

# Multilayer Ceramic Capacitors: Mitigating Rising Failure Rates

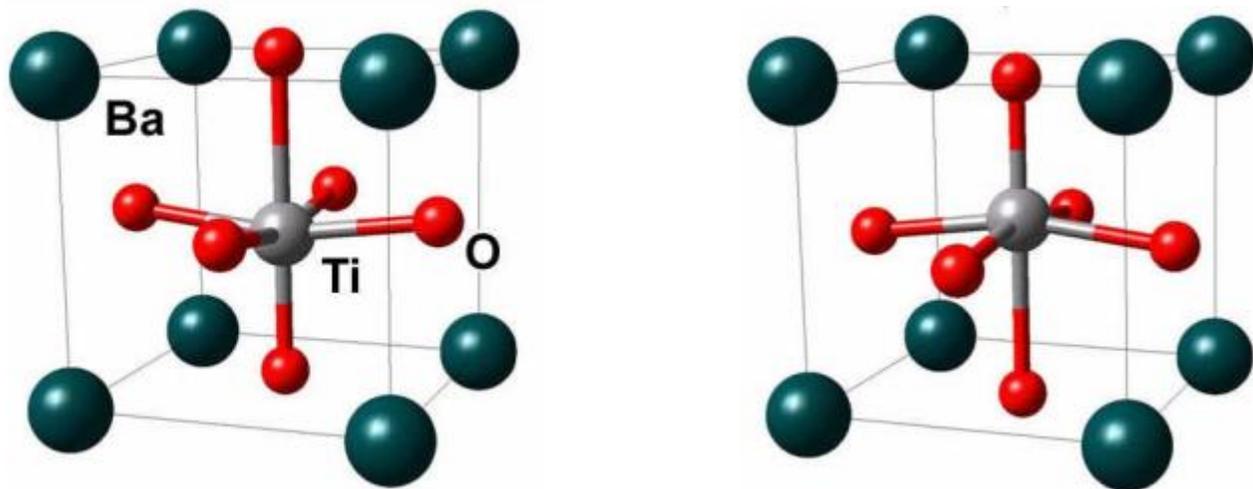
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## Abstract

The multilayer ceramic capacitor (MLCC) has become a widely used electronics component both for surface mount and embedded PCB applications. The MLCC technologies have gone through a number of material and process changes such as the shift from precious metal electrode (PME) configurations which were predominantly silver/palladium to base metal electrodes (BME) dominated by nickel. Each of these changes were accompanied by both quality and reliability problems. The MLCC industry is now in the midst of an unprecedented set of challenges similar to the Moore's Law challenges being faced by the semiconductor industry. While capacitor failures have historically been responsible for a significant percentage of product field failures (most estimates are ~30%) we are seeing disturbing developments in the low voltage (<250V) commodity part infant mortality and wearout failure rates.

## Introduction

Seven decades after its discovery, the ferroelectric material, barium titanate ( $\text{BaTiO}_3$ ) has established itself as the most widely used dielectric material used in the construction of multilayer ceramic capacitors (MLCCs) both because of its intrinsic properties and its amenability to property modification with dopant materials and process variants [1].



**Figure 1 – Electric Field Polarity Driven Displacement of Ti Cation within  $\text{BaTiO}_3$  Unit Cell Structure [2]**

Scaling up from the cell to the ferroelectric domain and crystal structure, the dielectric properties of  $\text{BaTiO}_3$  are dominated by the polarization versus electric field (P vs. E) hysteresis responses.

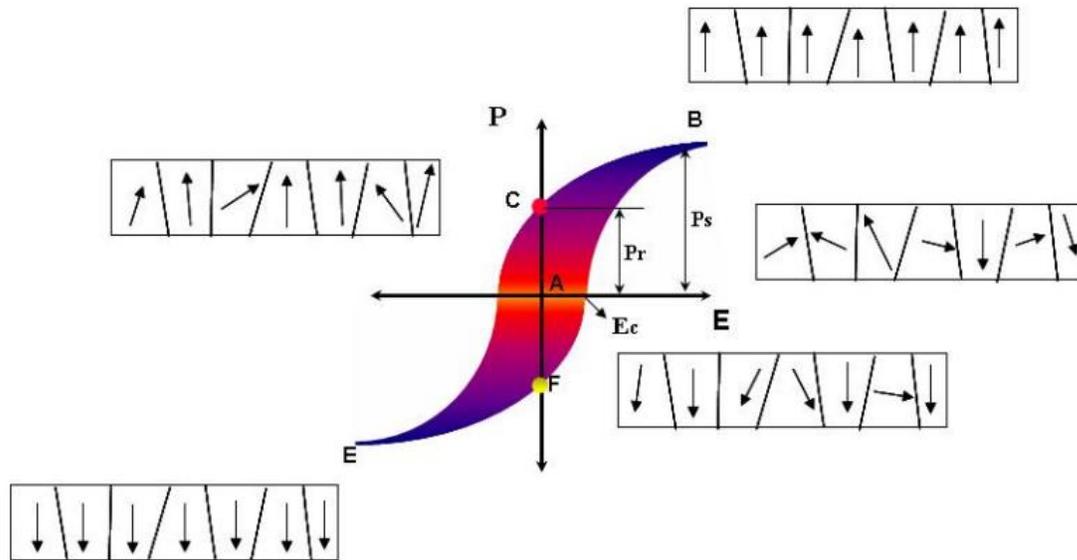


Figure 2 – Polarity Domain Structures and P vs. E Hysteresis [3]

The unit cell structure of  $\text{BaTiO}_3$  shifts with temperature into different crystalline phases, each having different electrical and mechanical properties. Of particular interest for the performance of MLCCs is the shift at the  $T_C$  Curie point ( $\sim 120^\circ\text{C}$ ) from  $\langle 100 \rangle$  polarized tetragonal at room temperature to non-polar cubic.

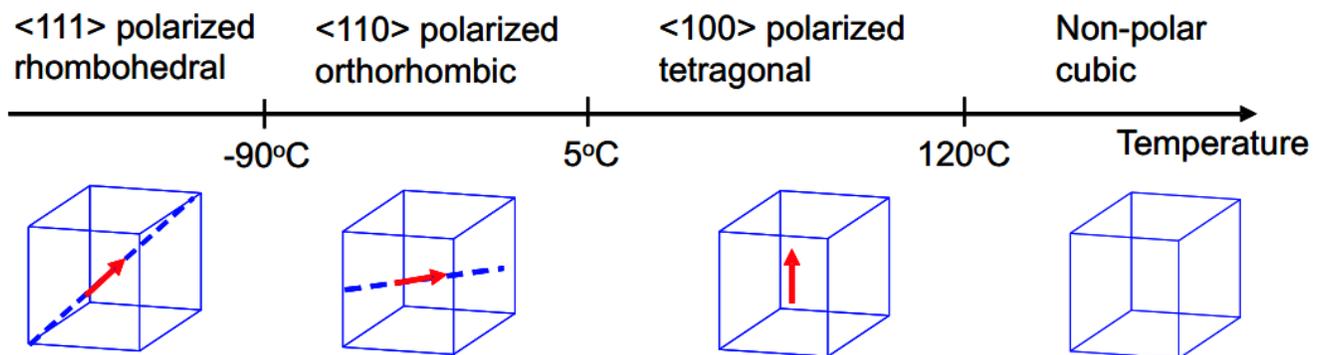


Figure 3 – Various Phases of  $\text{BaTiO}_3$  Unit Cell Structure [4]

The MLCC electrical performance is dramatically affected at temperature transitions above and below the Curie point because the capacitor's BaTiO<sub>3</sub> dielectric constant is likewise dramatically changed.

