Two Novel Very Low Fired High-K COG Dielectrics for High Frequency Capacitor Applications

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Abstract

Temperature stable dielectrics with low dielectric losses and high dielectric constant over 75 are key components of capacitors used in high frequency (up to 1GHz) applications such as consumer electronics, cellular phones, filters and so on. The vast majority of such capacitors are made with silver-palladium internal electrodes. With palladium prices exceeding 800 USD per troy ounce (January 2011), it is essential to reduce the palladium content in the electrodes from the traditional 30% down to at least 10%. This requires dielectric materials to be compatible with high silver content electrodes and to be able to sinter at, or below 1000°C. Moreover, recently adopted Restriction of Hazardous Substances (RoHS) regulations restrict the use of lead, cadmium and four other hazardous materials in manufacturing various types of electronic components, significantly reducing the selection of available dielectric materials on the market. This paper describes two newly developed RoHS compliant very low fired high-K COG dielectrics with dielectric constant over 80 and compares them with two traditional low and very low fired, RoHS and non-RoHS compliant high-K COG dielectrics.

Introduction

New microwave dielectric ceramics with high dielectric constant (K), low dielectric loss (tanδ) or high $Q*f_o$ (Q is a reciprocal tanδ at resonance frequency, f_o) and near zero temperature coefficient of resonance frequency (τ_f) are required to satisfy the needs of the rapidly growing telecommunication industry. In line with the available ceramic materials, pseudo-tungsten bronze-type $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R: rare earth elements) solid solutions are recognized for their unique and controllable dielectric properties, such as K = 70 – 110, $Q*f_o$ = 1200GHz – 10000GHz and small τ_f [1]. Since the pioneering investigation by Bolton [2] in 1968, on temperature stable and high permittivity tungsten bronze-structured $BaTiO_3$-R_2O_3-TiO_2, hundreds of new compositions have been developed and many of them have been successfully commercialized [3-5].

For high-frequency applications, it is a desire to have as high as possible electrical conductivity of metal electrodes embedded into the ceramic chips in order to reduce the overall equivalent series resistance (ESR) of the device. It is well known that the electrical conductivity of silver-palladium solid solution, primarily used for the internal electrodes in microwave devices, improves with increasing of silver content. In addition, with the increasing price of palladium (from 300 USD per troy ounce in January 2006 to 800 USD per troy ounce in January 2011), it is essential to reduce the palladium content in the electrodes from traditional 30% down to at least 10%. This requires dielectric materials to be compatible with high silver content electrodes and to be able to sinter at, or below 1000°C. Moreover, recently adopted Restriction of Hazardous Substances (RoHS) regulations restrict the use of lead, cadmium and four other hazardous materials in manufacturing various types of electronic components, significantly reducing the selection of available dielectric materials on the market. For example, due to high dielectric polarizability and compatibility with barium, lead was widely used in pseudo-tungsten bronze-type dielectric compositions with dielectric constant at or above 85 [6].

MRA Laboratories, Inc., a leading manufacturer of precious-metal electrode (PME) ceramic capacitor dielectric materials for specialty applications, offers a broad line of Class-I COG and Class-II X7R/X8R/BX type dielectrics with wide range of dielectric constant. This paper reviews two newly developed, RoHS compliant very low fired (VLF) high-K COG dielectrics with dielectric constant over 80 and compares them with two traditional low fired (LF) and very low fired, RoHS and non-RoHS compliant high-K COG dielectrics available on the market.

Experimental

Four Class-I COG air-fired dielectric formulations (EIA specification: ΔC/C within ±30ppm/°C between -55°C and +125°C, DF < 0.1%) were selected for side-by-side comparison in this study. Two of them, "VLF-085" and "Developmental VLF High-K COG" were the newly developed RoHS compliant VLF COG dielectrics manufactured by MRA Laboratories, Inc. These dielectrics were compared with traditional RoHS compliant LF high-K COG dielectric, "LF-085", manufactured by MRA Laboratories, Inc., and with another commercially available non-RoHS compliant VLF high-K COG dielectric, "Commercial", obtained from another dielectric materials manufacturer. The initial powder properties of dielectric materials used in this study are summarized in Table 1.

Table 1. Initial powder properties of dielectric materials used in this study.

