High Voltage Multi-Layer Ceramic Capacitors for Use at High Temperatures

Jim Magee, John Bultitude, Lonnie Jones, Mark Laps, Javier Zavala, Ana Garza, Glenda Torres, Wanda Andrews, Abhijit Gurav, Corey Antoniades and Reggie Phillips

KEMET Electronics Corporation, 2835 KEMET Way, Simpsonville, SC 29681, USA
Tel: +01-864-228-4052, Fax: +01-864-967-6823, e-mail: reggiephillips@kemet.com

Abstract

Multi-layer ceramic capacitors (MLCC) rated to 200Vdc for use at 200°C were developed using a high temperature C0G dielectric technology compatible with nickel electrodes. To meet the need for improved pulse detonator performance larger case size (2824 to 4540) capacitors rated to 2000Vdc at 200°C were then developed using this technology. The growing demand for higher temperature electronics capable of exploiting new reserves of oil and natural gas led us to develop a range of smaller case (0805 to 2225), high voltage designs (> 500V to 2000V). The electrical characteristics of these surface mounted MLCC, such as insulation resistance, voltage breakdown, impedance and ESR, are described. The basic properties of some selected capacitors are compared to MLCC made with precious metal electrodes at high temperatures to explain the performance enhancements of this new product range. Reliability data at 200°C is presented for some MLCC examples from the new product range and the mechanisms associated with reliable high temperature performance are reviewed. This new range of MLCC will allow designers of high temperature electronics to realize reliable, miniaturized circuit designs with stable capacitance at high voltage and high temperature.

Introduction

In a previous presentation[1] work to develop a range of high temperature capacitors based on a C0G type dielectric with nickel electrodes was described. The bulk dielectric material used in the dielectric formulation was calcium zirconate. The oxygen present is held tightly within the crystal lattice that results in a very low level of oxygen defects. Since the presence of these defects is minimized the migration of oxygen vacancies at elevated temperatures does not compromise the reliability of the BME MLCC as described for other more common types of dielectric such as X7R and X5R based on barium titanate. High temperature MLCC rated to 200V for use at 200°C were successfully qualified using a C0G dielectric formulation based on calcium zirconate. A range of higher voltage, large case size pulse detonation capacitors was subsequently developed to meet downhole market need for more reliable capacitors in this application. These developments and the application of this technology to smaller case size, high temperature rated MLCC are described below. The electrical properties are reviewed and compared to high temperature MLCC based on X7R dielectrics made with precious metal electrodes.

High Temperature C0G Dielectric Development

Multilayer ceramic capacitors using nickel base metal electrodes were originally developed using barium titanate based dielectrics. The high permittivity of these ferroelectric materials provided high capacitance; low voltage solutions in X5R and later X7R class 2 capacitors. To achieve reliable performance reduction resistant formulations were developed together with re-oxidation processes to replace vacancies formed during the high temperature firing in reduced atmosphere. This technology was applied to C0G dielectrics using calcium zirconate as the main component in order to replace the more expensive precious metal compatible systems that typically use barium-rare earth titanates[2]. The C0G dielectrics were also developed to be Pb-free unlike some of the precious metal compatible dielectrics. In later work[1] Highly Accelerated Life Testing (HALT) was performed on 50V rated MLCC made from the same batches of calcium zirconate based dielectric with and without re-oxidation. An example of this work is shown in Figure 1.