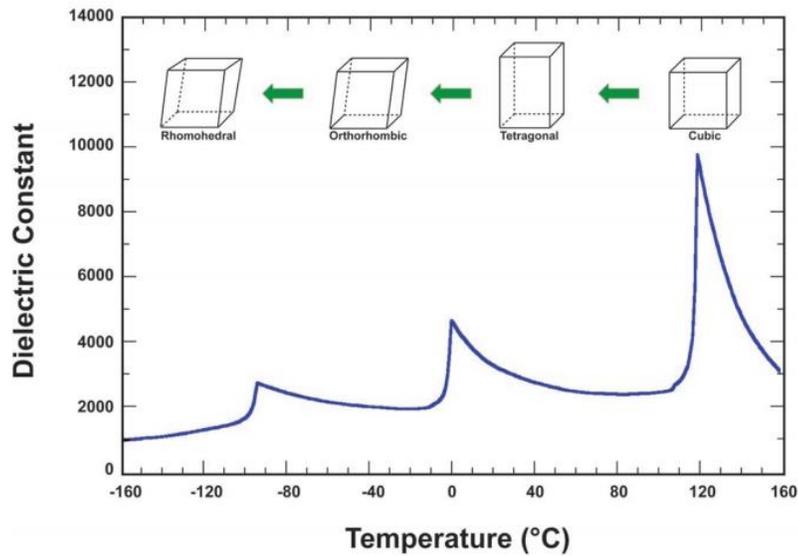


Figure 4 – Various Phases of BaTiO<sub>3</sub> Unit Cell Structure and Resultant Changes in Dielectric Constant [5]

### MLCC Configuration and Production

Capacitors consist of two or more conductive plates (also called internal electrodes) separated by a dielectric material. As clearly denoted by the term ‘multilayer ceramic capacitor’ the dielectric material for MLCCs is a ceramic. The structure is shown in Figure 5.

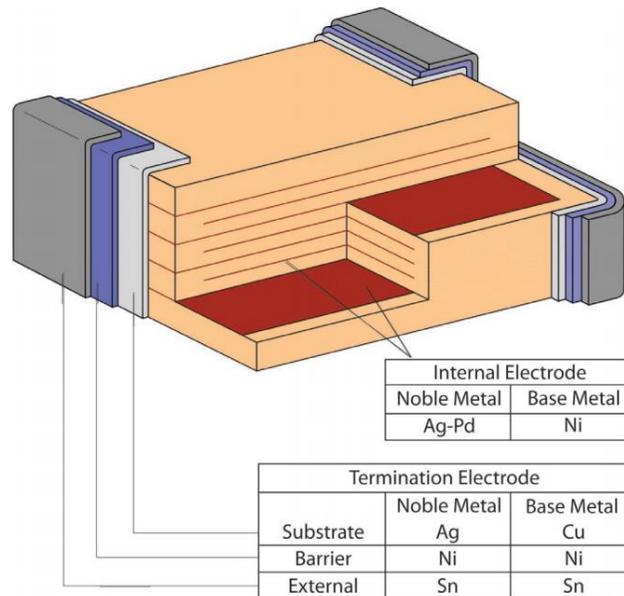


Figure 5 – MLCC Structure and Material Sets [5]

Most MLCCs are produced by a co-firing process where the internal electrodes and the ceramic materials are heated simultaneously. In such a process, the material integrity of the metallic and ceramic substances must be maintained which means choosing materials that do not substantially interact. Early MLCC conductive plates were made from precious metal electrode (PME) materials.

Previous work [6] introduced the CPS (conceptual product space) reliability model (Figure 6) as a practical visual representation of how the driving forces of technology, cost, and performance have merged to affect product reliability. These first MLCC parts, which had PME material sets, were suitable for harsh environment and long product lifetime applications. As the revenue center of gravity (RCG) shifted to consumer electronics and the PME materials, particularly palladium, became more expensive, demand rose for base metal electrode (BME) configurations.

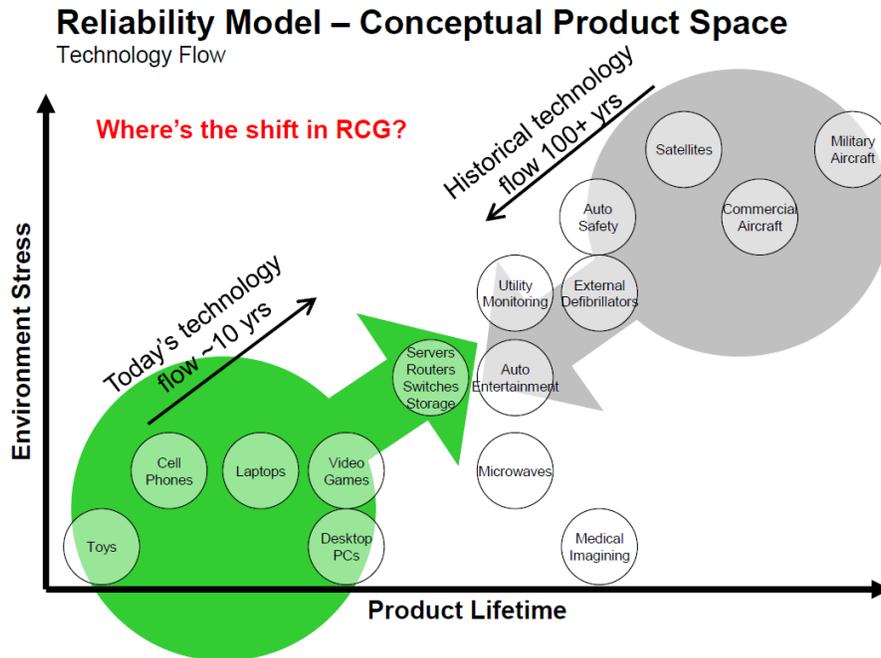


Figure 6 – Conceptual Product Space Reliability Model [6]

The production process for MLCCs typically begins with casting the dielectric from a ceramic slurry; the inner electrode materials are then printed onto the dielectric, which is stacked, laminated, cut into shape, the placed in an oven for binder burn out and sintering.

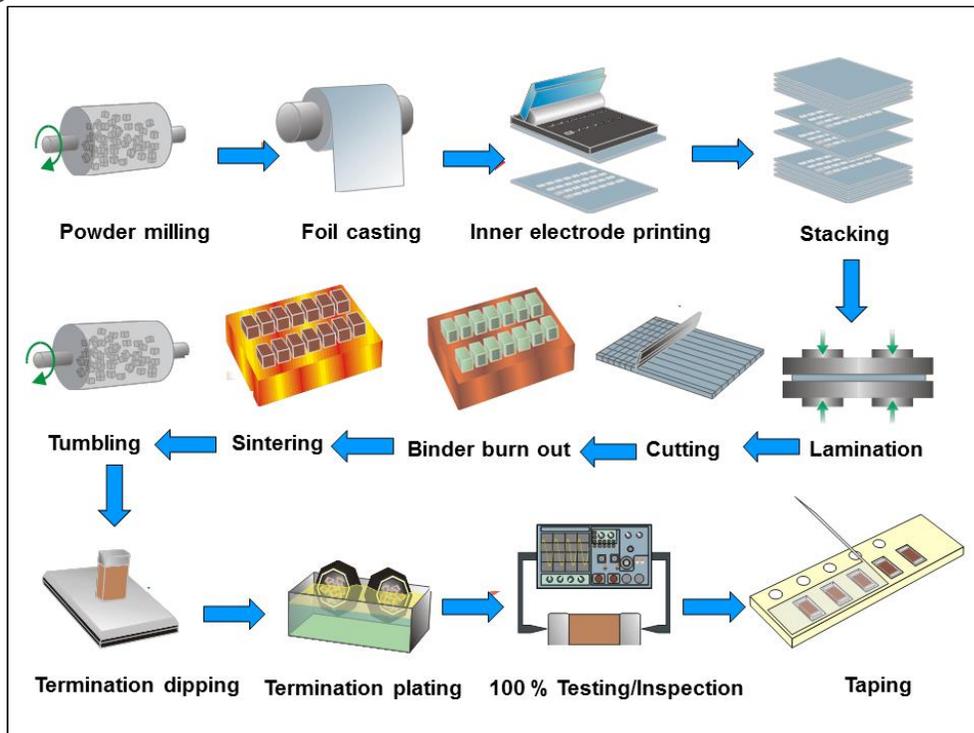


Figure 7 – Simplified MLCC Manufacturing Process [7]

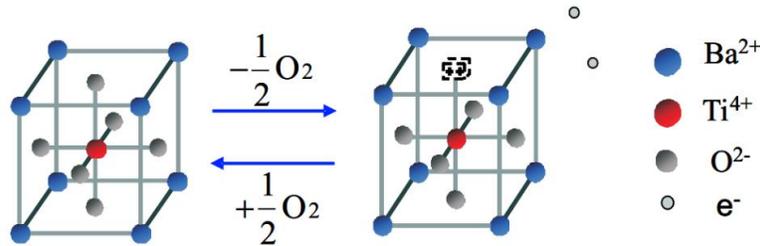
With the move from PME to BME configurations, new binder burn out and sintering processes were required. Whereas the PME parts required temperatures  $\sim 1100^{\circ}\text{C}$ , BME parts required temperatures  $\sim 1300^{\circ}\text{C}$ . The nickel in the BME electrodes readily oxidized during firing. This required changing the sintering atmosphere, see Table 1, in the processing kilns from the previous standard nitrogen/oxygen to a controlled chemically reducing atmosphere [8].

