

# Production and Characterisation of Composite Relaxor Ferroelectric Multi-layer Structures

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## Abstract

*The drive for miniaturisation of passive capacitor and filter devices requires dielectric materials with higher relative permittivities than can be attained using normal ferroelectrics. Relaxor ferroelectrics possess the required high relative permittivities but are incapable of being chemically doped to give a temperature stable capacitance. Work is presented detailing the design and development of a new class of temperature stable high volumetric efficiency multi-layer capacitors. Various compositions of high relative permittivity relaxor ferroelectrics are co-sintered in to a multi-layer capacitor with controllable temperature characteristics. The materials used are all doped perovskite  $Pb(Mg_{1/3}Nb_{2/3})O_3$  (PMN) compositions. The ceramic powder-processing route required to make such structures is summarised with reference to the unique device fabrication problems encountered. Dielectric measurements of the prototype devices are presented. © 1999 Elsevier Science Limited. All rights reserved*

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## 1 Introduction

In recent years research based on the class of ferroelectric ceramics known as relaxors has become widespread, both due to their potential in commercial applications and from scientific viewpoints.<sup>1</sup> The potential of relaxor materials stems from their high relative permittivities (10 000–35 000) and low losses.

Temperature stable (class II) capacitors are designed according to the Electrical Industries Association (EIA) classifications. One of the most

common of these is the X7R specification, with a  $\pm 15\%$  capacitance change allowable from the 25°C value over the temperature range  $-55$  to  $+125^\circ\text{C}$ . This paper describes the development of a new family of high volumetric efficiency composite multi-layer capacitors. The devices described are technology demonstrators and are precursors for commercial X7R devices.

The diffuse permittivity-temperature behaviour of relaxors coupled with their desirable volumetric efficiencies has pushed much research in the direction of compositional substitution. Such techniques have been used for many years to fabricate 'X7R barium titanate'. Attempts to synthesise a relaxor material conforming to X7R via compositional design have been unsuccessful. Most studies have focused upon the classical relaxor ferroelectric perovskite— $Pb(Mg_{1/3}Nb_{2/3})O_3$  (PMN). PMN substituent cations that are capable of diffusing the transition sufficiently, such as A-site  $La^{3+}$ ,  $Bi^{3+}$  or B-site  $Zr^{4+}$ , cause a dramatic loss in relative permittivity. The resultant temperature stable materials must be doped to a level where the permittivity is lower than that of normal ferroelectrics and the volumetric efficiency gains are lost.<sup>2,3</sup> Attempts have also been made to synthesise heterogeneous relaxor materials where the different phases present give rise to different maxima in the permittivity-temperature response. This is analogous to the method used to synthesise temperature stable normal ferroelectrics such as  $BaTiO_3$  and  $PbZr_xTi_{1-x}O_3$ . Unfortunately, the PMN structure provides high  $Pb^{2+}$  mobility when at sintering temperatures (1000–1300°C) such that the various compositions homogenise and the resultant dielectric response is a single peak corresponding to the dielectric characteristics of the average composition.

This paper reports on work on the development of a new class of device structure known as the *Multi-Composition Multi-Layer Structure* (MCMLS).<sup>4</sup> The structure is based on a standard multi-layer design

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(Fig. 1) but contains layers of various different relaxor ferroelectric compositions as shown in Fig. 2. The internal electrodes separate the different compositions. As the layers are connected in parallel, the total device capacitance is the sum of the individual layers. By engineering each of the compositions with carefully controlled temperature characteristics, when added together, the capacitance as a function of temperature response may be tailored exactly to device requirements. Using an adequate number of different compositions (usually 3 or 4) the X7R EIA specification can be attained. Since each composition selected has a relative permittivity far in excess of that of normal ferroelectrics, then the capacitive volumetric efficiency is increased (despite the use of more layers which of course temper the gains somewhat).

