Advances in Ceramic Capacitors for High Temperature Applications

Abhijit Gurav, Xilin Xu, Jim Magee, Reggie Phillips and Travis Ashburn
KEMET Electronics Corporation
2835 KEMET Way, Simpsonville, SC 29681, U.S.A.
Tel: +01-864-963-6300, Fax: +01-864-963-6492

Abstract

There is a growing need for capacitors for applications at temperatures of 150°C or above, such as electronics for down-hole drilling and exploration, geothermal energy generation and power electronics. Conventional X7R and X8R type ceramic capacitors are designed for applications up to 125°C and 150°C, respectively. At temperatures above 150°C, these types of capacitors typically suffer from degradation of reliability performance and severe reduction in capacitance, especially under DC bias conditions. Recently, a Class-I C0G dielectric has been developed using Nickel electrodes for high temperature application up to 200°C and beyond. Due to its linear dielectric nature, this material exhibits highly stable capacitance as a function of temperature and voltage. Multi-layer ceramic capacitors (MLCC) made from this material can be qualified as X9G with robust reliability. A Class-II modified-X7R dielectric composition with nickel internal electrodes showing robust reliability at 175°C has also recently been developed. This paper will report electrical properties and reliability test data on these Class-I C0G and Class-II ceramic capacitors at high temperatures of 150-200°C and above.

Key words: High temperature capacitor, BME MLCC, C0G, X9G, X7R, Ceramic Capacitor

1. Introduction

For applications in harsh environment conditions, such as down-hole oil exploration, industrial electronics, military devices and avionics, etc., the maximum operating temperature are commonly 175-200°C or higher. These industries need capacitors that are robust and reliable at these high temperatures. However, at these temperatures, dielectric materials either have significant capacitance variation with 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.

One commercially available solution for high temperature applications is KEMET's base-metal electrode (BME) C0G MLCC. This BME C0G typically uses a $CaZrO_3$-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, the maximum capacitance offering as well as reliability of this BME C0G are greatly improved compared to the traditional precious metal electrode (PME) C0G MLCC [6-7]. 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. Furthermore, development of high temperature Class-II X7R capacitors will be discussed which has a great potential for offering higher CV values due to its high dielectric constant of 2800-3000.

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) system and are compatible with precious metal electrodes (PME) such as Pd or Ag/Pd. To provide a more cost effective solution, MLCC manufacturers have mostly converted from PME to BME (mainly Ni electrodes). The BNT material has a dielectric constant (k) of ~70, while the k of $CaZrO_3$-based BME C0G material is ~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, it is possible to use thinner layers of $CaZrO_3$-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 μm, and that for the PME C0G 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 obtain useful failure rate data for modeling, the 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 C0G is a superior 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°C to +200°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°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 high temperatures.

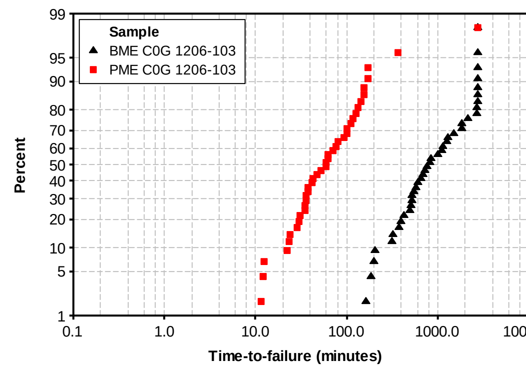

Figure 1. HALT for PME and BME C0G 1206/10nF MLCCs. (HALT conducted at 175°C and 400V.)

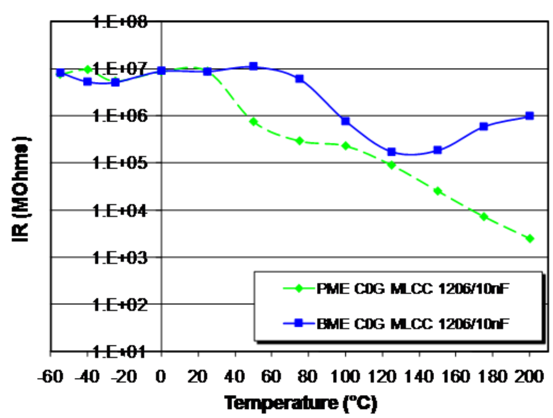

Figure 2. Dependence of IR on temperature with 25V DC bias for PME and BME C0G MLCC.

