

# **BME-X8R For Automotive and High Voltage Applications**

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## *Abstract*

The ongoing demand for more electronics in automotive applications increases the number of components that are located under the hood. This offers a challenge for the electronic industry to provide parts that are suitable to operate in this harsh environment (e.g. higher temperatures, chemical resistivity).

During last years, Ferro EMS developed a composition fulfilling the X8R specification with good reliability, suitable for Ni electrodes. Important for the composition was the role of BaTiO<sub>3</sub> and the control of the dielectric constant. It is demonstrated that an increase of the Ba/Ti ratio, in combination with milling, increases the Curie temperature, which is very helpful in fulfilling the X8R temperature specification. The role of small acceptor ions on the permittivity is discussed.

The optimised formulation was real X8R with promising properties, suitable for automotive applications, as well as for applications, where the increasing circuit board temperature limits the use of X7R capacitors. The high voltage breakdown of the material makes it probably applicable for high voltage X7R applications as well.

Keywords: BaTiO<sub>3</sub>, dielectric properties, capacitors, thermal properties, lifetime

## **Introduction**

The need for safer, more comfortable, pollution free and cost effective transportation has created a great opportunity for the electronic industry to develop new systems to fulfil these needs [1-3]. In the last decades the use of programmed fuel injection, antilock brake systems, cruise control, airbag systems, air conditioning and advanced entertainment systems became standard. And in the near future, more technology, like drive by wire, will be introduced.

These new and future technologies demand for more power and give rise to higher weight. Since every application is controlled from outside the engine room, an enormous amount of copper wires are used to connect the electronic system with the control unit.

The demand for more power with less weight will be solved by the change to a 42V system instead of the 14V nowadays. Secondly the introduction of a so-called bus system will result in a weight reduction as well. This system makes use of a network with addresses for each electronic device. A consequence is that more electronics can be found under the hood, near the engine. This also means that the electronics have to operate at higher temperatures.

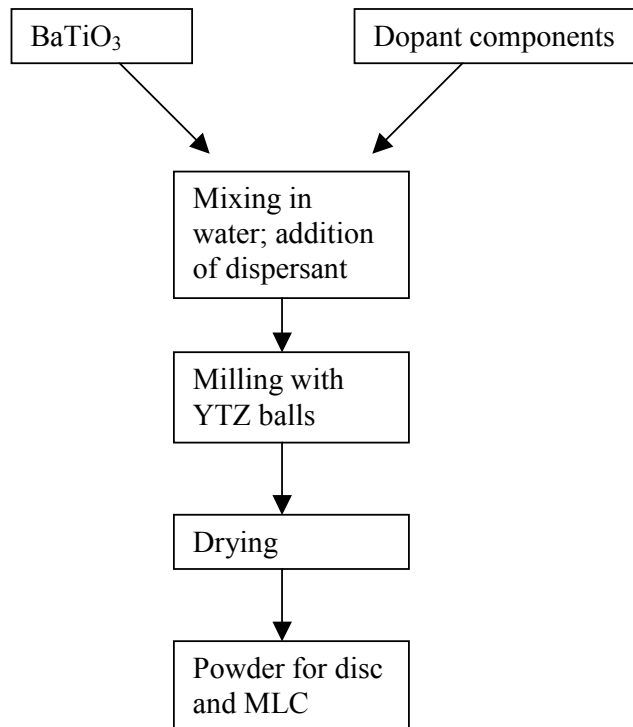
In order to extend the working range of the electronics to higher temperatures, it is desirable that X7R capacitors (-55°C-125°C,  $\square C/C_{ref} \pm 15\%$ ) is extended from 125°C to 150°C, the X8R temperature specification.

Noble metal X8R, based on PdAg electrode systems in combination with  $\text{Bi}_2\text{O}_3$ -(PbO)- $\text{TiO}_2$ , is currently available [4]. However, these parts are very expensive for higher layer count and larger amounts of MLC's due to the expensive Pd. However, BME MLC's have proven their reliability, also for automotive applications, for more than a decade and are now on the eve of emerging in X8R applications as well.