Dielectrics	Particle Size Distribution, µm			Surface Area, m^2/g	Powder Density, g/cm^3	RoHS Compliance
	D_{90}	D_{50}	D_{10}			
LF-085	1.97	0.81	0.29	1.83	5.76	Yes
VLF-085	0.87	0.47	0.28	6.05	5.55	Yes
Developmental VLF High-K COG	0.82	0.48	0.36	6.10	5.70	Yes
Commercial	0.63	0.52	0.43	6.33	5.80	No

To perform microstructural and electrical characterization of selected dielectric materials, 0805-type multilayer ceramic capacitor (MLCC) chips with ten active layers (~ 23µm sintered dielectric layer thickness) were fabricated using a traditional tape-cast process of solvent-based slurries formulated with PVB-type binder. "90%Ag–10%Pd"-based internal electrode paste was used with "VLF-085", "Developmental VLF High-K COG" and "Commercial" dielectrics, while "70%Ag–30%Pd"-based internal electrode paste was used with "LF-085" dielectric. For microwave frequency measurements, several 55mm x 55mm x 2mm laminated ceramic substrates (ceramic only) were fabricated from the cast dielectric tape. MLCC chips and ceramic substrates were sintered in air at 1000°C for 5 hours and at 1100°C for 3 hours respectively, for VLF- and LF-type of dielectrics.

Sinterability of the dielectric compositions (pressed powder pellets) was measured by a differential high resolution dilatometer (model Dilatronic II, Port Washington, NY, USA) during constant heating rate sintering, with 5°C/min heating rate to 1200°C in air. A scanning electron microscope (SEM, model ISI-100B, International Scientific Instruments, Pleasanton, CA, USA) equipped with an energy dispersive spectroscope (EDS, model PGT XS169, Princeton Gamma-Tech, Princeton, NJ, USA) was used to analyze the overall microstructure of sintered MLCC chips, their active dielectric layer thickness, as well as to estimate the compatibility of high silver content internal electrodes with dielectric compositions. Temperature coefficient of capacitance (TCC) and dissipation factor (DF) with and without dc-bias were measured by a Multi-Frequency Precision LSR meter (model HP/Agilent-4284A, Santa Clara, CA, USA) at both 1kHz and 1MHz frequencies, with 1Vrms over the temperature range from -55°C to 350°C using two environmental chambers – one capable of operating from -55°C to 200°C and the other from 25°C to 400°C. A dc-bias of 90V was applied by a 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. For ultimate breakdown voltage (UBV) measurements, each MLCC chip was flashed at 50Vdc and the voltage was slowly increased until the sample failed. The current was limited to 50mA. Measurements were performed using a special high voltage power supply (model PS-1067, Sprague Specialties, Co, North Adams, MA, USA) capable of providing 3000Vdc. The average UDV was estimated based on groups of twelve identical samples. The dielectric breakdown strength (DBS) was estimated by dividing UDV by dielectric thickness. The insulation resistance (IR) measurement was performed at 50V dc-bias, using a specially designed environmental chamber, capable of operating to 350°C. The insulation resistance reading was taken after 2 minutes of dc-bias applied. The reported average IR was based on a group of ten identical samples. Highly accelerated life test (HALT) was performed at three HALT conditions: 180°C/200Vdc, 180°C/400Vdc and 250°C/200Vdc for 100 hours using two life test systems – one was a commercially available HALT system (model 1025, Micro Instruments, Co, Canton, TX, USA), capable of operating to 180°C and the other was a specially designed high temperature HALT system, capable of operating to 350°C. A total of 20 MLCC chips per dielectric were used in each HALT run. The leakage current of each MLCC chip 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 at least two orders of magnitude increase of voltage across the resistor. Microwave measurements of ceramic substrates were kindly performed by Dielectric Laboratories, Inc., using a split-cavity resonance testing fixture and Network Analyzer (model HP 8722C Santa Clara, CA, USA) at 5GHz frequency.

Results and Discussion

In general, air-fired dielectric materials for high frequency applications are characterized by a group of properties, the most important being: dielectric sinterability and compatibility with Ag/Pd-based electrode systems, temperature coefficient of capacitance and dissipation factor with and without applied dc-bias, quality factor at high frequencies, dielectric breakdown strength, insulation resistance, and life time, or dielectric reliability. In this study, we used these sets of properties to comprehensively evaluate two newly developed RoHS compliant VLF high-K COG dielectric compositions and compare them with two commercially available analogs. In addition, some of the key properties were measured at temperatures up to 350°C, in order to estimate their high temperature dielectric performances.

