Evaluation of Case Size 0603 BME Ceramic Capacitors

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## List of Acronyms and Symbols

<table>
<thead>
<tr>
<th>A</th>
<th>area of cross-section</th>
<th>PME</th>
<th>precious metal electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>BME</td>
<td>base metal electrode</td>
<td>PWB</td>
<td>printed wiring board</td>
</tr>
<tr>
<td>C</td>
<td>capacitance</td>
<td>RT</td>
<td>room temperature</td>
</tr>
<tr>
<td>CTE</td>
<td>coefficient of thermal expansion</td>
<td>STD</td>
<td>standard deviation</td>
</tr>
<tr>
<td>DCL</td>
<td>direct current leakage</td>
<td>t</td>
<td>thickness of the dielectric</td>
</tr>
<tr>
<td>DWV</td>
<td>dielectric withstanding voltage</td>
<td>t_electr</td>
<td>electrification time</td>
</tr>
<tr>
<td>E</td>
<td>Young’s modulus</td>
<td>Tg</td>
<td>glass transition temperature</td>
</tr>
<tr>
<td>Ea</td>
<td>activation energy</td>
<td>TSD</td>
<td>terminal solder dip</td>
</tr>
<tr>
<td>HALT</td>
<td>highly accelerated life testing</td>
<td>T_sold</td>
<td>melting temperature of solder</td>
</tr>
<tr>
<td>HT</td>
<td>high temperature</td>
<td>VBR</td>
<td>breakdown voltage</td>
</tr>
<tr>
<td>HV</td>
<td>high voltage</td>
<td>VBR_{75}</td>
<td>third quartile of VBR distribution</td>
</tr>
<tr>
<td>IR</td>
<td>insulation resistance</td>
<td>VBR_{min}</td>
<td>minimal VBR in the group</td>
</tr>
<tr>
<td>LV</td>
<td>low voltage</td>
<td>V_{O}^{++}</td>
<td>charged oxygen vacancy</td>
</tr>
<tr>
<td>MLCC</td>
<td>multilayer ceramic capacitor</td>
<td>VR</td>
<td>rated voltage</td>
</tr>
<tr>
<td>N</td>
<td>number of layers</td>
<td>XRF</td>
<td>X-Ray Fluorescence</td>
</tr>
</tbody>
</table>
Abstract

High volumetric efficiency of commercial base metal electrode (BME) ceramic capacitors allows for a substantial reduction of weight and sizes of the parts compared to currently used military grade precious metal electrode (PME) capacitors. Insertion of BME capacitors in space applications requires a thorough analysis of their performance and reliability. In this work, six types of cases size 0603 BME capacitors from three vendors have been evaluated. Three types of multilayer ceramic capacitors (MLCCs) were designed for automotive industry and three types for general purposes. Leakage currents in the capacitors have been measured in a wide range of voltages and temperatures, and measurements of breakdown voltages (VBR) have been used to assess the proportion and severity of defects in the parts. The effect of soldering-related thermal shock stresses was evaluated by analysis of distributions of VBR for parts in “as is” condition and after terminal solder dip testing at 350°C. Highly Accelerated Life Testing (HALT) at different temperatures was used to assess the activation energy of degradation of leakage currents and predict behavior of the parts at life test and normal operating conditions. To address issues related to rework and manual soldering, capacitors were soldered onto different substrates at different soldering conditions. The results show that contrary to a common assumption that large-size capacitors are mostly vulnerable to soldering stresses, cracking in small size capacitors does happen unless special measures are taken during assembly processes.
Outline

- Introduction.
- Leakage currents and insulation resistance.
  - Absorption and leakage currents.
  - Temperature and voltage dependence of leakage currents.
- Breakdown voltages.
  - Initial evaluation.
  - Effect of TSD at 350°C.
- Degradation of leakage currents during HALT.
  - Activation energy of degradation.
  - Effect of HALT on breakdown voltages.
- Effect of soldering.
  - Manual and reflow soldering.
  - Effect of substrate temperature for manual soldering.
- Conclusion.

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Introduction

- Two major issues with MLCC:
  - Insulation Resistance (IR) degradation related to oxygen vacancies.
  - Failures related to soldering induced cracking.
- Due to the difference in electro-chemical behavior of Ni and Ag/Pd and formed products, the probability of low-voltage failures for BME is less than for PME capacitors.

Intrinsic wear-out failures caused by oxygen vacancies typically do not cause failures during applications.

