March 15-18, 2010 *CARTS USA 2010 Proceedings, p. 249-262* *New Orleans, LA*

Selection of Dielectric Materials for High Temperature Applications

Anton V. Polotai, Samir G. Maher, Jim M. Wilson and Riad G. Maher

MRA Laboratories, Inc.
15 Print Works Drive, Adams, MA, 01220
Tel: (413) 743-3927, Fax: (413) 743-0305, E-mail: apolotai@mralabs.com
www.mralabs.com

Abstract

The need for ceramic capacitors capable of operation at temperatures of 200°C and above continues to grow. These applications include avionics and aerospace, automotive, downhole drilling, mining and many others. In spite of the significant amount of research that has been done in recent years in this area, there has been very little commercialization of new materials. The biggest obstacle is to maintain acceptable levels of reliability, while keeping high volumetric efficiency and temperature stability of the dielectric constant. One of the alternative approaches is to use Class-I dielectrics, which lack high dielectric constant, but offer exceptional temperature stability, dielectric breakdown strength and reliability. This paper discusses the applicability of COG-type Class-I dielectrics for high temperature applications and compares their performance with Class-II X7R/X8R-type dielectrics. In addition, comparisons have been made between high temperature applicability of PME and BME-based dielectrics.

Introduction

Extreme environment applications require electronic systems capable of surviving beyond conventional Electronic Industry Alliance (EIA) or Military (MIL) standards operating temperature ranges of -55°C to +125°C. Applications such as downhole petroleum and geothermal production, distributed turbine engine controls in avionics and in military devices, multiple sensors and control circuitries in the automotive industry and many others, require robust electronic systems that can operate up to 200°C and beyond. Although the current market for high temperature electronics is relatively small compared to that for conventional electronics, the demand appears to growing significantly and many passive electronic manufacturing companies are trying to fill the gap.

Attempts to design a reliable high temperature dielectric with high volumetric efficiency for multilayer ceramic capacitors have been increasing in recent years. The traditional Class-II X7R/X8R dielectrics (EIA specification: $\Delta C/C$ within ±15% between -55°C and +125°C/+150°) based on barium titanate suffer from degradation of reliability performance and severe reduction of capacitance at temperatures above +125°C/+150°C. The high temperature reliability of X7R/X8R dielectrics can be improved to some extent by de-rating their rated voltage. However, the capacitance drop off at 200°C can be from 40% to up to 70%. An early effort to develop a special ceramic dielectric capable of operation at 200°C was a lanthanum-modified lead zirconate titanate (PLZT) developed by the late Dr. Galeb H. Maher [1-4]. This dielectric system showed considerably less variation in capacitance at 200°C than barium titanate dielectric systems. Capacitor made with this PLZT dielectric formulation met the EIA characteristic X9S (ΔC/C within ±22% between -55°C and +200°C) [5]. More recently, new relaxor-ferroelectric ceramics based on lead manganese niobate – lead titanate and barium bismuth sodium titanate systems have been developed [6-7]. They utilize high temperature ferroelectric phases in order to extend the ferroelectric region with high dielectric constant beyond 125°C. However, the biggest challenge is to maintain acceptable levels of reliability while keeping high volumetric efficiency and temperature stability of the dielectric constant, which prevents them from immediate commercialization.

One alternative approach is to use Class-I dielectrics. Class-I COG-type dielectrics (EIA specification: ΔC/C within ±30ppm/°C between -55°C and +125°C) do not possess ferroelectric properties and, therefore, lack high dielectric constant, but offer exceptional temperature stability, dielectric breakdown strength and reliability. It was recently reported that base-metal electrode (BME) COG dielectrics based on $CaZrO_3$ with dielectric constant around 32 are capable of operating at temperatures to 200°C [8]. These dielectrics are designed to work with Ni internal electrodes, which have a tendency to oxidize in air at relatively low temperatures [9]. This could significantly limit high temperature application of BME-type dielectrics in oxidizing atmospheres. On the other hand, precious-metal electrodes (PME) such as Ag, Ag-Pd, Au-Pt-Pd or Pd may operate continuously at much higher temperatures without oxidation and offer an advantage of higher electrical conductivity compared to Ni, which is especially important for high-frequency applications.

