COMPARISON OF PHYSICAL AND ELECTRICAL PROPERTIES OF LOW-FIRE X7R DIELECTRICS WITH "K" BETWEEN 4000 AND 5000 IN MLC WITH LAYER THICKNESS BETWEEN 5μ AND 15μ† *

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SUMMARY

The increasing demand for high volumetric efficiency multilayer ceramic capacitors (MLC) with X7R characteristics has expanded research in materials [1,2,3,4] as well as manufacturing technologies[5,6]. As dielectric formulations are designed for higher K, accompanying changes in temperature coefficient of capacitance (TCC) and dissipation factor (DF) need to be considered. As advances in manufacturing technologies make ever thinner active layers possible [7,8], the effect of ac signal strength on these dielectric properties ("K", TCC, and DF) must be taken into account.

Measurements on dielectric compositions (based on $BaTiO_3$) show that both "K" and DF increase with increasing ac signal strength accompanied with a clockwise rotation of the TCC curve. These changes with ac signal are stronger for dielectrics with higher "K".These effects arise due to the relative sensitivity of spontaneous polarization to the ac field. The relative change of K with ac signal field ($\Delta K/\Delta E$) is significantly higher at -55°C, than at 25°C and at 125°C. That is $\Delta K/\Delta E|_{-55°C} > \Delta K/\Delta E|_{25°C} > \Delta K/\Delta E|_{125°C}$. It is believed that these changes are related to the spontaneous polarization, P_s, of $BaTiO_3$ crystal at the three transition temperatures (-80°C, +25°C, +130°C). Due to these effects, $BaTiO_3$ based dielectric compositions, with K>4500, will not meet the X7R requirements at 1Vrms ac signal for thin (<5μ) active layer MLCs. A modified dielectric composition with "K" between 4000 and 4200 was found to meet the TCC X7R characteristics at 1V_{rms} in MLCs with 5μ active layer thickness.

A comparison of the relative costs of X7R MLCs manufactured with a low-fire dielectric using 70Ag/30Pd, a high-fire dielectric using 30Ag/70Pd, and a high-fire dielectric using Ni is presented. The analysis shows that low-fire dielectric compares favorably with the other two systems, both interms of cost and performance.

INTRODUCTION

We reported earlier on the properties of a 1μF capacitor in 1206 chip size consisting of 80 active layers of 10μ thickness[9]. This paper is a continuation of our research on the development of a series of compositions based on low-fire barium titanate dielectrics.

To achieve a high volumetric efficiency chip capacitor with X7R characteristics (i.e. 1206 - 2μF, 0805 - 1.0μF, and 0603 - 0.33μF), the "K" must be as high as possible and the layer thickness as small as possible. However, there are two problems that must be resolved. The combined effect of high K dielectrics and high signal strengths (due to thin active layers) causes (I) TCC curve to rotate clockwise and fall out of the X7R specification at 105°C, and (II) the DF increases to more than 3.5%.

Accordingly, the objective of this study is to explain the clockwise rotation of the TCC curve with

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increase of ac signal and to present the properties of a series of compositions which will meet the X7R characteristic with K >4000 and active layer thickness as low as 5μ. Data on the effect of ac signal strength on "K", DF and TCC for MLCs that have 5μ to 15μ thick active layers is presented.

RESULTS AND DISCUSSION

To demonstrate the effect of ac signal on "K", D.F. and TCC, we investigated three compositions with nominal "K" between 4000 and 5000. 70Ag/30Pd was used for internal electrode material. The first set of data shows the properties of 0805 chips with varying layer thickness between 5μ and 15μ, while the second set shows the properties of 0805 - 120nF capacitors with 8μ thick active layers.