In this paper we will address some issues, which were important in the development of Ferro's new BME-X8R material, applicable in 8-10  $\mu\text{m}$  MLC's. Special emphasis will be made for the importance of the selection of the appropriate barium titanate and a fine-tuning of the dopant composition.

### Experimental details

New compositions were obtained by mixing and milling dopant components and  $\text{BaTiO}_3$ . Oxides and carbonates were used as dopant components.  $\text{BaTiO}_3$  was selected from the extended Ferro's product line.



*Figure 1: sample preparation route*

In figure 1 the procedure for the preparation of the formulation is presented. After mixing the  $\text{BaTiO}_3$  with the dopant components, the material is milled down to the desired particle size.

Disc capacitors are prepared from granulated powder and pressed in a dye. Electrode ink was applied on each side of the disc capacitor.

MLC's were prepared from PVB based green tapes, stacked on a Keko Pal (IX), and using a Ferro pure Ni inner electrode paste. The plates were isostatically pressed and cut into individual MLC's. The layer thickness of the tape was targeted for 8-10  $\mu\text{m}$  after sintering

The firing atmosphere used for the disc capacitors and MLC's during sintering had an oxygen partial pressure of ca.  $1 \cdot 10^{-10}$  bar at 1300°C. The re-oxidation of the fired parts was done at 1000°C for 2 hrs in moistened  $\text{N}_2$ . After firing MLC's were tumbled and thereafter Cu-terminations (Ferro TM50-083) were applied.

The capacity was measured with an Agilent 4278A LCR meter. This bridge was connected to a Vötsch VT7004 in order to measure the temperature dependence of the capacitance. HALT (Highly accelerated lifetime testing) was performed by monitoring the insulation resistance at 140°C. A voltage of 50V/ $\mu\text{m}$  was applied during this test to be able to discriminate between different materials and to give an indication of the reliability at the severe application conditions.

## Results

### BaTiO<sub>3</sub> selection

Since the capacitance of doped BaTiO<sub>3</sub> drops sharply after the Curie temperature (tetragonal to cubic transition temperature), it is desired that the Curie temperature is as high as possible in order to fulfil the X8R temperature specification.

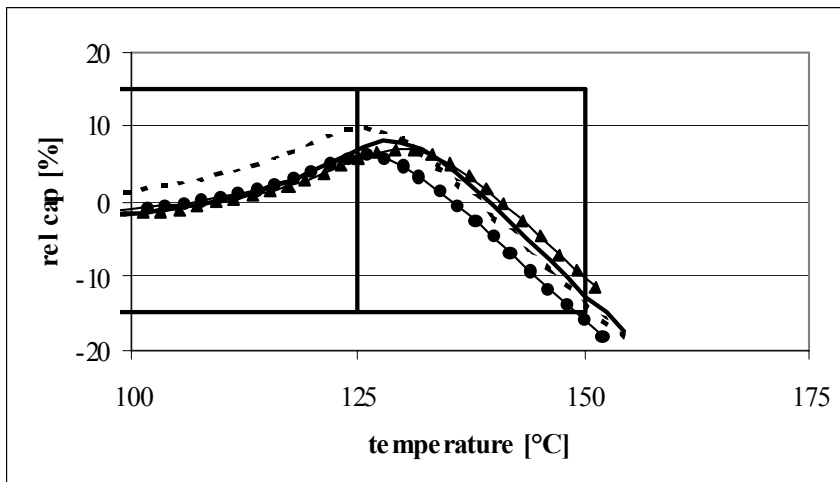


Figure 2: Four TCC curves for 4 different types of standard doped BaTiO<sub>3</sub>;

— (BT-A), -- (BT-B), • (BT-C) and ▲ (BT-D)

In order to indicate the influence of the barium titanate source, four different types of Ferro barium titanates have been tested. In figure 2 TCC curves of disc capacitors of these four barium titanates in combination with a standard dopant package [5], are presented. All samples were milled to the same D50 and disc capacitors were sintered at the same temperature.