MRA Laboratories, Inc, a leading manufacturer of PME ceramic capacitor dielectric materials for specialty applications, offers a broad line of Class-I and Class-II dielectrics with a wide range of dielectric constant. This paper discusses the applicability of COG-type Class-I dielectrics produced by MRA Laboratories, Inc for high temperature applications to 200°C and beyond, and compares their performance with other commercially available COG and Class-II X7R/X8R-type dielectrics. In addition, a comparison has been made between high-temperature applicability of PME and BME-based dielectrics.

Experimental

The samples used for high temperature performance comparison were 0805-size multilayer ceramic capacitor (MLCC) chips with 50V rated voltage, made with three PME COG-type dielectrics and one PME X8R dielectric. Each manufactured by MRA Laboratories, Inc. As counterparts, commercially available 0805-size, 50V rated MLCC chips made with BME COG, BME X7R and PME X8R dielectrics were purchased. Scanning electron microscopy (SEM, model ISI-100B, International Scientific Instruments, Pleasanton, CA, USA) with energy dispersive spectroscopy (EDS, model PGT XS169, Princeton Gamma-Tech, Princeton, NJ, USA) analysis was performed on the commercial MLCC chips in order to determine internal microstructure, dielectric thickness, type of electrodes and base dielectric composition. No attempts were made to quantify or copy the complete dielectric composition. The initial properties of MLCC chips used in this study are summarized in Table 1.

Table 1. Summary of the dielectric materials used in this study.

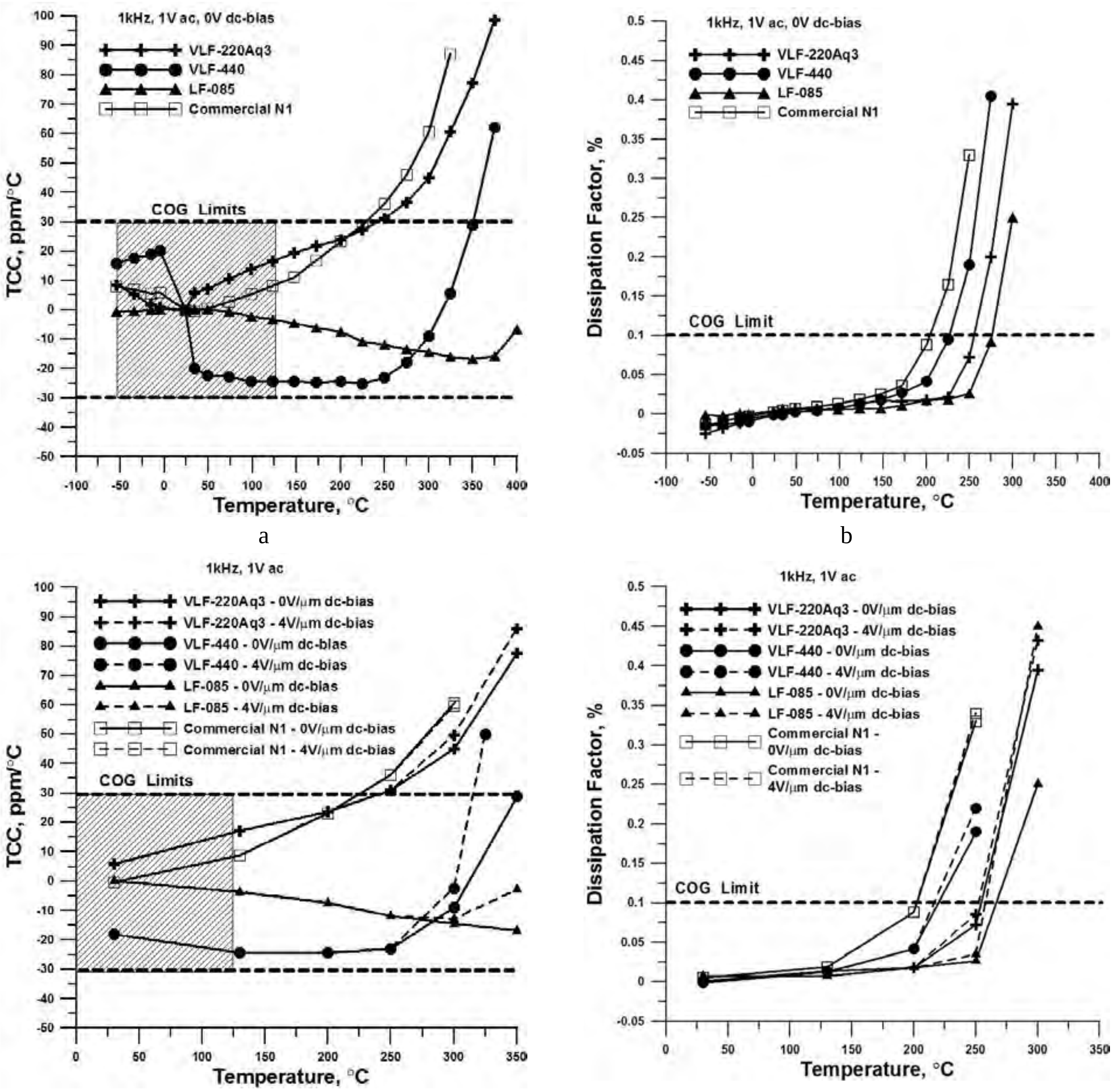
	Dielectric materials						
	VLF-220Aq3	VLF-440	LF-085	Commercial N1	LF-222	Commercial N2	Commercial N3
Dielectric Class	Class 1 COG	Class 1 COG	Class 1 COG	Class 1 COG	Class 2 X8R	Class 2 X7R	Class 2 X8R
Dielectric Base Material	(Mg,Zn)TiO_3-based	$Ba_2Ti_9O_{20}$-based	BaO-TiO_2-Bi_2O_3-Nd_2O_3-based	$CaZrO_3$-based	$BaTiO_3$-based	$BaTiO_3$-based	$BaTiO_3$-based
Internal Electrodes	PME 95%Ag-5%Pd	PME 95%Ag-5%Pd	PME 70%Ag-30%Pd	BME 100%Ni	PME 80%Ag-20%Pd	BME 100%Ni	PME 70%Ag-30%Pd
Dielectric Constant at RT	23	44	85	32	2300	2000	2150
Chip Size	0805 Parallel Capacitor Design	0805 Parallel Capacitor Design	0805 Parallel Capacitor Design	0805 Parallel Capacitor Design	0805 Parallel Capacitor Design	0805 Series Capacitor Design	0805 Parallel Capacitor Design
Dielectric Thickness, µm	17.4	19.0	24.1	19.0	19.7	15.3	20.3
Rated Voltage, V	50	50	50	50	50	50	50
Chip Capacitance at RT (1kHz), nF	0.08	0.10	0.21	0.12	6.54	6.50	1.90
Dissipation Factor at RT (1kHz), %	>0.01	>0.01	>0.01	>0.01	1.59	1.49	1.35