**Table 1 – Kiln Environment MLCC Manufacturing**

Operation	PME Atmosphere & Heating	BME Atmosphere & Heating
Sintering	Air at $1150^{\circ}\text{C}$	Nitrogen and hydrogen with $\text{PO}_2 < 10^{-8}$ atmosphere, $1350^{\circ}\text{C}$
Re-oxidation	Not required	Nitrogen and hydrogen with $\text{PO}_2 10^{-8}$ to $10^{-4}$ atmosphere, $1000^{\circ}\text{C}$

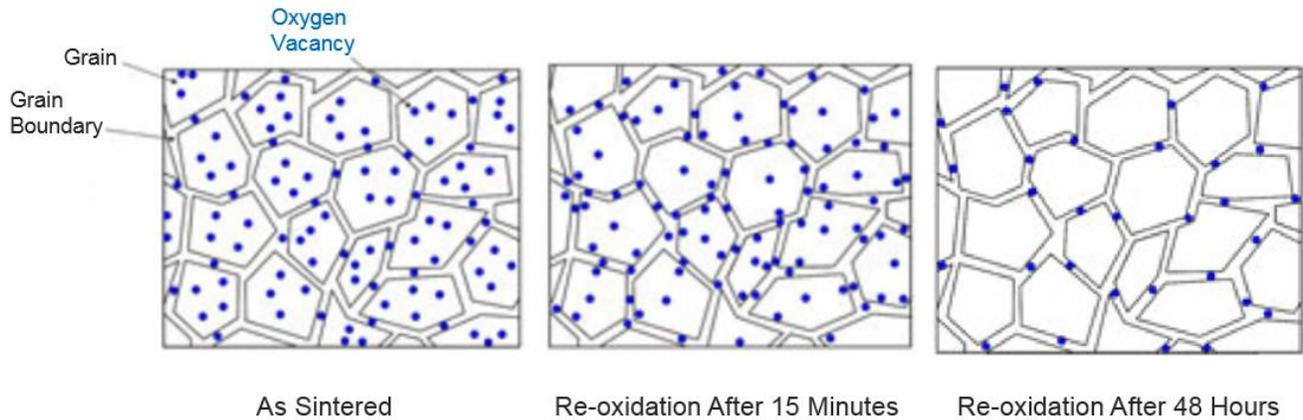
**Oxygen Vacancies: Migrations and Effects**

The chemically reducing kiln atmosphere doesn't just remove the oxygen from the BME structure; it also removed some of the oxygen from the  $\text{BaTiO}_3$  dielectric leaving oxygen vacancies behind. These oxygen vacancies not only disrupt the dielectric properties of the ceramic, but also induce a PN junction behavior and create asymmetrical insulation resistance.



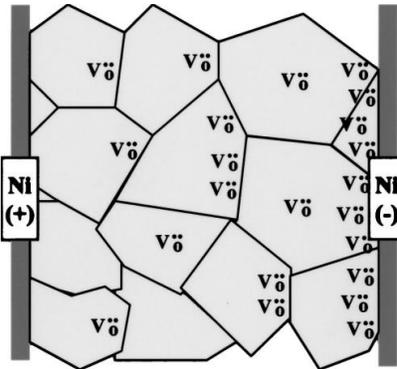
**Figure 8 – Creation of Oxygen Vacancies in  $\text{BaTiO}_3$  Unit Cell Structure [4]**

The re-oxidation operation noted in Table 1 is not 100% effective in returning the missing oxygen to the  $\text{BaTiO}_3$  dielectric and even after its successful completion, oxygen vacancies remain.



**Figure 9 – Effect of Re-oxidation Time on Oxygen Vacancy Distribution [9]**

Under the influence of time and voltage, those remaining oxygen vacancies migrate and preferentially collect at the interfaces of the inner electrodes and dielectrics.



**Figure 10 – Schematic Representation of Oxygen Vacancies ( $V_o$ ) Collecting at Ni- Electrode [10]**

### Industry Concerns

At the 2010 Capacitor and Resistor Technology Symposium (CARTS) industry concerns were raised about the effect of oxygen vacancy migration exacerbated by higher capacitance MLCCs appearing in smaller and smaller packages.

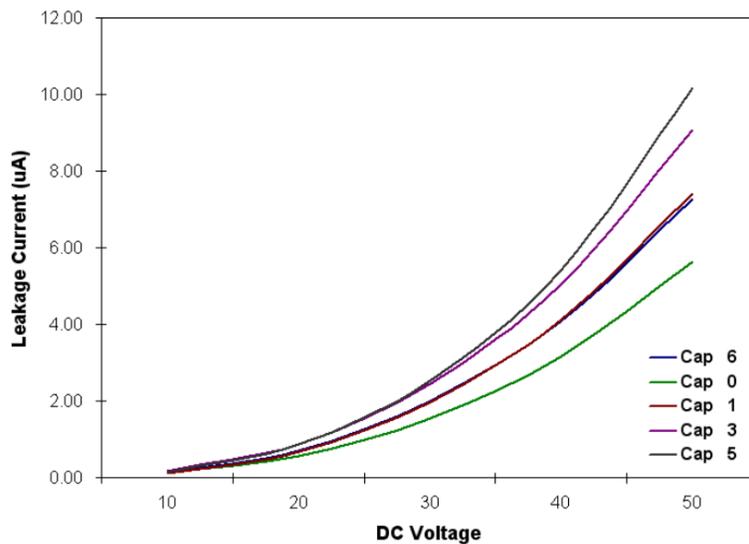
“Up until recently, failure due to dielectric wear out was not a concern for the capacitors used to support CPUs. Our reliability models showed that the capacitors could be used for thousands of years before the insulation resistance would begin to degrade. In the last five years, we have noticed a disturbing trend, as the capacitance density has increased; the usable life has reduced to hundreds, then tens of years and now even less than five years.

Going forward, we see reduced reliability margins impacting capacitor supplier roadmaps and posing an increased risk for applications using decoupling MLCCs. Many users don’t truly understand the risk they are taking because the industry standard Life Test is inadequate for describing the expected reliability of MLCCs.” [11]

This was followed by similar concerns. [12] [13]

### Failure Confirmation of Production MLCCs

Recent test and field failures of MLCCs have confirmed those concerns. All these failures have been loss of insulation resistance (IR) also described as DC leakage.



**Figure 11 – Confirmation of Oxygen Vacancy Migration Failure**

Field failures have been confirmed for MLCC applications where DC leakage fell substantially below the manufacturer’s datasheet specification in 14 months, far below the 5 to 8 years projected in [11]. One conclusion in that 2010 CARTS paper was, “given the complexity of today’s electronic devices and the reduced reliability margins of high CV capacitors, designers must pay special attention to reliability requirements of their system and the long term reliability of the capacitors . . .” To mitigate rising MLCC failure rates, that was advice worth heeding in 2010 and remains valid today.