Dielectric Sinterability and Ceramic Microstructure

Sinterability of four different COG dielectrics (in pressed pellets form) is presented in Figure 1 as a temperature dependence of linear shrinkage and linear shrinkage rate during sintering with constant heating rate of 5°C/min to 1200°C in air. According to the results, both “Developmental VLF High-K COG” and “Commercial” dielectrics exhibited similar densification temperature zones from about 700°C up to 1100°C and a slightly higher total linear shrinkage of ~15.1mm/mm%, compared to “VLF-085” dielectric, which showed densification from about 850°C to 1100°C and total linear shrinkage of ~12.2mm/mm%. On the other hand, the “LF-085” dielectric exhibited densification in the temperature range from about 950°C to 1200°C, with a total linear shrinkage compatible to "VLF-085". By the time dielectric compositions reached a soak temperature of MLCC sintering profiles (1000°C and 1100°C respectively for VLF- and LF-type dielectrics), their linear shrinkages were only about 50-80% of the total estimated linear shrinkage. These estimations are based on densification curves of pressed ceramic pellets, (Figure 1). It is generally recognized that the densification kinetics of thin dielectric layers in MLCC chips may be enhanced due to the presence of internal electrode layers [7], so the actual density of dielectric layers in MLCC chips at the beginning of high temperature soak may be significantly higher. Regardless, the density of dielectric layers in all four MLCC groups after sintering was estimated to be higher than 98% of theoretical density based on SEM microphotographs of sintered MLCC chips, (Figure 2). Average dielectric grain size was estimated at 0.99µm, 0.65µm, 0.68µm and 0.53µm respectively, for "LF-085", "VLF-085", "Developmental VLF High-K COG" and "Commercial" dielectrics based on SEM microphotographs of polished and thermally etched sintered MLCC chips. These grain size numbers are in good agreement with the initial particle size distribution of the dielectric powders, (Table 1), meaning that there is no significant grain growth taking place during sintering. Based on this information, it is possible to speculate that all four dielectrics may be potentially used in MLCC chips with dielectric layer thickness as low as 2-3 microns, to assure several dielectric grains across an active dielectric layer for better reliability [8]. EDS elemental analysis did not reveal any diffusion of Ag ions into the dielectrics or the formation of secondary phases at interfaces between dielectric and electrode layers, confirming that the new VLF high-K COG dielectrics are compatible with high silver content internal electrodes.

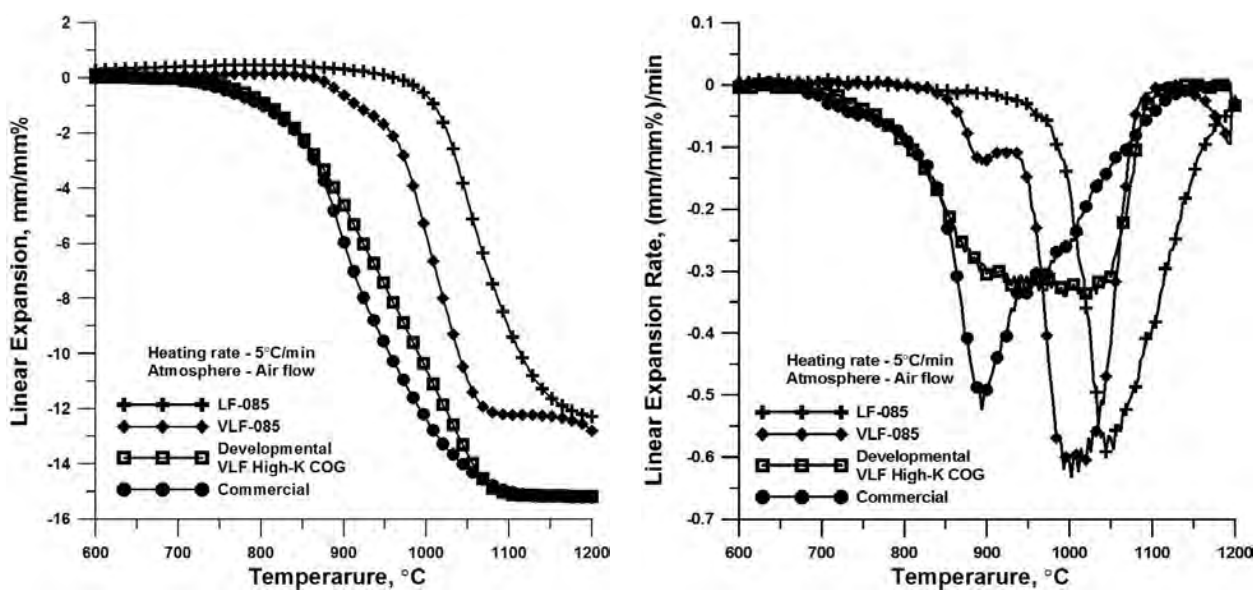

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Figure 1. Temperature dependence of (a) linear expansion and (b) linear expansion rate during sintering of dielectrics with constant linear heating rate in air.

