

# Advanced Ceramic Capacitor Solutions for High Temperature Applications

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## Abstract

*For high temperature applications at 150 °C or above, such as those in electronics for down-hole drilling, geothermal energy generation and power electronics, a robust dielectric material is necessary for capacitors. Ceramic capacitors using X7R and X8R type dielectrics are designed for applications up to 125 °C and 150 °C, respectively. At temperatures above 150 °C, these X7R/X8R types of ceramic capacitors typically suffer from degradation of reliability performance and severe reduction in capacitance, especially when bias is applied. Recently, a Class-I dielectric material has been developed using Nickel electrodes for high temperature application up to 200-250 °C. Due to its linear dielectric nature, this material exhibits highly stable capacitance as a function of temperature and voltage. This paper will report electrical properties and reliability test data on these Class-I type ceramic capacitors in SMD chip and leaded configurations at 150-200 °C and above, and discuss possible mechanisms behind the robust reliability of this high temperature dielectric.*

Key words: High temperature capacitor, Ceramic Capacitor, BME MLCC, C0G

## 1. Introduction

For applications in harsh environment conditions, such as down-hole oil exploration, automotive under the hood electronics, military devices and avionics, etc., the maximum operating temperatures can be 175-200 °C or higher. These industries need capacitors that are robust and reliable at such high temperatures. However, at these temperatures, dielectric materials either exhibit significantly lower capacitance compared to that at room temperature, or exhibit high dielectric losses, and hence, are not commonly available in the market [1-4]. Commercial C0G and X7R dielectrics are usually designed for applications up to 125 °C, while X8R dielectric is designed for applications up to 150 °C. One approach for using the X7R/X8R dielectric at temperatures above their design limit of temperature is by de-rating their rated voltages due to reliability concerns. For example, some X7R dielectrics can be used at 150 °C after 50% voltage de-rating [5]. Similarly, it may be possible to use some X8R capacitors at temperatures above 150 °C by appropriate voltage de-rating, however, there is

still a need for more robust ceramic capacitors for high temperature applications.

One commercially available solution for high temperature applications is KEMET's base-metal electrode (BME) C0G MLCC. This BME C0G typically uses a  $\text{CaZrO}_3$ -based linear dielectric material. Compared to Class-II dielectrics such as the X7R/X5R/X8R materials, the C0G dielectrics have the advantages of high stability of capacitance over temperature and voltage, no aging of capacitance, no micro-phonic effects, and low dielectric loss ( $DF$ ). In addition, with the progress in BME technology, both, the maximum capacitance offering as well as the reliability of this BME C0G are greatly improved compared to those for the traditional precious metal electrode (PME) C0G MLCC [6-7]. The BME C0G dielectric also exhibits high insulation resistance (or low leakage) at high temperatures, which is key to achieving excellent reliability at those temperatures. This paper will demonstrate the performance of BME C0G MLCC at temperatures up to 200 °C and compare it with PME C0G or X8R based MLCCs.

## 2. Electrical Performance at High Temperatures

### 2.1. BME C0G MLCC vs. PME C0G MLCC

Traditional C0G 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  $\text{CaZrO}_3$ -based BME C0G material is  $\sim 31$ . Although the BME-C0G system has a lower dielectric constant, due to the advancement of materials and processing technologies, the BME-C0G materials can be processed into MLCC with higher layer counts and thinner layers. Thus, we are able to use thinner layers of  $\text{CaZrO}_3$ -based materials compared to BNT, and still obtain higher insulation resistance (IR) and better reliability [6, 7]. Hence, for the same case size and voltage rating, BME C0G can offer much higher capacitance than PME because of its thinner, but high reliability dielectric layers [10]. For example, the Highly Accelerated Life Test (HALT) reliability of two 1206 case size 10nF MLCC samples (one is PME C0G and the other is BME C0G) is shown in Fig. 1. The dielectric thickness for the BME C0G MLCC is  $7.0 \mu\text{m}$ , and that for the PME C0G is  $11.6 \mu\text{m}$ . These two samples both passed the required QA life test, which was performed at  $125^\circ\text{C}$  and twice rated voltage for 1000 hours. In order to make these parts fail, the HALT test was conducted at  $175^\circ\text{C}$  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 BME 1206/10nF was 869.6 minutes, which is more than an order of magnitude of improvement in MTTF. This HALT result indicates that BME C0G will be a better material for high temperature applications than PME C0G. The topic of reliability of BME-C0G is discussed further in a later section on lifetime prediction study.

