HIGH VOLUMETRIC CAPACITANCE **
LOW FIRED X7R MLC CAPACITOR

Galeb H. Maher
Thomas I. Prokopowicz
Veerabhadrarao Bheemineni
MRA Laboratories, Inc.
North Adams, MA

ABSTRACT

A new low fired, high permittivity (K 4400) X7R dielectric suitable for use in MLC capacitors with active layer thickness of 10μ or less has been developed. The dielectric is based on fine grain barium titanate powder with small amount of sintering aid to promote densification of the MLCs at or below 1100°C. 70Ag/30Pd was used for the internal electrode.

MLCs in 0805 - 130nF and 1206 - 330nF chips gave an active volumetric capacitance in excess of 6000μF/in^3. The following is a summary of the properties: Fired density ≈97.5% of theoretical; Aging rate at 25°C is -2.0% per decade; Insulation resistance at 100 volts at 25°C, 2 minutes ≈ 10^5 ohm-farad; Ultimate dielectric breakdown ≈ 100V/μ. Other data is described in the text.

INTRODUCTION

The growing demand for a high volumetric efficiency multilayer ceramic capacitor (MLC) has accelerated research activities in raw materials and manufacturing technology of capacitors. In this paper we shall only consider the X7R type of the EIA classification.

To increase the volumetric efficiency of the capacitor there are two obvious parameters that can be changed: (a) Decrease the active dielectric thickness, and (b) increase the permittivity of the dielectric. In the past several years significant advances on both fronts have been reported.[1,2,3]

The bulk of the X7R MLC chips presently being produced are low fired dielectrics with "K" in the range 1500 to 2500, utilize 30Pd/70Ag internal electrodes, and are based on fine grain barium titanate. In addition, a substantial proportion of the X7R MLC chips currently being produced are high fired dielectrics with "K" in the range 3000 to 5000 and likewise are based on fine grain barium titanate[4,5,6,7]. Since sintering temperature is in the range 1275°C to 1325°C, these high fired dielectrics require internal electrodes high in palladium such as 70Pd/30Ag. For making high volumetric efficiency chip capacitors high fired, high "K" dielectric compositions are utilized.

While the demand to increase the volumetric efficiency continues to be major goal, reducing the cost of the MLC will always be a driving force in order to compete in the market place.

In the past several years we have been working on developing a low fired dielectric with a sintering temperature around 1100°C and based on fine powder barium titanate. A composition with a "K" nearly equal to that of high fired system was achieved. Some of the properties have been reported elsewhere[3,9].

Accordingly, the objective of this paper is to present some physical and electrical data of the new low fired K-4400 dielectric in 0805 and 1206 size MLC chips with 10μ active layer thickness.

EXPERIMENTAL SAMPLES

Although a variety of chips have been made and tested, we will only describe the results generated on 0805 (75nF and 130nF) and 1206 (330nF). These samples were manufactured on the prototype equipment umxng the "wet laydown process".[10] The internal electrode was a commercial 70Ag/30Pd system. After the binder was baked to 800°C, the samples were sintered at 1100°C with a 3 hour soak period at peak temperature.

The physical and electrical properties of these samples are summarized in Table 1.

Table 1
Summary of Electrical Properties

Sample	0805 75nF	0805 130nF	1206 330nF
Fired Density (gms/cc) (Ceramic only)	5.87	5.84	5.85
Capacitance nF at 1KHz, 1Vrms, 24hr aging	72	133	315
Dissipation Factor %	3.2	3.0	2.3
Dielectric Thickness μ	10	9.2	10
No. of Active Layers	20	34	45
Dielectric Constant	4200	4400	4500
Active Volumetric Capacitance (μF/in^3)	6200	6800	6300
Temperature Coefficient (TCC)	------ Fig. 1 -------		
Insulation Resistance (Ohm-Farad) (100V, 25°C, 2 minutes)	10^6	$4x10^5$	$2x10^5$
Life Test (Ohms) (100V, 150°C, 200 hours)	$5x10^9$	$3x10^9$	$7x10^8$

The microstructure of the as fired surface, fracture surface and polished cross section of the MLC are shown in figures 2 and 3. The average fired grain size ranges between 0.7μ and 1.0μ (figure 2), and the fracture surface (figure 3) gives an indication as to the relative fired density of the dielectric.

