

# Multilayer Ceramic Capacitor Case Study

## **Background**

A large variety of modern electronic devices required capacitors as part of their function. Perhaps most notable of these devices are mobile phones, which need large numbers of capacitors as well as those capacitors to be of a small size. For this task, multi-layer ceramic capacitors are better suited than single layer cylindrical capacitors, both due to their smaller size (for equivalent capacitance) and effective high frequency response.

## **Problems with MLCCs**

Multi layer ceramic capacitors (MLCCs) have traditionally been made with screen-printed layers of capacitor ceramic and palladium or platinum electrodes. While lead-based ceramics are available that work with different electrodes after sintering, environmental and health concerns have prevented these from becoming common. Instead, considerable effort has been placed on making conventional barium titanate ( $BaTiO_3$ ) MLCCs work with copper or nickel electrodes. As these electrodes need to be fired in a reducing environment so as to avoid oxidation of the metal making it ineffective, measures then need to be brought in to prevent the ceramic reducing and losing oxygen from its lattice, which can result in a semiconducting rather than capacitive behaviour.

To describe more fully – when exposed to a strongly reducing atmosphere at high temperatures, some of the oxygen atoms in the  $BaTiO_3$  escape the lattice. The vacancies left behind appear to have a charge of 2+ relative to the lattice as a whole (they are actually neutral, but occupy the location that should be held by a 2- oxygen). When the capacitor is in use, repeatedly charging and discharging, these vacancies can migrate as charge carriers (akin to holes in a semiconductor). The migration of oxygen vacancies to one electrode and of excess oxygen to the other results in the ceramic layer becoming similar to a PN junction and ceasing to be effective as a capacitor. As such, nickel electrode MLCCs have tended to display rather short lifetimes, especially when compared with palladium electrode base devices.

## **Solutions to the oxygen migration problem**

Research had found that adding yttrium (in  $Y_2O_3$ ) to the ceramic along with  $MnO$  could prevent the ceramic from reducing so easily when exposed to a reductive atmosphere for sintering. The suggestion was made that metals with ionic radii suitable to allow dissolution into either barium or titanium sites appeared to prevent reduction. The studies in this paper then investigated doping with a selection of Lanthanoid elements – lanthanum, neodymium, samarium, gadolinium, dysprosium, holmium and erbium. Dy, Ho and Er doped MLCCs all showed substantial improvements in lifetime.

Use of TEM and EDX analysis showed that the ceramic formed small grains when formed into the layers, with the grains themselves exhibiting a core-shell structure. The core contains almost pure  $BaTiO_3$  while the shell contains all the dopants – magnesium and the lanthanoid.

## **Effect of Lanthanoid Doping**

The doping showed an effect on resistivity of the ceramic. The larger ions produced relatively low resistivity compared to undoped, suggesting a large number of

oxygen vacancies in the material, while the dopants with ionic radii between those of *Ba* and *Ti* produced higher resistivities, similar to that of an undoped MLCC.

Studies were conducted into the capacitance change over a long cycle of use (up to around 1000 hours). *Ho*, *Dy* and to a lesser extent *Er* doped MLCCs showed relatively small capacitance changes. Hysteresis loops were measured of the different doped capacitors and found that the change in capacitance observed was related to increasing remnant polarization of the ceramic. Such permanent polarization is thought to be the result of the migration of oxygen vacancies. TEM analysis showed that the larger ion dopant samples (those with the greatest change in capacitance) exhibited small “dislocation loops” in their structure – artefacts produced by the collection and movement of oxygen vacancies. The *Ho*-doped sample however (the most stable over time) displayed none of these features, suggesting that *Ho* presence is the crystal structure of the shell reduced oxygen vacancy presence.

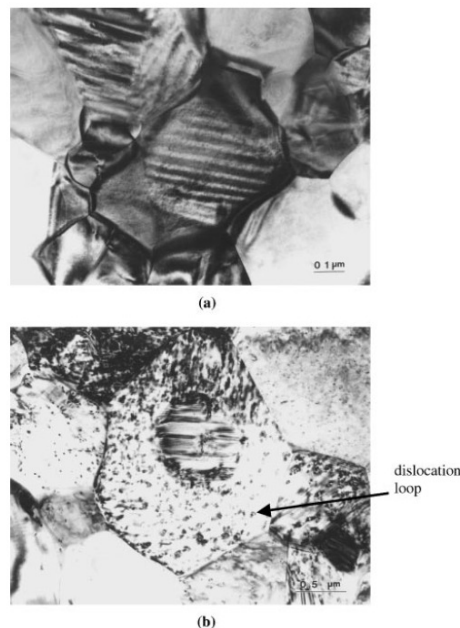


Fig. 10. TEM photographs of rare-earth-oxide-doped X7R ceramics. (a)  $\text{Ho}_2\text{O}_3$ , (b)  $\text{Sm}_2\text{O}_3$ .

### Other Dopants

Magnesium (in *MgO*) was also found to be a necessary dopant to create the correct properties in the ceramic. The presence of *Mg* reduces grain sizes and also appears to stop the lanthanoid ions from diffusing into the core.