Microstructures of BaTiO3 based PTC thermistors with Ca, Sr and Pb additions

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$BaTiO_3$-based PTC thermistors undergo a large and rapid increase in resistance just above the Curie temperature, T_C. The resistance increase is predominantly associated with an increase in grain boundary barrier height, and therefore it is important to gain information about the grain boundary character in these thermistors and to combine this understanding with electrical data. Increasingly complex formulations are being marketed commercially in order to tailor properties for specific applications and as well as varying the concentrations of donor and acceptor dopants, isovalent substitutions on the A-site are becoming more common.

In this study the microstructures of three different $BaTiO_3$ PTC thermistor formulations were compared by transmission electron microscopy. The samples differed in the A-site substitutions, giving the formulae: (1) $BaTiO_3$, (2) (Ba, Ca)TiO_3, (3) (Ba, Ca, Sr, Pb)TiO_3.

No grain boundary films were observed in any of the samples, although rounding of grains at the grain junctions was evidence of a liquid 2nd phase being present during sintering. EDX measurements were made across grain boundaries but no significant segregation of elements to the boundaries was observed.

All the samples had a spread of twin widths between a few 10s and a few 100s of nanometres wide. Ferroelectric, deformation and single annealing twins were observed in all samples. The $BaTiO_3$ sample also had double annealing twins.

In the Sr, Pb, Ca doped sample, some grains contained zones about 1 μm diameter, which were not twinned and had a similar composition to the surrounding grain. The interface with the host grain was sharp but contained a misorientation of a few degrees.