## 2 Experimental

Several new challenges were overcome in order to fabricate MCMLS devices. Firstly, as mentioned above, the mobility of lead based compounds are high at sintering temperatures. Each of the different compositions is subtly different and the tendency for compositional homogenisation during sintering is high. It is, therefore, crucial to ensure that the inter-layer inner electrodes act as diffusion barriers.

Secondly, although the various compositions are doped at low concentrations the alteration in sintering

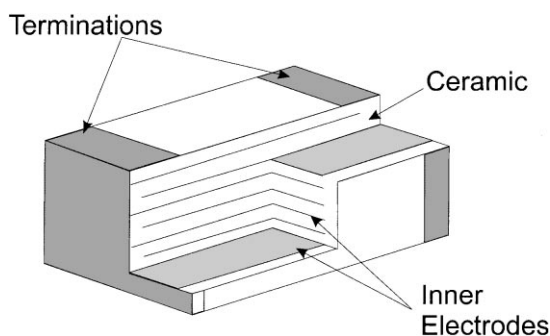


Fig. 1. Cut away view of a multi-layer ceramic capacitor (MLCC).

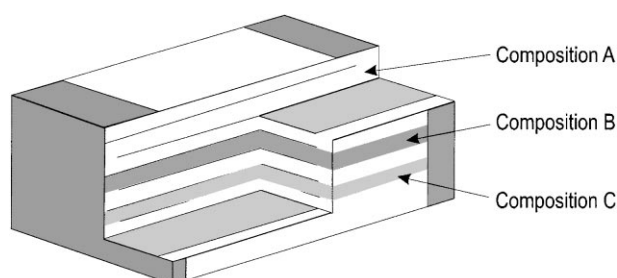


Fig. 2. Cut away view of a multi-composition multi-layer structure (MCMLS)

temperature is marked. This obviously leads to post-lamination processing difficulties. It is imperative that all the layers are of high density (>98% theoretical density is desirable) to maintain a high relative permittivity, good electric field tolerance and high mechanical strength. Slight differences in sintering temperature between compositions can lead to large density differences in the finished device resulting in useless, or worse, unpredictable performance. Careful powder preparation is, therefore, necessary to synthesise ceramics with controlled sintering behaviour. Powder particle size (controlled via precursor powder milling) has been used to control the sintering reactivity of the finished ceramic tapes. This ensures that the various compositions sinter to full density within a very small ( $\sim 10^\circ\text{C}$ ) temperature range. In addition, the multi-layer lamination process has been improved providing further density improvements. This work is described in full elsewhere.<sup>5,6</sup>

### 2.1 Composition

The exact compositions and configurations of X7R production devices will not be discussed here as they are the commercial property of our industrial partners<sup>7</sup> and marketed under the trade name Ceramox<sup>®</sup>-UHK. This paper documents the prototype research and developments conducted at Leeds to prove the MCMLS concept.

Two dopants were selected to demonstrate the MCMLS principle, namely, A-site lanthanum<sup>2,3,8</sup> and B-site titanium. The resultant materials (denoted PLMN and PMNT, respectively) along with undoped PMN are detailed in Table 1. These dopants were selected specifically to develop the MCMLS processing regime as they have widely differing sintering temperatures and present the most obstacles to co-sintering. These materials are good candidates to extend the temperature regime of operation since lanthanum doping reduces the temperature of the maximum permittivity whilst titanium increases it.<sup>9–11</sup> It is also important to note that titanium doped PMN also displays high strain electrostrictive behaviour. This expansion under applied field of up to 0.18% is utilised for actuator applications but would be catastrophic for a MCMLS device inside a close fitting filter connector. The electrostrictive expansion of PMNT in filter devices can be, however, neglected, since the electric field levels are low ( $< 0.1 \text{ M Vm}^{-1}$ ). In high voltage applications, the layer thickness is increased proportionally thus maintaining a low electric field.