## References

- [1] C. Randall, et. al., "History of the First Ferroelectric Oxide, BaTiO<sub>3</sub>," Materials Research Institute, Penn State, 2004
- [2] <http://www.materialsdesign.com/appnote/ferroelectric-properties-batio3>
- [3] M.Vijatović et al., "History and Challenges of Barium Titanate: Part I," Science of Sintering, 40 (2008) pp 155-165
- [4] Y. Xiao, "The influence of oxygen vacancies on domain patterns in ferroelectric perovskites," Diss. California Institute of Technology, 2005.
- [5] M. Pan, et. al., "A Brief Introduction to Ceramic Capacitors," IEEE Electrical Insulation, 26.3 (2010) pp 44-50
- [6] D. Brown, "The Astute Use of Commercial Off the Shelf Components," 2014 Medical Device Symposium, iNEMI/MEPTEC/SMTA.
- [7] <https://commons.wikimedia.org/wiki/File:MLCC-Manufacturing-Process.png>
- [8] D. Donahoe, "Moisture in Multilayer Ceramic Capacitors," Diss. umd.edu, 2005
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- [10] G. Yang, et. al., "Oxygen nonstoichiometry and dielectric evolution of BaTiO<sub>3</sub>. Part II—insulation resistance degradation under applied dc bias," Journal of Applied Physics, 96.12 (2004) pp 7500-7508
- [11] C. Hendricks, et. al., "*Reliability Challenges for CPU Decoupling MLCC,*" Proc. CARTS 2010, pp 279-288
- [12] D. Liu, et. al., "Some Aspects of the Failure Mechanisms in BaTiO<sub>3</sub>-Based Multilayer Ceramic Capacitors," Proc. CARTS 2012, pp 59-71
- [13] Y. Min, et. al., "*Embedded Capacitors in the Next Generation Processor,*" IEEE 63<sup>rd</sup> ECTC 2013, pp 1225-1229

# Multilayer Ceramic Capacitors: Mitigating Rising Failure Rates

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## A Little Cowboy Wisdom

- It ain't what we don't know that gets us into trouble.
- It's what we know that ain't so!
- Example: if it tests good, it is good



**Will Rogers**

**American Humorist**

# Systems of Materials, Processes, and Components

## **Historical Era (Pre-RoHS) – Highly Evolved**

- Gradual Change – 100 years of continuous improvement
- Circuit Geometries – large and stable, rule based design
- Selection Criteria – cost and reliability
- Solution Convergence – consumer, military, telecom & medical

## **Current Era (Post-RoHS) – Highly Suspect**

- Abrupt Change – 10 years of surprises
- Circuit Geometries – smaller and smaller, tool based design
- Selection Criteria – environment ♣ . . . \$ . . . . . reliability
- Solution Divergence – each market developing separately

## **A Little Professional Wisdom**

- **Essentially all models are wrong**
- **However, some are useful !**



**George Box**  
**Design of Experiments**

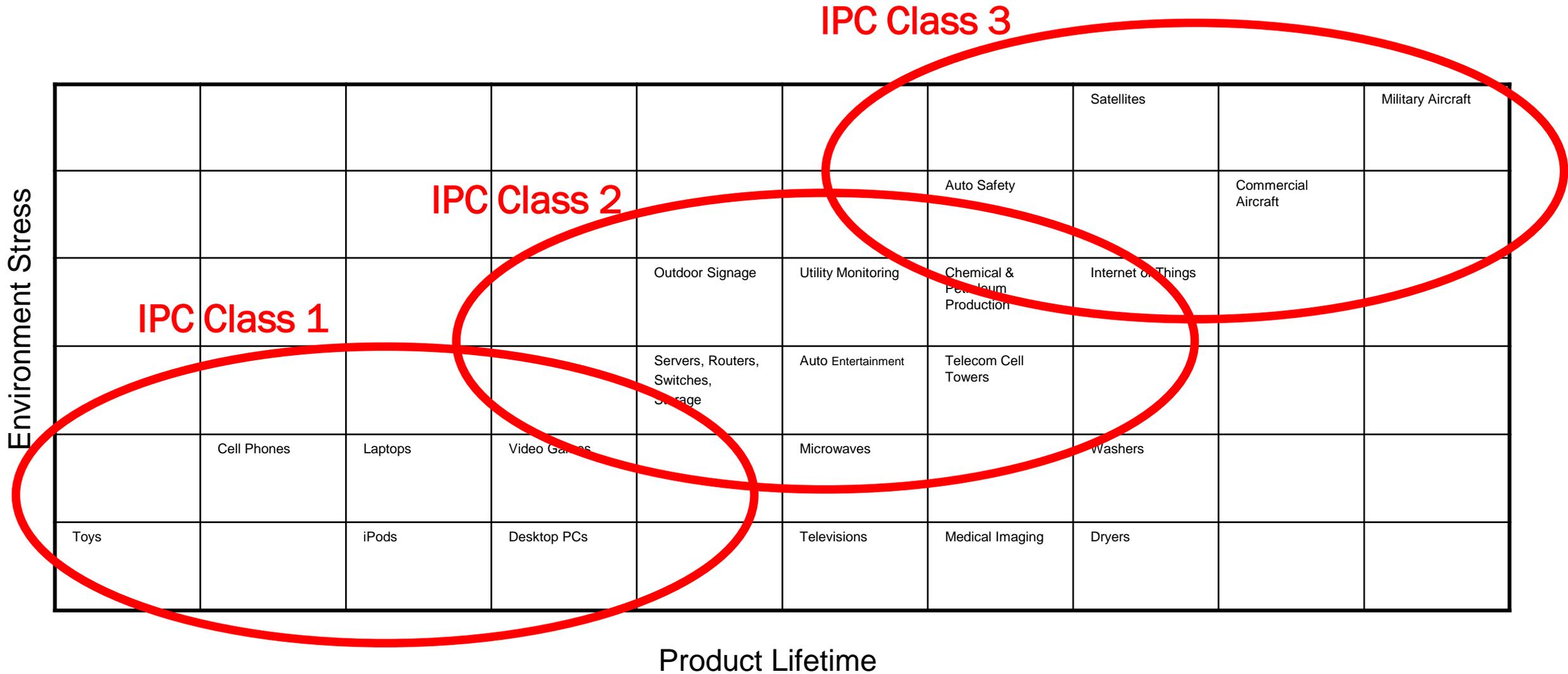
# Conceptual Product Space Model

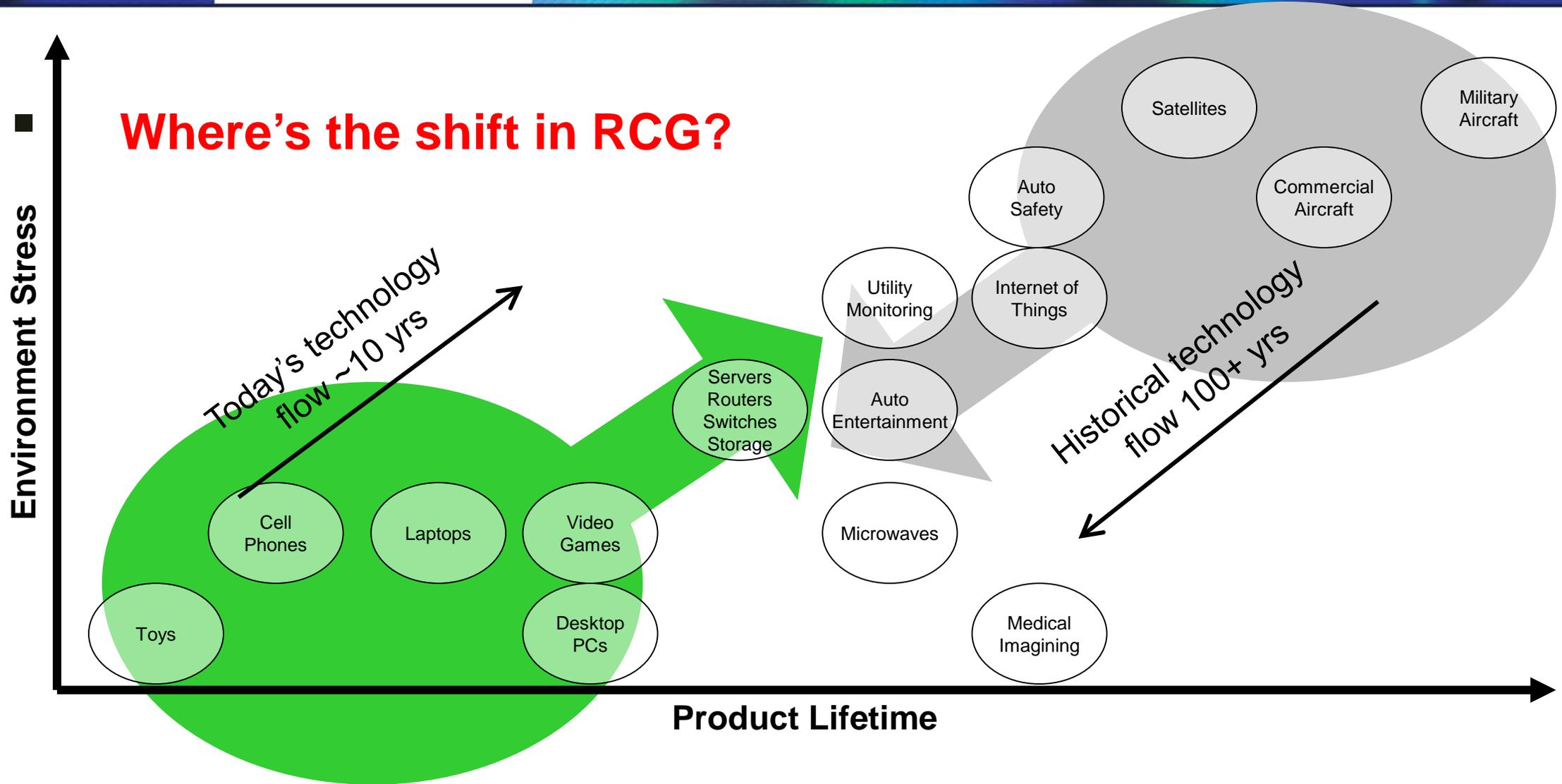
Product Use Conditions & Life Expectations