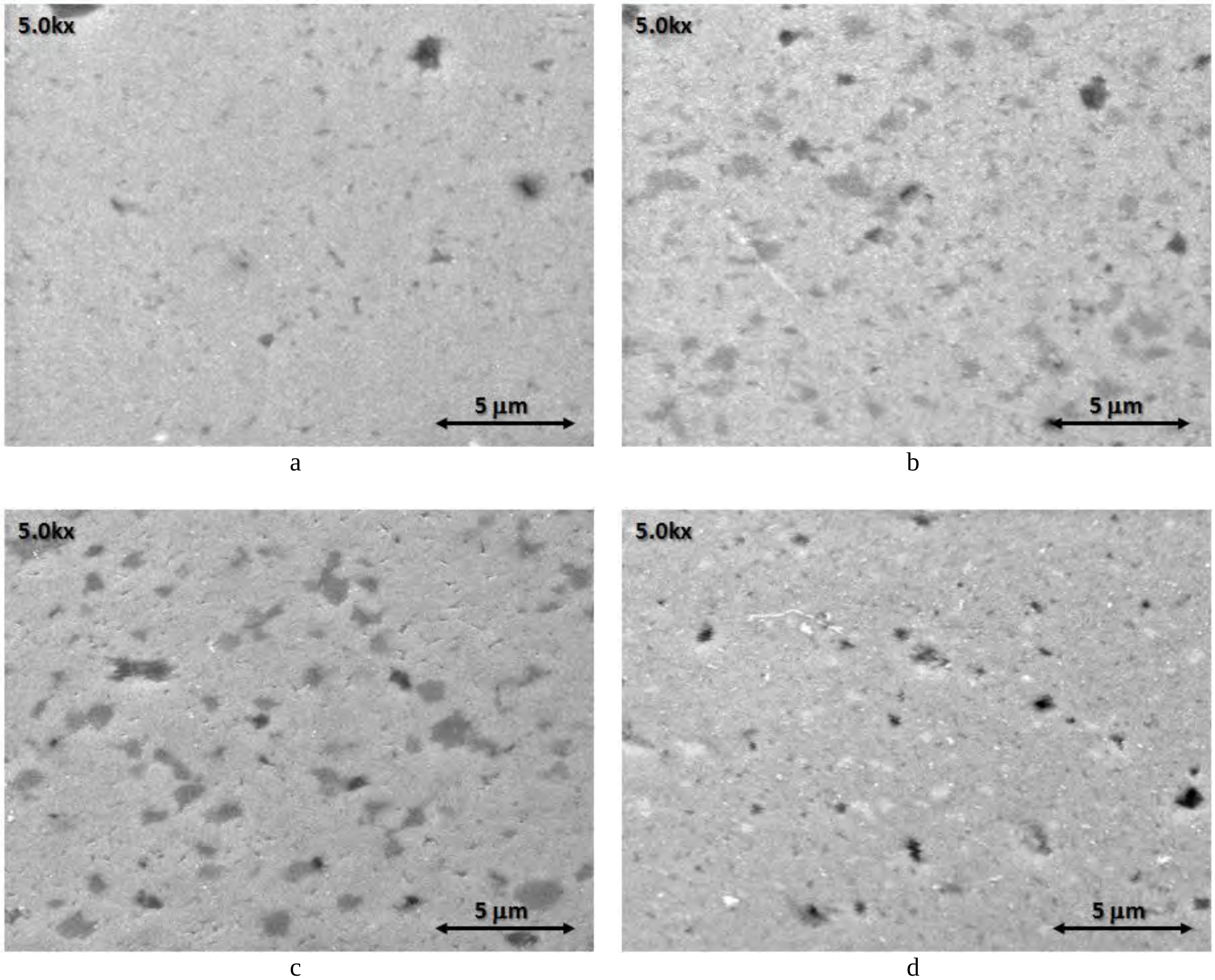


Figure 2. SEM microphotographs of sintered MLCC chips made with the following dielectrics: (a) “LF-085”; (b) “VLF-085”; (c) “Developmental VLF High-K COG” and (d) “Commercial”.

Basic Dielectric Properties

Table 2 summarizes sintering conditions, fired density, active dielectric layer thickness and basic dielectric properties for all four groups of MLCC chips measured at room temperature, while Figure 3 shows temperature coefficient of capacitance variation in the temperature range from -55°C to 125°C at 1MHz. All four dielectric compositions showed TCC and DF behaviors well within COG specification: $\Delta C/C$ within ±30ppm/°C between -55°C and +125°C and DF less than 0.1%. The highest estimated dielectric constant of 100 was observed in the “Commercial” dielectric, which contains some amount of PbO in the composition. “VLF-085” and “Developmental VLF High-K COG” dielectrics exhibited dielectric constants of 81 and 90 respectively, while “LF-085” showed dielectric constant of 86. Among others, the “Developmental VLF High-K COG” dielectric exhibited the smallest dielectric losses at 1MHz frequency. As expected, dielectric breakdown strength was found to be inversely proportional to the dielectric constant of compositions with similar sinterability – dielectrics with lower dielectric constant generally have higher breakdown strength. The highest breakdown strength was observed in the “LF-085” composition, which may be attributed to lower content of sintering aid used to enhance dielectrics sinterability.