The insulation resistance (IR) of these two samples of C0G1206/10nF were also measured in the temperature range of  $-55^\circ\text{C}$  to  $+200^\circ\text{C}$  under a DC bias of 25V, and are plotted in Fig. 2. 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  $120^\circ\text{C}$ . Due to its special composition and formulation, the IR of the BME C0G started to increase beyond  $120^\circ\text{C}$  (instead of decreasing), which resulted in more than two orders of magnitude higher IR than that of the PME C0G at  $200^\circ\text{C}$ . This

contributes to the robust reliability of the BME C0G at high temperatures.

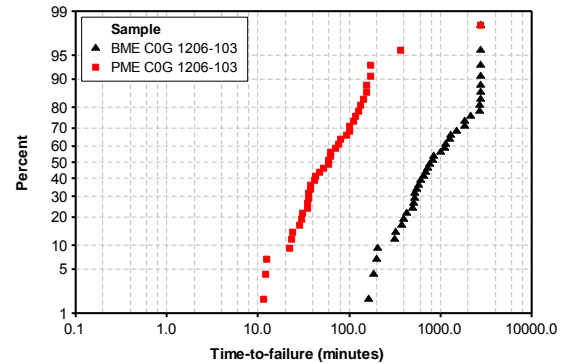


Fig. 1. HALT for PME and BME C0G 1206/10nF MLCCs. (HALT conducted at  $175^\circ\text{C}$  and 400V.)

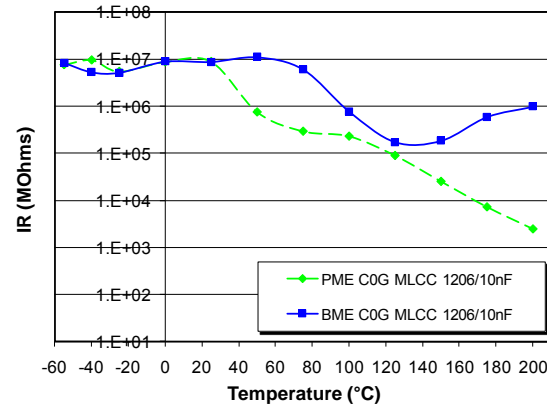


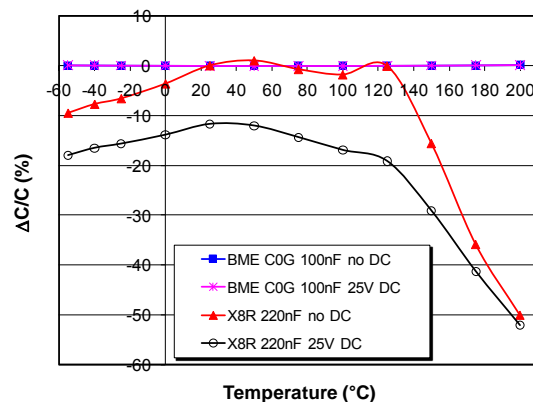
Fig. 2. Dependence of IR on temperature with 25V DC bias for PME and BME C0G MLCC.

### 2.2. BME C0G MLCC vs. X8R MLCC

The samples used for comparison are KEMET BME C0G MLCC (1206 case size, 100nF & 25V rated) and a commercially available X8R MLCC (1206 case size, 220nF & 50V rated). The dielectric thickness for the BME C0G MLCC was  $2.8 \mu\text{m}$ , and that for the X8R MLCC was  $11.2 \mu\text{m}$ , which is nearly four times thicker than the BME C0G MLCC.