Only a small temperature range of the full TCC curve is shown. However this range exhibits the important differences. Curve BT-D shows the maximum peak (Curie temperature) at the highest temperature, whereas BT-B exhibits the lowest peak temperature. Since all barium titanates are produced by the oxalate route under different processing conditions, it seems that these conditions and the underlying chemistry exhibit a major effect on the position of the Curie temperature.

During calcination of barium titanate, small grains are formed, which are sintered together to obtain clusters. That material has a Curie temperature of about 125°C, due to the delayed phase transition by the hindered mobility inside the grains. During milling, the smaller grains are separated from the clusters and the individual grains are free to move from the cubic to tetragonal phase at the temperature determined by the purity and chemistry (Ba/Ti ratio) of the material.

This is clearly demonstrated in figure 3. In this figure 2 graphs are presented in which the heat of transition, as measured by a differential scanning calorimeter (DSC), was plotted versus the temperature. The graphs are presented in an earlier paper by Baeten et al [6]. In the first graph, on the left, the influence of the Ba/Ti ratio (in solid state barium titanate) on the Curie temperature has been presented. It is shown that the Curie temperature increases with increasing Ba/Ti ratio. This is in agreement with results presented by Filimonov et al [7].

In the second graph of figure 3 (right) the influence of milling on the Curie temperature has been demonstrated. Barium titanate, obtained from the oxalate process, has been milled with 5 mm balls and samples have been taken at the times indicated in the figure. The Curie transition has been measured with the DSC. It has been shown that during milling the Curie temperature increases. This clearly demonstrates that both the chemical composition of the barium titanate and mechanical treatments are important for the selection of barium titanate for X8R applications.

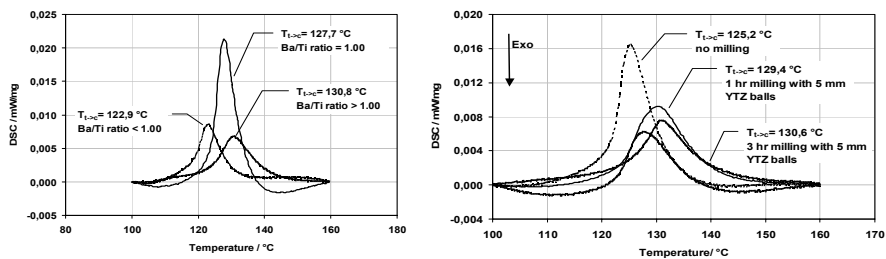


Figure 3: DSC measurements near the Curie temperature; effect of Ba/Ti ratio on Curie temperature (left), effect on milling on Curie temperature (right).

### Matching the X8R specification

Additional to a high Curie temperature, a dopant package that effectively controls the dielectric properties and reliability is required. One of the most important aspects to be considered is the dielectric constant, which should be high enough to allow the production of MLC's with reasonable capacity sizes, but not too high in order to fulfil to the X8R temperature specification in MLC's at the targeted thickness of 8-10 μm.

It is common knowledge that small acceptor ions like Mn, Mg, Cr, V, Fe, Co, Ni, Lu, Yb and Tm can significantly reduce the dielectric constant and reduce the polarisability of the material. This effect was also used to improve the TCC behaviour of our composition