The temperature variation of capacitance and dissipation factor with and without dc-bias was measured by Multi-Frequency Precision LSR meter (model HP/Agilent-4284A, Santa Clara, CA, USA) at 1kHz and 1Vrms over the temperature range from -55°C to 400°C using two environmental chambers – one capable of operation from -55°C to 200°C and the other from 25°C to 400°C. The dc-bias to 100V was applied by transistor power supply (model 212A, Electronic Measurements, Inc / TDK-Lambda, Inc, Pittsburgh, PA, USA). The data for each dielectric was averaged based on groups of four identical MLCC chips. A special sample holder for four MLCC chips was designed to perform high temperature ultimate breakdown voltage (UBV), and insulation resistance (IR) measurements up to 350°C. For UBD measurements, each MLCC chip was flashed starting at 50Vdc and continued to slowly increase the voltage until the sample failed. The current was limited to 50mA. Measurements were performed by a special high voltage power supply (model PS-1067, Sprague Specialties, Co, North Adams, MA, USA) capable of providing 3000Vdc. The average UDV and standard deviation were estimated based on groups of eight identical samples. The dielectric breakdown strength (DBS) was estimated dividing UDV by dielectric thickness. The IR measurements were performed at 50V dc-bias, using a megohmmeter (model L-10A, Beckman, Brea, CA, USA). The insulation resistance reading was taken after 2 minutes of dc-bias applied. The upper limit of the insulation resistance which this megohmmeter was capable of measuring is about $5*10^{12}\Omega$. The reported average IR was based on a group of eight identical samples. The highly accelerated life test (HALT) was performed at 180°C and various voltages (200V, 400V, 600V) for 100 hours using a life test system (model 1025, Micro Instruments, Co, Canton, TX, USA). A total of 20 MLCC chips per dielectric were used in each HALT run. The maximum temperature (180°C) and voltage (600V) used in this study were limited by the equipment capability. The leakage current of each MLCC was monitored during the test by measuring the voltage across 100kΩ resistors in series with the capacitors. A capacitor was considered failed when there was a 50% increase of voltage across the resistor. A dielectric was considered failed if any of chips from the group failed.