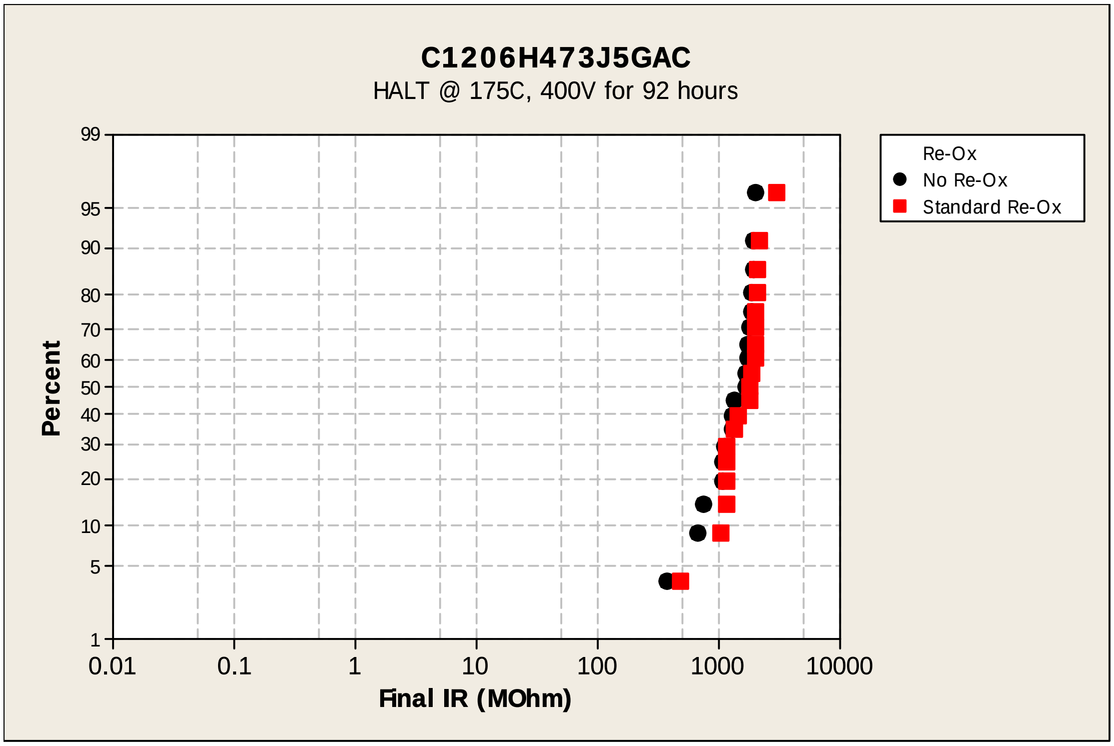

Figure 1. HALT test of 1206, 47nF, 50V rated C0G with and without re-oxidation

There was no degradation of IR with and without re-oxidation even at temperatures of 175°C at 12 x the rated voltage of the MLCC for 92hours. These results were attributed to the much higher affinities of calcium and zirconium for oxygen so tightly binding this within the crystal lattice of the dielectric. The low level of oxygen defects on processing allowed us to develop a range of MLCC based on this high temperature C0G technology. Initially this work was directed at rated voltages of ≤ 200V for use at 200°C but to meet the demand for pulse detonator capacitors larger, higher voltage MLCC were subsequently developed as described below.

High Voltage High Temperature MLCC Designs

The capacitor designs developed for use at 200°C at rated voltages ≤ 200V use a standard overlap design as shown in the example of a cross-section in Figure 2.

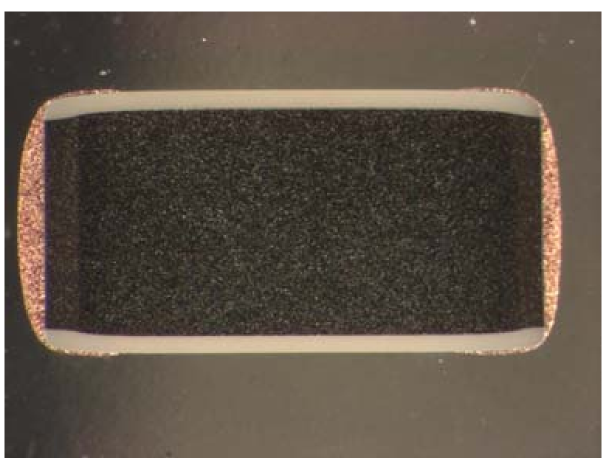

Figure 2. Cross–section 1206, 25V rated, 100nF MLCC rated for use at 200°C

Larger case size MLCC rated at voltages ≥ 500Vdc were then developed using this technology to meet a need for improved pulse detonator capacitors that serve to provide the energy to initiate explosions. Since the energy contained within the capacitor is given by $E = \frac{1}{2} CV^2$ the capacitor should operate at a high voltage to maximize the energy of the discharge current and help prevent any failures to detonate. Larger case sizes, ≥ 2824 are used to obtain a relatively high capacitance so the energy stored is adequate. In the case of downhole detonator applications the capacitor must be reliable at temperatures of 200°C. In these applications, such as fracking, the large case detonator capacitors usually only have to operate at high temperatures for a few hundred hours but they must function every time when needed. In these cases the high voltage is typically applied for a short time prior to detonation so there is little time for any migration processes to occur that can be a concern with high electric field between electrodes of opposed polarity. Even so these pulse detonator capacitors showed low failure rates in the field and during extended testing at 200°C at rated voltages. An example of a life test performed on 50pcs of 2824, 33nF, 630V rated pulse detonator capacitors is shown in Figure 3 and the cross section of one of these capacitors is shown in Figure 4.