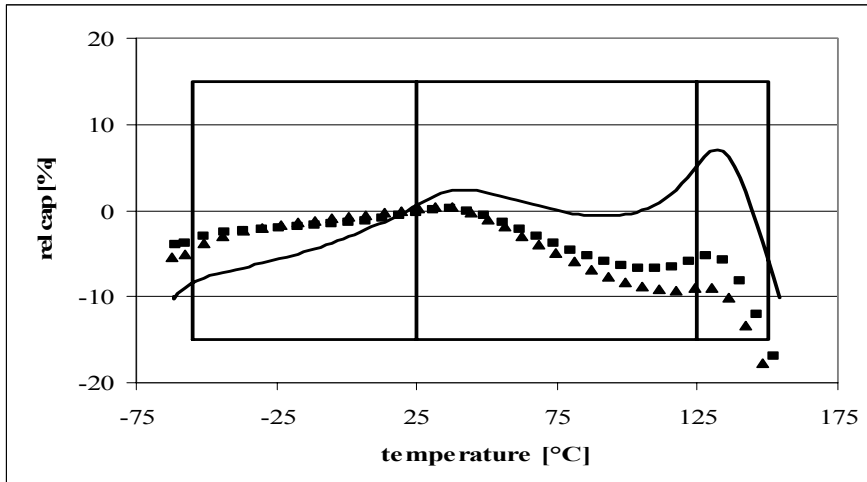


Figure 4: Effect of more or less polarisable material on MLC TCC

(■) MLC low K-value, (▲) MLC high K-value; solid lines corresponding disc capacitors

Figure 4 illustrates the impact of the dielectric constant on the TCC behaviour in MLC's. While the curves for the disc capacitor (thickness 1.8mm) are identical for the two materials, the MLC curves significantly differ as a result of the higher dielectric constant, in discs, (2300 compared to 2000) of the less doped material, showing a stronger clockwise rotation in the TCC. This makes such a material less desirable for X8R MLC applications.

Sato et al. [8] emphasize the role of small rare earth ions, like Tm, Lu and Yb, for a flatter TCC. However, our experiments demonstrate that also other acceptors can give the desired dielectric behaviour.

Ferro Electronic Material Systems is actually in the final stage of up scaling a new BME X8R material, AD202N, based on the optimisation of the dopants and physical properties of barium titanate. The new developed material is in compliance with RoHS. In table 1 the typical powder properties are presented. In table 2 typical electrical properties in MLC's are given. MLC data is obtained from 1206 40 nF capacitors. A typical micrograph is presented in figure 5. Very dense ceramic has been obtained after firing at about 1320-1350°C. The layer thickness is about 10 μm.

D50 [μm]	0.8
D90 [μm]	1.4
BET [m <sup>2</sup> /gr]	5.5

Table 1: Typical powder properties AD202N

K-value	2100
DF [%]	1.9
IR [GΩ] @ 25°C	66.5
RC [s] @ 25°C	~ 2400
RC [s] @125°C	200
VBD [V/□m]	122
HALT [hrs] 140°C, 50V/□m	> 100

Table 2: typical electrical properties of AD202N in 10□m 1206 MLC's

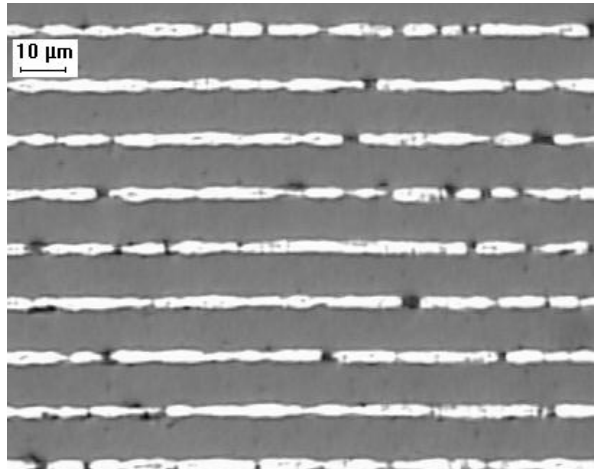


Figure 5: Cross section of AD202N multilayer capacitor

The temperature dependence of the formulation in disc and MLC is presented in figure 6. A flat TCC curve has been obtained for 10□m 1206 MLC's. The variation in capacity is only a few percentage over a wide temperature range (+ 7.5% -55°C to 125°C, X7F) and drops at temperatures above 130°C down to about -11% at 150°C, fulfilling the X8R temperature specification.

