Drift (due to Moisture) in Multilayer Ceramic Capacitors

IEEE CPMT - Santa Clara Valley Chapter
February 8, 2006

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I am most grateful for Professor Michael Pecht’s gracious permission to present this material to IEEE CPMT/SCV.

Background

• The continuing evolution of digital electronics has made capacitors the highest count piece part. The market for capacitors is US$ 9 billion per year\(^2\).
  – Approximately 1 trillion ceramic capacitors are sold each year\(^1\).
  – Multilayer ceramic capacitor use is growing at 25% per year\(^3\).
• The market price for palladium increased in the late 1990s. All multilayer ceramic capacitor (MLCC) manufacturers began to switch from precious metal (PME) to nickel electrodes (Base Metal Electrodes, BME) in 1998\(^4\).
• BME MLCCs require firing in a reducing atmosphere to avoid oxidation of the nickel electrode. PME MLCCs are fired in air\(^1\).\(^3\).
• Some equipment manufacturers are wary of BME capacitors\(^5\) in high humidity; the military has not qualified BME capacitors\(^6\).
• This work shows a new humidity driven capacitance degradation process in BME MLCCs not present in PME MLCCs.
Ferroelectric Effect and Barium Titanate

- Electric dipole moment at each unit cell\textsuperscript{37,38,39}
  - Electronic ceramics materials in capacitors are polycrystalline.
  - Each crystal spontaneously subdivides into 90° and 180° domains, without an external field, to minimize total energy.
    - Domains are separated by transitions called domain walls.
    - Mechanical stresses are coupled to the ferroelectric effect (FE) by the 90° domains.
  - Therefore, FE involves millions of atoms and more than one time scale.

- BaTiO\textsubscript{3} unit cell: Ba\textsuperscript{2+} on corners, Ti\textsuperscript{4+} in center and O\textsuperscript{2-} on faces
  - Phase transitions are atomic displacive transitions
  - In the tetragonal phase, the titanium ion moves ~0.1 Å (0.01 nm)

\begin{itemize}
  \item Tetragonal
    \begin{itemize}
      \item a = 3.99 Å
      \item c = 4.03 Å
    \end{itemize}

  \item Orthorhombic
  \item Rhombohedral
\end{itemize}

Vector is Polarization\textsuperscript{3}, \( p_s \approx 26 \text{ C/m}^2 \)
Dipole moment/cell \( \approx 2 \times 10^{-29} \text{ Cm} \)

Dielectric Constant vs. Temperature

- Graphically demonstrating [EIA] capacitor ratings\textsuperscript{40}
  - It would not be generally useful for maximum capacitance to occur at 120 °C. Therefore, dielectric “tuning” (doping) determines temperature range.
Capacitance Terminology

- Manufacturers typically produce MLCCs with temperature characteristics designated by COG, Z5U, X5R, X7R and Y5V\textsuperscript{11}.

<table>
<thead>
<tr>
<th>Low Temperature</th>
<th>High Temperature</th>
<th>Maximum Capacitance Change</th>
<th>Class</th>
</tr>
</thead>
<tbody>
<tr>
<td>[°C]</td>
<td>Symbols</td>
<td>[°C]</td>
<td>Symbols</td>
</tr>
<tr>
<td>-55</td>
<td>N/A</td>
<td>125</td>
<td>N/A</td>
</tr>
<tr>
<td>10</td>
<td>Z</td>
<td>85</td>
<td>5</td>
</tr>
<tr>
<td>-30</td>
<td>Y</td>
<td>125</td>
<td>7</td>
</tr>
<tr>
<td>-55</td>
<td>X</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

MLCC Construction\textsuperscript{7}

- EIA 0805 (0.08” by 0.05”) state of the art at 395 layers, 1.27 µm electrodes, 1.38 µm dielectric\textsuperscript{8}
- Work to shrink MLCC size is continuing\textsuperscript{10}. Murata introduced the EIA 01005 (0.01” by 0.005”) in 2003\textsuperscript{9}. 