Concentration of $V_O^{++}$ should be under control to reduce the probability of failures in the presence of defects.

$$TTF = TTF_0 \times \left( \frac{VBR_d}{VBR_i} \right)^n$$
The Significance of Breakdown Voltages

- In most cases distributions of VBR for BME capacitors are bimodal.
- The high voltage (HV) mode has tight distributions (STD/Mean ~4%) indicating intrinsic breakdown.
- The presence of low voltage (LV) subgroup is due to defects.

- The interception point of VBR distribution indicates the proportion of defects, and the spread of VBR towards low voltages indicates the significance of defects.
- Lot acceptance criterion: $VBR_{min}/VBR_{75} > 0.5$.
- Migration of $V_{O''''}$ in capacitors with defects results in IM failures.
Part Types Used in This Study

<table>
<thead>
<tr>
<th>application</th>
<th>Mfr.</th>
<th>C, µF</th>
<th>VR, V</th>
<th>t, µm</th>
<th>N plates</th>
<th>Margins, µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>auto</td>
<td>C</td>
<td>0.1</td>
<td>50</td>
<td>8</td>
<td>60</td>
<td>180 110 170</td>
</tr>
<tr>
<td>auto</td>
<td>M</td>
<td>0.1</td>
<td>50</td>
<td>9</td>
<td>62</td>
<td>125  70 120</td>
</tr>
<tr>
<td>auto</td>
<td>A</td>
<td>0.1</td>
<td>50</td>
<td>10</td>
<td>46</td>
<td>115 140 110</td>
</tr>
<tr>
<td>general</td>
<td>C</td>
<td>0.1</td>
<td>50</td>
<td>8</td>
<td></td>
<td>120 150</td>
</tr>
<tr>
<td>general</td>
<td>M</td>
<td>0.01</td>
<td>25</td>
<td>18</td>
<td>19</td>
<td>170 140 180</td>
</tr>
<tr>
<td>general</td>
<td>C</td>
<td>0.01</td>
<td>50</td>
<td>15</td>
<td>17</td>
<td>160 220 160</td>
</tr>
</tbody>
</table>

- X-Ray Fluorescence (XRF) analysis showed that barium titanate ceramics (BaTiO3) doped with different elements (mostly Zr, Y, W) is used in all parts.
- Same size and nominal auto and general purpose MLCCs have similar design and materials.
Absorption and Leakage Currents

Relaxation of leakage currents at room temperature

- Direct Current Leakage (DCL) at room temperature (RT) decreases with the electrification time, as $\sim 1/t_{electr}$.
- Absorption currents at VR prevail during first hours of electrification and depend mostly on the value of capacitance.
- Absorption currents are reproducible, increase with voltage, and stabilize at $V > \sim 2VR$.
- The larger $t_{electr}$, the better the sensitivity of the DCL/IR testing to the presence of defects.
- No significant difference in DCL for generic and auto capacitors.
Insulation Resistance

Relaxation of leakage currents at different temperatures and voltages

Effect of capacitance on IR in different types of BME capacitors

- At 125°C intrinsic currents prevail after ~ 100 sec of electrification.
- IR measurements in LV capacitors during mass production is a challenge. The test voltage should be increased.
- IR values for 0603 capacitors are within the range of values typical for different types of BME MLCCs, but some are out of the MIL limit.
- MIL requirements for IR do not allow sufficient margin for high volumetric efficiency BME capacitors. Murata auto limits are more reasonable.
Effects of Temperature and Voltage on Leakage Currents

Variations of leakage currents with voltage at different temperatures

- At high temperatures $I$-$V$ characteristics in all parts can be described with a power law, $I \sim V^m$.
- The exponent $m$ decreases with temperature.
- At 125°C $1.8 < m < 2.2$ and at 175°C $m \sim 1.5$.
- DCL at HT can be explained based on the space charge limiting model.
Effects of Temperature and Voltage on Leakage Currents, Cont’d

Variations of leakage currents with temperature at different voltages

✓ For BME capacitors activation energy of intrinsic leakage currents decreases with voltage.
✓ Ea for BME is less than for PME capacitors.
✓ Voltage and temperature dependencies for auto and general type capacitors are similar.
**Breakdown and Rated Voltages**

**Distributions of VBR for 0603 BME MLCCs**

- Tested lots did not have gross defects: $VBR_{\text{min}}/VBR_{75} > 0.5$.
- Thickness of the dielectric is not the only factor determining VBR.
- No significant difference between automotive and general types of BME capacitors.
- VR is 20 to 30 times less than VBR. One of the limiting factors for VR is voltage dependence of capacitance.
HALT, General Type BME Capacitors

- Step stress HALT was carried out at $T = 22^\circ C$, $125^\circ C$, $150^\circ C$, and $175^\circ C$, for 100hr and 200V at each step.
- Leakage currents were monitored through the testing.