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 μm, and that for the X8R MLCC was 11.2 μm, which is nearly four times thicker than the BME C0G MLCC.

Figure 3 shows the relative capacitance variation with reference capacitance at 25°C ($\Delta C/C$) versus temperature for BME C0G MLCC and X8R MLCC in the temperature range of −55°C to +200°C. The BME C0G MLCC exhibited extremely flat response over the entire temperature range whether with 25V DC bias applied or without any DC bias. The maximum temperature coefficient of capacitance (TCC) from −55°C to +200°C was found to be 13.4 ppm/°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 ± 30 ppm/°C (or $\Delta C_{Max}/C \leq 0.525\%$) over the temperature range of −55°C to +200°C). The X8R MLCC held its capacitance reasonably well below 125°C. However, at temperatures above 125°C, its capacitance decreased sharply. This is because at temperatures above the Curie point (125°C for $BaTiO_3$-based materials), the capacitance (C)–temperature (T) dependence for ferroelectric material follows the Curie-Weiss Law: $C \propto k \propto \Theta/(T\text{-}T_c)$, where k is the dielectric constant, Θ 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 its 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. At temperatures above 200°C, the capacitance of the X8R MLCC is expected to reduce to values below 100 nF. Thus, for high temperature applications, the actual capacitance under the use conditions needs a serious design 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 capacitors were under the same field strength as the BME C0G MLCC, their effective capacitance would have been even lower.

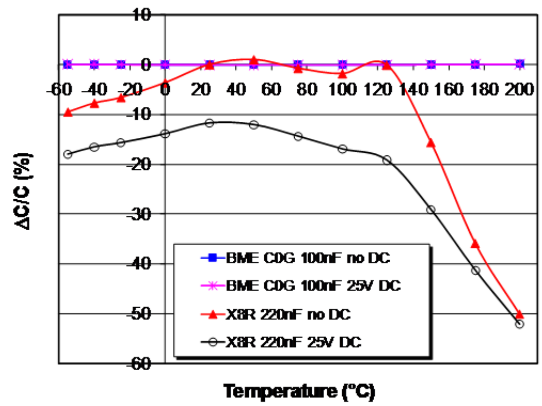

Figure 3. $\Delta C/C$ variation with temperature and DC bias.

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°C to +200°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 resulted in an R*C product (capacitance times IR) of only 0.67 MΩ•µF at 200°C, which should 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°C to +200°C as shown in this study.

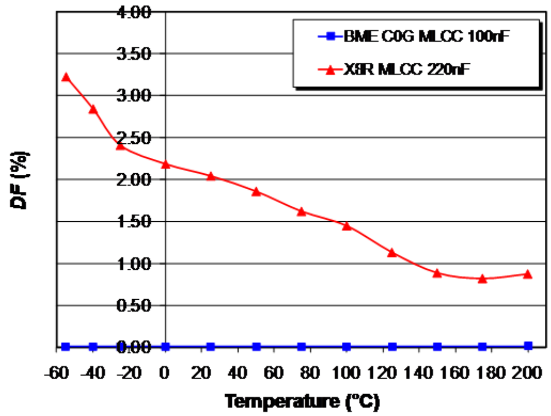

Figure 4. %*DF* dependence on temperature without DC bias.

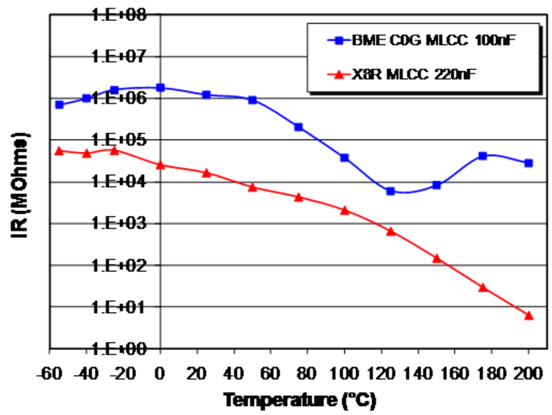

Figure 5. Dependence of IR on temperature with 25V DC bias.

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/µm to 207 Volts/µm, while that for the X8R MLCC dropped from 103 Volts/µm to 55 Volts/µm, 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].