** Presented and published - Electronic Components and Technology Conference, Lake Buena Vista, Florida, June 2-4, 1993.

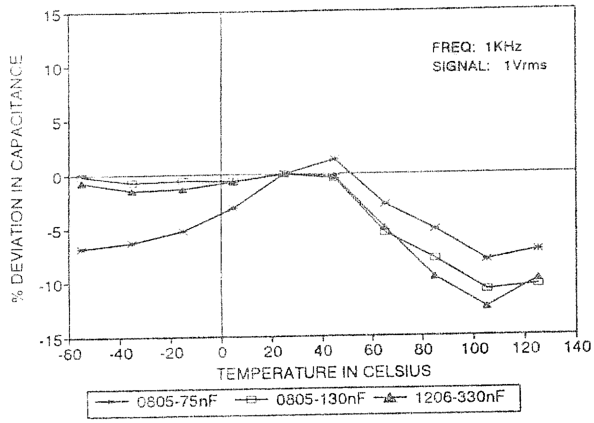

FIGURE 1. TEMPERATURE COEFFICIENT OF CAPACITANCE

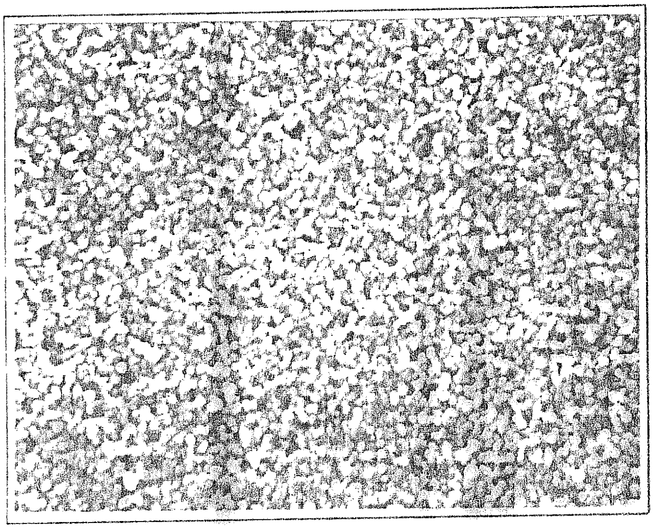

Figure 2a. As fired surface of MLCs
2000x Bar=1μ

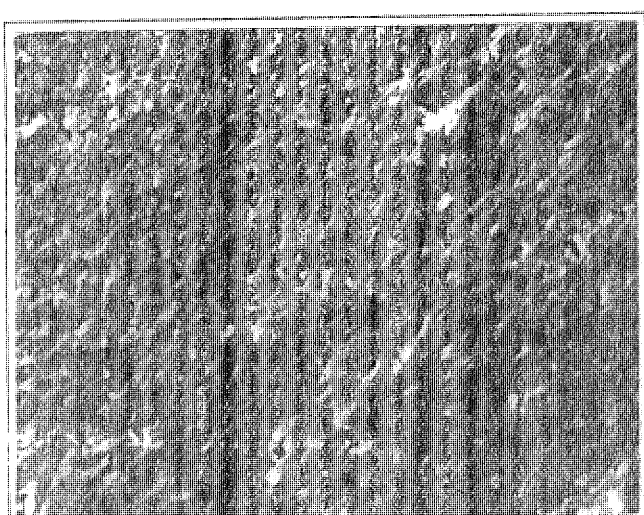

Figure 2b. Fracture surface of MLCs
2000x Bar=1μ

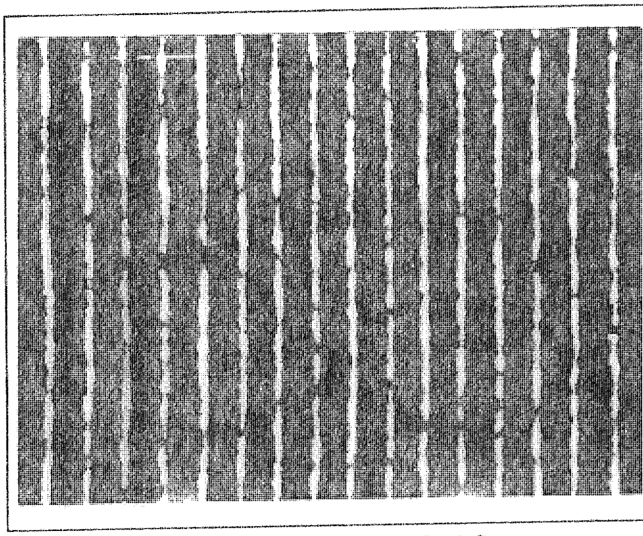

Figure 3a. Cross Section of MLCs
Sample: 1206 - 330nF; 10μ Active layer
500x Bar=10μ

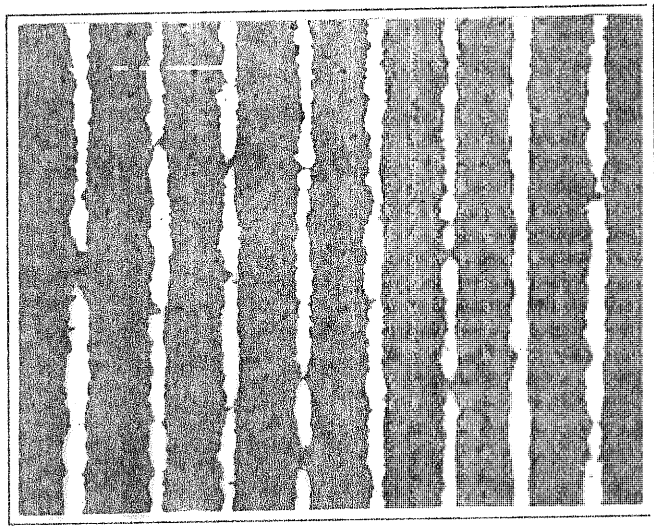

Figure 3b. Cross section of MLCs
Sample: 1206 - 330nF; 10μ Active layer
1000x Bar=10μ

The capacitance aging at room temperature was determined up to 1000 hours. This data is plotted in figure 4 and show an aging rate of about -2% per decade. This value is similar to that of high fired barium titanate based dielectrics with similar "K".[6]

The effect of AC signal at 1KHz on dielectric constant and dissipation factor is described in figure 5. These results are typical of ferroelectric dielectrics. It can also be seen that with further decrease in the active dielectric thickness to about 6μ, a dissipation factor of 3.5% can still be met at 1 Vrms.

The change in the capacitance and ESR with frequency for 1206 (330nF) and a special 35μF capacitor are shown in figure 6. These data were generated on a HP 4192A LF impedance analyzer using co-axial cable. The chips were soldered directly to the shield and the center conductor of the cable.

