The influence of grain boundary impedances on the electrical properties of $CaCu_3Ti_4O_{12}$ ceramics.

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There has been a lot of speculation regarding the electrical properties of an unusual perovskite (ABO_3)-type material, $CaCu_3Ti_4O_{12}$ which contains Ca and Cu(+II) ions on the A-site and Ti(+IV) on the B-site. Fixed frequency capacitance measurements in the kHz – MHz region show a dramatic decrease in permittivity from values as high as ~350,000 at room temperature to ~ 100 below ~ 100–150 K. $CaCu_3Ti_4O_{12}$ is centrosymmetric at room temperature (space group Im3) and does not exhibit any subambient crystallographic phase changes down to ~ 35K[1]. Despite the lack of any evidence for a lowering of crystal symmetry, this so-called 'giant dielectric effect' has been ascribed to an intrinsic phenomenon related to the high polarisibility of the Ti-ion in this unusual variant of the perovskite structure by several groups[1-3].

Recently we have used Impedance Spectroscopy (IS) to characterise the electrical microstructure of $CaCu_3Ti_4O_{12}$ ceramics[4,5] and have proposed a much simpler explanation for its dielectric behaviour. As opposed to fixed frequency measurements, IS requires the use of an equivalent circuit[6] (some combination of resistors and capacitors) to model the observed response over a wide range of frequency and temperature. This leads to a more comprehensive understanding of the electrical properties and shows $CaCu_3Ti_4O_{12}$ ceramics to be electrically heterogeneous and to consist of insulating grain boundaries and semi-conducting grains; an electrical microstructure which is consistent with that of an internal barrier layer capacitor.

Here we provide further evidence to support this model by showing how ceramic microstructure and the oxygen partial pressure in which ceramics are processed influence the electrical properties and in particular the grain boundary regions. Many unanswered questions remain regarding the electrical properties of $CaCu_3Ti_4O_{12}$. In particular, what is the origin of the bulk semiconductivity and what is the composition or nature (twinning) of the grain boundary regions? It is clear, however, that the giant dielectric effect is associated with an extrinsic phenomenon and that it is possible to generate room temperature (effective) permittivity values in excess of 250, 000 by processing ceramics in a single-step in air.

$CaCu_3Ti_4O_{12}$-based ceramics may represent an alternative to $BaTiO_3$-based materials currently used in internal barrier layer capacitor applications as these require complex, multi-stage processing routes to induce room temperature effective permittivity values of ~ 60,000 – 100,000.

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