Figure 3 shows the relative capacitance variation with reference capacitance at  $25^\circ\text{C}$  ( $\Delta\text{C}/\text{C}$ ) versus temperature for BME C0G MLCC and X8R MLCC in the temperature range of  $-55^\circ\text{C}$  to  $+200^\circ\text{C}$ . The BME C0G MLCC exhibit extremely flat response over the whole temperature range whether with 25V DC bias applied or without any DC bias. The maximum temperature coefficient of capacitance (TCC) from  $-55^\circ\text{C}$  to  $+200^\circ\text{C}$  is found to be 13.4 ppm/ $^\circ\text{C}$ , which indicates that this dielectric material

is not only compliant with the EIA C0G specification, but also can be extended to the X9G specification (capacitance variation from the reference point of 25°C should be within  $0 \pm 30$  ppm/°C (or  $\Delta C_{\text{Max}}/C \leq 0.525\%$ ) over the temperature range of  $-55^\circ\text{C}$  to  $+200^\circ\text{C}$ ). The X8R MLCC hold their capacitance reasonably well below 125°C. However, at temperatures above 125°C, their capacitance decreased sharply. This is because at temperatures above the Curie point (125°C for BaTiO<sub>3</sub>-based materials), the capacitance (C)–temperature (T) dependence for ferroelectric material follows the Curie-Weiss Law:  $C \propto k \propto \Theta/(T-T_c)$ , where  $k$  is the dielectric constant,  $\Theta$  is the Curie constant, and  $T_c$  is the Curie temperature. At 200°C, the capacitance of X8R MLCC dropped by 50.1% without DC bias, and by 52.1% while under 25V DC bias compared to their capacitance at 25°C. Hence, the 220 nF X8R MLCC had almost the same effective capacitance at 200°C as the 100 nF BME C0G MLCC. One can also expect that at temperatures above 200°C, the capacitance of the X8R MLCC will reduce to values lower than 100 nF. Thus, for high temperature applications, the actual capacitance under the use conditions needs a serious consideration because of the severe capacitance reduction with temperature (versus considering only the nominal capacitance value at room temperature). Another factor to note is that the actual electric field applied in the BME C0G MLCC was almost 4 times higher than that for the X8R MLCC because of the dielectric thickness difference. If the X8R MLCC were under the same field strength as the BME C0G MLCC, their effective capacitance would have been even lower.

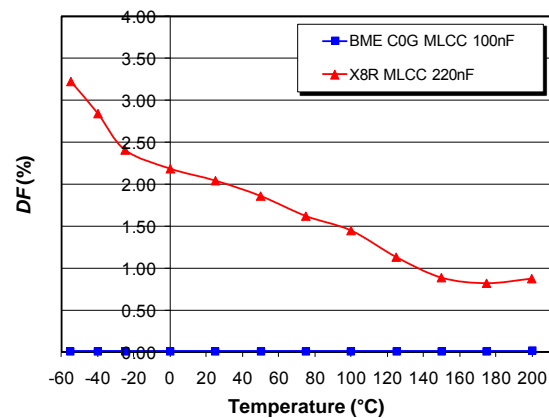


**Fig. 3.  $\Delta C/C$  variation with temperature and DC bias.**

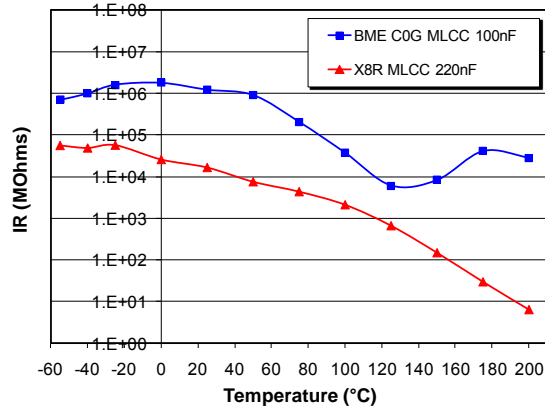
The measured dielectric loss or dissipation factor ( $DF$ ) of the BME C0G and X8R MLCC samples without DC bias in the temperature range of

