Base-Metal Electrode (BME) Ceramic Capacitors for High Reliability Applications

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ABSTRACT

The most common trend in electronics applications is reduction in feature sizes while growing functionality and the overall content of electronics. In the passive components category, Multi-Layer Ceramic Capacitors (MLCC) have followed this trend primarily due to the advent and growth of Base-Metal Electrode technology (BME, e.g., Nickel). Over the past 15 to 20 years, there has been significant advancement in the understanding of the materials, processing, properties and reliability of BME ceramic capacitors. This has led to their widespread use in applications such as electronics for automotive and implantable medical devices where long-term reliability is critical. Requirements for ceramic capacitors for high-reliability electronics for military and aerospace are also driving towards higher capacitance values in smaller case sizes which are difficult to achieve using conventional Precious-Metal Electrode (PME) ceramic capacitors. This paper will review various aspects of design and reliability test data of BME ceramic capacitors, and discuss their potential for high-reliability applications.

Key words: Base Metal Electrode, BME MLCC, BME Ceramic Capacitors, High Reliability, COG, X7R

INTRODUCTION

The world-wide production volume of Multi-Layer Ceramic Capacitors (MLCC) has reached about 2 trillion pieces per year, making them a key class of hybrid electronic components. The trends of miniaturization, enhanced functionality, connectivity, and reliability in consumer, industrial, automotive as well as military electronics have helped drive considerable amount of innovation and development in ceramic capacitor technology. Ceramic capacitors have been able to keep up with the trend of miniaturization due to the adoption and growth of Base-Metal Electrode technology (BME, e.g., Nickel). Over the past two decades, there has been significant advancement in the understanding of the materials, processing, properties and reliability of BME ceramic capacitors. This has led to their widespread use in applications such as electronics for automotive and implantable medical devices where long-term reliability is critical. Requirements for ceramic capacitors for high-reliability electronics for military and aerospace are also driving towards higher capacitance values in smaller case sizes which are difficult to achieve using conventional Precious-Metal Electrode (PME) ceramic capacitors. This paper reviews various aspects of design and reliability test data of BME ceramic capacitors, and discusses their potential for high-reliability applications.

BASE-METAL ELECTRODE (BME) COG

The Base-Metal Electrode (BME) COG MLCC typically use a CaZrO3-based linear dielectric material. Compared to the Class-II dielectrics such as X7R (BX) or X8R materials, the COG dielectrics have the advantages of high stability of capacitance over temperature and voltage (temperature coefficient of capacitance, TCC \leq 30ppm for the

range -55°C to 125°C), no aging of capacitance, no micro-phonic effects, and low dielectric loss (DF). In addition, with the progress in BME technology, the maximum capacitance offering as well as reliability of BME COG are greatly improved compared to the traditional precious metal electrode (PME) COG MLCC [1-2].

BME COG MLCC vs. PME COG MLCC

Traditional COG dielectric materials are mainly based on the barium neodymium titanate (BNT) and are compatible with precious metal electrodes (PME) such as Pd or Ag/Pd. To provide a more cost effective solution, the MLCC manufacturers have mostly converted from PME to BME (mainly Ni electrodes). The BNT material has a dielectric constant (k) of \sim 70, while the k of CaZrO₃-based BME COG material is \sim 31. Although the BME-COG system has a lower dielectric constant, due to the advancement of materials and processing technologies, the BME-COG materials can be processed into MLCC with higher layer counts and thinner layers. Thus, it is possible to use thinner layers of CaZrO₃-based materials compared to BNT, and still obtain higher insulation resistance (IR) and better reliability [1-2]. Hence, for the same case size and voltage rating, BME COG can offer much higher capacitance than PME because of its thinner, but high reliability dielectric layers. For example, the Highly Accelerated Life Test (HALT) reliability of two 1206 case size 10nF MLCC samples (one is PME COG and the other is BME COG) is shown in Fig. 1(a). The dielectric thickness for the BME COG MLCC is 7.0 µm, and that for the PME COG is 11.6 µm. These two samples both passed the required QA life test, which was performed at 125°C and twice rated voltage for 1000 hours. In order to make these parts fail, a HALT test was conducted at 175°C and 400V. Figure 1 shows that the BME 1206/10nF sample exhibits markedly longer time-to-failure (TTF) values compared to the PME version. The median time-to-failure (MTTF) at HALT for PME 1206/10nF was 62.6 minutes, while that for the BME1206/10nF was 869.6 minutes, which is more than an order of magnitude of improvement in MTTF. This HALT result indicates that BME COG will be a better material for high temperature applications than PME COG.