Table 2. Summary of dielectric properties of MLCC chips measured at room temperature.

Dielectric	Sintering Conditions	Fired Density, g/cm^3	Active Dielectric Layer Thickness, µm	MLCC Capacitance Value, pF at 1MHz, 1Vrms	Dissipation Factor, % at 1MHz, 1Vrms	Estimated Dielectric Constant	Dielectric Breakdown Strength, Vdc/µm
LF-085	1100°C/3h	5.65	23.5	211.0	0.028	86	100.4
VLF-085	1000°C/5h	5.53	23.6	186.9	0.026	81	95.1
Developmental VLF High-K COG	1000°C/5h	5.72	23.6	226.1	0.012	90	84.7
Commercial	1000°C/5h	5.95	21.1	277.9	0.033	100	69.9

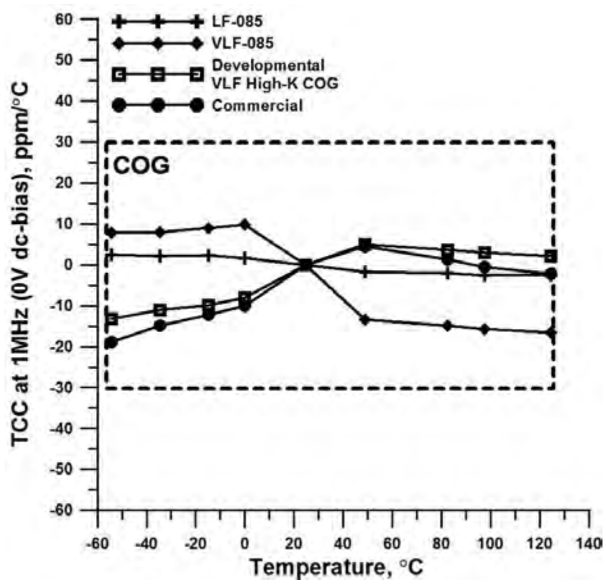


Figure 3. Temperature variation of capacitance of dielectrics at 1MHz, 1Vrms and 0V dc-bias.

Dielectric Properties at Microwave Frequency

Table 3 summarizes the results of microwave frequency measurements of dielectric ceramic substrates (ceramic only) at around 5GHz of resonance frequency using 3rd resonance (TE01 mode). The dielectric constant at microwave frequencies was found to be slightly lower compared to the estimated dielectric constant at 1MHz, (Table 2), meaning that these compositions do not have significant contributions from low frequency polarization mechanisms, such as interfacial or dipole polarizations typical for Class-II dielectrics. The quality factor, $Q*f_o$, of VLF-type dielectric compositions almost linearly decreased with increasing of dielectric constant, while “LF-085” dielectric showed the highest $Q*f_o$ among all materials evaluated in this study. This result was expected because both foreign ions used to increase dielectric constant in pseudo-tungsten bronze-type dielectrics, as well as sintering aid additions used to decrease its sintering temperature, all reduce quality factor at microwave frequencies. We believe that the newly developed RoHS compliant VLF high-K COG dielectrics, capable of sintering at 1000°C, exhibited competitive microwave properties for their dielectric constant range. Among 210 pseudo-tungsten bronze-type dielectric compositions listed by Sebastian [1], 26 compositions with dielectric constant from 80 to 90 and small τ_f have $Q*f_o$ in the range from 5500GHz to 10500GHz. However, those compositions were sintered at very high temperatures, i.e. 1350°C for several hours or higher. Very low fired versions of pseudo-tungsten bronze-type dielectrics with the same dielectric constant generally have a dielectric quality factor in the range between 1000GHz and 3500GHz [1].

Table 3. Dielectric properties of ceramic substrates at 5GHz frequency.

Dielectrics	Resonance Frequency, f_o, GHz	Estimated Dielectric Constant	Quality Factor, $Q*f_o$, GHz
LF-085	5.83	77.3	6317.7
VLF-085	5.28	70.1	4690.5
Developmental VLF High-K COG	5.59	84.6	2019.5
Commercial	4.63	98.9	1318.9