Increasing volumetric charge efficiency with dielectric classes
BME MLCC Cross Section

- Epoxy encapsulated and lapped Kemet 0805 Y5V 1000 nF (1 µF)
- It has 65, 2 µm thick nickel electrodes, 10 µm thick dielectric layers with copper terminations on each end.
- Large capacitance MLCC dielectrics are doped barium titanate, such as \((\text{Ba}_{1-a-b-c-d-e-f} \text{Ca}_{a} \text{Sr}_{b}) (\text{Ti}_{1-c-d-e-f} \text{Zr}_{c} \text{Al}_{d} \text{Mn}_{e} \text{Nb}_{f}) \text{O}_{3+\delta}\)

**Known MLCC Capacitor Aging**

- Aging is time dependent logarithmic degradation of capacitance in all barium titanate based capacitors.
  - Aging is due to motion of domain walls within the crystals reducing net polarization with time counted from the time of last heat (TOLH) to the Curie point.
  - Dielectric temperature characteristics designations:

<table>
<thead>
<tr>
<th>Dielectric</th>
<th>Maximum Percent Capacitance Loss per Decade Hour, k</th>
</tr>
</thead>
<tbody>
<tr>
<td>COG</td>
<td>0</td>
</tr>
<tr>
<td>X7R</td>
<td>2.5</td>
</tr>
<tr>
<td>Y5V</td>
<td>7.0</td>
</tr>
</tbody>
</table>

\[
\frac{C(t)}{C_0} = 1 - k \log t,
\]

- Specified capacitance is guaranteed at 1000 hours at room temperature.
- Capacitors can be de-aged by heating above the Curie point (125 °C for 4 hours or 150 °C for 1 hour).
Industry Testing Practice

<table>
<thead>
<tr>
<th>Moisture Resistance</th>
<th>Load Humidity</th>
<th>Life Test</th>
<th>Thermal Shock</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 °C, 95 % RH</td>
<td>85 °C, 85 % RH</td>
<td>Maximum operating temperature (e.g., 85 °C for Y5V)</td>
<td>-55 to 125 °C (-30 to 85 °C for Y5V)</td>
</tr>
<tr>
<td>500 hours, unpowered</td>
<td>500 (to 1000) hours, 1X rated voltage</td>
<td>1000 hours, 2X rated voltage</td>
<td>5 cycles, unpowered</td>
</tr>
</tbody>
</table>

- Additional industry highly accelerated life test (HALT) does not include humidity
  - HALT is based on the model by Prokopowicz and Vaskas²¹
  - Typical HALT uses 140 °C with a voltage ratio of 8 times the rated voltage

Observations from Initial Humidity Investigation

- Samples of X7R and Y5V PME and BME MLCCs were exposed to two 100 % relative humidity (RH) environments: room temperature and 120 °C (autoclave) for over 6 months.
  - Parts were optically inspected for cracking. No cracking was observed.
- Capacitances were well below nominal values at the end of the test period (data on the following slide)
  - The PME parts had less capacitance degradation than the BME parts
  - The BME parts exposed to the autoclave degraded more than the room temperature parts.
  - The BME parts degraded below their tolerance limits.
Initial Humidity Investigation