Figure 1. Comparison of PME and BME C0G 1206/10nF/rated voltage 25V Ceramic Capacitors: (a) HALT at 175°C and 400V, and (b) Insulation resistance versus temperature from -55°C to 200°C.

The insulation resistance (IR) of the PME and BME C0G1206/10nF capacitors were also measured in the temperature range of -55° C to $+200^{\circ}$ C under a DC bias of 25V (rated voltage), and are plotted in Fig. 1(b). Even with a much thinner dielectric thickness, the BME C0G typically shows higher IR than the PME C0G in the whole temperature range, especially at temperature above 120°C. Due to its special composition and formulation, the IR of the BME C0G started to increase beyond 120°C (instead of decreasing), which resulted in more than two orders of magnitude higher IR than that of the PME C0G at 200°C. This contributes to the robust reliability of the BME C0G

at 125°C as well as at higher temperatures of 200°C and above. The BME C0G capacitors also maintain their high insulation resistance and TCC within +/-30 ppm at cryogenic temperatures down to -196°C (Liquid N₂ temperature).

Another important aspect of the BME COG dielectric is its high breakdown voltage (BDV) per micron (or per mil) and its ability to maintain BDV above 200V/micron at 150°C and above. Measured BDV values for BME COG 1206/100nF capacitors (rated voltage 25V) are shown in Fig. 2. This property is important while considering the BME COG capacitors for applications at high temperatures such as 125°C and 200°C, and in energy storage and pulse applications. A detailed HALT reliability and modeling study of the BME COG system was published elsewhere [3].



Figure 2. Dielectric Breakdown Voltage (V/micron) of BME C0G 1206/100nF Ceramic Capacitors (rated voltage 25V) at 25°C and 150°C.

The robust reliability of BME COG is attributed to several factors. Ceramic capacitors using BME technology are typically fired under a reducing atmosphere, and then, exposed to a well-controlled re-oxidation process to alleviate any oxygen vacancies that might have formed in the dielectric. The CaZrO₃-based formulation is highly reduction resistant. This is evident from extensive studies of transmission electron microscopy (TEM) of the fired dielectric and dielectric/electrode interfaces, as well as from highly accelerated life tests on BME COG capacitors fired with and without reoxidation treatment. Figure 3(a-b) show typical interfaces of Nickel electrode and BME COG dielectric which show the clean interfaces without any signs of reduction of the dielectric or any spurious Ni/Ca/Zralloy or mixed oxide formation. Figure 4 (a-b) shows insulation resistance of BME COG 1206/47nF/50V and 0805/22nF/50V capacitors fired with and without reoxidation treatment and then HALT tested for 92 hours at 175°C and 400V. These IR results indicate that this dielectric has robust reliability when processed with or without reoxidation. In the CaZrO₃, the Oxygen ions are tightly bound in the perovskite crystal structure due to the high affinities of Calcium and Zirconium ions for Oxygen. This factor, along with the reduction resistant formulation and the wide band gap nature of Zirconium make this BME COG highly reduction resistant, and reliable under bias and elevated temperature conditions. The BME COG capacitors still receive an optimized reoxidation treatment during their manufacturing. The BME COG capacitors are also proven to be extremely robust under long term humidity testing at 1x and 2x rated voltages as well as under low-voltage humidity testing (1.5-1.7V).