### 2.2 Tape fabrication

Ceramic slip preparation, the initial step for tape casting,<sup>12,13</sup> was carried out according to the standard

**Table 1.** Materials used for prototype investigation

Acronym	Dopant & concentration	Formula
PMN	–	$\text{Pb}(\text{Mg}_{0.333}\text{Nb}_{0.666})\text{O}_3$
PLMN-01	1 mol% La (A-Site)	$\text{Pb}_{0.99}\text{La}_{0.01}(\text{Mg}_{0.336}\text{Nb}_{0.663})\text{O}_3$
PMNT-06	6 mol% Ti (B-Site)	$\text{Pb}(\text{Mg}_{0.313}\text{Nb}_{0.626}\text{Ti}_{0.060})\text{O}_3$
PMNT-20	20 mol% Ti (B-Site)	$\text{Pb}(\text{Mg}_{0.266}\text{Nb}_{0.553}\text{Ti}_{0.200})\text{O}_3$
PMNT-23	23 mol% Ti (B-Site)	$\text{Pb}(\text{Mg}_{0.256}\text{Nb}_{0.515}\text{Ti}_{0.230})\text{O}_3$

commercial route of our industrial collaborators. Slips<sup>14</sup> were prepared by adding an appropriate amount of ceramic powder into an organic mix, consisting of trichloroethene, xylene, MEK resin (methyl ethyl ketone) and butyl benzyl phthalate as a binder and plasticiser. Batches were usually made with 100 or 200 g of powder with 50 wt% of additives. Higher volume fractions of organics yielded a more robust tape but green density and dielectric properties were reduced dramatically. The mixed slips were ball milling with  $\text{ZrO}_2$  media in a plastic mill for 12 h, with viscosity maintained in the range of 1000–4500 cps (measured at 2.5 rpm at room temperature). As produced slurries were tape cast to produce thin green ceramic sheets. The tape caster was built ‘in house’ and contains a steel blade box with a gap of 200  $\mu\text{m}$  and a speed-controllable drive. A polypropylene film carrier with a width of 100 mm and average thickness of 30  $\mu\text{m}$  was used as a support layer. Casting speed was used to control the tape thickness and was between 2.5 and 10 mm s<sup>-1</sup>. The thicknesses of the resultant green tapes were controlled between 50 and 80  $\mu\text{m}$ .

### 2.3 Screen printing

The material selected for use as internal electrodes is required to be of high electrical conductivity, be chemically inert at sintering temperatures and to provide a diffusion barrier between layers of different compositions. Prototype devices have been fabricated using platinum electrodes. In view of the high cost of platinum, experiments have also been carried out using Ag/Pd inks that are more suitable for commercial production. Electrodes were printed using a bench top manual machine using 65-390 Polyester 45° 10  $\mu\text{m}$  mesh. As-printed sheets were placed on a flat glass surface for drying and levelling at room temperature for 20–30 min in air.

### 2.4 Device fabrication

The electroded sheets were manually sliced using a steel blade and stacked carefully one by one. As-stacked samples were compacted by cold isostatic pressure (300 MPa at room temperature for 30 s). Previous experiments have shown that higher pressures provide improved density and microstructures in multi-layer devices.<sup>4,5</sup> A five-step multistage binder burn-out process was employed

to ensure that the organic components were removed without risk of multi-layer delamination. Heating rates of 5°C h<sup>-1</sup> were used with ramp dwells of 5 h at 180, 250, 350 and 450°C. Green devices were sintered surrounded by PMN atmosphere powders, in  $\text{Al}_2\text{O}_3$  lidded crucibles as described elsewhere.<sup>2,3</sup>

## 2.5 Dielectric and electrical characterisation

Measurements of relative permittivity (via capacitance) as a function of temperature and angular frequency were made using the Leeds *PermT* dielectric measurement system.<sup>9</sup> Each sample was also pass/fail tested for suitable insulation resistance at 500 V which proved to be a good check of device integrity and saved valuable characterisation time.

