

# A quick method to determine the capacitance characteristics of thin layer X5R multilayer capacitors

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## Abstract

The effect of  $Y_2O_3$  concentration on the dielectric properties of ceramic disc capacitors and multilayer capacitors containing 50 dielectric layers with an approximate thickness of  $3\ \mu\text{m}$  were investigated. The relative permittivity and temperature coefficient of capacity of multilayer capacitors at low and high applied field suggest that two types of microstructures formed, depending on yttrium doping concentration. Yttrium concentrations of 1.5–2.0 mol% yielded identical relative permittivities over a wide temperature range. The permittivities at  $Y$  concentrations of 2.6–3.0 mol% were also identical, but somewhat higher. The relative permittivity of ceramic disc capacitors of similar composition, determined from hysteresis loop measurements as function of applied field, was compared with field-dependent permittivity measurements on multilayer capacitors. The results indicate that polarization measurements on CDCs are a good indicator for the relative permittivity values of MLCCs.

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**Keywords:** BaTiO<sub>3</sub>; Y<sub>2</sub>O<sub>3</sub>; Hysteresis loop; Dielectric properties; Capacitors

## 1. Introduction

Developments in the electronics industry are driven by miniaturization, the addition of more functionality in electronic devices, and cost reduction. As a consequence passive components like multilayer ceramic capacitors (MLCC) should achieve an increasingly high volumetric efficiency. There is an ongoing demand to increase the volumetric density by using thinner dielectric layers and higher layer numbers in successively smaller case size capacitors. Currently the thickness of dielectric layers of high capacitive MLCCs has already been reduced to below  $1\ \mu\text{m}$  and the number of active layers can range from 500 to 1000. Furthermore, the demand of temperature stable capacitors and high relative permittivity increased over the last decade. The dielectrics should also perform better and their electrical properties should be more reliable. Thus,

capacitors having X5R characteristics are being used in electronic applications.<sup>1–4</sup> The X5R capacitors, as specified by the Electronics Industries Alliance (EIA), show a capacitance drift that may not exceed 15% of the nominal capacitance value at 25 °C in a temperature range from –55 to 85 °C. These types of dielectrics are based on modified BaTiO<sub>3</sub> with a microstructure of core–shell grains. The core–shell grains consist of a ferroelectric core of almost pure BaTiO<sub>3</sub> and a para-electric shell of doped BaTiO<sub>3</sub>, which is formed by controlled addition of various elements.

Nowadays X5R multilayer capacitors are produced with nickel electrodes because of their low cost. Sintering of MLCCs therefore has to be carried out in an atmosphere having a low oxygen partial pressure ( $pO_2$ ) in order to prevent nickel from oxidizing. Numerous studies on the development of high permittivity dielectrics with high insulation resistivity values and good stability regarding temperature and applied electrical fields have been carried out since the 1980s. For X5R capacitors with base metal electrodes typically dielectrics based on BaTiO<sub>3</sub>, doped with MgO, MnO, SiO<sub>2</sub> and one of the ‘magic’ dopants, Ho<sub>2</sub>O<sub>3</sub>, Dy<sub>2</sub>O<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub>, are used.<sup>5–10</sup>

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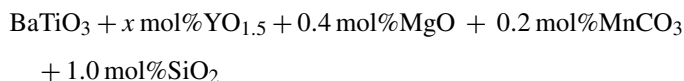
When the thickness of the dielectric layers in MLCCs is decreased, the electrical field is increased accordingly when a specific alternating current (AC) or direct current (DC) is applied. Therefore changes in dielectric properties occur, e.g. permittivity, loss factors, temperature stability, and reliability. Furthermore, the temperature independency of the dielectric constant is affected by changes of applied electrical field. It has nonetheless been possible to make temperature stable dielectrics for ultra thin layers with X5R characteristics by modifying the chemical composition and microstructure of the ceramics.

It is common in materials development to examine the properties of dielectrics in terms of electrical characteristics like relative permittivity and temperature coefficient of capacitance (TCC) directly on multilayer capacitors having ultrathin dielectric layers. However, the making of multilayer capacitors is laborious and costly. If ceramics disc capacitors (CDC) could be made and their electrical properties could be correlated directly with the behaviour in MLCCs, development time could be reduced significantly.