A. 0805 MLCs with 10 active layers of 5μ, 10μ and 15μ

These MLCs were made from a dielectric composition with a nominal "K" of 4800. All samples were sintered at the same time & temperature. Table 1 shows a summary of the properties of this dielectric while Figures 1 & 2 show the effect of ac signal strength (Vrms/μ) on "K" and D.F., and Figure 3 on "K" at varying temperatures (-55°C, 25°C and +125°C). Similar size MLCs were made and evaluated with a "K" 4200 dielectric composition. The results are shown in Table 2 and the effect of ac signal strength is shown in Figures 4, 5 and 6 respectively. Figure 7 shows SEM image of a fracture surface of MLC of the K4200 with 5μ, 10μ and 15μ layer thickness.

These data clearly show that both the "K" and D.F. increase significantly with increase in ac signal strength and the TCC curve rotates clockwise.

The reason for the rotation of the TCC curve as shown in Figures 8 & 9 can be explained by the relative sensitivity of "K" to ac signal strength at three temperatures. These are related to the ferroelectric transition temperatures of $BaTiO_3$ (at -80°C, +25°C, and +125°C).

As shown in Figure 3, for the K-4800 composition, the slope $M = \Delta K/\Delta E$ at -55°C is about 5000, at +25°C is about 3000 and at +125°C is about

Table 1. Properties of K-4800 Dielectric

Chip Size	0805
No. Of active layers	10
Sintering Condition	1110°C, 3Hr
Electrode System	70Ag/30Pd
Fired Density	5.85 gms/cc

AD Thickness	15μ	10μ	5μ
Capacitance @ 1KHz, 1Vrms, 24hr aging	23nF	33nF	73nF
%DF	1.95	2.5	4.7
K	4700	4800	5180
TCC @ 1KHz, 1Vrms			
-55°C	-4.2%	-2.1%	+2.6%
-35°C	-4.9%	-3.1%	+0.6%
-15°C	-3.9%	-2.8%	+0.3%
+25°C	0	0	0
+45°C	+0.9%	-0.3%	-0.9%
+85°C	-9.3%	-10.4%	-12.7%
+105°C	-11.2%	-13.2%	-16.6%
+125°C	-6.2%	-9.0%	-15.4%
IR @ 150V, 125°C ΩF	350	300	-
UDBV (V/μ)	100	70 -	-

1600. It should be noted, however, that at a signal strength greater than 0.3Vrms/μ, the "K" starts to saturate, especially at 125°C.

In determining the TCC curve the room temperature "K" value is usually used as reference. Thus, the rotation of the TCC curve with increasing ac signal strength is shown to be related to the relative slopes of the "K" at -55°C and +125°C.

The effect of the ac signal strength, on K at the three transition temperatures, can be explained by the relative sensitivity of the spontaneous polarization P_s to the ac signal field.

At -55°C, the dielectric constant is mostly influenced by the rhombohedral/orthorhombic crystallographic transition which is at -80°C for pure

Table 2. Properties of K-4200 Dielectric

Chip Size	0805
No. Of active layers	10
Sintering Condition	1110°C, 3Hr
Electrode System	70Ag/30Pd
Fired Density	5.88 gms/cc

AD Thickness	15μ	10μ	5μ
Capacitance @ 1KHz, 1Vrms, 24hr aging	19nF	28nF	67nF
%DF	1.6	2.1	3.9
K	4000	4200	4500
TCC @ 1KHz, 1Vrms			
-55°C	+3.3%	+4.8%	+8.7%
-35°C	+0.4%	+1.4%	+4.6%
-15°C	-1.3%	-0.6%	+1.7%
+25°C	0	0	0
+45°C	+1.3%	+1.1%	-0.1%
+85°C	-5.8%	-6.1%	-8.0%
+105°C	-6.2%	-7.0%	-9.8%
+125°C	+0.7%	-1.2%	-7.6%
IR @ 150V, 125°C	400	300	-
UDBV (V/μ)	90	70	-

$BaTiO_3$ and is at higher temperature for X7R dielectric due to the chemical inhomogeneity of the grains. Near this temperature it is likely that most of the P_s is along the <111> direction. Similarly near +25°C, the K is mostly influenced by the orthorhombic/tetragonal transition and the polarization, P_s, direction is along the <110> direction, while at 125°C, the K is influenced by the tetragonal/cubic transition and P_s direction is along the <100> direction. The lower ac field strength required to saturate polarization and lower values of $\Delta K/\Delta E$ at higher temperatures (Figure 3) may be due to changes in crystal structure and/or due to the higher thermal energy available (to the dipoles) at higher temperature.