Environment Stress

							Satellites		Military Aircraft
						Auto Safety		Commercial Aircraft	
				Outdoor Signage	Utility Monitoring	Chemical & Petroleum Production	Internet of Things		
				Servers, Routers, Switches, Storage	Auto Entertainment	Telecom Cell Towers			
	Cell Phones	Laptops	Video Games		Microwaves		Washers		
Toys		iPods	Desktop PCs		Televisions	Medical Imaging	Dryers		

Product Lifetime



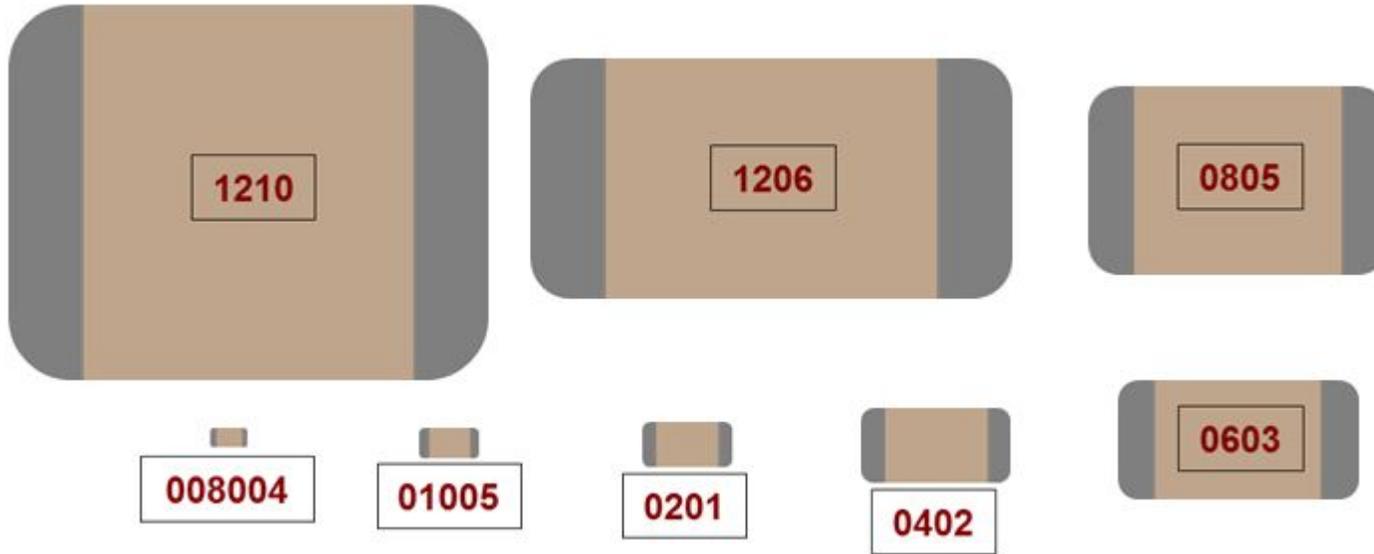