In the present study a method is proposed to evaluate the relative permittivity ( $\epsilon_r$ ) of CDCs in response to an applied AC electrical field by measuring the polarization versus applied electrical field. The slope of the hysteresis loops corresponds to  $\epsilon_r \cdot \epsilon_0$ , where  $\epsilon_0$  is the permittivity of vacuum.<sup>3</sup> These results are compared to the results from relative permittivity measurements on MLCCs versus applied AC electrical field.

## 2. Experimental

The ceramic disc capacitors (CDC) were made starting from powders of BaTiO<sub>3</sub> (NCI) and Y<sub>2</sub>O<sub>3</sub> (Rhodia), SiO<sub>2</sub> (Degussa, Aerosil R975), MnCO<sub>3</sub> (J.T. Baker, 99.0%) and MgO (Konoshima, 99%). The powders were weighed according to the formula



where  $x = 3.0, 2.6, 2.1$  or  $1.5$ . The powders were ball-milled with 2 mm YTZ beads in an ethanol–toluene solvent mixture until a  $D_{50}$  of 0.2  $\mu\text{m}$  was reached. The powders were dried, grounded and then the powders were pressed uniaxially (Fontijne SRA100) into pellets of 10 mm diameter  $\times$  2 mm height. Nickel electrodes were applied and the CDCs were sintered in a tube kiln (Carbolite) at 1280 °C for 2 h in a wetted 0.3% H<sub>2</sub>/N<sub>2</sub> atmosphere. They were then re-oxidized at 1000 °C for 2 h in wetted N<sub>2</sub>. The  $P$ – $U_{\text{applied}}$  hysteresis loops were measured at AC fields of 50, 150, 300, 450, 800, 900 and 1000 V mm<sup>−1</sup> with an RT6000 HVS-2 analyzer (Radiant Technologies Inc.).

Green MLCC chips of above-mentioned compositions were produced on regular production equipment at Yageo in Roermond, The Netherlands. The MLCCs of 3.2 mm  $\times$  1.6 mm  $\times$  0.4 mm in size consisted of 50 electrode layers. The dielectric thickness of the MLCCs after sintering were between 2.2 and 2.6  $\mu\text{m}$ ; the electrode thickness was around 1  $\mu\text{m}$ . Copper terminations were applied onto the chips, which were cured at 900 °C in a N<sub>2</sub> atmosphere.

The capacitances were measured at 1 kHz and under an applied electrical field ranging from 0.02 to 5 V<sub>rms</sub> using a HP4284A LCR meter. The temperature coefficients of capacitance (TCC) of the samples were measured by measuring the capacitances respectively at 1 kHz/1 V<sub>rms</sub> and 1 kHz/0.02 V<sub>rms</sub> from −55 to +125 °C using a HP4284A LCR meter. The temperature was controlled using a Keithley 740 system scanning thermometer. This measurement setup was controlled by a computerized control system with data acquisition. The microstructures of the ceramics were examined using a scanning electron microscope (Philips XL20) after the MLCC samples were chemically etched for several seconds using a 1% HCl/1% HF solution. The  $I$ – $V$  curves were measured by determining the leakage current at 150 °C using a setup consisting of a Keithley K617 electrometer and an oven.