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 $BaTiO_3$ based BME X7R/X5R dielectric materials, oxygen vacancy is not

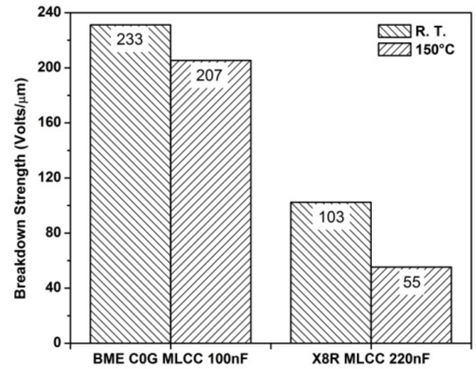

Figure 6. Dielectric breakdown strength at room temperature and 150°C.

a concern for reliability in BME C0Gs based on $CaZrO_3$. In order to estimate the lifetime in high temperature applications, a highly accelerated life test (HALT) study was conducted. 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.

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

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 (8.62×10^{-5} eV/K),
T_i = absolute temperature for condition i.

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

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

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

$$Ln[t] = Ln[A] - n\,Ln[V] + \frac{E_a}{kT} \qquad (4)$$

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 MΩ.

Figure 7 shows the HALT time-to-failure distributions for part type 0805-2200 pF-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 0402-100 pF - 50V and 0603- 470 pF - 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 200 hrs 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 (50th percentile) needed to model the median-time-to-failure (MTTF) data. Thus, their HALT distribution fitting cannot 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 (4000hrs), 150°C and 200°C (2000hrs) without any failures or degradation of electrical characteristics such as capacitance, %DF or insulation resistance.

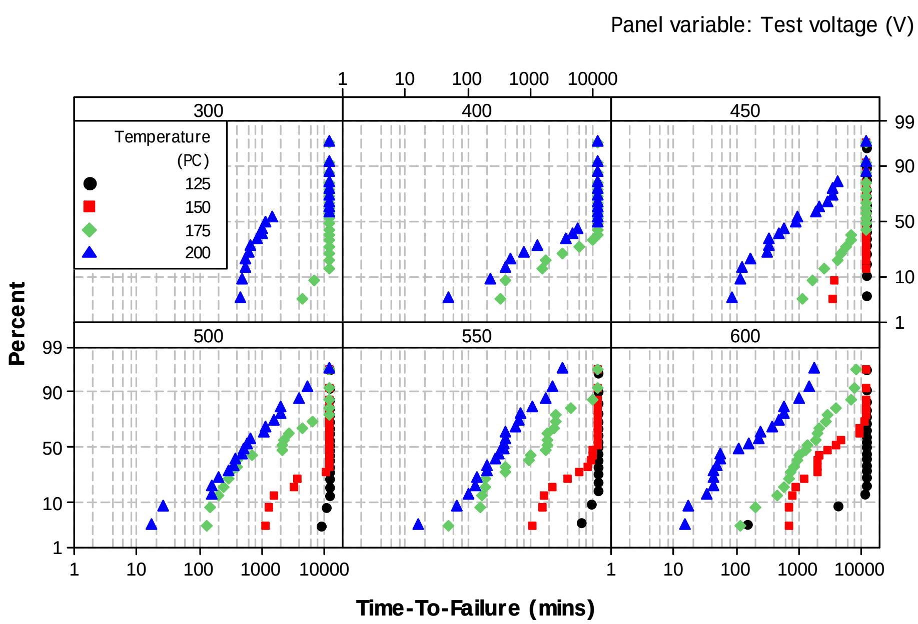

Figure 7. HALT distributions at various test conditions for 0805- 2200 pF 50V.

Table I. Multi-regression Results for HALT-TTF P-V Model for 0805- 2200 pF 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 0805-0805- 2200 pF 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

