多层片式陶瓷电容器（MLCC）

技 术 交 流

如何理解电容器的容量老化

How To Understand Aging

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如何理解电容器的容量老化

铁电体陶瓷电容器的容量和介质损耗会展现出随时间延长而衰减的趋势。这种被称为老化的现象是可逆的，其产生的原因在于铁电体晶体结构随温度而变化。

铁电介质以钛酸钡（$BaTiO_3$）为主要成分，加入一定的氧化物以改变材料晶体惯态和对称性，产生出铁电畴。在居里点（120℃）附近，$BaTiO_3$晶体结构由四方相转变为立方相，自发极化不再发生。而当冷却通过居里点时，材料晶体结构又重新由立方相转变为四方相，其点阵结构中不存在对称中心。Ti^{4+}离子可以占据两个非对称位置中的一个，从而导致永久性电偶极。由于相邻晶胞相互作用的影响足以建立起极化畴，因此这些电偶极是自发产生和略微有序的。平行极化畴是随机取向的（在没有外加电场作用的情况下），给系统提供应变能。而应变能的松弛正是材料介电常数老化的原因，具有下列时间关系：

$$K = K_0 - m \log t$$

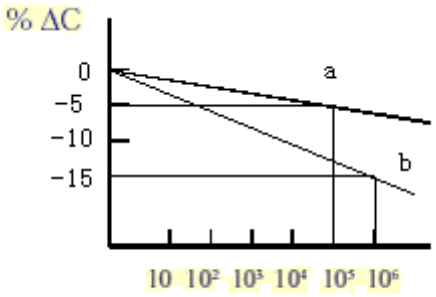
这里 K = 任意时间 t 处的介电常数

K_0 = 时间t_0（$t_0 < t$）处的介电常数

m = 衰减速率

上面公式是对数关系，如果采用半对数图处理所得数据，其结果将会近似于一条直线，正如下图所示。每十倍时内 K（或电容量）变化的百分数可以通过计算得出，用做衡量瓷料优劣的一个指标。

与微观结构有关，进而对极化产生影响的的因素（材料纯度、晶粒尺寸、烧结情况、晶界、空隙率，内应力）同样也决定了畴壁移动和重新取向的自由程度。



铁电体的老化

例 (a) 老化速率 = -5% / 5 十倍时 = 1.0% / 十倍时（小时）

例 (b) 老化速率 = -15% / 6 十倍时 = 2.5% / 十倍时（小时）

由此可知，材料老化的速率与材料组分和工艺过程密切相关，同时对那些影响材料介电常

数的因素也非常敏感。

铁电体容量的时间损耗是不可避免的，尽管通过把介质加热到居里点以上，使材料晶体结构变回“顺电”立方态的方法可以得到恢复。但一旦冷却下来，材料晶体结构再次转变为四方相，自发极化再次出现，产生的新极化畴使得老化过程重新开始。

顺电体，例如 NPO，中由于不存在自发极化的机制，因此观察不到老化现象。老化速率受电容器“电压状态”的影响。元件在高温（低于居里温度）直流偏压负荷试验中表现出了容量损耗，但老化速率很低。从理论上讲，高温下的电压负荷会促进极化畴的的弛豫。当然，如果实际温度超过了居里点，电压效应则会消失。

How To Understand Aging

Ceramic capacitors made with ferroelectric formulations display a decay of capacitance and dielectric loss with time. This phenomenon, called aging, is reversible and occurs due to the crystallographic changes of ferroelectrics with temperature.

The ferroelectric group of dielectrics is based on barium titanate (BaTiO3) as the main constituent, an oxide which undergoes changes in crystal habit or symmetry that give rise to ferroelectric domains. At the Curie Temperature of 120°C, BaTiO3 transforms from a tetragonal to a cubic crystal habit, and spontaneous polarization no longer occurs. On cooling through and below the Curie point, the material again transforms from a cubic to a tetragonal crystal configuration in which the lattice has no center of symmetry and the Ti4+ cation can occupy one of two asymmetrical sites, giving rise to a permanent electric dipole. These dipoles form spontaneously and are somewhat ordered, as adjacent unit cells influence one another sufficiently to interact and create domains of similar polarity. The domains of parallel electrical polarity are random in orientation (without the influence of an electric field) and impart a certain strain energy to the system. The relaxation of this strain energy is attributed to be the mechanism of aging of the dielectric constant, and is found to have the following relationship with time:

$K = Ko - m \log t$

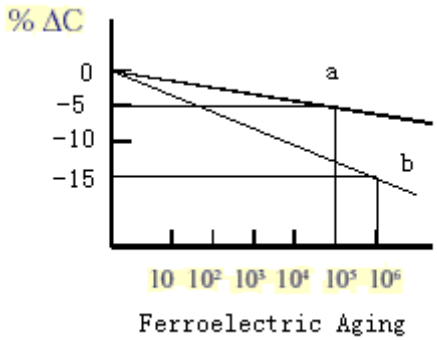
where K = dielectric constant at any time t

Ko = dielectric constant at time t,(to<t)

m = rate of decay

The above relationship is logarithmic, and data will approximate a straight line when

plotted on semi log paper as illustrated in below Figure. The percent change of K (or capacitance) per decade can be calculated and used as a figure of merit for dielectric formulations. The microstructure details which affect polarization (material purity, grain size, sintering, grain boundaries, porosity, internal stresses) also determine freedom of domain wall movement and reorientation, and it is found that the aging rate is composition and process dependent and is sensitive to variables which also influence the dielectric constant of the material.



Ferroelectric Aging

Example (a) Aging Rate = -5% / 5 decades = 1.0%/decade hr.

Example (b) Aging Rate = -15% / 6 decades = 2.5%/decade hr.

The loss of capacitance with time is unavoidable with ferroelectric formulations, although it can be reversed by heating the dielectric above the Curie Point and reverting the material back to a “Para electric” cubic state. On cooling, however, spontaneous polarization will again occur as the material transforms to the tetragonal crystal habit, and new domains recommence the aging process.

As is expected, no aging is observed only in paraelectric formulations, such as NPO, which do not possess the mechanism of spontaneous polarization. The rate at which aging may occur can be influenced by “voltage conditioning” of capacitors. It is found that units stressed by a dc voltage at elevated temperature (below the Curie Point) will experience a loss of capacitance, but with a consequently lower aging rate. It is theorized that the voltage stress at the elevated temperature accelerates the domain relaxation process. This voltage conditioning effect is, of course, eliminated if the. unit ever experiences temperatures exceeding the Curie Point.

Capacitor manufacturers compensate for capacitance loss of ferroelectric dielectrics by adjustment of the testing limits, such that units do not age out of tolerance over a long time

period. For example, for a dielectric with a 1.5%/decade aging rate, the testing limits are raised 3%, i.e. two decades of time. Units tested 100 hours after last exposure to the Curie Temperature therefore will remain within tolerance for another two decades or 10,000 hours.