## 3. Results and discussion

The relationship between relative permittivity and applied AC field was investigated for X5R dielectrics with varying Y<sub>2</sub>O<sub>3</sub> concentrations. The relative permittivity values of the ceramic disc capacitors were determined by polarization hysteresis loops of samples at electrical fields strengths of 50–1000 V mm<sup>−1</sup>. Fig. 1 shows an example of polarization ( $P$ ) versus applied electrical field ( $U_{\text{applied}}$ ) curves for a CDC sample measured at various electrical fields. The  $P$ – $U_{\text{applied}}$  loops were measured at 1 kHz. From the slope of the  $P$ – $U_{\text{applied}}$  curves the relative permittivity was calculated by dividing the maximum polarization by the maximum applied electrical field. Fig. 2 shows the results of the relationship between  $\epsilon_r$  and  $U_{\text{applied}}$  of the four CDC samples. The  $\epsilon_r$ – $U_{\text{applied}}$  dependency seems to have a maximum at 500–700 V mm<sup>−1</sup>. At low  $U_{\text{applied}}$  the value of  $\epsilon_r$  is low because of random polarization in the domains. When  $U_{\text{applied}}$  is increased the domain walls shift and an enhanced polarization is accomplished due to an increase of dipole motion, until a maximum polarization is reached at a certain  $U_{\text{applied}}$ . At even higher electrical fields the relative permittivity is decreased due to the non-linearity of the  $P$ – $U_{\text{applied}}$  curve. The results in Fig. 2 also show that the  $\epsilon_r$ – $U_{\text{applied}}$  curves vary depending on the Y<sub>2</sub>O<sub>3</sub> concentration in the compositions. The value of  $\epsilon_r$  of dielectrics with a low Y<sub>2</sub>O<sub>3</sub> concentration show low dielectric constants compared to the dielectrics with higher Y<sub>2</sub>O<sub>3</sub> concentration.

The dependency between  $\epsilon_r$  and applied AC electrical field was also examined for the same dielectrics via measurements on MLCCs. The results in Fig. 3 indicate a similar relationship between applied electrical field and relative permittivity. Initially an increase of the relative permittivity versus  $U_{\text{applied}}$  is seen, until a maximum  $\epsilon_r$  is reached at a certain applied electrical field. When higher AC fields were applied the  $\epsilon_r$  decreased to lower values. This trend is similar as in CDCs.

The  $\epsilon_r$ – $U_{\text{applied}}$  curves of the dielectrics with 1.5 and 2.0 mol% yttrium were similar. At higher Y concentrations the values of  $\epsilon_r$  at given  $U_{\text{applied}}$  were higher. At electrical field strengths below  $\sim 0.8 \text{ V } \mu\text{m}^{-1}$ , the permittivity seems to be slightly lower for dielectrics having 2.6 mol% Y than for dielectrics with 3.0 mol% Y. Above 1 V  $\mu\text{m}^{-1}$ , the dielectrics with 3.0 mol% Y had slightly lower  $\epsilon_r$  values than the dielectrics

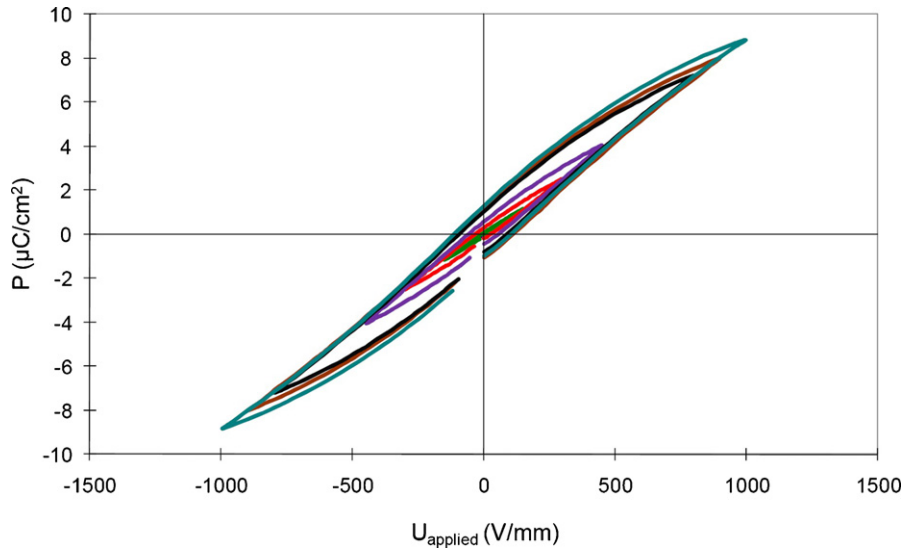


Fig. 1. Hysteresis loop of CDC sample containing 1.5 mol%  $Y_2O_3$ .