<table>
<thead>
<tr>
<th>Electrode Type</th>
<th>Dielectric</th>
<th>Sample Size: Autoclave /Room Temperature</th>
<th>Nominal Capacitance [nF]</th>
<th>Capacitance after 3500 Hours Autoclave [nF]</th>
<th>Capacitance after 4900 Hours Room Temperature and 100% RH [nF]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PME</td>
<td>X75</td>
<td>24/24</td>
<td>22</td>
<td>22</td>
<td>21</td>
</tr>
<tr>
<td>PME</td>
<td>X75</td>
<td>0/22</td>
<td>10</td>
<td>N/A</td>
<td>9.9</td>
</tr>
<tr>
<td>PME</td>
<td>X75</td>
<td>0/24</td>
<td>22</td>
<td>N/A</td>
<td>21</td>
</tr>
<tr>
<td>PME</td>
<td>Y5V</td>
<td>0/24</td>
<td>100</td>
<td>N/A</td>
<td>95</td>
</tr>
<tr>
<td>BME</td>
<td>X75</td>
<td>15/10</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>BME</td>
<td>X75</td>
<td>15/11</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>BME</td>
<td>X75</td>
<td>15/8</td>
<td>10000</td>
<td>8600</td>
<td>9200</td>
</tr>
<tr>
<td>BME</td>
<td>Y5V</td>
<td>43/33</td>
<td>1000</td>
<td>710</td>
<td>860</td>
</tr>
<tr>
<td>BME</td>
<td>Y5V</td>
<td>44/34</td>
<td>1000</td>
<td>560</td>
<td>610</td>
</tr>
</tbody>
</table>

Problem Statement

- Compare and explain the difference between PME and BME MLCC humidity induced degradation.
- Determine the root cause that explains the difference in capacitance degradation for BME and PME MLCCs.
- Investigate why the industry standard qualification may have failed to completely characterize humidity induced degradation.
Objectives

• Determine the rate and extent of capacitance degradation of MLCC BME exposed to high relative humidity.
• Contrast degradation observations to the known logarithmic aging process for barium titanate capacitors.
  – Can the degradation be explained by the known process or is it a new phenomenon?
  – Investigate whether BME MLCCs can be de-aged (rejuvenated) by heating after exposure, as with the known aging mechanism for PME MLCCs.
  – Explain why BME and PME MLCCs degrade differently.
• Find how reliability assessment of BME MLCCs can be improved.
  – Are modified MLCC qualification testing procedures required, and what would they entail?
  – How can the supply chain verify whether MLCC parts are BME or PME without destroying the parts?

Approach (1 of 2)

• Hypothesized that capacitance degradation was due to the ingress of moisture (flow by Darcy’s Law). The capacitance degradation is caused by one of the following:
  – Introduction of water along an electrode-dielectric interface flow path changing the effective dielectric constant of barium titanate by hydration or by polarization effects of the adsorbed water layers (perhaps interface voiding is due the absence silver diffused into the dielectric)
  – Moisture induced nickel electrode oxidation along interface of barium titanate and the electrode causing increased electrode to electrode spacing (also changing the state of stress in the barium titanate) changing the effective dielectric constant of barium titanate
  – Separation of the termination from the barium titanate body due to the influence of moisture creating stress by means of a pinching action on the capacitor body by the constraining terminations. The stress may result in a change in the dielectric constant.
Approach (2 of 2)

• Hypothesized that capacitance degradation was due to ionic diffusion driven by reduction of barium titanate on the surface with capacitance degradation caused by one of the following:
  – Nickel electrode oxidation along interface of barium titanate and the electrode causing increased electrode to electrode spacing (and changed the state of stress in the barium titanate) modifying the effective dielectric constant of barium titanate
  – Oxygen vacancy ordering beginning with random oxygen defects from firing and moving vacancies to align along ferroelectric domain walls within barium titanate grains thereby reducing the effective dielectric constant of barium titanate

Experimental Approach

• Exposed samples of BME MLCCs found most prone to degradation to autoclave (121 °C/100% RH) environment with periodic capacitance monitoring to investigate their response to humidity.
  – Prepared samples by restoring them to initial capacitances by heating to the Curie temperature (de-aging)
  – Monitored weight of capacitors
  – After long term autoclave exposure, applied heat to determine if the parts could be de-aged
• Analyzed the morphology of the MLCC by
  – Cleaved and sectioned capacitors exposing internal surface for microscopy and spectroscopy by Energy Dispersive Spectroscopy (EDS).
  – Encapsulated and lapped cross sections for Focused Ion Beam (FIB), Scanning Electron Microscope (SEM) and Electron Backscatter Diffraction (EBSD)
  – Analyzed the post autoclaved MLCCs for chemical changes by spectroscopy X-ray Photoelectron Spectroscopy (XPS)
Capacitor Cleaving Device