Results and Discussion

In general, dielectric materials for multilayer ceramic capacitor applications are characterized by a group of properties, the most important of which are: temperature coefficient of capacitance (TCC) and dissipation factor (DF) with and without applied dc-bias, dielectric breakdown strength, insulation resistance, and life time or dielectric reliability. Historically, these parameters are well defined for the normal operating temperatures, from -55°C to 125°C. However, no clear standards exist for high temperature applications as of yet. Therefore, for this study, the Class-I and Class-II dielectric materials were compared based on acceptability limits defined for the normal operating temperatures. One exception was made for the dielectric insulation resistance. For the IR acceptability limit, the conditional boundary between insulation materials and semiconductors (electrical conductivity equals to 10^{-8}S/cm) was used [10].

The temperature coefficient of capacitance and dissipation factor of Class-I COG dielectrics to 400°C with and without dc-bias is shown in Figure 1. All four COG dielectrics fully satisfied COG requirements: TCC within ±30ppm/°C from -55°C to +125°C with DF < 0.1%. However, at higher temperatures they behaved differently. The “Commercial N1” BME COG dielectric based on $CaZrO_3$ first intersected the extended COG TCC limit of +30ppm/°C at ~ 225°C independently on the applied 4V/μm dc-bias (Fig. 1a and 1c). The dissipation factor of this dielectric crossed COG limit at even lower temperature, ~205°C (Fig. 1b and 1d). All three PME COG dielectrics showed better high temperature stability. “LF-085” PME COG dielectric based on the $BaO\text{-}TiO_2\text{-}Bi_2O_3\text{-}Nd_2O_3$ system maintained COG TCC requirements up to 400°C and intersected COG DF requirements at ~260°C, under the applied dc-bias condition. In general, all COG dielectrics tested did not show any dc-bias dependence and remained linear up to 200°C-250°C (Fig. 1c and 1d).



a b

c d

Figure 1. Dielectric properties of COG-type dielectrics at high temperatures: a) TCC without dc-bias; b) DF without dc-bias; c) TCC with dc-bias and d) DF with dc-bias.

The temperature coefficient of capacitance and dissipation factor of Class-II X7R/X8R dielectrics to 400°C with and without dc-bias is presented in Figure 2. Two PME X8R dielectrics, “LF-222” and “Commercial N3”, completely satisfied X8R requirements (TCC within ±15% between -55°C and +150°C, DF < 2.5%) independently, whether or not the 50V dc-bias was applied. The “Commercial N2” BME X7R dielectric, on the other hand, did not meet X7R requirements under the 50V dc-bias test condition, but met “BX” military requirements (TCC within +15%/-25%

between -55°C and +125°C, DF < 2.5% at RT at rated voltage) (Fig. 2c) and showed the earliest rise of DF compared to both PME X8R dielectrics (Fig. 2b and 2d). Due to the fact that X7R/X8R dielectrics were formulated based on ferroelectric barium titanate, their TCC behavior fell rapidly above 125°C/150°C, following the Currie-Weise Law. At 200°C, for example, the capacitance of "LF-222", "Commercial N2" and "Commercial N3" MLCC chips dropped by 47.6%, 62.8% and 43.5% respectively, without dc-bias and by 40.2%, 58.5% and 37.1% respectively, while under the 50V dc-bias, compared to their capacitance at 25°C, as shown in Fig. 2c.