Dielectric Properties at High Temperatures

In order to evaluate high temperature properties of air-fired high-K COG dielectrics, temperature coefficient of capacitance and dissipation factor with and without dc-bias, as well as insulation resistance and RC time constant were measured from room temperature up to 350°C, (Figures 4 and 5). In contrast to other VLF low- and mid-K COG dielectrics, which we had evaluated in a previous paper [9], all four high-K COG dielectric compositions maintained their TCC behavior within COG limits of ±30ppm/°C up to 350°C, (Figure 4a). The dielectric losses crossed the COG limit of 0.1% at the temperature range from 250°C to 275°C, (Figure 4c), similar to what we previously observed for "VLF-220Aq3" low-K COG dielectric [9]. Application of 90V dc-bias revealed that TCC and DF had not been compromised up to about 200°C for the "Commercial" dielectric and up to about 275°C for "LF-085", "VLF-085" and "Developmental VLF High-K COG" dielectrics, (Figures 4b and 4d). Even at 350°C, TCC dependence on dc-bias was very small, in the range from 0.03(ppm/°C/V dc-bias) to 0.14(ppm/°C/V dc-bias), meaning that 100V dc-bias may change TCC only by 3ppm/°C for "LF-085" and "VLF-085", and up to 14ppm/°C for "Commercial" dielectrics.

The comparison of temperature behavior of insulation resistance and RC time constant are presented in Figure 5. 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/Ω) 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. The "Commercial" dielectric was found to have higher insulation resistance and, due to higher dielectric constant, it showed better RC time constant compared to other high-K COG materials, (Figure 5a and 5b). All four dielectrics reached the insulator-semiconductor conditional boundary in the 230°C-260°C temperature range. These numbers are lower compared to "VLF-220Aq3" low-K COG dielectric ($T_{semicond.}$ = 340°C), but higher than "LF-222" Class-II X8R dielectric ($T_{semicond.}$ = 200°C), confirming that the insulation resistance generally degrades with increasing of dielectric constant [9].

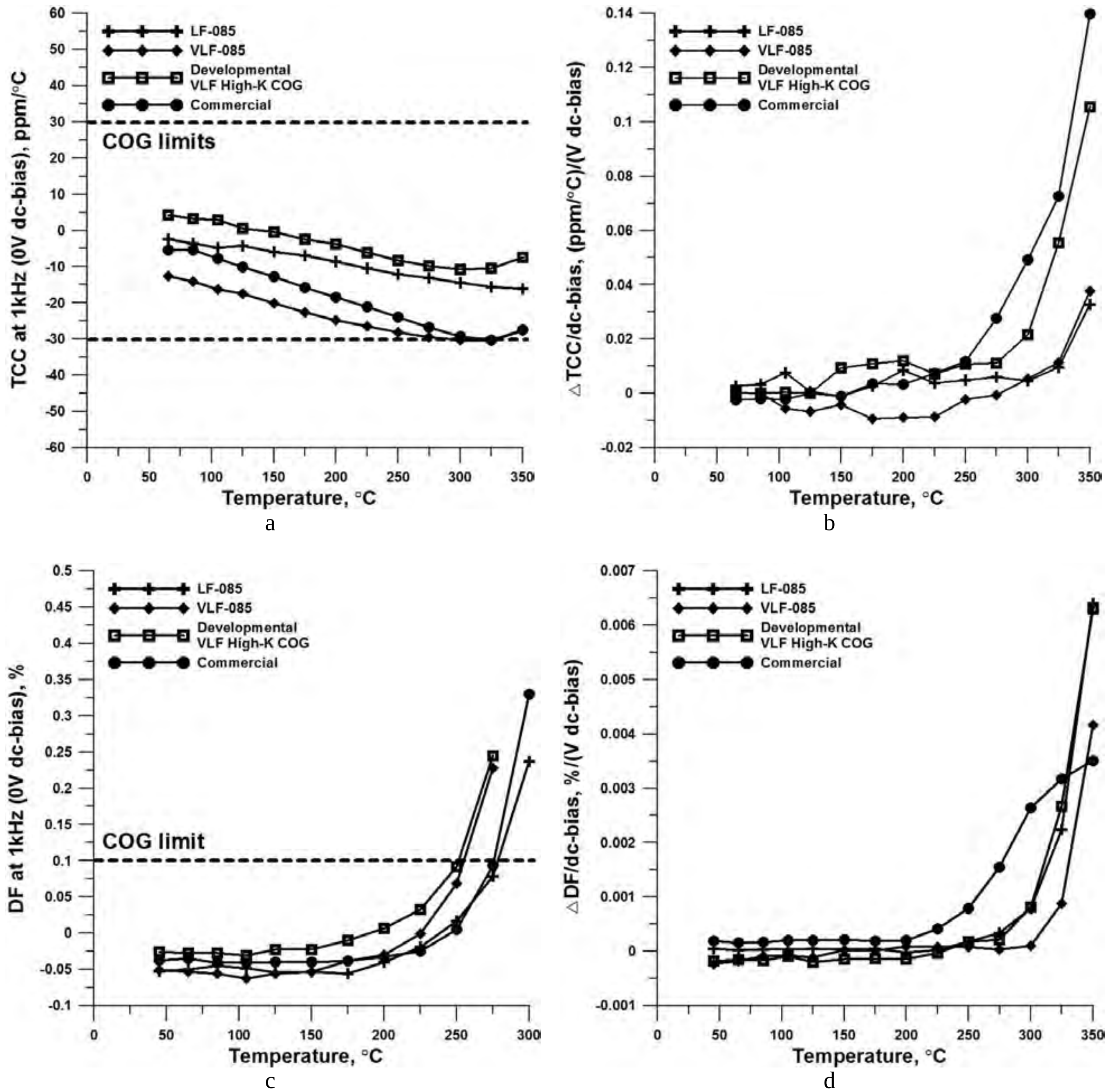
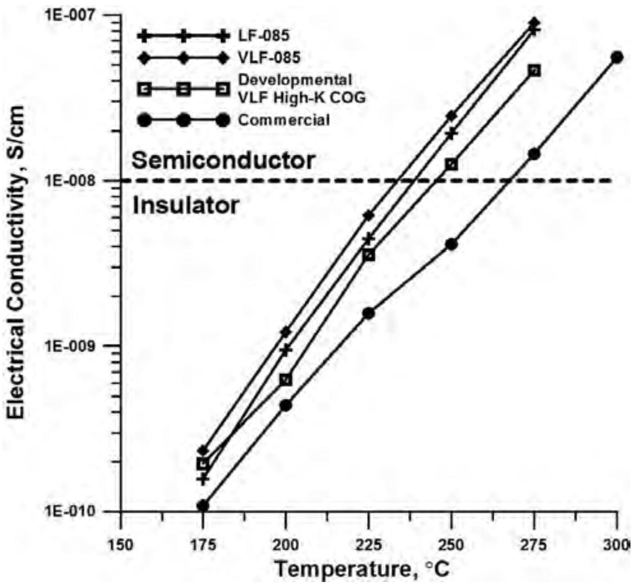