- Device used to cleave MLCCs for microscopy and spectroscopy, however cleaved surfaces are rough

Focused Ion Beam (FIB)

- FIB cuts into upper left quadrant of sectioned Kemet 0805 BME
SEM of FIB Cut at Termination Interface

• FIB aided inspection of interface by going below lapped surface, because polishing can introduce damage

EBSD Analysis

<table>
<thead>
<tr>
<th>Kemet 1 μF Y5V BME MLCC</th>
<th>Crystal Orientation of Dielectric</th>
<th>Observations and Conclusions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>• The dielectric crystal orientation is random.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Dielectric thickness is 9.9 μm, typically 12 grains between electrodes. The grain diameter mode is 1.9 μm.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• The electrode is nickel, one grain thick. Copper is diffused into the electrode.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Analysis of a PME MLCC showed no silver migration into dielectric</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Conclusion 1: Dielectric is not permeable, no interconnected flow path.</td>
</tr>
</tbody>
</table>
Capacitors Subjected to Autoclave

<table>
<thead>
<tr>
<th>Vendor</th>
<th>Electrode Alloy</th>
<th>Termination Alloy</th>
<th>Dielectric Temperature Characteristic</th>
<th>Nominal Capacitance [nF]</th>
<th>Capacitor Tolerance</th>
<th>Sample Size</th>
<th>Dielectric Thickness [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kemet</td>
<td>Ni</td>
<td>Cu</td>
<td>Y5V</td>
<td>1000</td>
<td>+80, -20%</td>
<td>86</td>
<td>10</td>
</tr>
<tr>
<td>Murata</td>
<td>Ni</td>
<td>Cu</td>
<td>Y5V</td>
<td>1000</td>
<td>+80, -20%</td>
<td>106</td>
<td>7</td>
</tr>
<tr>
<td>Kemet</td>
<td>PdAg</td>
<td>PdAg</td>
<td>Y5V</td>
<td>100</td>
<td>+80, -20%</td>
<td>100</td>
<td>13</td>
</tr>
<tr>
<td>TDK</td>
<td>Ni</td>
<td>Cu</td>
<td>X7R</td>
<td>100</td>
<td>-10%</td>
<td>23</td>
<td>46</td>
</tr>
</tbody>
</table>

- BME are nickel with copper terminations.
- PME are palladium-silver with silver terminations (into which palladium intrudes).

Kemet 1 µF with Error Bands, as Aging

\[
\frac{C(t)}{C_o} = 1 - k\log t
\]

- Autoclave results using industry standard aging representation show increased aging ($r^2=0.71$).
• Autoclave results using industry aging representation show an increase in aging \( r^2=0.69 \).

\[
\frac{C(t)}{C_0} = 1 - \log t
\]

• Autoclave results with the best curve fit \( r^2=0.95 \) reveal a time constant of 225 hours, reaching a steady state.

\[
C = 380 \exp\left(\frac{-t}{225}\right) + 600
\]
Autoclave results with the best curve fit ($r^2=0.95$) reveal a time constant of 270 hours, reaching a steady state.

After 2600 hours of autoclave exposure, average capacitor degradation is within the known aging logarithmic rule.

At 1200 and 2600 hours, only one sample had dropped below specification limit.
• PME average degraded by 13%, still within specification.
• Both brands of BMEs degraded below specification of 800 nF, converging to 600 nF.