BME COG MLCC processed with standard reoxidation

BME C0G MLCC processed without reoxidation

Figure 3 (a-b). Typical Transmission Electron Microscopy (TEM) Micrographs of Electrode/Dielectric Interfaces in Nickel-BME COG Ceramic Capacitors



Figure 4 (a, b). Insulation Resistance of BME C0G Capacitors Processed With and Without Reoxidation: HALT at 175°C and 400V for 92h (a) BME C0G 0805/22nF/rated 50V (b) BME C0G 1206/47nF/rated 50V

Long Term Life Testing of BME C0G Capacitors

Over the past several years, numerous HALT based studies have been published on the BME COG ceramic capacitors [1-3]. A large number of the BME COG capacitor part types have also been qualified through automotive AEC-Q200 qualification protocols and load (bias) life tests for 1000h and 2000h at 125°C, and then at 200°C. However, it is essential to test the performance through 4000 hour life tests at twice rated voltages at 125°C to verify potential for high reliability applications. Figure 5 (a, b) show typical life test results on BME COG capacitors 0805/10nF/rated50V and 1206/22nF/rated25V through 4000 hours at twice rated voltages at 125°C. The plots of insulation resistance verify no failures or degradation of IR occurred through these life test conditions. Table 1 shows a summary of life test results on various part types of BME COG ceramic capacitors through 4000 hours at twice rated voltages at 125°C. The BME COG capacitors including part types such as 1210/104/25V and 0805/103/50V have performed well through 4000 hour life tests with zero failures.



Figure 5 (a, b). Life test results on BME C0G 0805/10nF/rated 50V and 1206/22nF/rated 25V through 4000 hours at twice rated voltages at 125°C.

Part Type	Rated Voltage	Life Test Voltage Test Temp = 125C	1000 hr	2000 hr	3000 hr	4000 h r
C0G 0603 / 680	100	200	0/100	0/100	0/100	0/100
C0G 0603 / 181	50	100	0/100	0/100	0/100	0/100
C0G 0603 / 391	50	100	0/100	0/100	0/100	0/100
C0G 0603 / 392	50	100	0/100	0/100	0/100	0/100
C0G 0603 / 562	25	50	0/100	0/100	0/100	0/100
C0G 0805 / 103	50	100	0/100	0/100	0/100	0/100
C0G 0805 / 103	25	5 0	0/100	0/100	0/100	0/100
C0G 1206 / 182	100	200	0/100	0/100	0/100	0/100
C0G 1206 / 272	50	100	0/100	0/100	0/100	0/100
C0G 1206 / 183	50	100	0/100	0/100	0/100	0/100
C0G 1206 / 223	25	50	0/100	0/100	0/100	0/100
C0G 1210 / 223	50	100	0/100	0/100	0/100	0/100
C0G 1210 / 104	25	50	0/100	0/100	0/100	0/100

Table 1. Summary of Life Test Results on BME C0G Ceramic CapacitorsThrough 4000 hours at Twice Rated Voltages at 125°C

Reliability Testing of BME COG Ceramic Stacks

In the field of ceramic capacitors, it is common to achieve higher capacitance by stacking more than one ceramic chip in the form of capacitor stacks by attaching leadframes to the terminations of the chips. Such stacks can be fabricated in various configurations using suitable feeder chips and leadframe designs. It is important to evaluate life test reliability when ceramic chips are formed into ceramic stacks. Life test results on two types of BME COG stacks are reported below. First, stacks were built using BME COG chips based on dimensions recommended for Case Code 4 stacks as per MIL-PRF-49470. Each stack consisted of 5 chips of case code 4 each having a capacitance of 0.5μ F and thickness of 0.1 inch. These Case Code 4 BME COG stack had a capacitance of 2.5μ F and a rated voltage of 50V. These stacks passed life test at 125° C through 4000hrs without any failures or degradation of insulation resistance as shown in Fig. 6.



Figure 6. Life test at 125°C through 4000hrs on Case-Code-4 BME C0G stacks 2.5µF/rated 50V.