## 3 Results

### 3.1 Electron probe micro-analysis

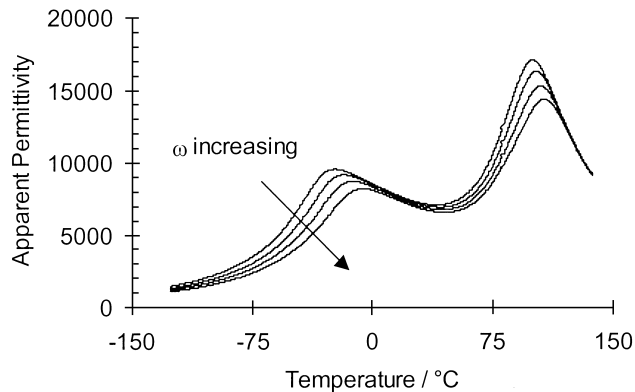
Electron probe micro-analysis (EPMA) was used to assess the diffusion barrier properties of various electrode materials. Pure platinum was found to provide a total barrier to Pb diffusion and was selected for this study. High density (>94%) multi-layer samples with Pt electrodes were found via EPMA to possess little or no interlayer diffusion—certainly not enough to seriously affect the dielectric properties. This contrasts with approximately 40  $\mu\text{m}$  penetration of Ti into the PMN layer observed without electrodes or with low density samples when the electrodes are not continuous. The work focussed on electrode improvements and the use of reduced cost electrodes is beyond the scope of this paper and will be detailed elsewhere.

### 3.2 Dielectric measurements

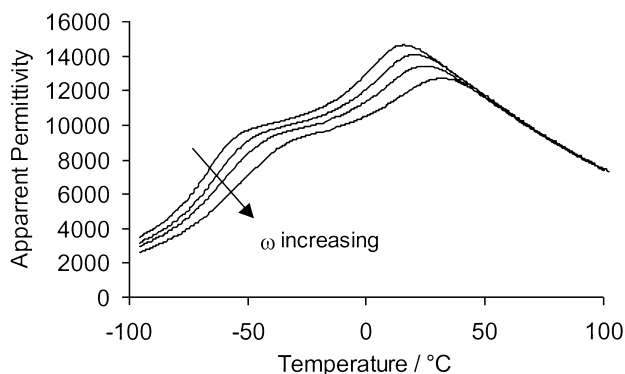
Figures 3–5 show apparent permittivity as a function of temperature and frequency for various prototype MCMLS devices. Measurements were made over decades of frequency from 100 Hz to 100 kHz.

In order to accurately compare MCMLS performance compared to existing devices and materials, the relative permittivity should be used. Apparent permittivity is a new term coined to describe the *apparent* relative permittivity of the new MCMLS devices. The apparent permittivity of a MCMLS device is the sum of the constituent relative permittivities (at any given temperature) divided by the number of layers present. This, therefore, allows the volumetric efficiencies of MCMLS devices to be directly compared to conventional devices.

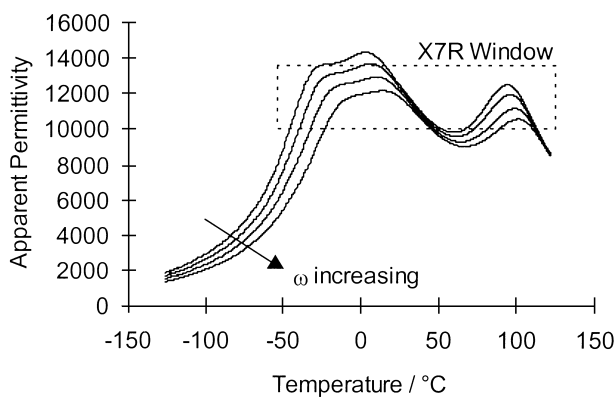
Figure 3 shows the response of the prototype sample P33 containing 1 layer of PMNT-20 and 1



**Fig. 3.** Apparent permittivity as a function of temperature and angular frequency (100 Hz, 1 kHz, 10 kHz, 100 kHz) for device P33.