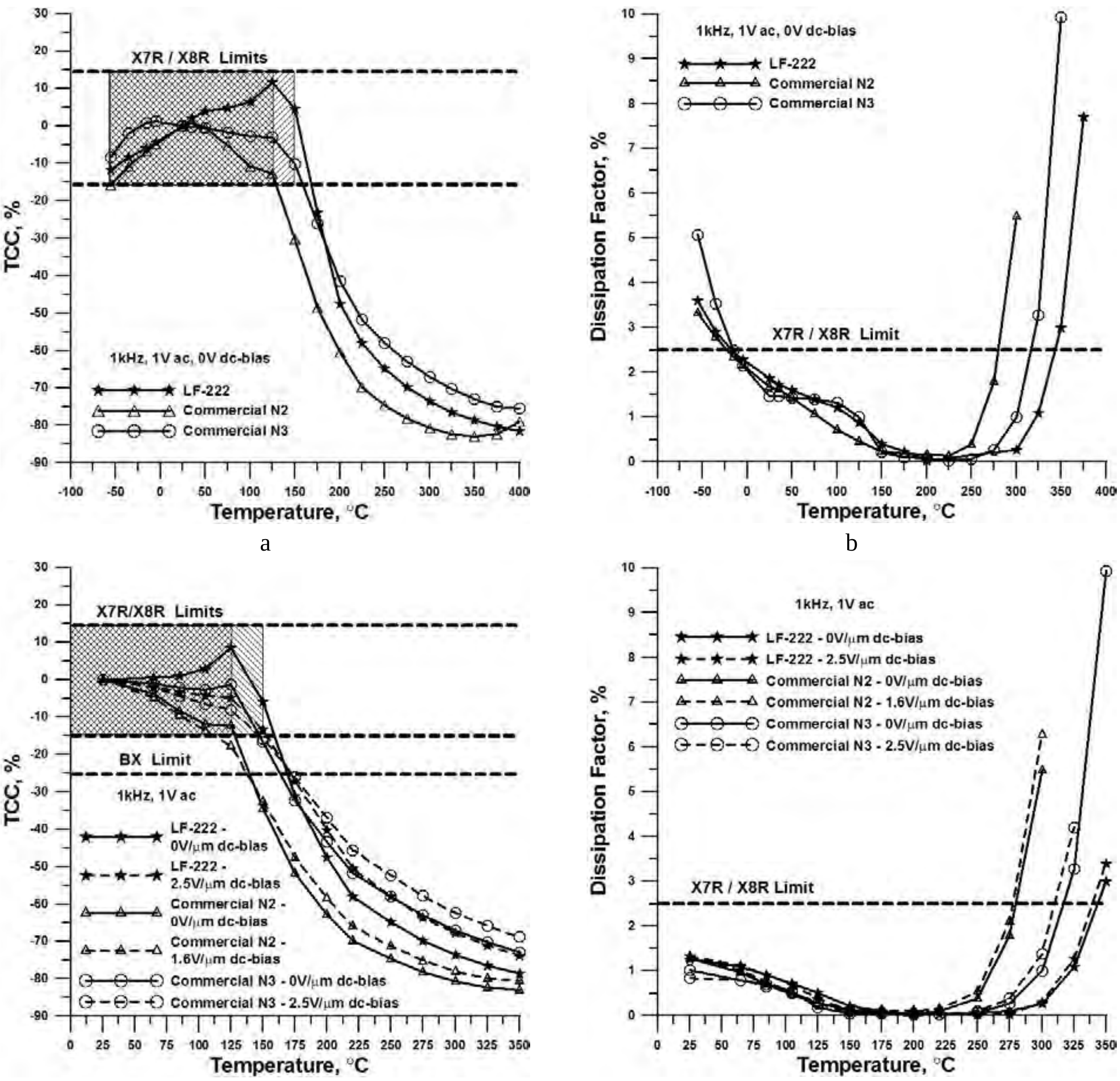


Figure 2. Dielectric properties of X7R/X8R-type dielectrics at high temperatures: a) TCC without dc-bias; b) DF without dc-bias; c) TCC with dc-bias and d) DF with dc-bias.

In essence, a 200nF X7R/X8R would have virtually the same effective capacitance at 200°C as a 120nF COG MLCC. At higher temperatures, the capacitance of X7R/X8R dielectrics continues to fall and, at 250°C, the effective capacitance of 200nF X7R/X8R MLCC chips corresponded to ~80nF COG MLCC's.