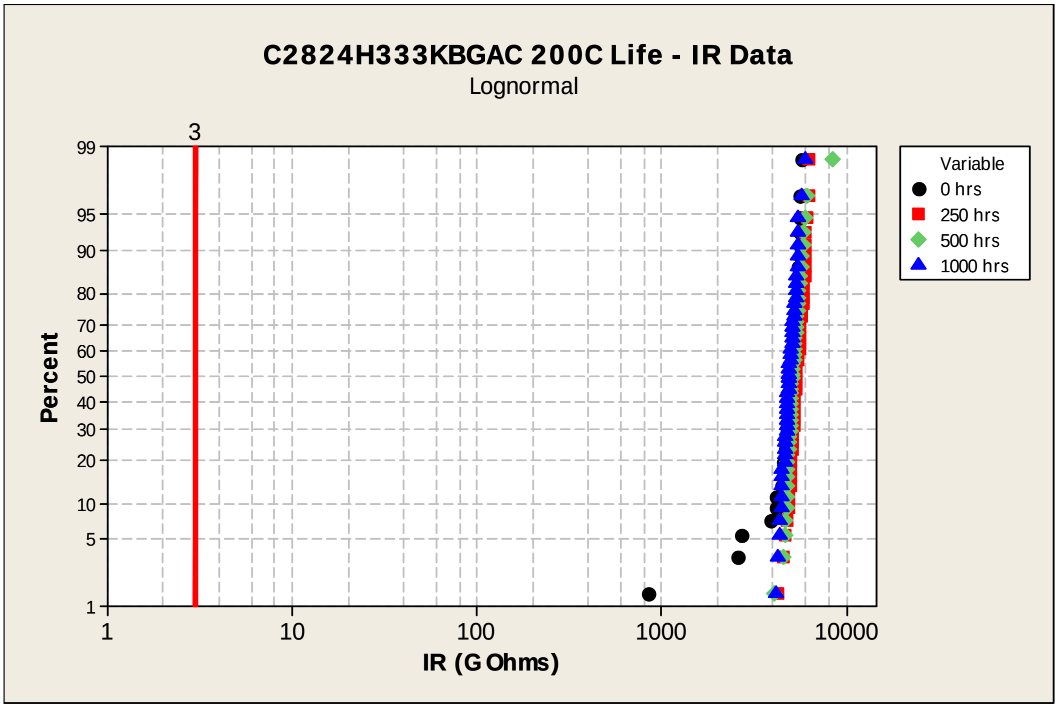

Figure 3. Life Test at 200°C/630V for 2824, 33nF, 630V rated pulse detonator capacitors

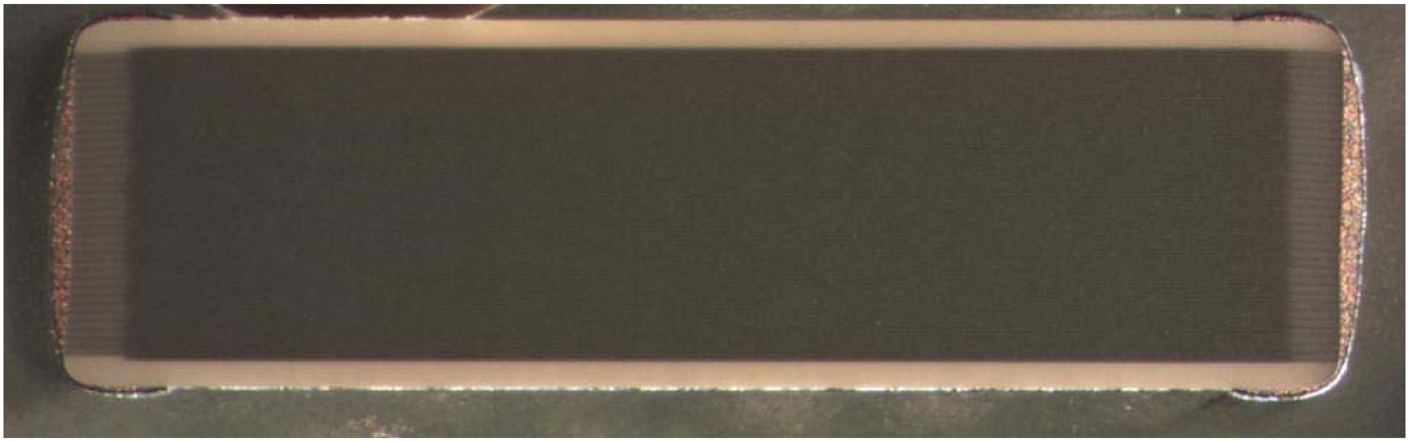

Figure 4. Cross-section of a 2824, 33nF, 630V rated pulse detonator capacitor

Since the larger case pulse detonator capacitors showed no significant deterioration in insulation resistance after 1000hours at 200^{o}C with rated voltage applied we concluded that this technology was suitable for further development of other high temperature, high voltage capacitors. In a response to requests from downhole customers for smaller MLCC with high voltage capability to perform as snubbers and smoothing capacitors in other tools we decided to develop a range of smaller surface mounted MLCC. Case sizes from 0805 through to 2225 with ratings of 500V to 2000V were manufactured applying the same designs as for the larger case detonator capacitors. In the case of higher voltage surface mount MLCC a common practice for many years has been to arrange the electrodes to form two or more capacitors in series[3]. These designs are also known as "cascade" or "floating electrode" designs. This serial arrangement within the MLCC reduces the voltage by the reciprocal number of capacitors in series although the effective capacitance is also lowered. However, we selected this design type because of the many years of proven capability in the field in high voltage applications. This type of design was used in the 1000V rated 1808 MLCC shown in cross-section in Figure 5.