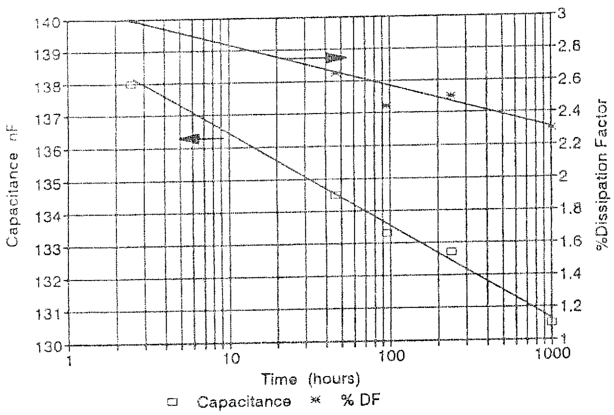

Figure 4. Aging data for 0805 - 130nF MLC at 1KHz, 1Vrms, 21°C

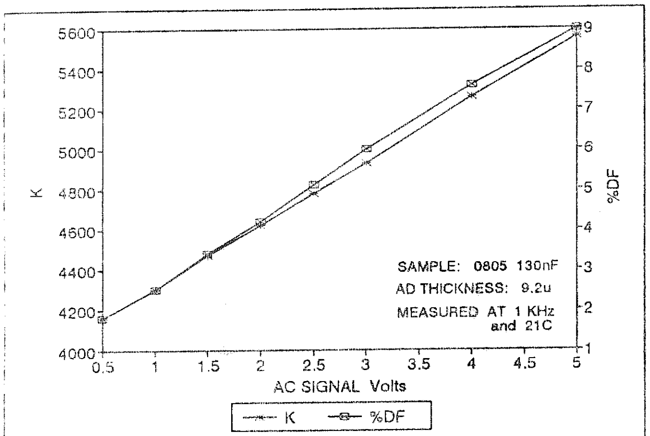

FIGURE 5. EFFECT OF AC SIGNAL VOLTAGE ON K AND %DF

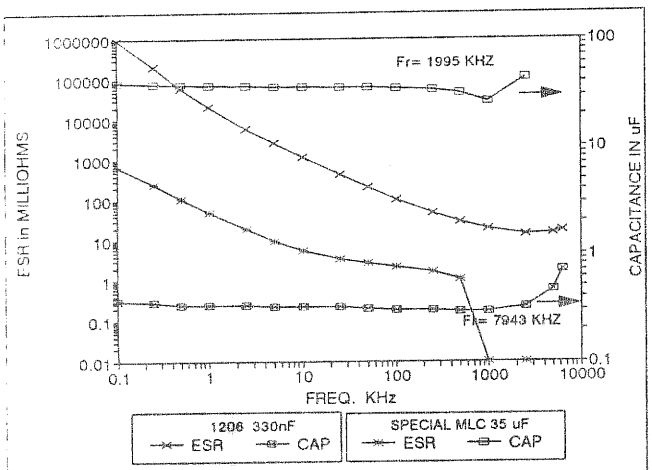

FIGURE 6. CHANGE IN ESR AND CAPACITANCE WITH FREQUENCY

The steady state insulation resistance as a function of temperature (120°C to 160°C) was determined for a 300nF configuration (4 0805-75nF chips in parallel) between 50V and 400V. The results are described in figure 7. These data clearly show that the conduction mechanism of this dielectric remain nearly constant even to a field as high as 40 Volts/μ. The leakage current follows an arrehenius relationship with temperature. The activation energy of the steady state conduction was found to be about 0.9 electron volts.

The ultimate dielectric breakdown was determined on the 0805 75nF chips. The results are shown in figure 8. The mean of the distribution is about 800 volts while the ultimate breakdown is near 1100 volts (110V/μ).

In order to determine the inherent capability of this dielectric at high voltage and temperature, a highly accelerated life test (HALT) was performed at 350V to 450V and 125°C to 150°C. These data are shown in figures 9a and 9b. As can be seen from the time to failure distribution, the acceleration factor is similar to that reported for high fired X7R barium titanate dielectric[11].

Using the time-to-failure distribution function[12,13], the acceleration factor (AC) can be represented as follows:

$$AC = \frac{(V_t)^n}{(V_o)^n} e^{-\frac{Ea}{K}\left(\frac{1}{T_t} - \frac{1}{T_o}\right)}$$

Where V_o, T_o are rated voltage and temperature (°K)
V_t, T_t are accelerated voltage and temperature.

From figure 9a the voltage acceleration factor, n was calculated to be about 4.0 (between 350V and 450V) and from figure 9b, the activation energy was about 1.21 electron volts (between 126°C and 150°C). Further study is being done with different active layer thickness MLC. The results will be reported in the near future.

