative local R–T measurements were made in the central and near-surface regions of the thermistor (Fig. 6). The 25μm separation of the electrode pairs used for each measurement corresponds to approximately six

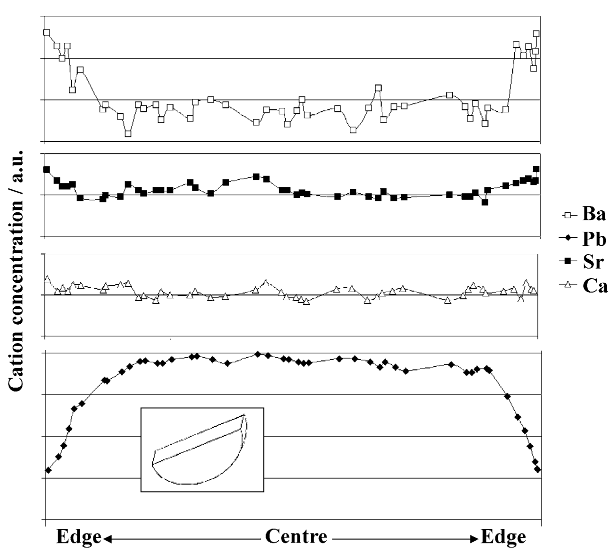

Fig. 5. Compositional variation of Pb, Sr, Ca, Ba with distance between disk faces.

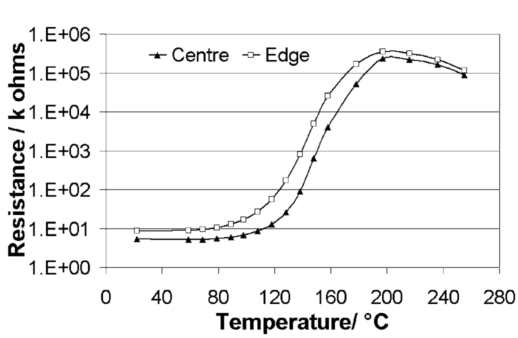

Fig. 6. Local R–T responses from the centre and near-surface regions of the thermistor.

grain diameters within the specimen. A PTC effect was observed in both regions, but T_C was found to be lower near the surface, which is consistent with the decreased levels of Pb in this region. Additionally the resistance below T_C was found to be lower at the centre of the pellet and the peak resistance was higher in the near-surface region, concurring with earlier work examining the effect of lead and strontium additions on the bulk PTCR response of $BaTiO_3$ based samples.[12]

By extrapolating the linear section of each R–T characteristic above T_C (Fig. 6) back to an appropriate baseline, an approximate value for the T_C offset between the central and near-surface regions of the thermistor was calculated and found to be 11 °C. This may be compared with a value calculated from the compositions of the thermistor at the points where the R–T measurements were made, and adjusting the value of T_C according to the relationships shown in Fig. 1. At the position of the near surface electrodes the lead content was depleted by approximately 3.4 at.%, and the strontium enhanced by approximately 1 at.% compared with the centre of the pellet. By referring to Fig. 1 we can estimate a decrease in T_C of 17 °C due to the reduction in lead concentration, and an increase in T_C of 5 °C due to the strontium substitution near the surface. Consequently, the predicted T_C offset between the centre and edge regions, based on the compositional analyses, is 12 °C. Hence the difference in T_C observed between the R–T measurements can be attributed solely to the compositional inhomogeneity introduced during sintering.

The lowering of T_C near the surface of the thermistor disk will result in a locally inhomogeneous R–T response during high current excursions, since in this region it will switch into the high resistance state at a lower temperature. This may lead to inhomogeneous Joule heating rates across the pellet and thus generate non-uniform stress concentrations in the component.

4. Conclusions

Large compositional variations were found to be present in a commercial thermistor disk, primarily due to lead loss by volatilization above 1150 °C during sintering. The lead loss near the surface is predominantly compensated by barium enrichment, with some increase in strontium and calcium, forming a 'shell' region approximately 300 μm thick at the sample surface. The grain size of the thermistor was found to decrease slightly from 4.0 μm at the centre to 3.7 μm near the surface.

Measurement of local R–T characteristics in the centre and near-surface regions of the thermistor disk show a suppression of T_C in the lead depleted edge region of approximately 12 °C compared with the central region.

Acknowledgements

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