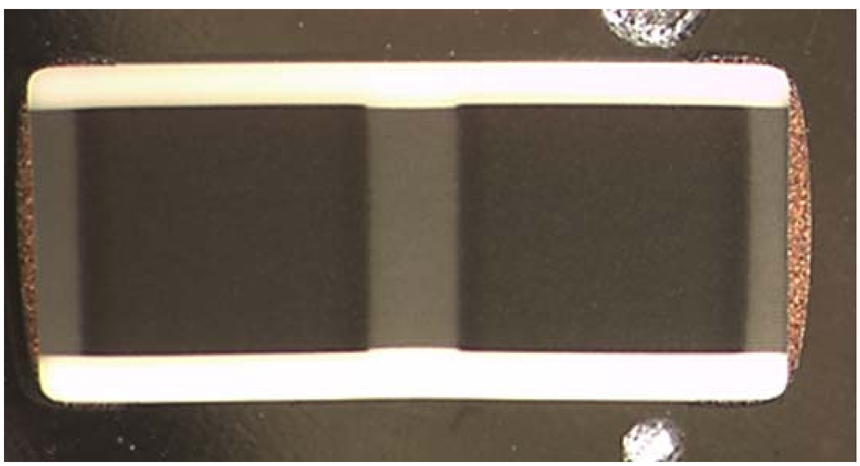

Figure 5. Cross–section of 1808, 2.9nF, 1000V rated MLCC

The electrical characteristics of the three MLCC parts described above are compared in Table 1 below. These are all mean values measured over sample sizes >20. Insulation Resistance (IR) means from measurements at 60 seconds at 500V and Voltage Breakdown at a ramp rate of 300V/second.

Product Type	Low Voltage Development	Large Case Detonator	Small Case Development
Part Number	C1206H104J3GAC	C2824H333KBGAC	C1808H292JDGAC
Capacitance (nF)	97.31	34.17	2.70
DF (%)	0.0040	0.0097	0.0210
Active Thickness (µm)	2.54	21.34	13.72
Rated Voltage	25V	630V	1000V
Effective V/µm	9.84	29.53	36.45
IR @ 25°C (GΩ)	2,546	2,869	70,312
IR @ 200°C (GΩ)	16	10	2,271
Temperature Coefficient of Capacitance in PPM/°C (-55°C, +125°C)	-14.21, 1.11	-8.60, 22.94	-12.05, 10.01
Mean Voltage Breakdown @ 25°C (Volts)	588	1,792	2,931
Mean Voltage Breakdown @ 200°C (Volts)	563	1,849	2,863

Table 1. Electrical Property Comparison of High Temperature C0G MLCC

It can be seen that the effective V/µm is higher as the rated voltage increases (Table 1.) so there were concerns with the potential for degradation of MLCC properties after prolonged exposure at 200°C. The IR of the small case size high voltage 1808 MLCC is above the lower voltage ratings and remains higher at 200°C. The voltage breakdown for all three capacitors does not show a significant degradation even at 200°C. To confirm the longer term reliability of the high voltage 1808 small case capacitors MLCC from 2 batches, 50 pieces each, were life tested at 200°C, rated voltage (1000V) for 1000hours (Figure 6.).