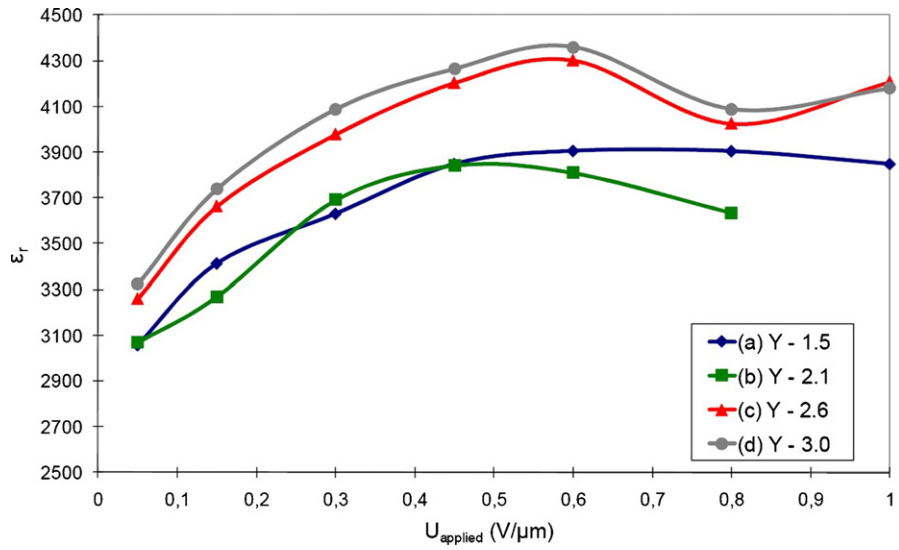


Fig. 2. Relative permittivity as function of applied electrical field in CDC samples.

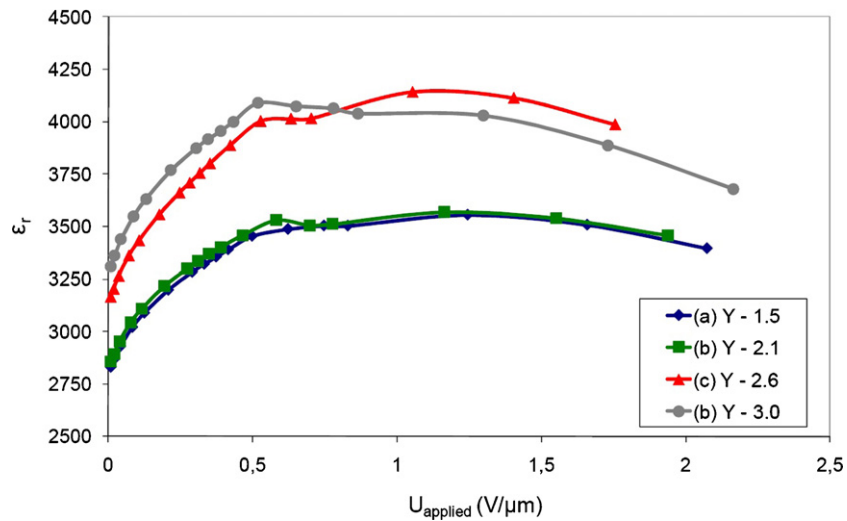


Fig. 3. Relative permittivity as function of applied electrical field in MLCC samples.