$-55^\circ\text{C}$  to  $+200^\circ\text{C}$  is shown in Fig. 4. The BME C0G MLCC has a maximum  $DF$  of 0.016% over the temperature range investigated. Such extreme low dielectric loss is in good agreement with the  $D-E$  curve analysis, which showed almost zero loop area at high temperatures. The  $DF$  of the X8R MLCC was 2.04% at 25°C and decreased with increasing temperature because of the easier rotation of ferroelectric domains at increasing temperatures. However, the X8R MLCC still showed a  $DF$  of 0.87% at 200°C.

The comparison of insulation resistance (IR) was quite revealing between the BME C0G and X8R MLCC, as shown in Fig. 5. From room temperature to 200°C, the IR of BME C0G MLCC measured at 25V changed from 1.22 TΩs to 28.3 GΩs. The X8R MLCC sample used in this study was originally rated at 50V for applications below 150°C. In these IR measurements, a voltage of only 25V DC was applied. Even then, the IR of X8R MLCC decreased more than 3 orders of magnitude to 6.3 MΩs at 200°C. This results in an  $R \cdot C$  product (capacitance times IR) of only  $0.67 \text{ M}\Omega \cdot \mu\text{F}$  at 200°C, which will be of great concern for the majority of high temperature applications. Thus, the X8R MLCC would need to be de-rated in voltage rating for high temperature applications above 150°C, while the BME C0G capacitors are expected to hold their capacitance,  $DF$  as well as IR reasonably well over the temperature range of  $-55^\circ\text{C}$  to  $+200^\circ\text{C}$  as shown in this study.

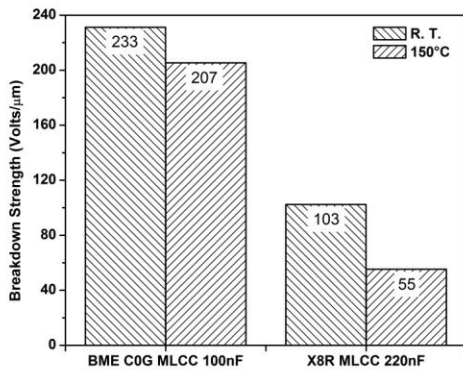


**Fig. 4. % $DF$  dependence on temperature without DC bias.**



**Fig. 5. Dependence of IR on temperature with 25V DC bias.**

The dielectric breakdown strength of the BME C0G and X8R MLCC samples was also investigated, and results are shown in Fig. 6. From room temperature to 150°C, the breakdown strength of BME C0G MLCC only dropped from 233 Volts/ $\mu\text{m}$  to 207 Volts/ $\mu\text{m}$ , while that for the X8R MLCC dropped from 103 Volts/ $\mu\text{m}$  to 55 Volts/ $\mu\text{m}$ , which was a reduction of 46%. At 150°C, the breakdown strength of BME C0G MLCC is 3.7 times higher than the X8R MLCC. Breakdown test for X8R MLCC could not be conducted at temperatures above 150°C due to its high leakage. The high breakdown strength of BME C0G capacitors make them more attractive for energy storage applications [8-10].