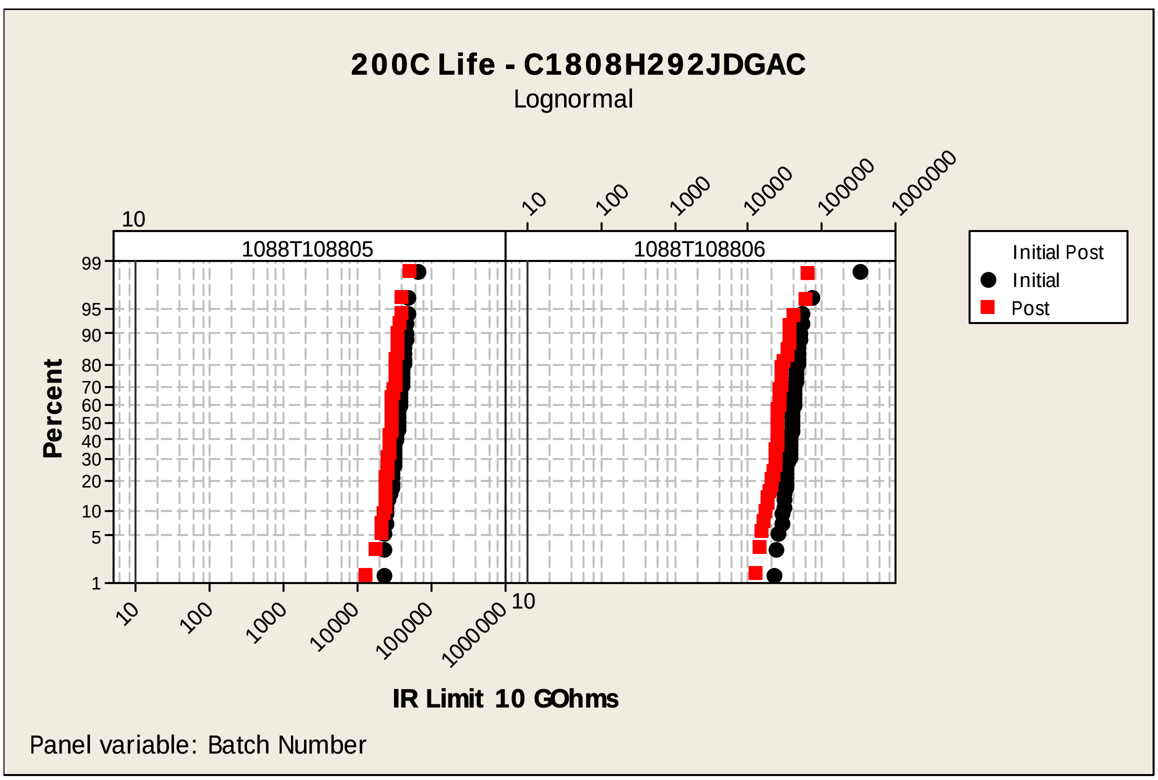

Figure 6. Life Tests of 1808, 2.9nF, 1000V rated MLCC at 200°C/1000V for 1000hours

The life testing of shows no sign of degradation of insulation resistance even after 1000hours at 1000V and 200°C. A range of small case size high voltage MLCC for use at 200°C were identified and characterized and selected parts were similarly tested as shown in the following section.

Smaller Case Size C0G MLCC for High Temperature High Voltage Applications

The life test data at 200°C for 1000 hours at rated voltage and 200°C for selected f smaller case size C0G MLCC are shown in Table 2 together with other characteristic electrical data.

Part Number	C1206H332JCGAC	C1210H472JBGAC	C1813H332JFGAC	C2220H332JGGAC
Case Size	1206	1210	1813	2220
Rated Voltage	500V	630V	1500V	2000V
Capacitance (nF)	3.29	4.81	2.98	3.31
DF (%)	0.0200	0.0182	0.0200	0.0200
IR @ 25°C (GΩ)	44,001	35,422	59,159	63,039
Temperature Coefficient of Capaciance in PPM/°C (-55°C , +125°C)	-10.56, 10.65	-10.96, 10.17	-10.63, 11.15	-11.77, 9.42
Mean Voltage Breakdown @ 25°C (Volts)	1,825	2,000	3,519	4,116
Mean Voltage Breakdown @ 200°C (Volts)	2,289	2,134	3,522	3,798
Life Test 1000 hrs/ 200°C/Rated Voltage*	0/100	0/100	0/100	0/100
* For each part number 2 Batches, 50 pieces each				

Table 2. Electrical Characteristics and Reliability of Selected Small Case Size High Temperature C0G MLCC

The voltage breakdown performance for the different high voltage rated small case size MLCC shown in Table 1 and 2 was measured at 4 temperatures, 175, 200, 225 and 250°C using 5 pieces of each part number and the mean values compared to 25°C in Figure 7.