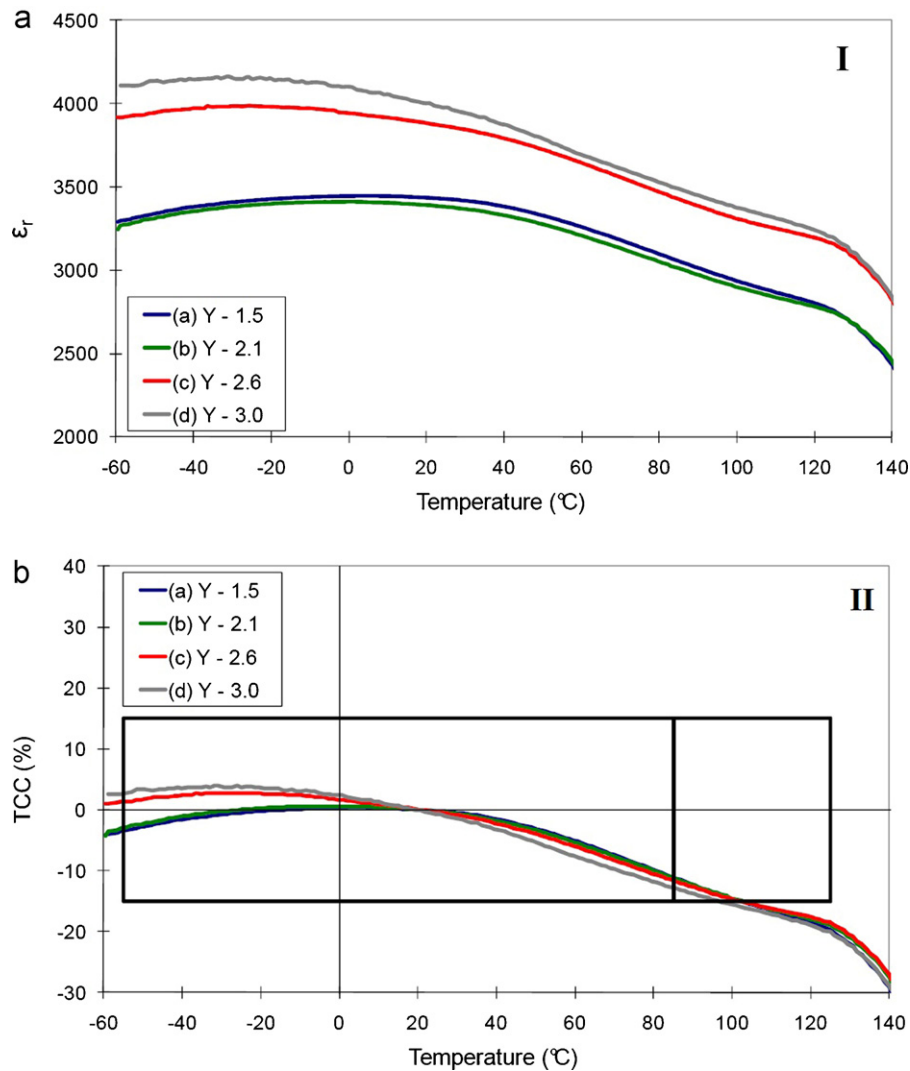


Fig. 4. (a) Relative permittivity and (b)  $\Delta C/C$  of MLCCs as function of temperature measured at  $0.4 \text{ V}/\mu\text{m}$  and  $1 \text{ kHz}$ . The X5R and X7R specification boxes are highlighted.

with 2.6 mol% Y. In any case the difference between the two curves was small and we assume that these curves are identical within experimental error.

The results shown in Fig. 3 suggest that two distinct types of microstructures formed, depending on yttrium concentration. The microstructure with low concentrations of yttrium had low permittivities, while the microstructure with high concentrations of  $\text{Y}_2\text{O}_3$  showed higher permittivities. The difference between the  $\epsilon_r-U_{\text{applied}}$  characteristics of samples with lower (1.5–2.0 mol%) and higher (2.4–3.0 mol%) Y concentrations were also observed in Fig. 2. Because both trend and absolute  $\epsilon_r$  values were approximately similar for the series of measurements on CDCs and MLCCs, it can be concluded that direct measurements on CDCs are a good indicator for the  $\epsilon_r$  values of MLCCs.

The temperature dependency of  $\epsilon_r$  of MLCCs is very dependent on field strength. Because the core consists of ferroelectric  $\text{BaTiO}_3$  the applied field strength dictates the  $\epsilon_r$ .<sup>3</sup> To study the effect of field strength on the  $\epsilon_r-T$  relationship, measurements were performed on MLCCs at both high and low applied field,

employing field strengths of  $0.4 \text{ V}/\mu\text{m}$  and  $0.008 \text{ V}/\mu\text{m}$ , respectively. The frequency in both measurements was  $1 \text{ kHz}$ . Fig. 4I and II show the temperature dependency of  $\epsilon_r$  and TCC of the MLCC samples measured at high field. The results in Fig. 4I shows that the TCC curves of the four samples are relatively flat and that the capacitors can meet the X5R specification. Fig. 4I shows that the  $\epsilon_r-T$  curves are dependent on the  $\text{Y}_2\text{O}_3$  concentration and the  $\epsilon_r-T$  curves of the four samples follow a similar trend in relation to temperature change above room temperature.