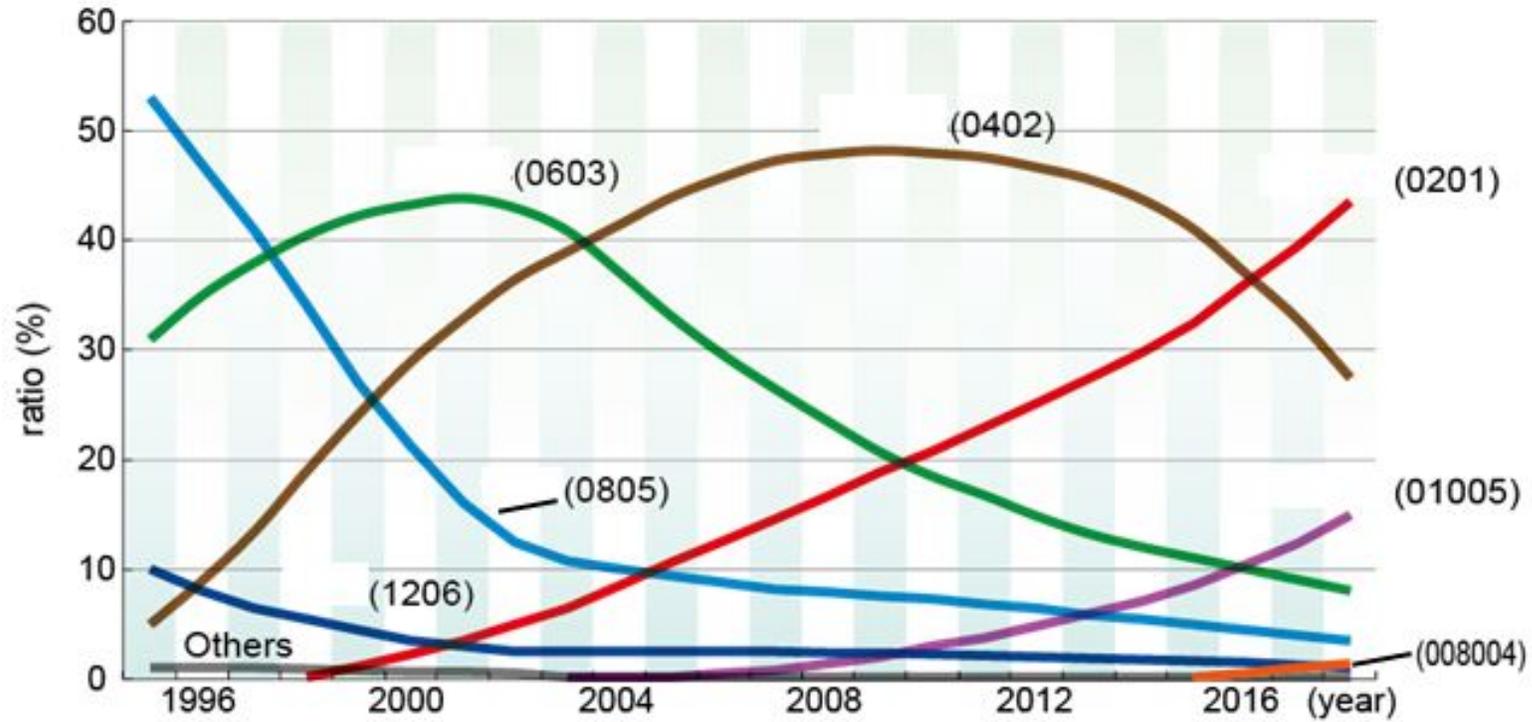
# Multilayer Ceramic Capacitors

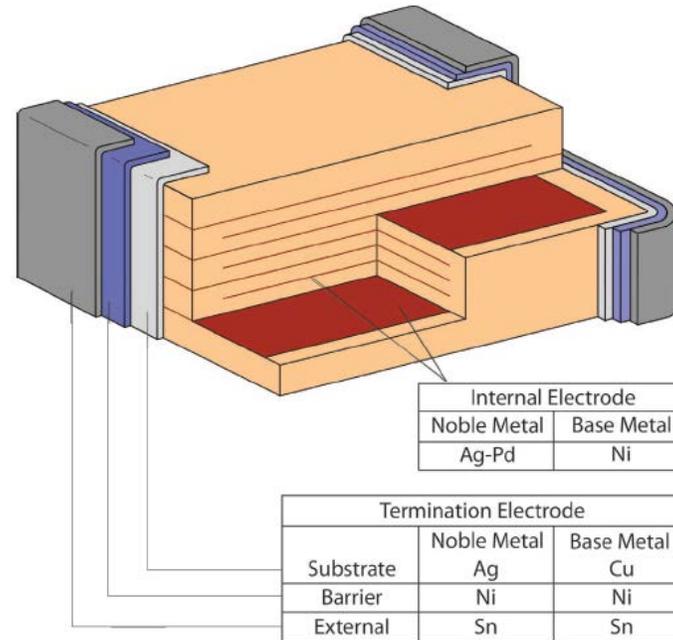
MLCCs: the basics



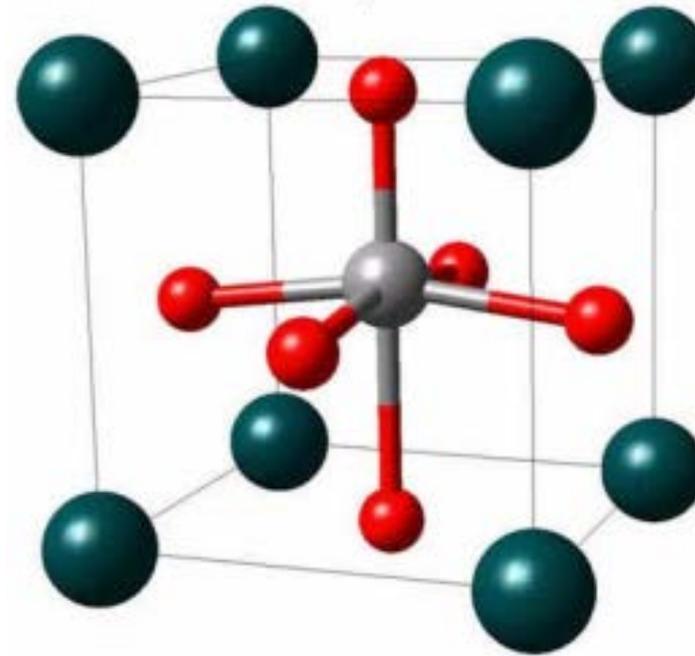
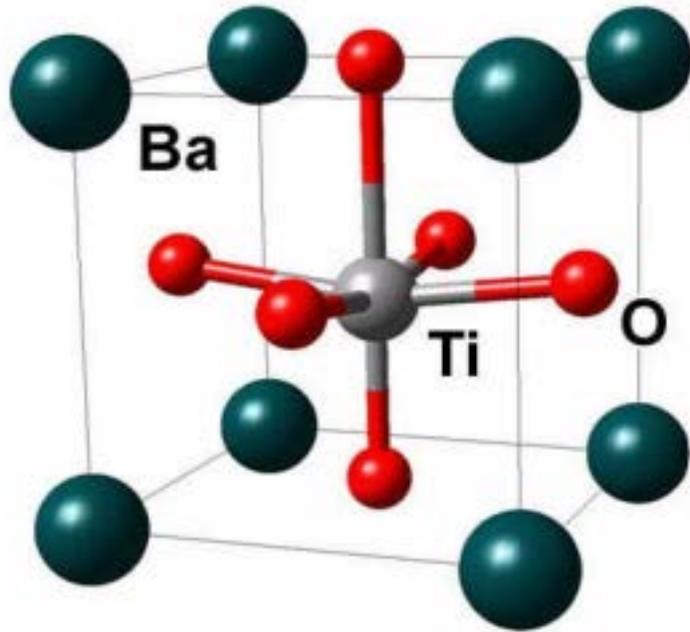
They look so simple, what could go wrong?



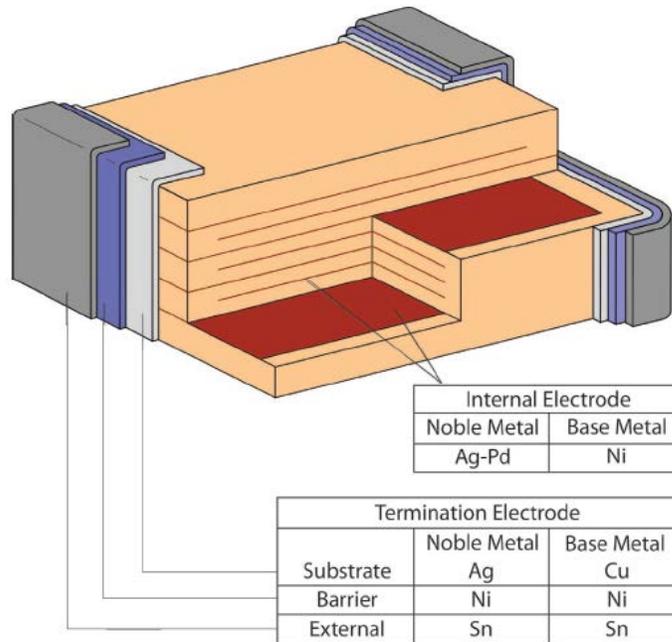




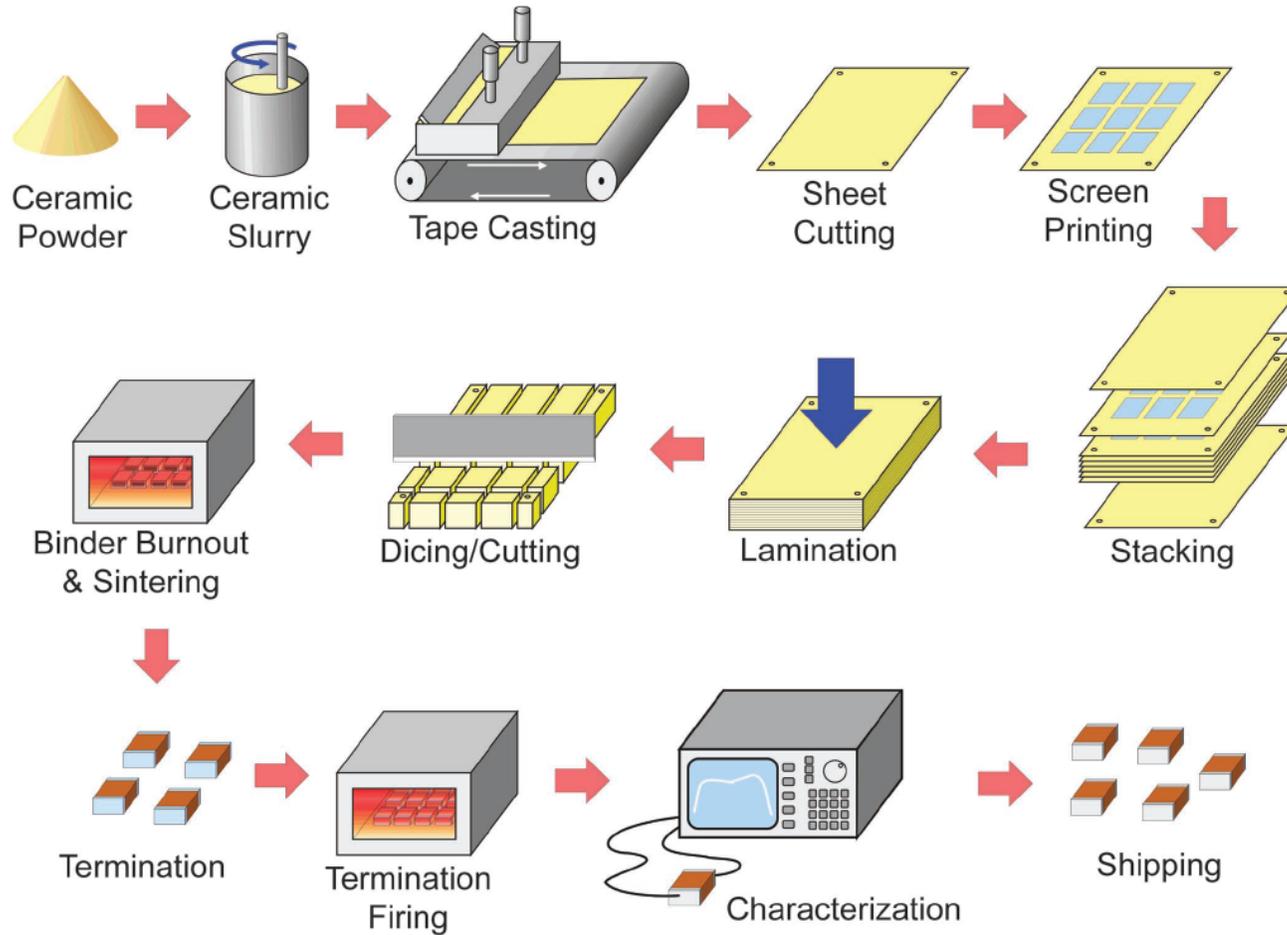
Orange Material – common class II ceramic dielectric:  $\text{BaTiO}_3$