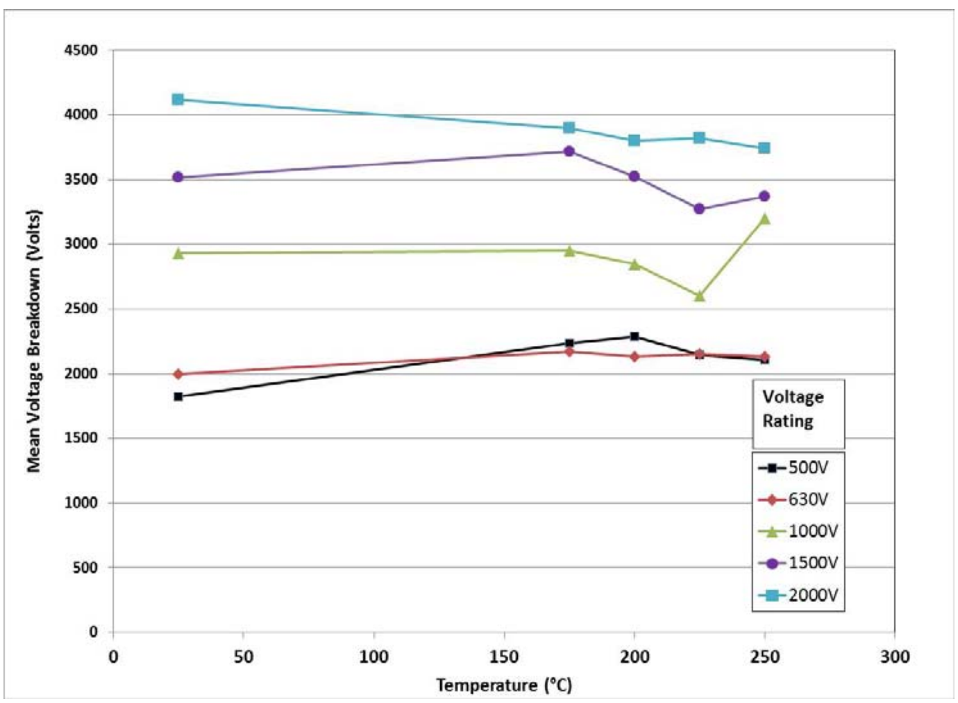

Figure 7. Voltage Breakdown vs. Temperature for Small Case Size High Temperature C0G MLCC

The voltage breakdowns of all the small case size MLCC remain high at temperatures up to 250°C with no significant degradation. The variance at different temperatures is believed to be related to the relatively small sample size used. As expected the voltage breakdowns of the 500 and 630V ratings are close since these MLCC designs are very similar.

Performance Comparison of Smaller Case Size C0G to Leaded X7R MLCC

The available competitive product with equivalent capacitance and voltage rating are leaded MLCC made with X7R or X8R MLCC using precious metal technology. Some competitor 200°C, 500V rated leaded X7R products were obtained with nominal capacitances of 220nF and 120nF and compared to a small case 2220, 33nF, 500V rated C0G. These parts are shown in Figure 8 and a comparison of their dimensions and electrical properties is shown in Table 3.

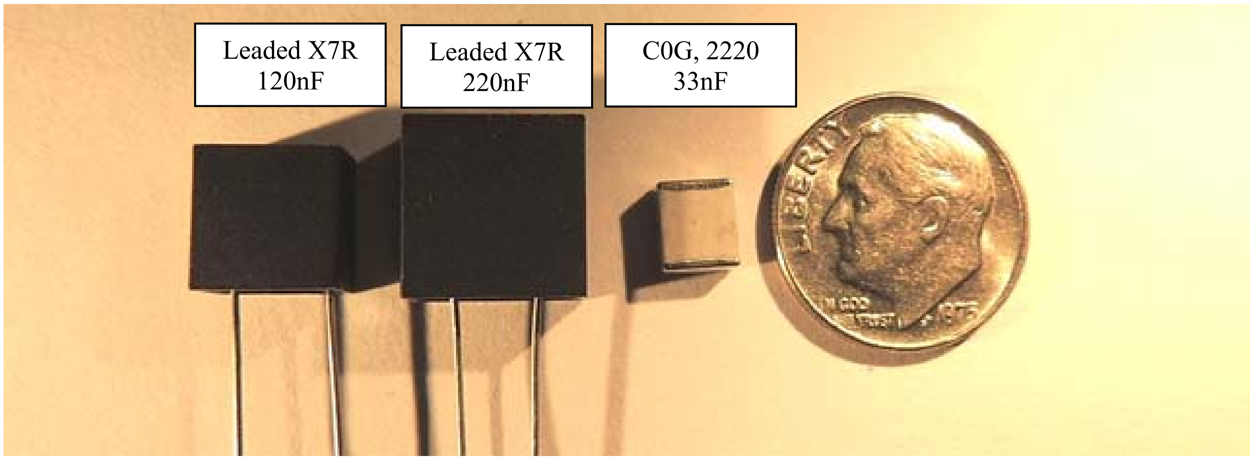

Figure 8. 500V rated C0G, 2220, 33nF and Leaded X7R

Part	C0G, 2220, 33nF	Leaded X7R 220nF	Leaded X7R 120nF
Capacitance (nF)	32.68	220.3	121.4
DF (%)	0.02	1.25	1.24
IR @ 25°C (GΩ)	5,592	277	411
IR @ 200°C (GΩ)	105	0.338	0.354
Temperature Coefficient of Capaciance in % (-55°C , +200°C)	0.08, 0.42	-8.31, -46.15	-8.69, -46.13
Mean Voltage Breakdown @ 25°C (Volts)	1,819	1,730	1,703
Mean Voltage Breakdown @ 200°C (Volts)	2,226	2,850	3,270
Length (mm)	5.9	11.4	8.9
Width (mm)	4.9	11.4	8.9
Thickness (mm)	2.5	5.1	5.1
Volume (mm^3)	72	663	404

Table 3. Electrical Properties and Dimensions of 500V rated capacitors

At first, apart from the opportunity to use automated surface mounting in the case of the smaller case size C0G MLCC, it would seem these offer little advantage in terms of capacitance although dissipation factor is lower than X7R. However, the X7R capacitance is significantly reduced at high temperature as can be seen in the TCC measurements. In all 3 cases the voltage breakdown increases with temperature but the IR for the C0G is nearly 300X higher than the X7R at 200°C. The capacitance and IR differences were examined in more detail.