Figure 3 shows temperature dependence of dielectric breakdown strength for different COG and X7R/X8R dielectrics. As expected, the dielectric breakdown strength was found to be inversely proportional to the dielectric constant (K) – dielectrics with lower dielectric constant generally have higher breakdown strength. The superior DBS of "Commercial N2" BME X7R dielectric compared to both PME X8R dielectrics is very likely attributed to the series vs. parallel design of the various MLCC's, as stated in Table 1. It is important to note that DBS for all dielectrics did not degrade at 250°C and, in some cases, were even superior to DBS at room temperature. At 350°C, however, most dielectrics showed substantial degradation of their breakdown strength. Only "VLF-220Aq3" PME COG and "LF-222" PME X8R dielectrics showed compatible breakdown properties at 350°C and 25°C. There is a direct correlation between the level of high temperature dielectric losses and the high temperature DBS at 350°C – dielectrics with higher losses showed higher degradation of dielectric strength (Fig. 1b, 2b and 3). In general, Class-I COG dielectrics exhibited 1.5-3 times better DBS compared to Class-II X7R/X8R.

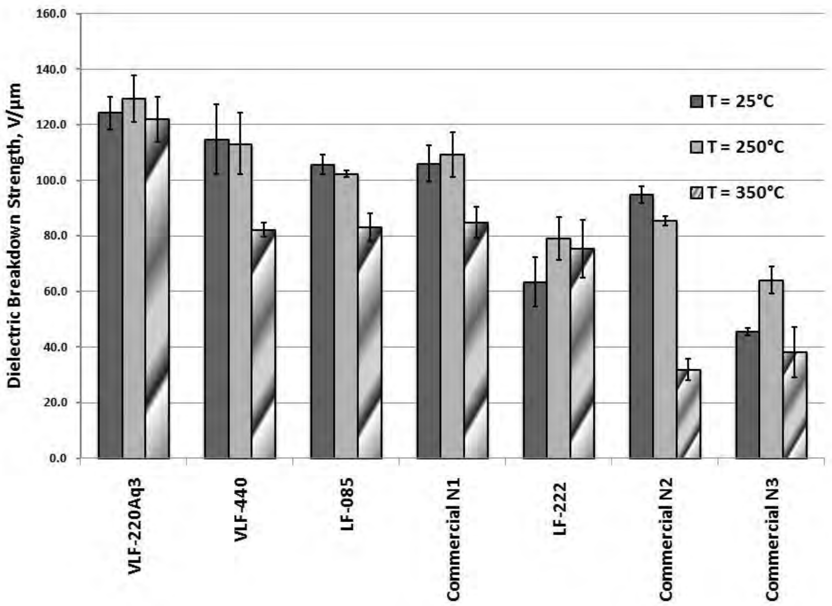
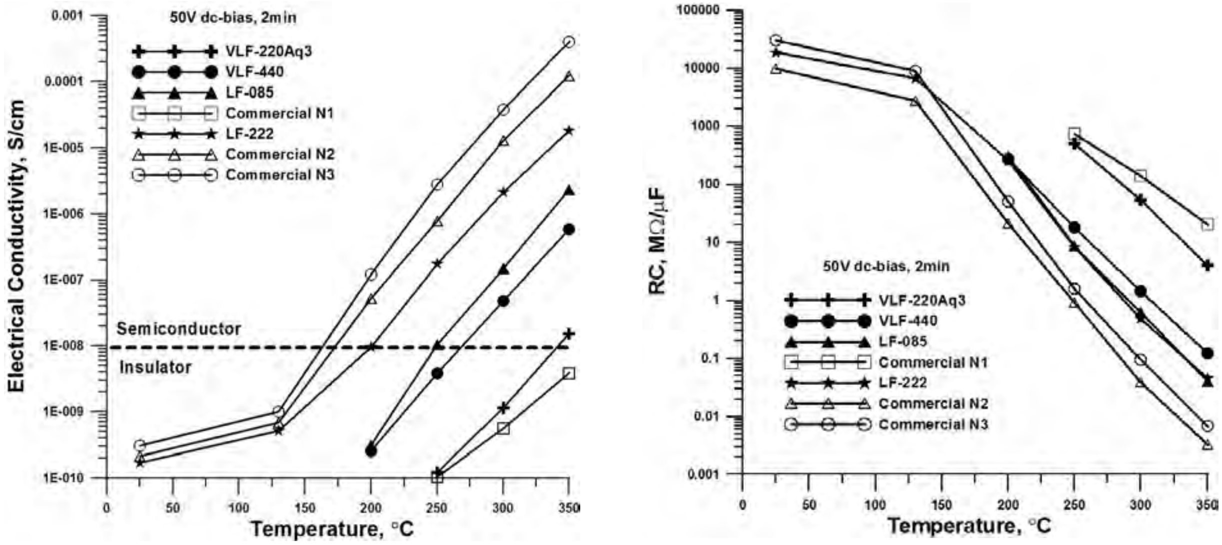


Figure 3. Dielectric breakdown strength of COG and X7R/X8R dielectrics at high temperatures.