Custom stacks were also built using 30 chips of BME COG case size EIA1812/0.22 μ F/50V. The chips were arranged in two rows of 15 chips each. The stacks had a length of 0.98in and a width of 0.20in. These stacks had a capacitance of 6.6 μ F and were rated at 50V. Life test was conducted at rated voltage (50V) at a temperature of 225°C for 1000hr. Test sample size of six stacks was limited due to the dimensions of the test chamber. The results shown in Fig. 7 indicate that the BME COG stacks passed life test at 225°C and rated voltage of 50V through 1000hr without any issues.



Fig.. 7. Life test at 225°C and 1000h on custom BME C0G stacks with capacitance of 6.6µF and rated voltage of 50V.

BASE-METAL ELECTRODE (BME) X7R Material and Microstructure Design of BME X7R Ceramic Capacitors

During the past two decades, the majority of research and development in the field of ceramic capacitors has focused on understanding and improving BME ceramic capacitors with respect to their raw materials, processing and equipment for superior dispersion, build-up and thermal treatment, as well as to improve their reliability performance. Although some of these efforts were driven by efforts towards lower cost and large scale manufacturing, they have led to significant knowhow for tailoring the design of capacitors ceramic for high reliability applications. Figure 2(a-c) demonstrates some of the key improvements in the raw materials and microstructure design employed in the BME X7R ceramic dielectric. Depending on the design thickness of the dielectric, Barium Titanate (BaTiO₃) powders of high crystallinity and narrow particle size distribution are chosen for the dielectric (available down to 150nm. 200nm, 250nm size, etc.). Highly sophisticated milling, dispersion and coating techniques allow molecular- and nanometer-level dispersion of dopant elements and additives within the BaTiO₃-based ceramic. This helps to achieve a core-shell type microstructure in the ceramic dielectric with a core of high crystallinity barium titanate, and a uniform grain size within the fired or sintered ceramic dielectric.



(c) Core-Shell Microstructure



Figure 8 (a-c) Some of the key material design features for improving the microstructure, performance and reliability of BME MLCC

Long Term Life Testing of BME X7R Capacitors

Similar to the BME COG system, a large number of the BME X7R capacitor part types have also been qualified through automotive AEC-Q200 qualification protocols and load (bias) life tests for 1000h and 2000h at 125°C. A subset of the X7R part types have also been qualified through 1000 hour life tests at 150°C, and are classified as X8L type since their TCC is between -15% and +15% at 125°C, but the TCC at 125°C -150°C is between +15% and -40%. The BME X7R type capacitors have been used successfully in automotive applications for over 10 years.

Although it is possible to make high capacitance value BME X7R MLCC due to the advancement in materials, processing and testing/screening, a systematic and rigorous approach is required to design and evaluate BME X7R capacitors for high reliability applications. Some examples of the scrutiny and improvements based on material selection and tailoring of ceramic dielectric microstructure were already described above. In addition, detailed part type specific reliability studies using HALT and life testing are conducted to ascertain and optimize various chip design and processing parameters for robust long term reliability of the capacitors. These parameters include dielectric thickness, sintered ceramic grain microstructure, chip designs and build up conditions, thermal processing parameters, and conditions for electrical testing, screening and burn-in. Finally, it is essential to test the reliability performance through 4000 hour load (bias) life tests at twice rated voltages at 125°C to verify potential for high reliability applications.



Figure 9 (a-d). Insulation Resistance Plots at 25°C (a and c) and 125°C (b and d) on BME X7R capacitors 1206/1µF/Vr50V tested at 100V and 1206/2.2µF/Vr16V tested at 32V through 4000 hours at 125°C.