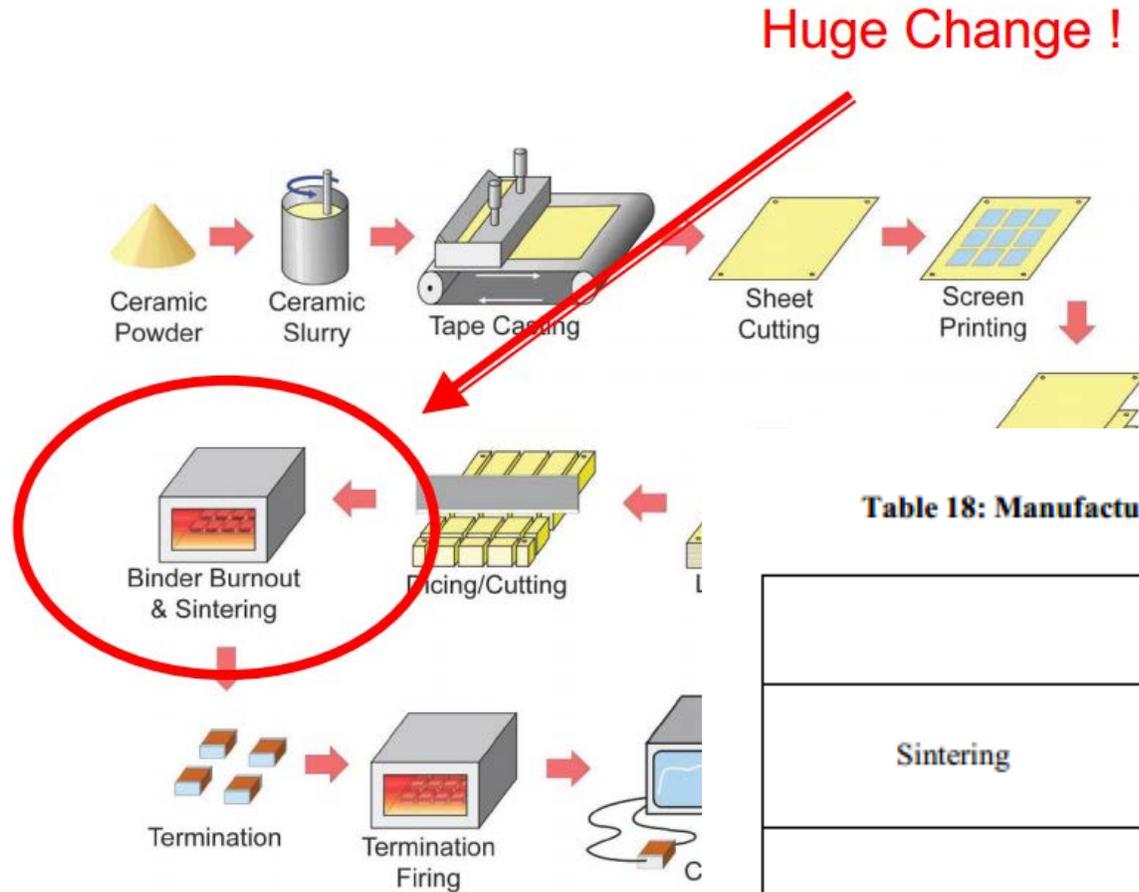


BaTiO<sub>3</sub> – how it works



- Historical Era Material
  - Noble metal electrodes
  - Ag-Pd
- Current Era Material
  - Base metal electrodes (BME)
  - Ni
- We might ask ourselves,  
“Why use precious metals?”





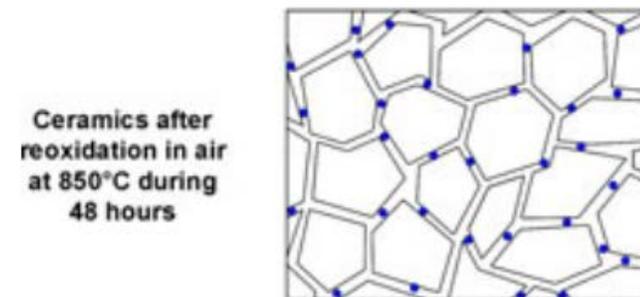
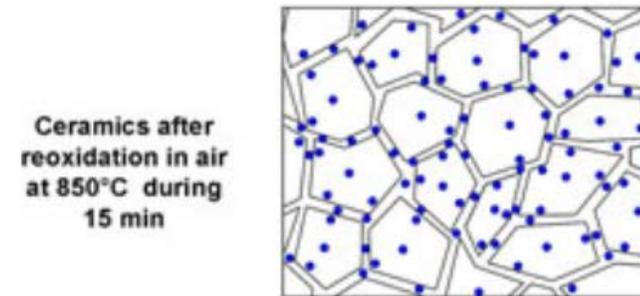
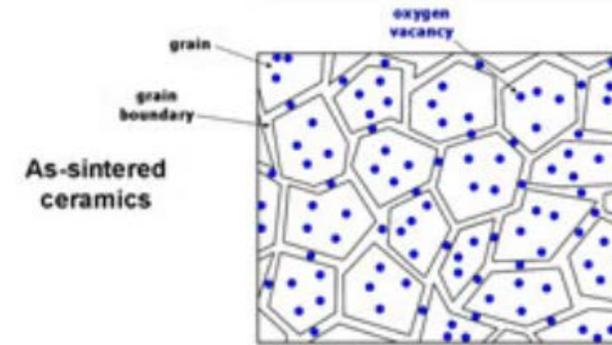
**Table 18: Manufacturing Changes from PME to BME that Introduce Oxygen Vacancies**

	Low Palladium Content PME Heating Atmosphere [16] [76] [80]	BME Heating Atmosphere [63]
Sintering	Air at approximately 1150 °C for silver-palladium with less than 35 atomic percent palladium	Humidified nitrogen and hydrogen with partial pressure of oxygen less than $10^{-8}$ atmospheres, 1350 °C
Re-oxidation	Step not required	Humidified nitrogen and hydrogen with partial pressure of oxygen between $10^{-7}$ and $10^{-4}$ atmospheres, 1000 °C