The capacitance differences at 25°C and 200°C with and without 500V applied are shown in the form of a bar chart in Figure 9.

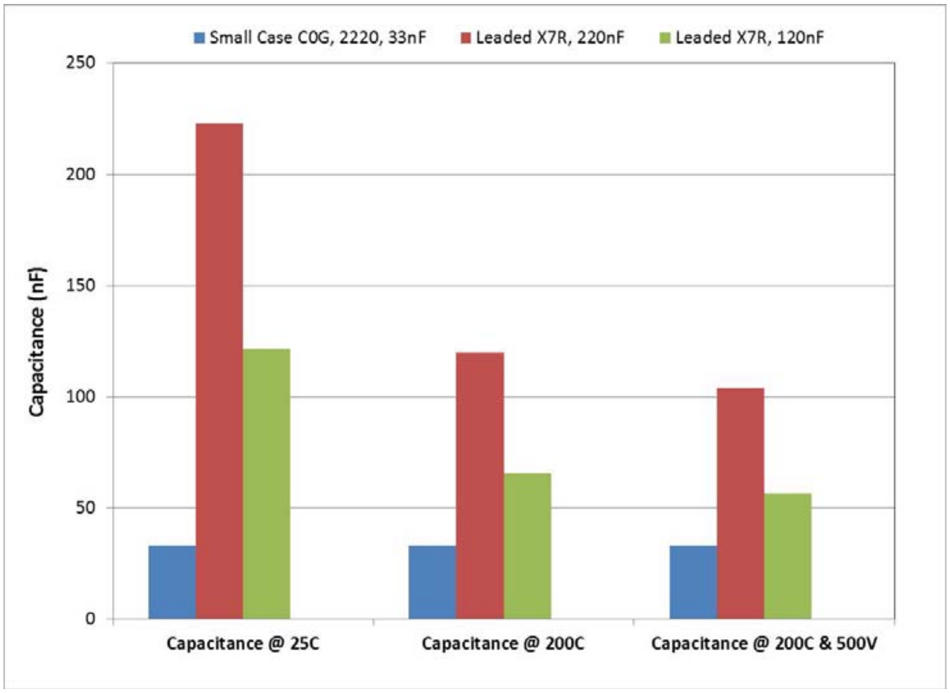

Figure 9. Comparison of Capacitance

The C0G capacitance is not significantly changed at 200°C or when 500V is applied at this temperature. The capacitance of leaded X7R MLCC at 200°C is reduced by 46% compared to the value at 25°C then by a further 7% with applied voltage. Even so the available capacitance of the leaded X7R remains higher than the C0G. However, if the same data is shown by capacitance per unit volume (Figure 10.) then the C0G clearly has a superior volumetric efficiency.

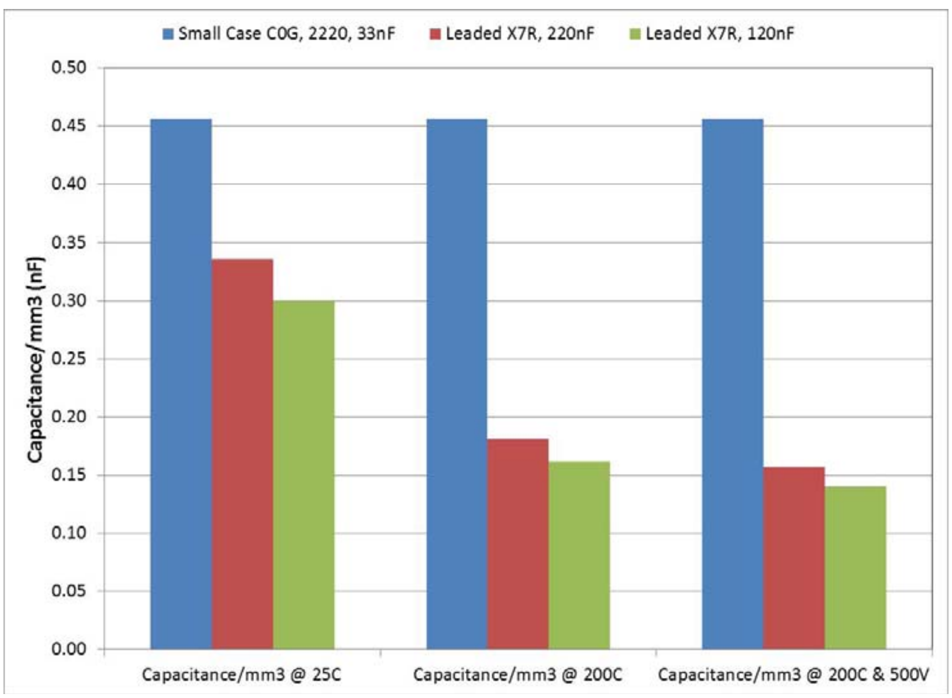

Figure 10. Comparison of Capacitance per unit volume

The RC factors for these capacitors calculated at 25°C and at 200°C & 500V are shown in Figure 11.