- At $125^\circ C$ some degradation was observed in 0.1$\mu F$ 50V capacitors only.
- At $150^\circ C$ degradation in 0.1$\mu F$ 50V capacitors was noticeable and some parts failed.
- All 0.1$\mu F$ 50V capacitors failed at $175^\circ C$, but 0.01 $\mu F$ capacitors, both 25V and 50V, increased currents ~ 50% only.

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- All 0.1$\mu F$ 50V capacitors failed at $175^\circ C$, but 0.01 $\mu F$ capacitors, both 25V and 50V, increased currents ~ 50% only.
**HALT, Automotive Grade BME Capacitors**

**Variations of leakage currents in 0.1\(\mu\)F 50V size 0603 BME auto capacitors at 200V with time at 125°C and 150°C**

- No current increase for capacitors from Mfr.M that had minimal IR. It is possible that large intrinsic currents mask degradation.
- Some degradation can be observed at 125°C for Mfr.A and C.
- Degradation and failures in parts from Mfr.C at 150°C are similar to generic capacitors from the same manufacturer.
- Comparison of results for Mfr.C 0.1\(\mu\)F and 0.01\(\mu\)F capacitors indicates the effect of dielectric thickness on degradation processes.
Activation energy of degradation is consistent with the migration of positively charged oxygen vacancies model.

Degradation at life test and operating conditions is negligibly small.

At $E_a \sim 1.6 \text{ eV}$, the predicted degradation rate at 125°C and 200V is $\sim 1.3 \times 10^{-13} \text{ A/sec}$. Using a conservative estimation for the voltage acceleration constant, $n = 3$, the rate at 2VR would be $\sim 1.5 \times 10^{-14} \text{ A/sec}$. At this rate it would take $\sim 2 \times 10^6$ years for the current to increase by 1 μA during life testing.
Effect of HALT on VBR

Comparison of initial and post_HALT distributions of VBR.

- Parts with higher rate of degradation had a more substantial decrease of VBR.
- Post-HALT degradation of VBR is consistent with the defect-related failure model:
  An IM failure occurs when accumulation of $V_{O}^{++}$ at a defect site would be sufficient to increase current density to a level necessary to initiate a local thermal run-away process.
Effect of Soldering Thermal Shock on Breakdown Voltages

- 30 capacitors of each type were stressed by the terminal solder dip testing at a solder pot temperature of 350°C (10 cycles).
- The effect was evaluated by visual examinations and by comparing initial and post-terminal solder dip (TSD)350 distributions.

- No substantial variations in distributions of breakdown voltages after thermal shock testing.
- TSD_350 does not generate cracks on 0603 BME capacitors.
Effect of Manual Soldering

- It is often assumed that large size MLCCs (1210 and above) are more susceptible to cracking.
- Insertion of BME MLCCs in hi-rel applications means extensive use of small size capacitors (below 0805). Are they less vulnerable to cracking?

Experiment: Groups with 14 to 12 samples of 0.1 μF, 50V, size 0603 BME MLCCs were soldered manually onto FR4 PWBs using recommended precautions and a soldering iron set to 315°C.

<table>
<thead>
<tr>
<th>MLCC</th>
<th>Open circuit</th>
<th>Short circuit</th>
<th>Intermittent</th>
<th>Total failures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mfr. C</td>
<td>3/14</td>
<td>2/14</td>
<td>0/14</td>
<td>5/14</td>
</tr>
<tr>
<td>Mfr. M</td>
<td>1/14</td>
<td>2/14</td>
<td>5/14</td>
<td>8/14</td>
</tr>
<tr>
<td>Mfr. A</td>
<td>3/12</td>
<td>0/12</td>
<td>2/12</td>
<td>5/12</td>
</tr>
</tbody>
</table>

- Manual soldering can cause failures of small size capacitors.
- Out of 40 samples of 0603 size MLCCs soldered with a soldering iron at 315°C 70% were electrical failures.
Effects of manual and reflow soldering were compared by measurements of VBR for case size 0603 BME 0.01uF, 25V capacitors from Mfr.M soldered onto the same FR4 PWB.