Figure 9 (a-d) show life test results on BME X7R capacitors $1206/1\mu$ F/rated voltage 50V tested at 100V and $1206/2.2\mu$ F/rated voltage 16V tested at 32V through 4000 hours at 125° C. The plots of insulation resistance verify no failures or degradation of IR occurred through these life test conditions. Table 2 shows a summary of life test results on various part types of BME X7R ceramic capacitors through 4000 hours at twice rated voltages at 125° . Some part types with somewhat aggressive chip designs (higher capacitance values) were also included in this load life testing and were tested at more than one life test voltage. Among all the part types and life test conditions chosen, only one piece failed in X7R 0805/2.2\muF. This part type was life tested at 20V and 13V, and the only

failure that occurred was when tested at the higher voltage of 20V. The failure occurred between 2000h and 3000hr into the life test at 20V and was found to be a small dielectric breakdown. However, these BME X7R 0805/2.2 μ F ceramic capacitors passed 4000 hour life tests with zero failures when tested as 6.3V rated capacitors (life test at 13V). A growing list of BME X7R capacitors (Table 2) including part types such as 1210/4.7 μ F and 1206/2.2 μ F have performed well through 4000 hour life tests with zero failures. Thus, the BaTiO₃-based BME X7R dielectric offers great options for extending capacitance ranges in BX/X7R for high reliability applications. Work continues to include additional batches and part types in this evaluation.

Part Type	Rated Voltage	Life Test Voltage Test Temp = 125C	1000 hr	2000 hr	3000 hr	4000 hr
X7R 0603 / 154	16	32	0/100	0/100	0/100	0/100
X7R 0603 / 154	25	50	0/100	0/100	0/100	0/100
X7R 0603 / 224	10	20	0/100	0/100	0/100	0/100
X7R 0603 / 224	10	20	0/100	0/100	0/100	0/100
X7R 0603 / 224	16	32	0/100	0/100	0/100	0/100
X7R 0805 / 684	25	50	0/100	0/100	0/100	0/100
X7R 0805 / 105	10	20	0/77	0/77	0/77	0/77
X7R 0805 / 105	16	32	0/77	0/77	0/77	0/77
X7R 0805 / 105	10	20	0/140	0/140	0/140	0/140
X7R 0805 / 105	10	20	0/140	0/140	0/140	0/140
X7R 0805 / 225	10	20	0/77	0/77	1/77	1/77
X7R 0805 / 225	6.3	13	0/77	0/77	0/77	0/77
X7R 1206 / 684	50	100	0/200	0/200	0/200	0/200
X7R 1206 / 105	50	100	0/100	0/100	0/100	0/100
X7R 1206 / 105	25	50	0/100	0/100	0/100	0/100
X7R 1206 / 225	16	32	0/140	0/140	0/140	0/140
X7R 1206 / 225	25	50	0/100	0/100	0/100	0/100
X7R 1206 / 225	16	32	0/150	0/150	0/140*	0/140*
X7R 1210 / 475	10	20	0/77	0/77	0/77	0/77
X7R 1210 / 475	16	32	0/77	0/77	0/77	0/77
X7R 1210 / 475	25	50	0/77	0/77	0/77	0/77
X7R 1812 / 475	10	20	0/100	0/100	0/100	0/100
X7R 1812 / 475	16	32	0/100	0/100	0/100	0/100
X7R 1812 / 475	25	50	0/100	0/100	0/100	0/100

Table 2. Summary of Life Test Results on BME C0G Ceramic Capacitors through 4000 hours at Twice Rated Voltages at 125°C

* 10 pcs removed for other testing (ESR)

SUMMARY

Criteria have been redesigned for chip designs, dielectric thickness and ceramic dielectric microstructures to assure robust reliability of BME COG and X7R MLCC. Reliability evaluations were based on extensive HALT and Life Test studies. In the case of the CaZrO₃-based BME COG dielectric, various HALT studies as well as load life tests at 125°C through 4000h as well as at 200°C for 2000h on MLCC and stacked capacitors demonstrate the robust reliability of this system. This COG material meets the EIA X9G specification with TCC \leq 30ppm from -196°C to +200°C, possesses high insulation resistance over this temperature range, shows zero VCC and no piezoelectric effects (non-ferroelectric material). Through systematic optimization of materials, microstructure, processing and

testing, the $BaTiO_3$ -based BME X7R dielectric and the corresponding chip designs have been optimized for enhanced reliability. The 4000 hour life test results indicate that the BME X7R system offers great options for extending capacitance ranges in the BX/X7R family of capacitors.

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