Figure 4. Temperature and dc-bias variation of capacitance and dissipation factor at 1kHz: (a) and (b) temperature variation of capacitance without and with dc-bias, respectively; (c) and (d) temperature variation of dissipation factor without and with dc-bias, respectively.



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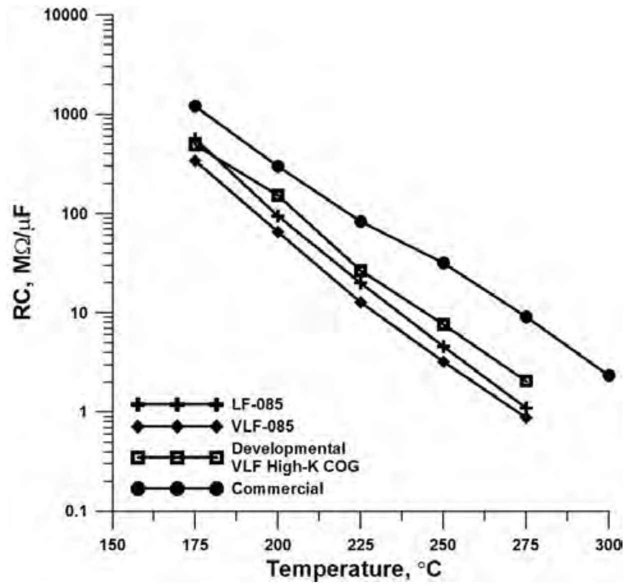

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Figure 5. Insulation resistance of dielectrics at high temperatures: (a) electrical conductivity; (b) RC time constant.

Dielectric Reliability

A critical parameter for most applications in the electronic industry is long term reliability. A highly accelerated life test (HALT) at three different acceleration conditions, 180°C/200V, 180°C/400V and 250°C/200V, for 100 hours was used to estimate the robustness of the dielectrics. Both nickel-tin plated and non plated MLCC chips were used in the study. As mentioned previously, 20 MLCC chips per group were used for each run and a capacitor was considered failed when there was at least 2 orders of magnitude increase of voltage across the resistor. Results are summarized in Table 4. The table presents the following information: i) mean time to failure (MTTF - 50% failures among the chip population) and the total number of failed chips after 100 hours; ii) initial average insulation resistance of MLCC chips (IR initial) at the beginning of the test and iii) final average insulation resistance (IR final) of the surviving chips when MTTF was reached, or at the end of 100 hours. HALT results revealed that both newly developed RoHS compliant VLF High-K COG dielectrics passed the most severe HALT conditions at 180°C/400V for plated chips and 250°C/200V for non plated chips. The "LF-085" dielectric was able to pass 180°C/200V HALT conditions for plated chips, while the "Commercial" dielectric failed all test conditions. The calculation of dielectric life time using the HALT equation was not performed due to an insufficient amount of data. We also HALT tested plated "VLF-085" chips at 180°C/400V during 1000 hours, and accumulated only 2 failures out of 20 chips. These results suggest very high reliability of both newly developed VLF High-K COG dielectrics compared to their commercially available analogs. Comparing to other dielectrics reviewed in our previous study [9], the reliability of VLF High-K COG was found to be slightly lower compared to "VLF-440" mid-K and "VLF-220Aq3" low-K COG dielectrics, which were found to be capable of passing 180°C/600V HALT test conditions.