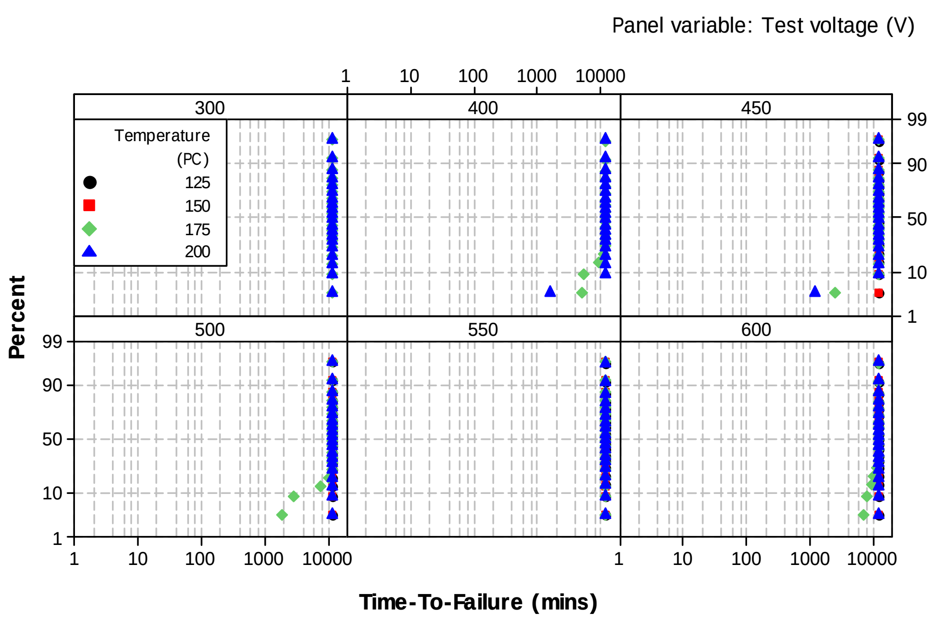

Figure 8. HALT distributions at various test conditions for 0603-470 pF-50V.

4. High-Temperature-X7R Class-II Dielectric

Although the high-temperature C0G capacitors discussed in previous sections have been a greatly successful product, this dielectric has a dielectric constant of 32.5. There will always be a need for higher capacitance MLCCs in electronics for surface and sub-surface downhole drilling and geothermal energy applications especially for temperatures up to 175C. Recently, a modified-X7R dielectric compatible with nickel internal electrodes has been developed to design robust reliability in this Class-II dielectric at high temperatures such as 175°C. This new dielectric has a dielectric constant of ~3000.

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 improved dispersion, build-up and thermal treatment, as well as to improve reliability performance. Figure 9(a-c) demonstrates some of the key improvements employed in the raw materials and microstructure design for the high reliability BME X7R ceramic dielectric. Depending on the design thickness of the dielectric, Barium Titanate ($BaTiO_3$) powders of high crystallinity and narrow particle size distribution were chosen for the dielectric (available down to 150nm, 200nm, 250nm size, etc.). Special combinations of dopant chemistries and a precisely controlled firing process were developed to achieve high reliability in this modified-X7R system at high temperatures. Highly sophisticated milling, dispersion and coating techniques allow molecular- and nanometer-level dispersion of dopant elements and additives within the $BaTiO_3$-based ceramic. This helped in achieving 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.

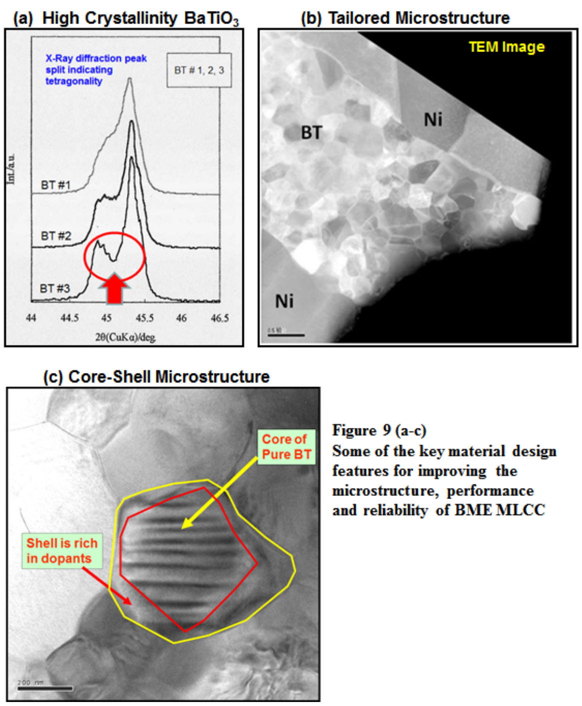

Figure 9 (a-c)
Some of the key material design features for improving the microstructure, performance and reliability of BME MLCC