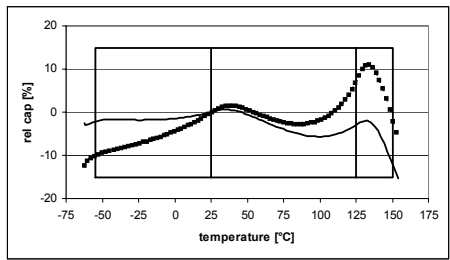


Figure 6: TCC curve of AD202N —: MLC, --- disc capacitor

Electrical properties of the material indicate the potential of this material. Typical K-values in combination with DF is given in table 2. K-value is sufficiently high for applications in 10 $\mu$ m 0603 47nF capacitors. The RC value at room temperature is higher than 2000 seconds and at 125°C about 200 s.

The good temperature behaviour of the material makes the material not only suitable for automotive applications but also for other applications where the temperature limits the use of X7R capacitors. The increasing circuit board temperature of many electronic applications asks for components suitable for high temperature applications.

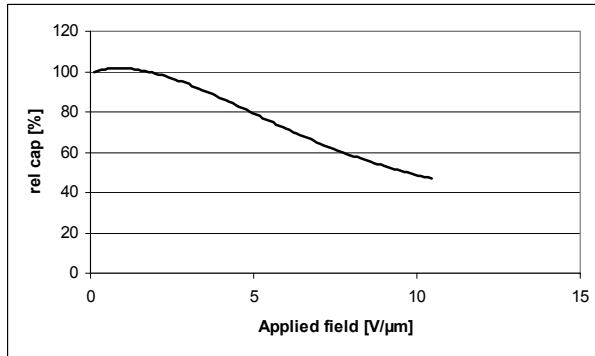


Figure 7: DC bias curve of AD202N

A high voltage breakdown above 120V/ $\mu$ m implies the possibility of high voltage applications X7R.

This is supported by the DC bias behavior of MLC's with 10 $\mu$ m dielectric thickness, as shown in figure 7. From this curve it is shown that for 50 V (5V/ $\mu$ m) 80% of the initial capacity is available and for 100V (10V/ $\mu$ m) still 50% of the capacity is present. Aging tests, figure 8, indicates that the aging is about 1% from 24 to 240 hours

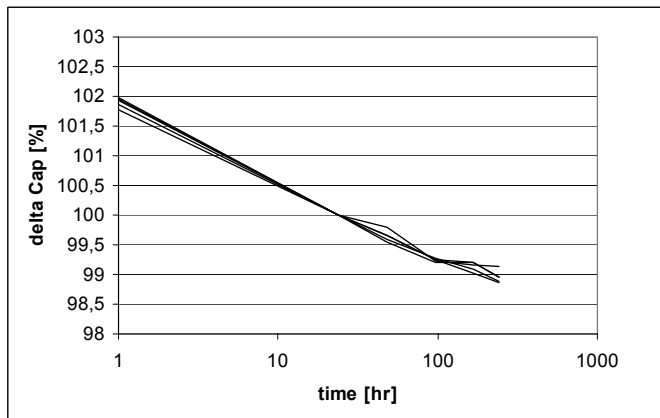


Figure 8: Aging curve of AD202N

## Conclusions

In this paper the development of a new X8R composition for automotive applications has been described. Important aspects discussed are the selection of BaTiO<sub>3</sub> and the control of permittivity. It is

shown that processing of the BaTiO<sub>3</sub> affects the Curie temperature. Permittivity control has been done by the use of small acceptors in the dopant package.

It is further demonstrated that with a suitable formulation a new BME-X8R material can be obtained with promising dielectric properties and thermal stability. The material also looks promising for high voltage X7R applications. AD202N is RoHS compliant.

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