The comparison of insulation resistance was also quite revealing between the two classes of dielectrics, as shown in Figure 4. Since there are no standard rules set describing how to define the acceptable minimum of insulation resistance of dielectric materials for high temperature applications, the conditional boundary between insulation materials and semiconductors (electrical conductivity is equal to 10^{-8}S/cm. Siemens (S) = $1/\Omega$) was used. The temperature dependence of insulation resistance of all dielectrics was measured at 50V (2min) and then converted to the electrical conductivity, dividing total reciprocal IR by dielectric thickness (Fig. 4a). The RC time constant is also shown in Figure 4b. Similar to the dielectric breakdown strength, the insulation resistance was found to be inversely proportional to the dielectric constant. The low-K COG dielectrics, “VLF-220Aq3” PME COG with K = 23 and “Commercial N1” BME COG with K = 32, showed the lowest electrical conductivity and highest RC time constant at high temperatures. They became semiconductors in the 340°C-370°C temperature range. On the other hand, the “Commercial N3” PME X8R dielectric became semiconducting at 165°C. It is interesting to note that in spite of the higher electrical conductivity of “LF-222” PME X8R dielectric, its RC time constant is almost identical to the RC time constant of “LF-085” PME COG dielectric.



a b

Figure 4. Insulation resistance of COG and X7R/X8R dielectrics at high temperatures: a) electrical conductivity; b) RC time constant

A critical parameter for high temperature application is the long term reliability. A highly accelerated life test (HALT) at 180°C and with different dc-bias conditions from 200V up to 600V for 100 hours was used in the effort to estimate the robustness of dielectrics. Results are summarized in Table 2. As mentioned previously, 20 MLCC chips per group were used for each run. A capacitor was considered failed when there was a 50% increase of voltage across the resistor. A dielectric was considered failed if any of chips from the group failed. HALT results revealed that all three low-K COG dielectrics, “VLF-220Aq3”, “VLF-440” and “Commercial N1”, passed the most severe HALT condition at 12X rated voltage. The high-K COG dielectric, “LF-085”, failed 600V testing but passed the 400V test. Among Class-II X7R/X8R dielectrics, the most robust dielectric was “LF-222”. This dielectric passed at 400Vdc, or 8X rated conditions. Two other Class-II dielectrics were able to pass only 200V tests. The 180°C test condition was limited by the equipment capability. However, the results suggest very high reliability of all COG dielectrics and “LF-222” dielectric at temperatures around 200°C and above, under normal operating voltages.

Table 2. Highly Accelerated Life Test of COG and X7R/X8R dielectrics at 180°C for 100 hours.

Dielectrics	Applied dc-bias, V		
	200	400	600
VLF-220Aq3	Passed	Passed	Passed
VLF-440	Passed	Passed	Passed
LF-085	Passed	Passed	Failed
Commercial N1	Passed	Passed	Passed
LF-222	Passed	Passed	Not Tested
Commercial N2	Failed	Failed	Not Tested
Commercial N3	Passed	Failed	Not Tested

As mentioned previously, dielectric materials for multilayer capacitor application are characterized by a group of properties, the most important of which are: temperature coefficient of capacitance (TCC) and dissipation factor (DF) with and without applied dc-bias, dielectric breakdown strength, insulation resistance, and life time or dielectric reliability. Each property has its own temperature range when it satisfies applicability criterion. Figure 5 shows a comparative bar chart representing acceptable temperature ranges for each dielectric property. The dielectric reliability (life time) was excluded from this chart due to the fact that actual life time was not modeled based on various HALT conditions.