Figure 10 shows a time-to-failure plot of highly accelerated life test (HALT) on X7R 0603-0.1µF capacitors rated for 25V. This test was performed at 175°C for 92 hours with 300V, 400V, 450V and 500V applied voltages. No failures occurred during the HALT test at 300V (12X rated voltage) after 92 hours. Figure 11 is the life test plot for these capacitors at 175°C, with an applied voltage of 50V. After 1000 hours of testing, no failures occurred, and there was no evidence of degradation in the insulation resistance (or leakage current) of the capacitors. The HALT and life test data demonstrate that this modified-X7R dielectric material is very robust for applications at high temperatures such as 175°C. Testing continues at temperatures up to 200°C to evaluate this modified-X7R Class-II ceramic further for applications in extreme environments.

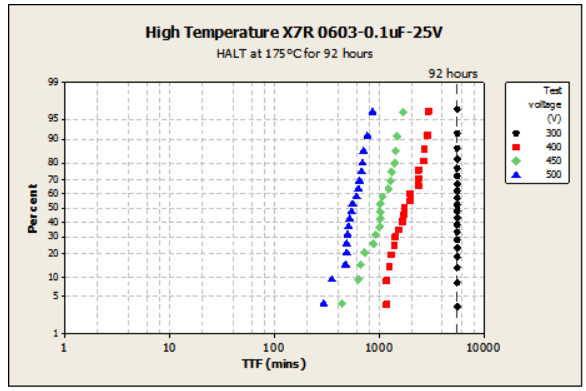

Figure 10. HALT testing time-to-failure (TTF, minutes) plot for Modified-X7R 0603-0.1µF capacitors (rated at 25V) at 175°C for 92 hours

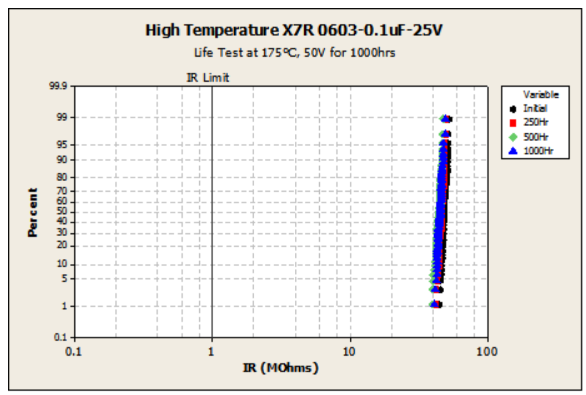

Figure 11. Insulation resistance (IR) plot after Life Test of Modified-X7R 0603-0.1µF capacitors (rated 25V) at 50V and 175°C for 1000hrs hours

5. Summary

(1) The $CaZrO_3$ based BME C0G dielectric material showed 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 ± 30 ppm/°C (or $\Delta C_{Max}/C \leq 0.525\%$) over the temperature range of −55°C to +200°C) and exhibits good long term reliability.
(2) The $CaZrO_3$-based BME C0G chips of various case sizes, capacitance and rated voltages have been tested through long term life tests at 125°C (4000hrs), 150°C and 200°C (2000hrs) without any failures or degradation of electrical characteristics such as capacitance, %DF or insulation resistance.

(3) Traditional $BaTiO_3$-based X7R and X8R dielectrics suffer from severe capacitance reduction, insulation resistance deterioration, and breakdown voltage reduction at high temperatures above 150°C. The newly developed *modified-X7R Class-II* ceramic with a dielectric constant of ~3000 showed robust reliability at high temperatures such as 175°C, and is capable of extending the capacitance offerings by 10 to 20 times compared to the high-temperature-BME-C0G capacitors.

6. References

[1] E. F. Alberta, et al., "High Temperature Ceramic Multilayer Capacitors," p69-72, *Proceedings of the 24th 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 12th 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 27th Symposium for Passive Components (CARTS USA 2007)*, Albuquerque, NM, USA, 2007.

[7] A. Gurav, et al., "Characteristics of $CaZrO_3$-Based BME C0G Dielectric," p359-362, *Proceedings of the 13th 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 $PbHfO_3$ 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 C0G MLCC and SMD Film Capacitors," p449-461, *Proceedings of the 28th 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 5th SMTA Medical Electronics Symposium*, Anaheim, CA, USA, 2008.