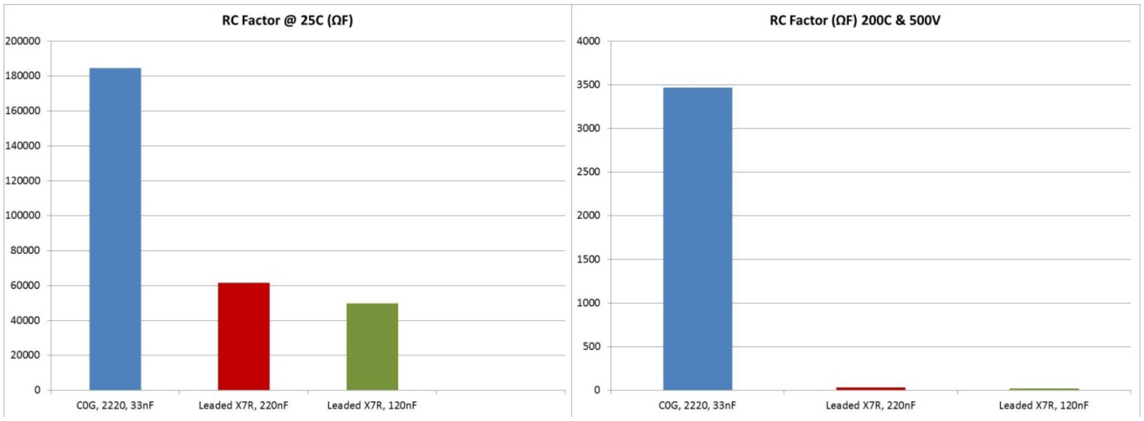

Figure 11. RC Factors at 25°C and 200°C & 500V

The RC factors for the X7R at high temperature and rated voltage are ≤ 35 ΩF because of the lower IR and capacitance at these measurement conditions whereas the RC of the C0G is approximately 100 X higher.

The ESR and Impedance of these capacitors were measured under ambient conditions and are shown in Figure 12. Measurements were made from 100Hz to 3GHz.

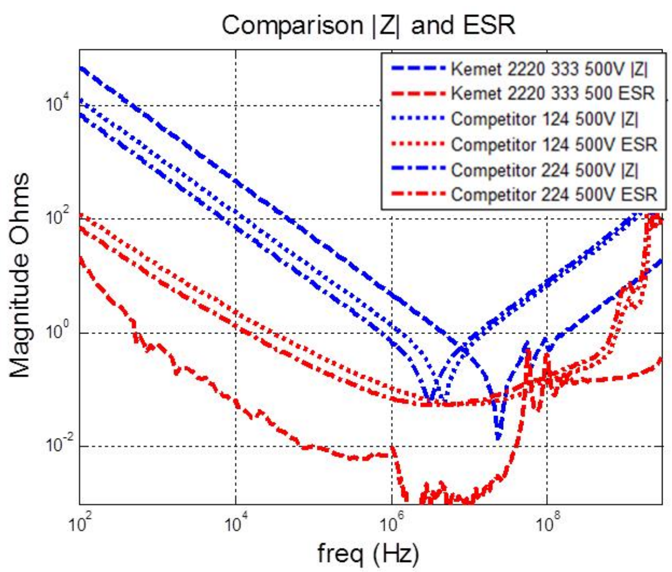

Figure 12. Comparison of ESR and Impedance

As expected the higher capacitance of the X7R correlates to a lower self-resonant frequency. The C0G part type has an ESR that is about an order of magnitude lower than both X7R capacitors.

Summary and Conclusions

A range of surface mountable, high voltage capacitors has been developed for use at 200°C using high temperature BME C0G technology that have stable capacitance with temperature and voltage, high insulation resistance and low dissipation factors. These capacitors have low ESR and impedance and passed life testing for 1000 hours at 200°C rated voltage. The

BME C0G MLCC were shown to have a higher volumetric efficiency when compared to competitor leaded X7R rated at 500V so more capacitance can be achieved in a smaller space. This new range of high voltage MLCC will allow designers of high temperature electronics to realize reliable, miniaturized circuit designs.

Acknowledgements

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References

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