**Fig. 6. Dielectric breakdown strength at room temperature and 150°C.**

### 3. Lifetime Prediction at High Temperatures

One of the key parameters for high temperature applications is the long term reliability. As reported earlier [6, 7], unlike the typical BaTiO<sub>3</sub> based BME X7R/X5R dielectric materials, oxygen vacancy is not a concern for reliability in BME C0Gs

based on CaZrO<sub>3</sub>. In order to estimate the lifetime in high temperatures applications, a highly accelerated life test (HALT) study was used. The HALT data under various temperature and voltage conditions was used to extrapolate the reliability of the capacitor at typical use conditions. The detailed principle and procedures of this kind of study have been well reported [11-13], and will be only summarized in this paper. An empirical equation by Prokopowicz and Vaskas (P-V equation), shown in equation (2), is employed to correlate the reliability behavior under accelerated test conditions to operating conditions.

$$\frac{t_1}{t_2} = \left( \frac{V_2}{V_1} \right)^n \exp \left[ \frac{E_a}{k} \left( \frac{1}{T_{1abs}} - \frac{1}{T_{2abs}} \right) \right] \quad (2)$$

where:

- $t_i$  = time to failure under conditions  $i$ ,
- $V_i$  = voltage under condition  $i$ ,
- $n$  = voltage stress exponential,
- $E_a$  = activation energy for dielectric wear out,
- $k$  = Boltzmann's constant ( $8.62 \times 10^{-5}$  eV/K),
- $T_i$  = absolute temperature for condition  $i$ .

The P-V equation can be simplified to equation (3):

$$t = A \frac{1}{V^n} \exp \left( \frac{E_a}{kT} \right) \quad (3)$$

where  $A$  is the time constant. Equation (3) can also be put into the following natural log form for easy experimental data multi-regression.

$$\ln[t] = \ln[A] - n \ln[V] + \frac{E_a}{kT} \quad (4)$$

Typically the time ( $t$ ) used for reliability modeling is the median time to failure (MTTF). By running HALT at multiple combinations of voltages and temperatures, the median time to failure data at each combination can be obtained from the time-to-failure data distribution fitting if more than 50% of the parts failed during testing. Using the multi-regression tool in a commercial software package, parameters such as  $A$ ,  $n$ , and  $E_a$  can be determined. Thus, from equation (3), a lifetime can be predicted under given use conditions (voltage  $V$  and temperature  $T$ ).

Three BME C0G MLCC part types, 0402-101-50V, 0603-471-50V and 0805-222-50V were tested under HALT conditions at 4 temperatures (125°C, 150°C, 175°C, and 200°C) and 6 voltages (300V, 400V, 450V, 500V, 550V, and 600V) for 200 hours. The maximum temperature (200°C) and maximum voltage (600V) used in this study were limited by the equipment capability. A sample size of 20 pieces was used in each HALT run. HALT

time-to-failure (TTF) was recorded when IR at test temperature dropped below 4.28 M $\Omega$ .

Figure 7 shows the HALT time-to-failure distributions for part type 0805-222-50V under various temperature and voltage conditions. Following the steps described above, a time constant  $A$ , voltage exponential  $n$ , and the activation energy  $E_a$  were obtained by multi-regression and are listed in Table I. The  $R$ -Sq. of this regression was 94.7%. By substituting values of  $A$ ,  $n$  and  $E_a$  parameters back into equation (3), MTTF can be calculated for various use conditions. Some of these use conditions are listed in Table II as examples. At 150°C and 50V, the predicted lifetime is over 52.6 million years, and even at 200°C and 50V, the predicted median lifetime is 1.48 million years.

HALT testing was also conducted on part types 0402-101-50V and 0603-471-50V at several combinations of temperatures and voltages. As shown in Fig. 8, there were not enough failures under

even the most severe HALT conditions used up to 200hrs of test time. While this is a strong proof of the robust reliability of these BME C0G capacitors under the accelerated test conditions, these tests still could not cause the required number of failures (50<sup>th</sup> percentile) needed to model the median-time-to-failure (MTTF) data. Thus, their HALT distribution fitting can not be performed. This also indicates that it is not necessary to de-rate the voltage rating for the BME C0G MLCC tested in this study for high temperature applications, which is a clear advantage over the MLCCs based on X7R/X8R dielectrics. It is important to mention that BME C0G chips of various case sizes, capacitance and rated voltages have been tested through long term life tests at 125°C, 150°C and 200°C without any failures or degradation of electrical characteristics such as capacitance, %DF or insulation resistance.