Conclusions (Continued)

• Conclusion 2: The capacitance of base metal electrode multilayer ceramic capacitors degraded in the autoclave environment according to a decaying time constant, coming to a steady state value in one month in the experiments.
  – Under known aging, Y5V MLCCs would not reach this value in at least 25 years
• Conclusion 3: Electrical design should allow added capacitance margin for BME MLCCs in high humidity, because more familiar precious metal electrode capacitors do not degrade according to this rule.
• Conclusion 4: Capacitor electrode type cannot be distinguished by electrical instrument measurements or mechanical inspection. A nondestructive magnetic method of separating the capacitor types has been invented. This process can be readily automated for volume production.
## Recovery after Autoclave

<table>
<thead>
<tr>
<th></th>
<th>Starting Value</th>
<th></th>
<th>After 480 Hours</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>After Initial</td>
<td></td>
<td>Auto clave 125°C</td>
</tr>
<tr>
<td></td>
<td>125°C Bake</td>
<td>Average Capacitance</td>
<td>Bake 125°C</td>
</tr>
<tr>
<td></td>
<td>(147 Hours)</td>
<td>(Standard Deviation)</td>
<td>(24 Hours)</td>
</tr>
<tr>
<td></td>
<td>Number of</td>
<td>[nF]</td>
<td>Number of</td>
</tr>
<tr>
<td></td>
<td>Samples</td>
<td></td>
<td>Samples</td>
</tr>
<tr>
<td>Kemet BME</td>
<td>32</td>
<td>946 (103)</td>
<td>30</td>
</tr>
<tr>
<td>Murata BME</td>
<td>37</td>
<td>1246 (61)</td>
<td>21</td>
</tr>
<tr>
<td>Kemet PME</td>
<td>24</td>
<td>106 (6)</td>
<td>21</td>
</tr>
</tbody>
</table>

- Conclusion 5: The BME MLCC degradation due to autoclave was not reversed by de-aging at 125 °C (or by increasing the temperature 45 °C) contrary to PME MLCCs.

## Acceleration Factor for 0805 Y5V

<table>
<thead>
<tr>
<th></th>
<th>1 μF BME</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{C}{C_0} ) for 85/85 at 1060 hours</td>
<td>.90</td>
</tr>
<tr>
<td>( \frac{C}{C_0} ) for Autoclave at 125 hours</td>
<td>.90</td>
</tr>
<tr>
<td>Acceleration factor (AF = 1060/125)</td>
<td>8.5</td>
</tr>
</tbody>
</table>

- Testing at 85 °C/85 RH for 500 hours can be accelerated to only 60 hours using the autoclave.
Acceleration Factor for 0805 Y5V

- Approximate curve fit test results for Kemet 0805 Y5V used in acceleration factor calculation.

![Graph showing C(t)/C0 vs Time (Hours) for different conditions: Lower Tolerance, Standard Log, Room Temperature, Autoclave, and 85 C/85 RH.]

Conclusions (Continued)

- Conclusion 6: An acceleration factor for humidity induced aging of the 0805 size for 85 ºC/85 RH to autoclave is 8.
- Conclusion 7: The standard industry testing, per specifications, is not sufficient to detect susceptibility to humidity degradation (because life testing is based on the model of Prokopowicz and Vaskas is based on temperature and voltage).
- Conclusion 8: Designers of high value infrastructure electronics that may experience harsh environments with high humidity should consider using precious metal multilayer capacitors.
  - Since the capacitor industry has completed the transition to base metal electrodes, military specification parts are the only certain source for precious metal capacitors.
  - Even military multilayer parts should be screened by the electrode distinguishing method to verify that they are not counterfeit, unless integrity of the supply chain is certain.
### Impedance

#### MLCC Electrical Model:

\[
Z = R_{ESR} + j \left( \frac{1}{2\pi f C} \right)
\]

- **Plot** shows Kemet’s 1 µF Y5V BME in terms of real and imaginary parts across frequencies of 100 Hz to 100 kHz.
- Increasing slopes reflect aging as lower dielectric constant.

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### Theories of Degradation

- The non-reversibility and exponential nature of the new degradation cannot be explained by the known aging mechanism.