Fig. 5I and II shows the results of temperature dependency of  $\epsilon_r$  and TCC of MLCCs at low applied field. The permittivity  $\epsilon_r$  of these samples is less dependent on  $T$  than at higher AC field. However, due to the smaller field the  $\epsilon_r$ -values dropped, especially when measured well below the Curie temperature of  $125^\circ\text{C}$ .

Around and above  $125^\circ\text{C}$   $\epsilon_r$  was not influenced by an AC field. The Curie temperature of the core phase did not change due to the presence of Y. At lower temperatures  $\epsilon_r$  is much more dependent on the applied AC electrical fields due to the occur-

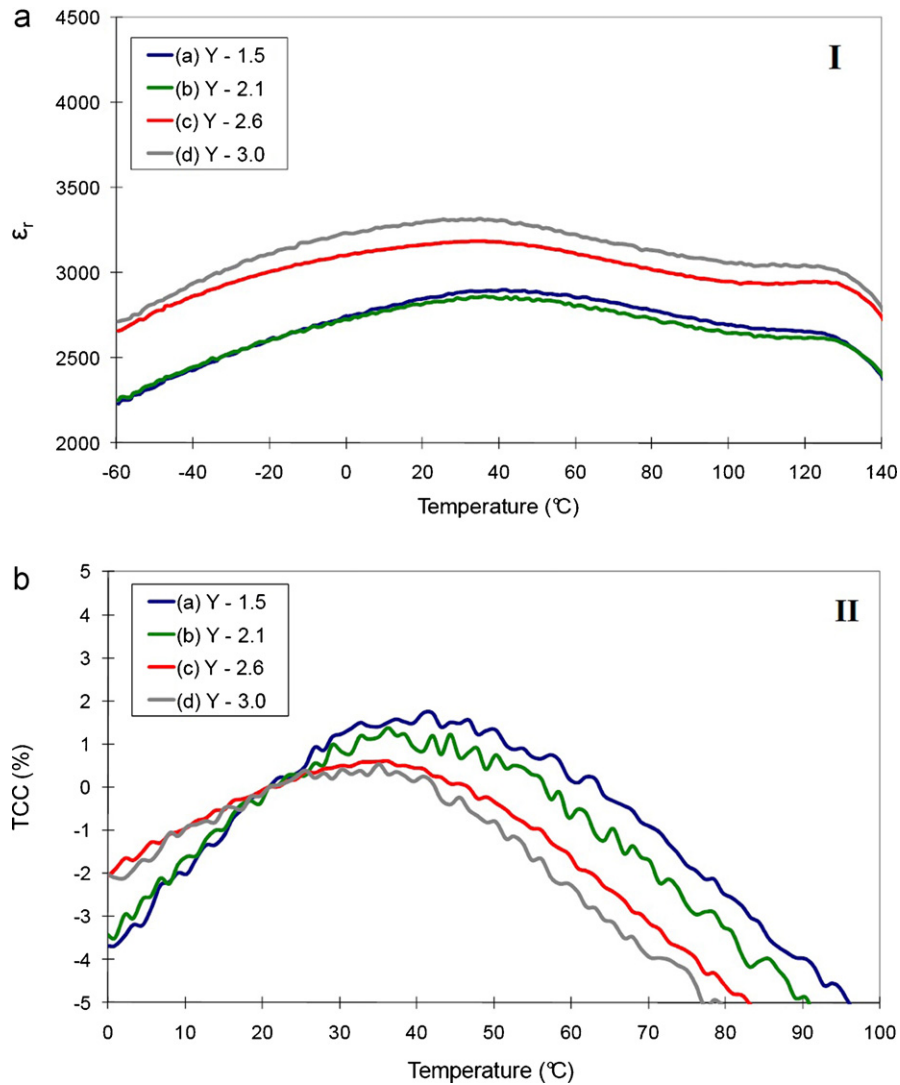


Fig. 5. (a) Relative permittivity and (b)  $\Delta C/C$  of MLCCs as function of temperature measured at 8 mV/ $\mu\text{m}$  and 1 kHz.

rence of ferro-electricity, which is related to the tetragonal and orthorhombic crystal structure of  $\text{BaTiO}_3$ .