The K-4200 composition shows a similar trend, but as shown in Figure 6, the magnitude of the slopes at -55°C, +25°C and +125°C are significantly lower (3160, 2160 and 1060 respectively). The K for this composition is reduced by modifying the ratio of core volume to shell volume in the core- shell structure of the $BaTiO_3$ grain. The "K" of this composition shows a higher linearity with ac field (up to 0.4Vrms/μ), as compared to the K-4800 composition which reached saturation at about 0.3Vrms/μ. This characteristic along with lower values of $\Delta K/\Delta E$ is the reason why an MLC with 5μ thick active layers will meet the X7R specification at 1Vrms.

B. 0805 - 120nF MLCs With 25½ Layers of 8μ Thickness

Based on the results of part A, MLCs in 0805 chip size were made with three different dielectric compositions. Except for the dielectric, all the design and processing parameters were kept the same through out. The design capacitance was 120nF. Internal electrodes were 70Ag/30Pd. Results for these MLCs are summarized in Table 3.

As can be seen from the data, the K-4800 could be used for MLCs with layer thickness of $>12\mu$, K-4500 for layer thickness $>8\mu$ and K-4200 for layer thickness $>5\mu$.

Table 3. Properties of 0805 Chip Size 120nF MLCs with Varying K

Chip Size	0805
Active Area / Layer	$0.94mm^2$
No. of Layers	25½
Layer Thickness	8μ
Sintering Condition	1110°C, 3Hr
Electrode System	70Ag/30Pd

Dielectric System	K-4800	K-4500	K-4200
Density gm/cc	5.85	5.88	5.92
%Theoretical	97.5	98	98.5
Capacitance @ 1KHz, 1Vrms, 24hrs	139nF	127nF	120nF
%D.F.	3.2	2.8	2.7
Calculated K	5000	4560	4300
TCC	See Figure 10		
Microstructure	See Figure 11		
IR @ 50V, 125°C ΩF	556	508	360
Aging Rate %/decade	-2.6	-2.4	-1.85

C. Comparison of Relative Costs of X7R MLCs Manufactured With Low-Fire Dielectric & 70Ag/30Pd, High-Fire Dielectric & 30Ag/70Pd, and High-Fire Dielectric & Ni

Although it is difficult at this time to arrive at an accurate cost for these dielectric/electrode systems, we have made an attempt to compare the key factors. This analysis, shown in Table 4, is based on the following assumptions:

- The dielectrics represent a high quality fine grain barium titanate of equivalent cost.

- Similar overall chip yield for the same layer thickness, ignoring the effect of layer count on yield.

- Capital allocations of cost differential for firing equipment is not considered.

Table 4. Relative Costs of X7R MLCs With Various Dielectric /Electrode Systems

Dielectric System	Low Fired	High Fired (10,11, 12, 13)	High Fired (14,15, 16)
Electrode System	70Ag/ 30Pd	30Ag/ 70Pd	Ni
K	4200	4000	2800
Active Layer Thickness	8μ	8μ	8μ
Relative Electrode Cost/100nF	1	2	0.35
Capacitance Volumetric Efficiency	1	0.95	0.62
Relative Labor Cost/100nF	1	1.05	1.61
Machine Utilization Efficiency	1	0.95	0.62
Sintering Atmosphere	Air	Air	$H_2/H_2O/N_2$
Gas Cost	-	-	?

As can be seen from Table 4, the relative cost of the Ni electrode system is about 1/3 that of the low-fire 70Ag/30Pd version. However, all other costs are significantly higher. Based on this analysis we believe that the low-fire X7R dielectric will compete in cost and performance with the Ni electrode system and offer a wide range of dielectric constants to meet the demands of various MLC manufacturing capabilities.

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