Manual soldering was carried out with different tip sizes (0.03” and 0.08”) and different temperatures of the board (cold, 22°C, and hot, 150°C).

- No defects were observed in MLCCs after solder reflow and after manual soldering onto a board preheated to 150°C.
- Soldering iron tips of larger size increase the probability of failures from ~20% for 0.03” to ~70% for 0.08”.

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Post Soldering Stresses

- Tensile strength of X7R ceramics is 70 to 250 MPa.
- PWB with coefficient of thermal expansion \((\text{CTE})_{PWB} > \text{CTE}_{\text{cap}}\) create compressive stresses \((\sigma > 0)\) in MLCCs after reflow soldering.
- Ceramic substrates with \(\text{CTE}_{PWB} < \text{CTE}_{\text{cap}}\) create tensile stresses \((\sigma < 0)\) that are much more dangerous.
- The level of stresses caused by solder reflow and manual soldering onto a cold board can be estimated using a one-dimensional model:

\[
\sigma_{\text{coldPWB}} = \frac{\alpha_{\text{cap}} \times (T_{\text{sold}} - T_r)}{(E_{\text{cap}})^{-1} + \left(E_{PWB} \times A_{PWB} / A_{\text{cap}}\right)^{-1}} \quad \sigma_{\text{reflow}} = \frac{(\alpha_{PWB} - \alpha_{\text{cap}}) \times (T_g - T_r)}{(E_{\text{cap}})^{-1} + \left(E_{PWB} \times A_{PWB} / A_{\text{cap}}\right)^{-1}}
\]

Mechanical characteristics used for stress calculations

<table>
<thead>
<tr>
<th>Material</th>
<th>E, GPa</th>
<th>CTE, ppm/°C</th>
<th>Tg/Tsold</th>
</tr>
</thead>
<tbody>
<tr>
<td>PWB (FR4)</td>
<td>17</td>
<td>15</td>
<td>150</td>
</tr>
<tr>
<td>Alumina</td>
<td>360</td>
<td>7.7</td>
<td>230</td>
</tr>
<tr>
<td>MLCC</td>
<td>100</td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>

Mechanical stresses in MLCCs assembled by reflow and manual soldering (3mm FR4, 1mm alumina)

- Reflow soldering onto a PWB creates relatively small compressive stresses in case of FR4 and tensile stresses in case of alumina board.
- Manual soldering onto cold PWB creates significant tensile stresses.
- Post manual soldering stresses are greater for small size MLCCs.
Effect of Substrate and Type of MLCC

0.01µF 25V capacitors were soldered onto alumina and FR4 PWBs manually (350°C)

Manual soldering onto alumina board resulted in less damage compared to FR4 PWB. A contradiction with the model is likely due to a much higher thermal conductivity of alumina (increase T of the board).

All case size 0603 0.01 µF 50V capacitors passed DWV test after reflow soldering. However, contrary to 0.1 µF 50V MLCCs, ~10% of capacitors had defects.
Failures Caused by Manual Soldering

Typical soldering thermal shock cracks in large MLCCs

Post soldering cracks in small size MLCCs

- Contrary to the annular thermal stress cracks in large size capacitors, cracks in 0603 capacitors occur along the terminations.
- Termination cracks are not specific for BME MLCCs only. They were also observed in small-size PME capacitors.
Conclusion

- Design, materials, leakage currents and breakdown voltages in automotive and general application capacitors are similar.

- Leakage currents:
  - at RT absorption currents prevail over intrinsic conduction currents that are several orders of magnitude less than currents measured within 2 min of electrification;
  - Ea decreases with voltage from ~ 0.9 eV at 0.5VR to ~ 0.5 eV at 4VR.
  - I-V characteristics at HT follow a power law with the exponent decreasing from ~3 at 85°C to ~ 1.5 at 175°C.

- Degradation of DCL and failures were observed during HALT in parts having minimal thickness of the dielectric. Activation energy of degradation is large, ~1.6 eV, so no intrinsic wear-out failures are expected at life testing or normal operating conditions.

- 0603 MLCCs are vulnerable to manual soldering and more than 50% of capacitors can fail in case of soldering onto a cold PWB.

- Board preheating is critical to reduce the probability of failures.

- Post-soldering fracturing along the terminals is a specific feature of small-size capacitors.