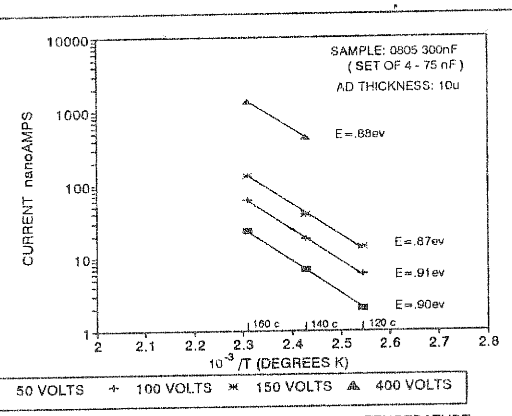

FIGURE 7. STEADY STATE LEAKAGE CURRENT vs TEMPERATURE AT VARIOUS VOLTAGES

A sample of the 0805 130nF chips was electroplated with a nickel barrier layer and 60Sn/40Pb solder. The electrical properties before and after electroplating are summarized in table 2. The slight increase in capacitance and dissipation factor are caused by de-aging. The insulation resistance at 25°C and 150°C were identical for the plated and silver terminated samples.

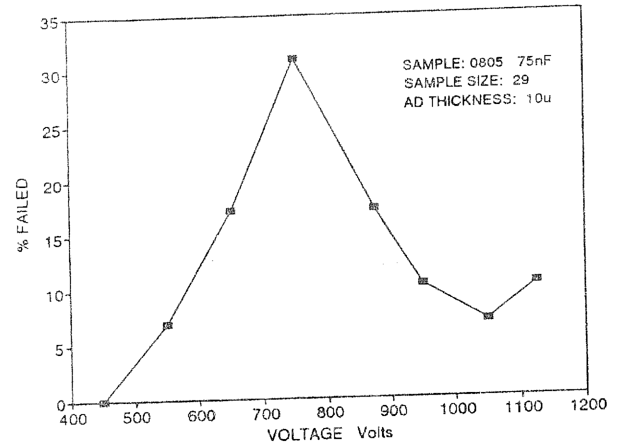

FIGURE 8. DIELECTRIC BREAKDOWN DISTRIBUTION

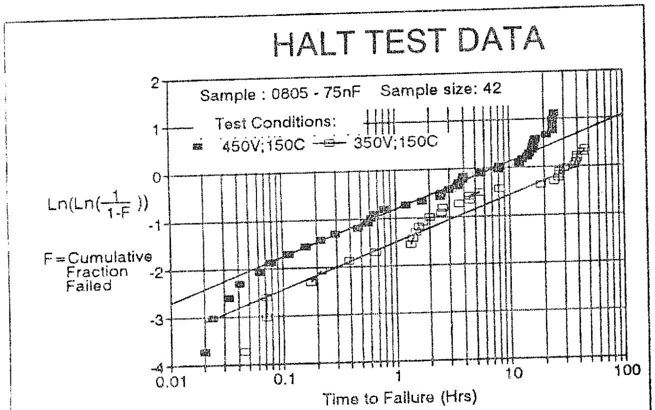

Figure 9a. Distribution of failure times under HALT

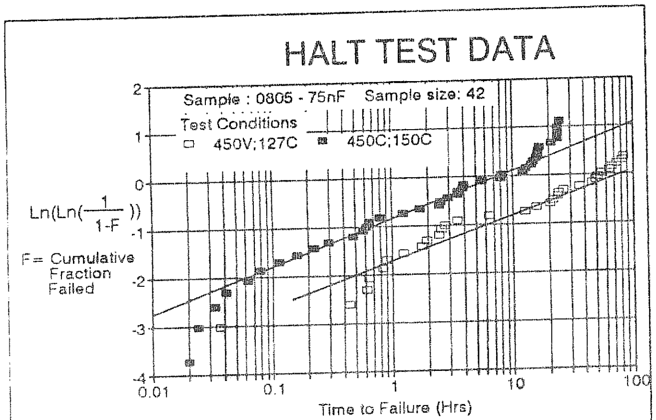

Figure 9b. Distribution of failure times under HALT

Table 2
Electrical Properties of Ni-Sn/Pb Electroplated Chips
(Sample: 0805 - 130nF)