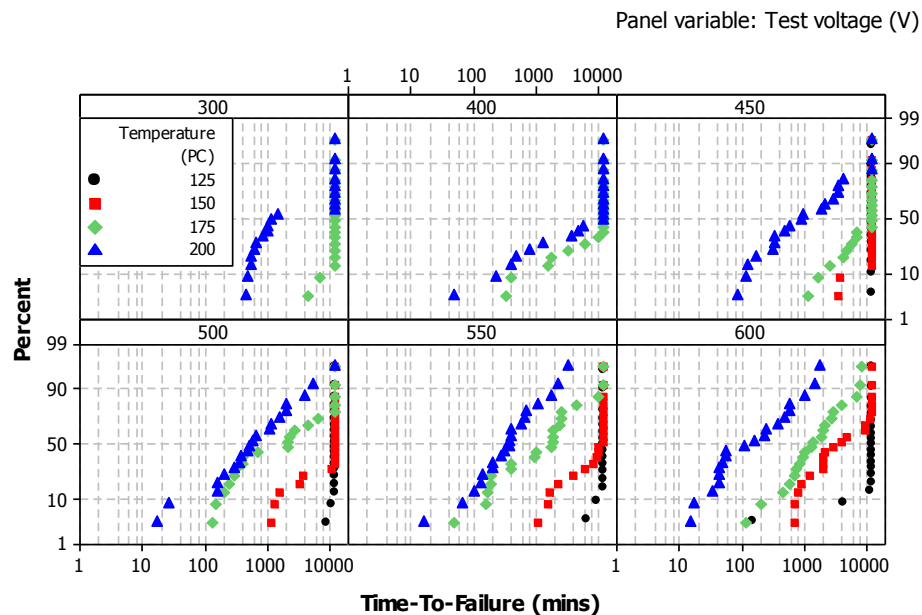


Fig. 7. HALT distributions at various test conditions for 0805-222-50V.

Table I. Multi-regression Results for HALT-TTF P-V Model for 0805-222-50V

Part Type	A (mins)	n	$E_a$ (eV)	$R^2$
C0805C222J5GAB	1.30E+14	9.0	1.23	94.7%



Table II. Lifetime Prediction from MTTF Model for 0805-222-50V

Part Type	CAP (nF)	Rated Voltage	Application Temperature (°C)	Application Voltage	MTTF (Years)
C0805C222J5GAB	2.20	50	25	50	7.47E+13
				25	3.91E+16
			125	50	4.39E+08
				25	2.29E+11
			150	50	5.26E+07
				25	2.75E+10
			175	50	7.98E+06
				25	4.17E+09
			200	50	1.48E+06
				25	7.73E+08