**Fig. 4.** Apparent permittivity as a function of temperature and angular frequency (100 Hz, 1 kHz, 10 kHz, 100 kHz) for device P41.



**Fig. 5.** Apparent permittivity as a function of temperature and angular frequency (100 Hz, 1 kHz, 10 kHz, 100 kHz) for device P35. The box marks limits of the EIA X7R specification.

layer of PMN. This result clearly demonstrates the principle of peak addition in a composite MCMLS device. The differences in relative permittivity between the two compositions are also evident. Undoped PMN has a maximum relative permittivity of  $\sim 18\,500$  but sample P33 shows a maximum low

temperature permittivity of  $\sim 10\,000$ . This is because at the peak permittivity of PMN ( $\sim -15$  to  $-20^\circ\text{C}$ ), the PMNT-20 layer is contributing a relative permittivity of approximately 1500. The apparent permittivity at the low temperature peak is, therefore, approximately  $(18\,500 + 1500)/2 = 10\,000$ . This highlights the care that must be taken when designing MCMLS devices to ensure that enough compositions are used such that more than one of these is contributing to the device response at any given temperature.

Consequently, a prime factor in the design of MCMLS devices is using the correct ratios of different layers to achieve a temperature stable capacitance response. Under commercial production, this may be also achieved by casting layers of different thickness according to the relationship:

$$C = \frac{\epsilon_r \epsilon_0 A}{t} \quad (1)$$

where,  $A$  = electrode area,  $t$  = layer thickness

Figure 4 shows the relative permittivity as a function of temperature for prototype P41. This device demonstrates the use of lanthanum doped material to extend the device response to lower temperatures. Device P41 contained 3 layers of PLMN-01 and 1 layer of PMNT-06. As in Fig. 3, the difference in relative permittivities of the two constituent materials is apparent. Clearly, in order to flatten the dielectric response 4–5 layers of PLMN-01 must be used per layer of PMNT-06. This highlights another physical limitation of the MCMLS principle namely that the apparent permittivity of the device is limited by the relative permittivity of the material with the lowest peak permittivity.

The final prototype example, device P35, contained layers of PMN, PMNT-06 and PMNT-23 in a 1:1:1 ratio. This device demonstrates the advantage that can be gained by using more materials in the device such that the *tails* of the permittivity peaks overlap. Whilst not intended as a practical X7R device, this prototype is remarkably close to the specification. The dotted rectangle shows the limits of the X7R specification ( $\pm 15\%$  of the  $25^\circ\text{C}$  value).

## 4 Conclusions

The combination of compositionally different substituted-PMN relaxor ferroelectric materials in a composite multi-layer structure has been successfully demonstrated to yield devices with uniquely high volumetric efficiencies.

The main processing difficulties, namely inter-layer Pb diffusion and differential sintering character-

istics, have been overcome via careful control of the oxide powders and screen print inks. The multi-composition multi-layer structure (MCMLS) may be easily applied to niche applications where accurate control of the capacitance–temperature response is required and the increased cost can be borne.

The high apparent permittivities, and so volumetric efficiencies, of MCMLS devices also means that to achieve a given capacitance within a certain size device, the layer thickness may be increased several fold. This introduces the possibility of operating devices at much higher working voltages due to the ability to use thicker layers without compromising capacitance. This is particularly applicable to MCMLS devices as the higher production cost is warranted for high value added components such as high voltage—close pitch filter arrays for EMI/RFI suppression in avionics.

Further publications will detail compositional modifications made to the constituent materials in order to achieve a practical X7R device. This of course includes consideration of dielectric losses. The design of MCMLS devices means that several loss peaks can occur within the operating range and these must be minimised dependent upon the application.

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