	Silver Termination	Ni-Sn/Pb Plated Termination
Capacitance nF	131	132
Dissipation Factor %	2.4	2.6
Insulation Resistance (Ohms)		
at 100V, 25°C	10^{11}	10^{11}
at 100V, 150°C	$3x10^9$	$3x10^9$
Life test	No degradation	No degradation
IR at 100V, 150°C, 100hrs	$3x10^9$	$3x10^9$

CONCLUSION

A new low fired, K 4400, X7R type dielectric, based on fine grain barium titanate, has been developed. MLC capacitors with 10μ layer thickness in 0805 130nF and 1206 330nF gave an active volumetric capacitance in excess of 6000μF/in^3.

The basic physical and electrical characteristics of this dielectric are comparable to the high fired version of the commercial X7R system. The temperature coefficient of capacitance is well within the X7R specification of $\pm$15%. The life test at 100V and 150°C showed no degradation in insulation resistance even up to 1000 hours.

The steady state activation energy of conduction between 50 and 400 volts and 120°C and 160°C was nearly constant at about 0.9 electron volts.

The preliminary results of highly accelerated life test (HALT) between 350V and 450V and 125°C and 150°C showed a voltage dependence exponent (n) of about 4.0 and activation energy for conduction of 1.21 electron volts.

Electroplating of Ni and Sn/Pb on silver termination showed no change in the electrical properties as compared to unplated chips.

ACKNOWLEDGEMENT

We wish to thank Dr.George Shirn for the fruitful discussions and Messrs. Kamlesh Shah and John Martin for sample preparation and characterization.

REFERENCES

1. G.H.Maher "MLC Capacitor with 6 Micron Active Dielectric and X7R Electrical Characteristics", Ceramic Transactions, Vol.II,pp. 429-435.

2. G.H.Maher "Liquid Phase Assisted Sintering of Ceramic Dielectric for Low Fired MLC Application", Ceramic Transactions, Vol. 20, pp. 365-386.

3. G.H.Maher "Capacitor with Fine Grained $BaTiO_3$ Body and Method of Making", U.S. Patent # 5010443, 1991

4. M.Chu et al "Dielectric Ceramic Composition with High Dielectric Constant and Flat TC characteristics", U.S. Patent # 4882305, 1989.

5. T.Dean "Process for Producing Dielectric Ceramic Composition with High Dielectric Constant, Low Dissipation Factor, and Flat TC Characteristics", U.S. Patent # 4939108, 1990.

6. D.Swanson et al "Chemical Precipitation and Coating Processes for Synthesis of Next Generation Dielectric Powders", Proceedings of Fifth U.S.-Japan Seminar on Dielectric and Piezoelectric Ceramics, Kyoto, Japan, December 1990.

7 Sasaki et al "Dielectric Composition", U.S. Patent # 5086021, 1992.

8. J.Wilson "X7R Dielectric Ceramic Composition and Capacitor Made Therefrom", U.S. Patent # 5128289, 1992.

9. G.H.Maher et al "Comparison of Ag/Pd and Au/Pt/Pd Internal Electrode in MLC X7R Capacitor", 12th Capacitor and Resistor Technology Symposium, 1992.

10. T.Hurley et al "Ceramic Slip Composition", U.S. Patent # 3717487, 1973

11. J.Canner et al "Use of Highly Accelerated Life Test (HALT) to Determine Reliability of Multilayer Ceramic Capacitor", Proceedings of Fifth U.S.-Japan Seminar on Dielectric and Piezoelectric Ceramics, Kyoto, Japan, December 1990.

12. T.Prokopowicz et al "Intrinsic Reliability of Subminiature Ceramic Capacitor", Final Report, ECOM 90705-F NTIS AD-864068, 1969, p.175.

13. W.Minford "Accelerated Life Testing and Reliability of High K Multilayer Ceramic Capacitors", IEEE Transactions on CHMT, 5(3), September 1982, pp 297-300.