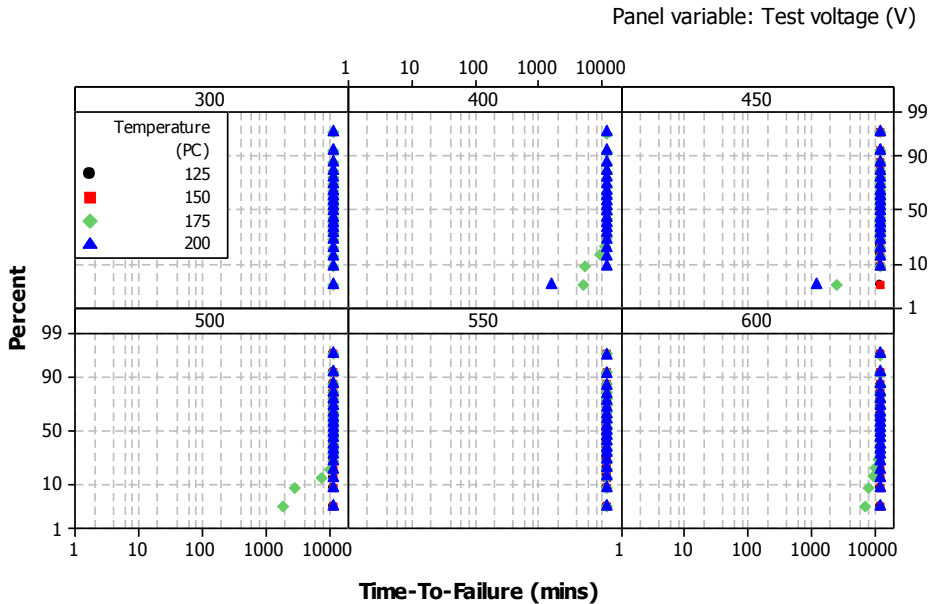
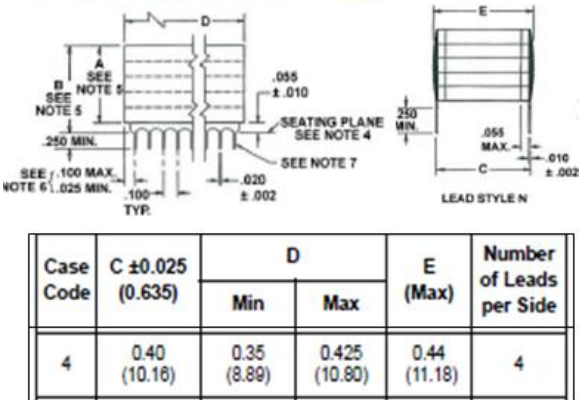


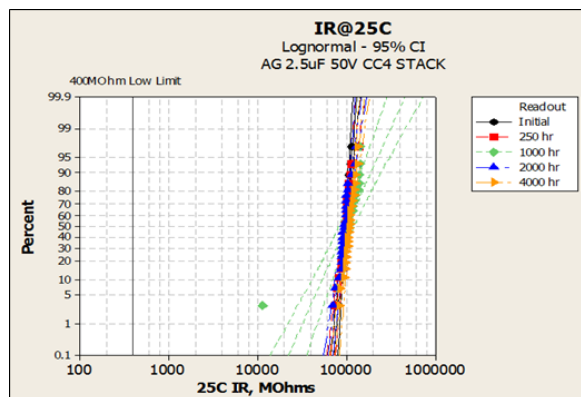
Fig. 8. HALT distributions at various test conditions for 0603-471-50V.

4. Reliability Testing of 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 0.5 $\mu$ F and thickness of 0.1 inch. Such Case Code 4 BME COG stack had a capacitance of 2.5 $\mu$ F and 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. 9.

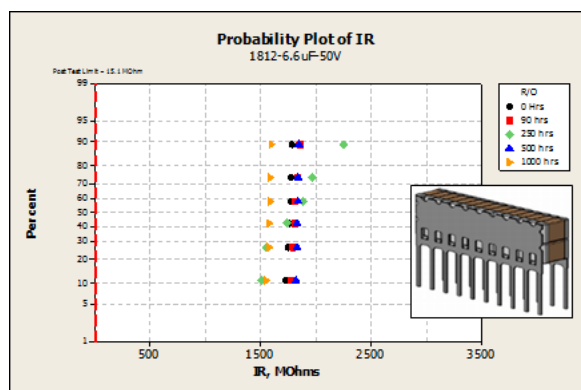
BME COG Stack construction similar to MIL-PRF-49470 Stacks





**Fig. 9. 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 C0G case size EIA1812/0.22µF/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 6.6µF 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. 10 indicate that the BME C0G stacks passed life test at 225°C at rated voltage of 50V through 1000hr without any issues.



**Fig. 10. Life test at 225°C through 1000hrs on custom BME C0G stacks with capacitance of 6.6µF and rated voltage of 50V.**

## 5. Summary

1. The CaZrO<sub>3</sub> based BME C0G dielectric material shows robust performance for high temperature applications. At temperature up to 200°C, it meets the EIA X9G specification (capacitance variation from the reference point of 25°C should be within  $0 \pm 30$  ppm/°C (or  $\Delta C_{\text{Max}}/C \leq 0.525\%$ ) over the temperature range of -55°C to +200°C) and exhibits good long term reliability.