- Two ionic diffusion theories were investigated.
  - Electrodes oxidation caused an increase of the dielectric spacing, thus reducing capacitance.
  - Mobile oxygen vacancies join into planes along ferroelectric domain walls by a process called oxygen vacancy ordering, reducing the dielectric constant.
Testing Nickel Oxide Theory

- If nickel were oxidizing in the capacitor due to humidity exposure, nickel oxide could be detected by x-ray photoelectron spectroscopy (XPS) by ion etching into the body. The surface would initially have nickel oxide from the atmosphere. If there were no internal oxide, nickel oxide would diminish with etch time.
- BME MLCCs were split into halves (exposing electrodes) using a custom tool in order to expose electrodes to x-rays and ion etch.

### Ion Etch Direction

- Cleaved Face
- Etch Depth
- Half Height
- MLCC Body

Post Autoclaved BME MLCC

- Example of an XPS plot: nickel bonds after 5th ion etch of cleaved face
- Nickel oxide data analysis on following slide
XPS Analysis for Nickel Oxide

- XPS data analysis shows nickel oxide reducing to extinction with each successive 15 minute ion etch.
- Conclusion 9: The interior electrodes have not been oxidized by exposure to humidity. The oxidized electrode hypothesis can be rejected.

BME MLCC Manufacturing Steps

- Manufacturing and testing will be key to my conclusions

```
Blending Powders → [Heat Applications] → Polishing
    ↓ Wet Milling    ↓ Dicing         ↓ Add Terminations
    ↓ Calcinining   ↓ Laminating → MLCC Testing
    ↓ Grinding      ↓ Electrode Printing
    ↓ Mixing into Paste ↓ Tape Casting
```
### Process Difference

**-PME versus BME-**

<table>
<thead>
<tr>
<th>Sintering</th>
<th>Low Palladium Content PME Heating Atmosphere(^{27, 28, 29})</th>
<th>BME Heating Atmosphere(^{26})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Air (approx. 1150 °C for silver-palladium with &lt; 35 at% Pd)</td>
<td>Humidified nitrogen and hydrogen with the partial pressure of oxygen less than (10^{-8}) atmospheres (1350 °C)</td>
</tr>
<tr>
<td>Re-oxidation</td>
<td>Step Not Required</td>
<td>Humidified nitrogen with partial pressure of oxygen between (10^{-7}) and (10^{-4}) atmospheres (1000 °C)</td>
</tr>
</tbody>
</table>

### Ellingham Diagram

- A reducing firing atmosphere and addition of a reduction inhibitor are required due to the proximity of the Ni-NiO and equilibrium lines for the reduction of barium titante\(^{13,36}\)
Oxygen Vacancy Theory

- Theorized to be responsible for the reduction of capacitance in the presence of humidity, oxygen vacancy ordering\textsuperscript{16,18,19} due to two factors.
  - The loss of capacitance for a single crystal barium titanate capacitor in the presence of water was first observed in 1955\textsuperscript{15}. Barium titanate reduction on the surface of the MLCC creates oxygen vacancies\textsuperscript{20,22}.
  - The propensity for reduction of titanium oxide is shown by the Ellingham diagram. As a result, oxygen vacancies appear as random defects remaining from firing in BME MLCCs\textsuperscript{13}.
- This theory does not invalidate any observations.
  - Oxygen movement is by ionic diffusion, an exponential solution would be expected.
  - The diffusion path between electrodes is long
- The oxygen vacancy ordering must be a lower energy state at room temperature, and it, therefore, is not reversible by heating to 125 °C.

Conclusions (Continued)

- Conclusion 10: Capacitance degradation is theorized to be caused by ionic motion within the body of the capacitors. Since degradation effect is driven by surface conditions, each new generation of miniaturized high value capacitance BME multilayer capacitors must be assessed for susceptibility to humidity degradation.
References (1 of 4)


References (2 of 4)

References (3 of 4)


References (4 of 4)