# MLCCs and Oxygen

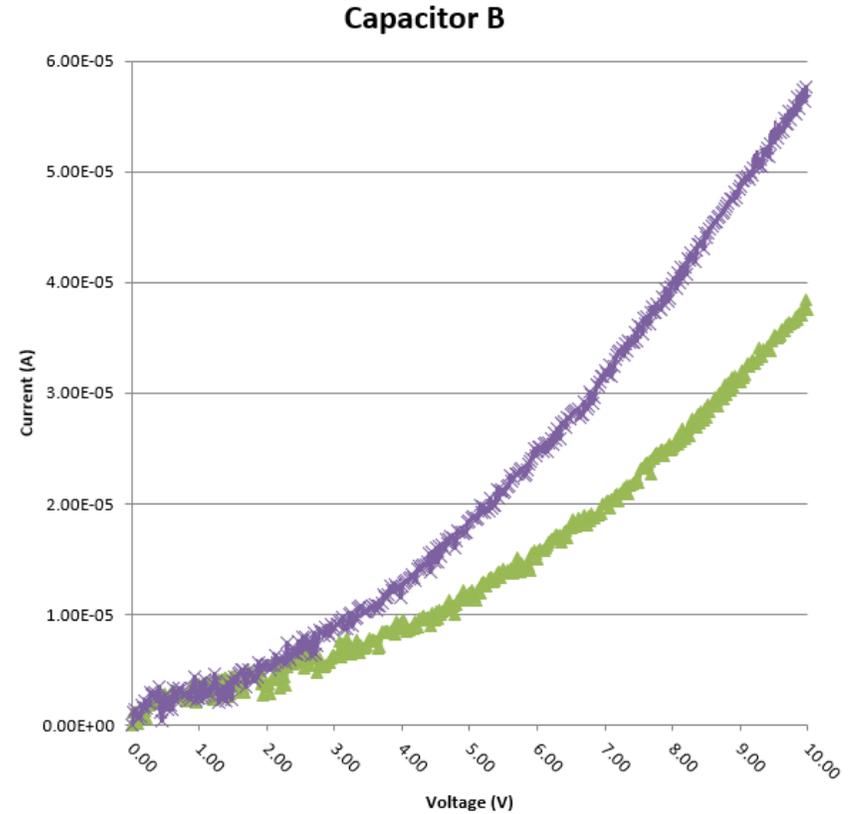
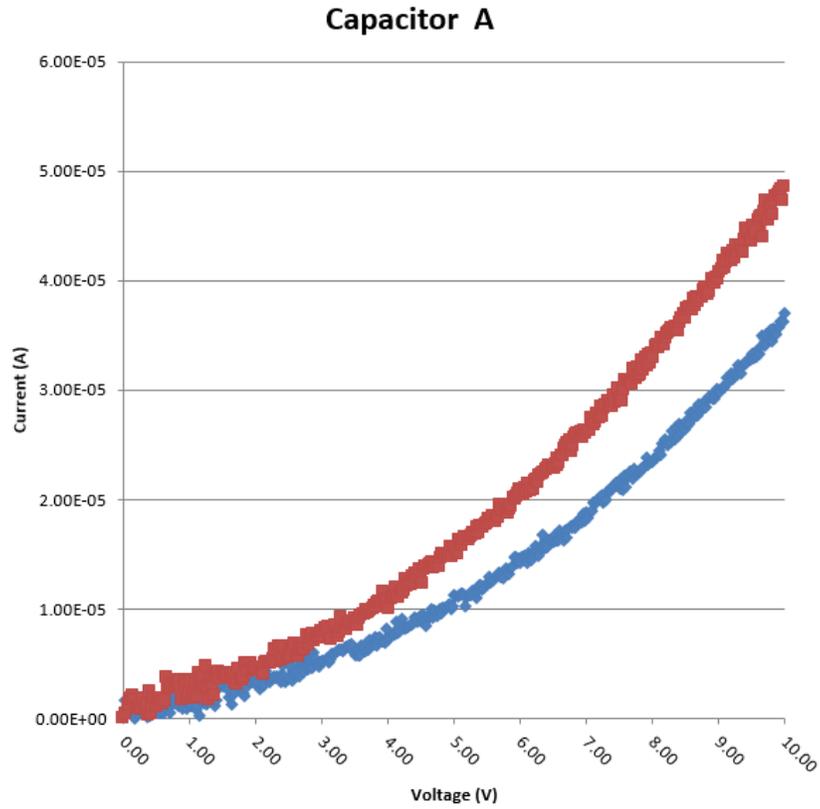
- **MLCC Electrode (capacitor plate) Configurations**
  - *Precious Metal Electrode (PME) silver/palladium (Ag/Pd)*
  - *Base Metal Electrode (BME) nickel (Ni) – most common*
  
- **During ceramic firing, Ni cannot be allowed to oxidize**
  - *Firing oven is chemically reducing atmosphere to remove and exclude O<sub>2</sub> from Ni electrode structures*
  - *Ceramic contains oxygen: barium titanate – BaTiO<sub>3</sub>*
  - *Reducing atmosphere removes some of the O from BaTiO<sub>3</sub> resulting in oxygen vacancies in the ceramic*
  - *That missing oxygen is replaced by a re-oxidation process*
  - *Re-oxidation is not 100% perfect leaving some remaining oxygen vacancies*

- Fired in chemically reducing atmosphere
  
- Re-oxidation started
  
- Re-oxidation completed



# Oxygen Vacancy Migration

- Those remaining oxygen vacancies can move; rate is influenced by:
  - *Temperature*
  - *DC voltage field*
- That movement is called electro-migration; its effects are:
  - *Reduces the MLCC insulation resistance*
  - *Causes a PN junction-like effect*
- Dopants – retard or pin vacancy migration
- That PN junction-like effect means when the insulation resistance (IR) is measured, the IR measurement will change when the polarity of the instrument is reversed



**Oxygen Vacancy Migration – Electrical Effects**

# Previously Reported Work

- Many users don't truly understand the risks they are taking because the industry standard life test is inadequate for describing the expected reliability of MLCCs
- MLCCs placed under a DC bias eventually fail due to insulation resistance degradation
- Significant variation in useful life can exist between suppliers

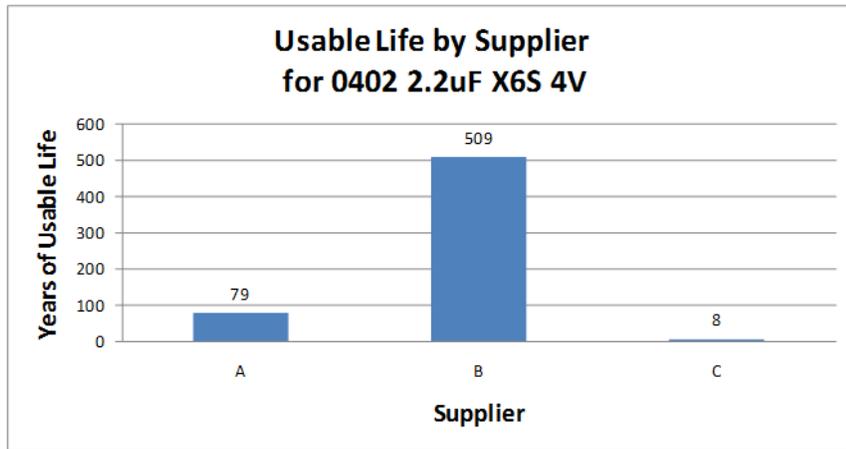


Figure 4  
Predicted life times of capacitors, manufactured at different companies.

- Supplier 'A' – 79 years
- Supplier 'B' – 509 years
- Supplier 'C' – 8 years

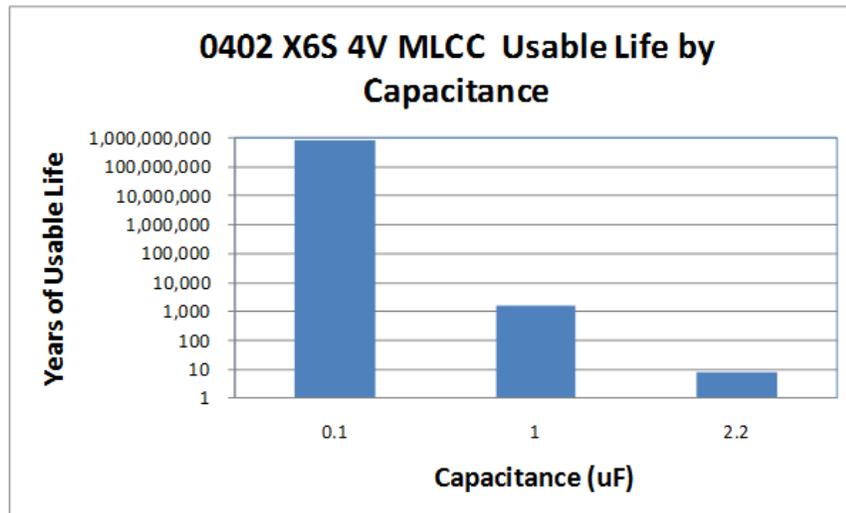


Figure 5  
As Capacitance Density Increases Usable life decreases.

- 0.1  $\mu$ F ~ 1,000,000,000 years
- 1.0  $\mu$ F ~ 1,000 years
- 2.2  $\mu$ F ~ 10 years

- **Summary and Conclusions**

- *Products passed final acceptance test*
- *Failed in the field due to oxygen vacancy migration*
- *Some MLCC datasheets don't even specify IR or leakage!*
- *Conduct MLCC design and review activities with oxygen vacancy migration in mind*
- **KNOW YOUR MLCC SUPPLIERS !!**

# Questions ?

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