Table 4. Summary of Highly Accelerated Life Test results performed at three test conditions.

HALT Conditions	Measured Parameters	Dielectrics			
		LF-085	VLF-085	Developmental VLF High-K COG	Commercial
250°C/200V/100h	MTTF, h	9h (20F/20) Non plated	>100h (0F/20) Non plated	>100h (0F/20) Non plated	5h (20F/20) Non plated
	IR initial, Ω	$9.5*10^{9}$	$7.44*10^{9}$	$8.82*10^{9}$	$4.88*10^{10}$
	IR final, Ω	$1.8*10^{9}$	$7.32*10^{9}$	$8.16*10^{9}$	$2.57*10^{10}$
180°C/400V/100h	MTTF, h	>100h (8F/20) Plated	>100h (0F/20) Plated	>100h (0F/20) Plated	3h (20F/20) Plated
	IR initial, Ω	$4.35*10^{11}$	$1.95*10^{11}$	$1.08*10^{11}$	$1.34*10^{11}$
	IR final, Ω	$1.43*10^{11}$	$1.75*10^{11}$	$9.01*10^{10}$	$6.31*10^{9}$
180°C/200V/100h	MTTF, h	>100h (0F/20) Plated	>100h (0F/20) Plated	>100h (0F/20) Plated	92h (13F/20) Plated
	IR initial, Ω	$4.90*10^{11}$	$2.83*10^{11}$	$1.11*10^{11}$	$2.01*10^{11}$
	IR final, Ω	$2.35*10^{11}$	$2.71*10^{11}$	$9.33*10^{10}$	$5.84*10^{10}$

Summary

Two new RoHS compliant air fired COG dielectric compositions compatible with 90%Ag-10%Pd internal electrodes and having dielectric constant over 80 were developed by MRA Laboratories, Inc. Comprehensive evaluation of their basic dielectric properties vs. properties of two commercially available analogs revealed that the new materials exhibit comparable dielectric performances at MHz and GHz frequencies, but offer significant advantages in terms of RoHS compatibility, sintering temperature and dielectric reliability. Moreover, the combination of reviewed high temperature properties suggests that these two materials may be used for high temperature applications up to 200°C and beyond, depending on flexibility of electrical circuit board design.

Acknowledgments

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References

1. M.T. Sebastian, “Dielectric Materials for Wireless Communication”, book, 1st edition, p.671, 2008.
2. R.L. Bolton, “Temperature Compensating Ceramic Capacitors in the System Barium-Rare Earth Oxide-Titania”, Ph.D. Thesis, The University of Illinois, 1968.
3. H. Ohsato, “Research and Development of Microwave Dielectric Ceramics for Wireless Communications”, J. Ceram. Soc. Of Japan, 113, vol.11, p. 703-711, 2005.
4. H. Ohsato, “Science of Tungsten Bronze Type Like $Ba_{6-3x}R_{8+2x}T_{18}O_{54}$ (R = Rare Earth) Microwave Dielectric Solid Solutions”, J. Europ. Ceram. Soc., 21, p. 2703-2711, 2001.
5. G.H. Maher, “Capacitor and Dielectric Ceramic Powder Based Upon a Barium Borate and Zinc Silicate Dual-Component Sintering Flux”, U.S. Patent 6,251,816, 2001.
6. J.M. Wilson, “Temperature Stable Monolithic Capacitors and Ceramic Compositions for Producing Same”, U.S. Patent 4,500,942, 1985.

7. A. Mohanram, S.H. Lee, G.L. Messing and D.J. Green, "Constrained Sintering of Low-Temperature Co-Fired Ceramics", J. Am. Ceram. Soc., 89, vol. 6, p. 1923-1929, 2006.
8. R. Waser, R. Hagenbeck, "Grain Boundaries in Dielectric and Mixed Conducting Ceramics", Acta Mater., 48, p. 797-825, 2000.
9. A.V. Polotai, S.G. Maher, J.M. Wilson and R.G. Maher, "Selection of Dielectric Materials for High Temperature Applications", proceeding of CARTS USA 2010 conference, New Orleans, LA, USA, p. 249-262, 2010.