2. The CaZrO<sub>3</sub> based BME C0G MLCCs exhibit good potential for energy storage applications even when used at temperatures above 150°C. This is complimented by their stable dielectric constant, low dielectric losses, high IR, high breakdown strengths and good reliability at high temperatures.

3. Traditional BaTiO<sub>3</sub>-based X7R and X8R dielectrics suffer from severe capacitance reduction, insulation resistance deterioration, and breakdown voltage reduction at high temperatures above 150°C. Thus, their nominal capacitance and the voltage rating should be carefully investigated if applications involve temperatures above 150°C.

## 6. References

- [1] E. F. Alberta, et al., "High Temperature Ceramic Multilayer Capacitors," p69-72, *Proceedings of the 24<sup>th</sup> Symposium for Passive Components (CARTS USA 2004)*, San Antonio, TX, USA, 2004.
- [2] C. J. Stringer, et al., "New Relaxor Dielectrics for High Temperature Capacitors," p381-384, *Proceedings of the 12<sup>th</sup> US-Japan Seminar on Dielectric and Piezoelectric Ceramics*, Annapolis, Maryland, USA, 2005.
- [3] E. F. Alberta, et al., "High Temperature Ceramic Capacitors," p471-477, *International Conference and Exhibition on High Temperature Electronics (HiTEC 2006)*, Santa Fe, NM, Mexico, USA, 2006.
- [4] W. Schulze, et al., "High Temperature Capacitor - Sodium Bismuth Titanate – Idea to Application," p478-484, *International Conference and Exhibition on High Temperature Electronics (HiTEC 2006)*, Santa Fe, NM, Mexico, USA, 2006.
- [5] <http://www.epcos.com/inf/20/10/ds/MLSC.pdf>.
- [6] X. Xu, et al., "High CV BME C0G," p179-188, *Proceedings of the 27<sup>th</sup> Symposium for Passive Components (CARTS USA 2007)*, Albuquerque, NM, USA, 2007.
- [7] A. Gurav, et al., "Characteristics of CaZrO<sub>3</sub>-Based BME C0G Dielectric," p359-362, *Proceedings of the 13<sup>th</sup> US-Japan Seminar on Dielectric and Piezoelectric Ceramics*, Awaji Island, Hyogo, Japan, 2007.

- [8] N. H. Fletcher, et al., "Optimization of Energy Storage Density in Ceramic Capacitors," *J. Phys. D: Appl. Phys.*, 29, 253-258 (1996).
- [9] M. D. Waugh, et al., "Structure-Property Investigation of a Modified PbHfO<sub>3</sub> Composition for High Energy Storage", p153-163 in *Ceramic Transactions, Vol. 90, Manufacturing of Electronic Materials and Components*, The American Ceramic Society, 1998.
- [10] X. Xu, et al., "Advances in Class-I COG MLCC and SMD Film Capacitors," p449-461, *Proceedings of the 28<sup>th</sup> Symposium for Passive Components (CARTS USA 2008)*, Newport Beach, CA, USA, 2008.
- [11] T. Prokopowicz and A. Vaskas, "Research and Development, Intrinsic Reliability, Subminiature Ceramic Capacitors," Final Report, ECOM-9705-F, 1969 NTIS AD-864068.
- [12] J. L. Paulsen, et al., "Highly Accelerated Life Testing of KEMET Base Metal Electrode (BME) Ceramic Chip Capacitors," p265-270, *CARTS 2001*.
- [13] T. Ashburn, et al., "Highly Accelerated Testing of Capacitors for Medical Applications," *Proceedings of the 5<sup>th</sup> SMTA Medical Electronics Symposium*, Anaheim, CA, USA, 2008.