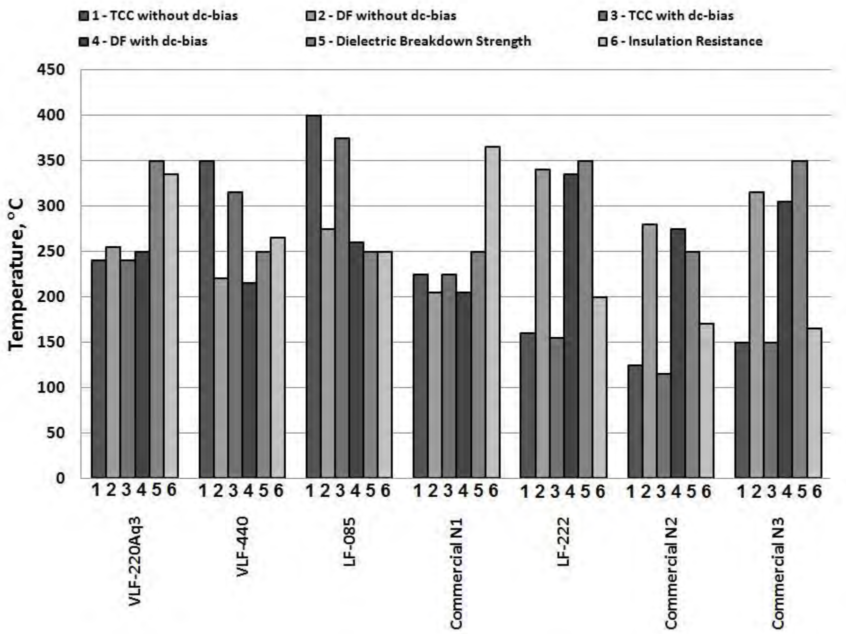


Figure 5. Comparative chart of acceptable temperature ranges for each main dielectric property.

The maximum acceptable application temperature was estimated based on the criterion that all main dielectric properties have to satisfy general EIA standards for COG and X7R/X8R dielectrics (Fig. 6). However, high temperature circuit designers may decide to sacrifice one or more of these properties. For example, temperature coefficient of capacitance may be compromised in order to increase maximum applicability temperature. Figure 6 shows that PME COG dielectrics may work continuously up to 250°C, while BME COG is limited to about 200°C. If the TCC limitation for Class-II dielectrics is sacrificed, the maximum application temperature, for example, for "LF-222" dielectric may be extended up to 200°C.

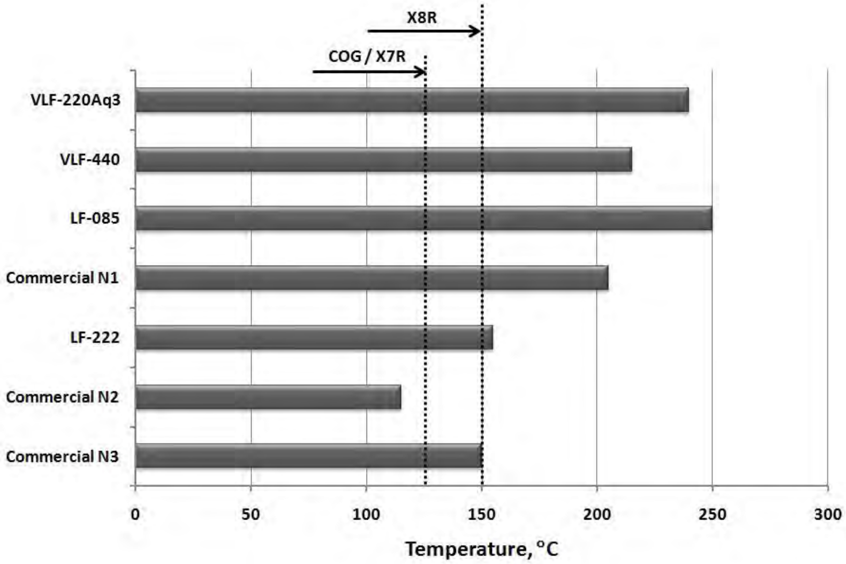


Figure 6. Estimation of maximum temperature where all main properties met standard EIA specifications.

Summary

The comparison of high temperature performance of commercially available Class-I COG and Class-II X7R/X8R dielectrics made with PME and BME technology revealed that the their applicability temperature ranges may be extended up to 200°C and beyond, depending on the flexibility of electrical circuit board design. In general, PME COG dielectrics exhibited equal or superior performance compared to the BME COG dielectric at 200°C. However, for higher temperature applications, PME dielectrics should likely be selected due to the potential susceptibility to oxidation of internal Ni electrodes in oxidizing atmospheres.

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