When foreign elements are reacted with  $\text{BaTiO}_3$ , then a shell of inhomogeneously distributed chemical composition with different properties than the core phase forms. The incorporation of foreign elements usually shifts the Curie temperature. When the TCC of the samples were measured at low AC field the shift of the Curie temperature of the shell phase could be determined. The results are shown in Fig. 5I. The TCC of the various MLCC samples show a maximum that represents the Curie temperature of the shell phase. The results show that with increasing amount of  $Y$  the Curie point shifts to lower temperatures (see Table 1).

As the dielectric properties can be controlled by adjusting the formulation, the influence of  $Y$  concentration on microstructure was examined. Fig. 6 shows the SEM micrographs of various dielectric ceramics sintered at  $1280^\circ\text{C}$ . The  $Y_2O_3$  concentration is important as grain growth of the core-shell grains can be largely influenced by the ratio and amount of added elements like  $\text{MgO}$ ,  $Y_2O_3$  or  $\text{Mn}_3O_4$ . From our results, it was observed that dielectrics having an  $Y$  concentration of 3 mol% had a relatively

fine grain structure of small grains combined with few larger grains. When the  $Y_2O_3$  concentration was smaller, the average grain size was slightly larger. However, this slight variation of grain size will have an effect on the electrical characteristics of the dielectrics.

To realize highly reliable dielectrics,  $\text{MgO}$ ,  $\text{Mn}_3O_4$  and one of the magic dopants,  $Y_2O_3$ ,  $\text{Ho}_2O_3$  or  $\text{Dy}_2O_3$ , are usually added to produce core-shell X5R dielectrics. The electrical resistivity of these types of dielectrics is determined by the chemistry of the grain boundaries and generally show varistor-like  $I$ - $V$  characteristics.<sup>11</sup> Therefore, the  $I$ - $V$  characteristics were measured

Table 1  
 $T_c$  of shell phase.

$YO_{1.5}$ (mol%)	Curie temperature ( $^\circ\text{C}$ )
1.5	42.0
2.1	38.0
2.6	36.2
3.0	35.0

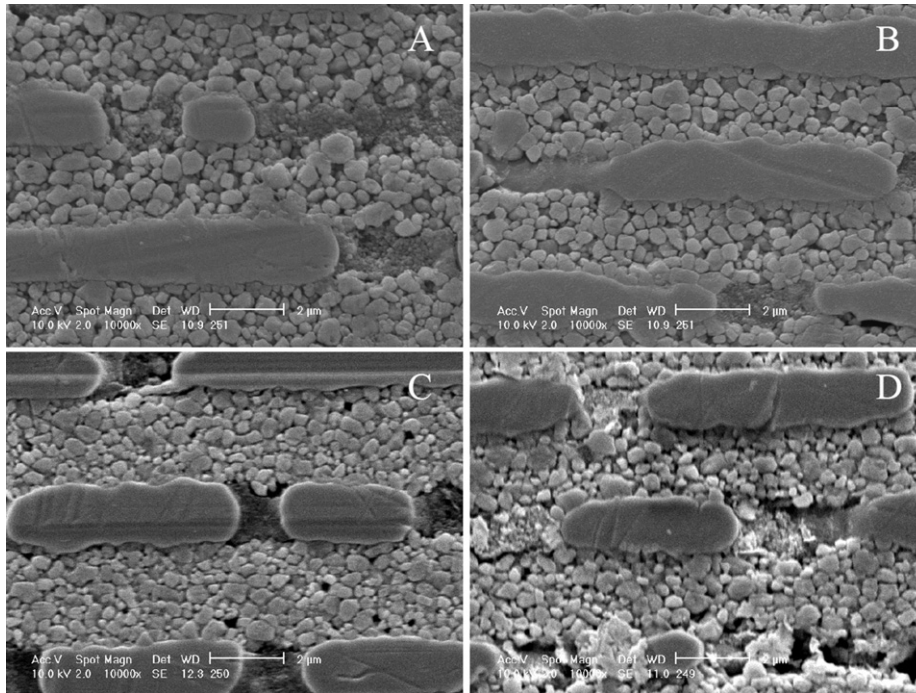


Fig. 6. SEM micrographs of X5R dielectrics with a concentration of (a) 1.5 mol% Y, (b) 2.1 mol% Y, (c) 2.6 mol% Y and 3.0 mol% Y. The MLCCs were sintered at 1280 °C in a wetted 0.3% H<sub>2</sub>/N<sub>2</sub> atmosphere.

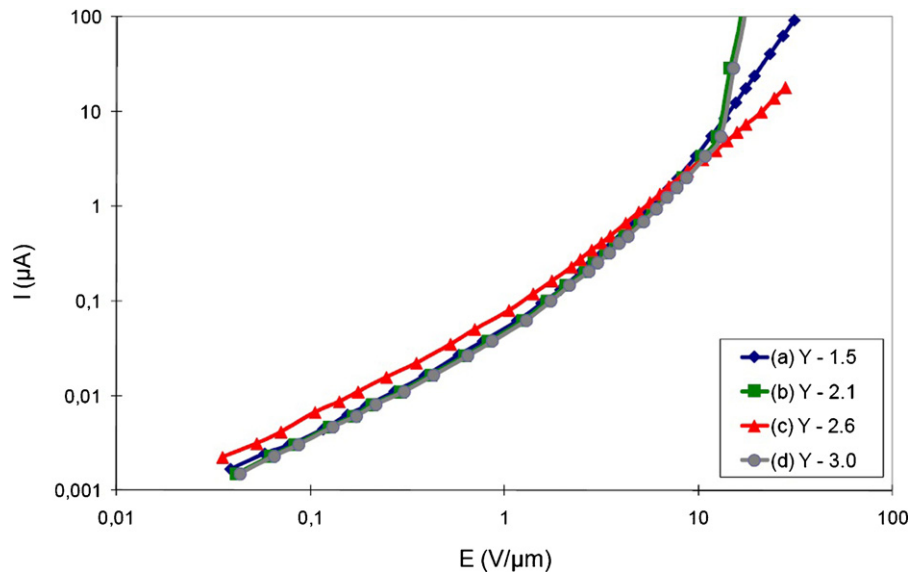


Fig. 7.  $I$ – $V$  curves of MLCCs with a concentration of (a) 1.5 mol% Y, (b) 2.1 mol% Y, (c) 2.6 mol% Y and 3.0 mol% Y in the dielectric composition. The MLCCs were sintered at 1280 °C in a wetted 0.3% H<sub>2</sub>/N<sub>2</sub> atmosphere.

at 150 °C. The results are shown in Fig. 7. The data show that there is no large difference between the four dielectric compositions when the DC electrical field was increased up to 10 V/μm. A gradual increase of the current was observed. The leakage current increases sharply at DC fields >10 V/μm, indicating that the current passes via the grain boundaries and the resistivity of the dielectrics was decreased considerably. Thus, the concentration of Y<sub>2</sub>O<sub>3</sub> has no significant influence on the  $I$ – $V$  characteristics.

#### 4. Conclusions

The relative permittivity as function of the AC electrical field dependency was determined by measuring the  $P$ – $U_{\text{applied}}$  hysteresis loops on CDCs. The results were compared with  $\epsilon_r$  versus  $U_{\text{applied}}$  measured on MLCCs. Comparison of data from these two methods showed that the trends in  $\epsilon_r$  versus AC field strength were similar. This suggests that the  $\epsilon_r$  of dielectric compositions can be determined directly on CDCs, thereby avoiding the

laborious fabrication of MLCC samples to examine the electric properties of their ultra thin dielectrics.

The electrical measurements also showed that the relative permittivity at room temperature increased with increasing  $Y_2O_3$  concentration. A distinct difference was observed between  $\epsilon_r$  values of different compositions. Two types of microstructures could be distinguished. Microstructure analysis showed that the dielectrics consist of small grains and that the  $Y_2O_3$  concentration has a very small effect on the average grain size. With increasing concentration of  $Y_2O_3$  the average size decreased only slightly.

The Curie point of the dielectrics at 125 °C did not shift upon variation of the Y concentration, except at low AC fields, where a shift of the Curie point to lower temperatures was observed when more yttrium was incorporated in the ceramics.

The MLCC made from these dielectrics had good insulation resistance properties. The  $I$ – $V$  measurements at 150 °C showed that the yttrium concentration had almost no effect on the leakage current of the ceramics.

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