Mechanism of aging characteristics in capacitors

The capacitance of a high dielectric constant type ceramic capacitor (its typical main material is $BaTiO_3$ with temperature characteristics of X5R, X7R, Y5V, etc) tends to decrease with the passage of time. This characteristic is called capacitance aging. Capacitance aging is a unique phenomenon of ferroelectric ceramics having spontaneous polarization. When a ceramic capacitor is heated above the Curie point (the temperature where crystalline structure changes and spontaneous polarization disappears (approximately 150 °C)) and left without load until it cools below the Curie point. It becomes more difficult for spontaneous polarization to reverse with the passage of time, which, as a result, is measured as the decreased capacitance with time.

This phenomenon is observed not only in Murata products but in high dielectric constant type ($BaTiO_3$) ceramic capacitors in general. An appendix is attached with some public standards regarding capacitance aging (Monolithic ceramic capacitor: IEC384-10 Appendix B, etc.). When a ceramic capacitor with decreased capacitance due to aging is re-heated above Curie point and allowed to cool, the capacitance recovers. This is called de-aging and after de-aging the normal aging process starts again.

<Spontaneous polarization and ferroelectricity of $BaTiO_3$ type ceramics>

As seen in Figure 1, $BaTiO_3$ type ceramics possesses perovskite type crystalline structure. It is cubic at temperature over Curie point, and Ba is in peak, O is in face center and Ti is in body center.

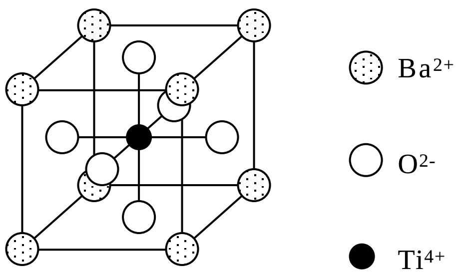


Figure 1　Crystalline structure of $BaTiO_3$ type ceramics

When within the normal temperature range below Curie point, one of the axes (C axis) stretches about 1% and other axes shrink slightly to become tetragonal (Figure 2 on the next page). In this case, the Ti^{4+} ion will occupy the position near the O^{2-} ion being displaced by 0.12Å from the body center, in the direction of stretched axis. This displaces the center of gravity for negative and positive electric charges, causing polarization. Polarization is caused by asymmetry of the crystalline structure, which exists from the outset without applying an external electric field or pressure. This type of polarization is called spontaneous polarization.

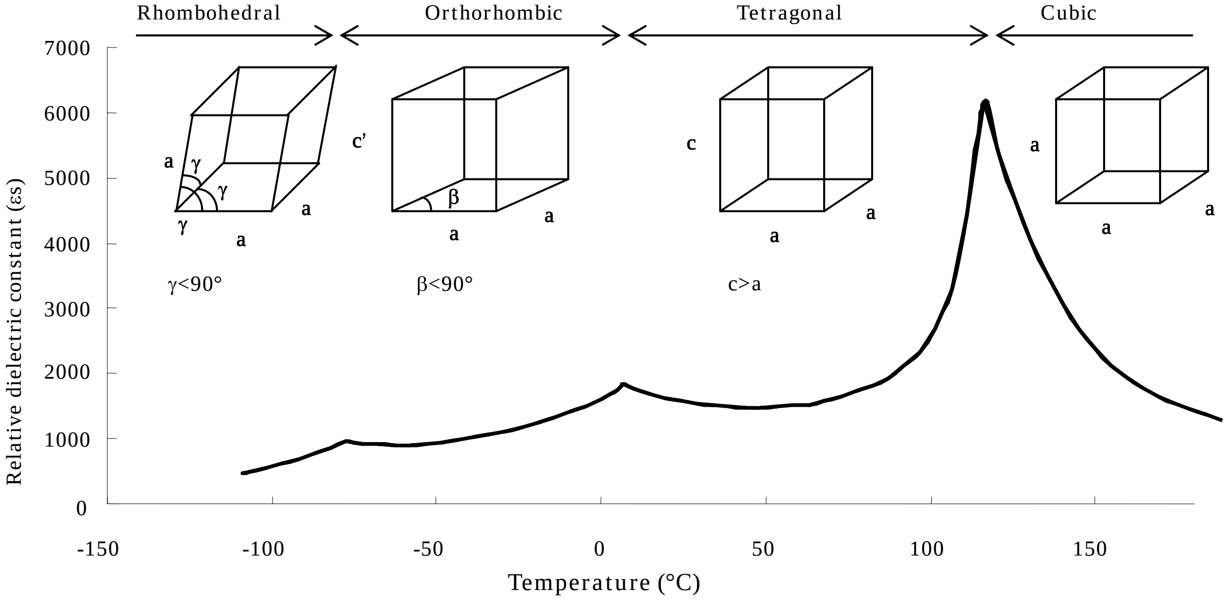


Figure 2　Change in crystalline structure and relative dielectric constant on temperature (pure $BaTiO_3$)

The direction of spontaneous polarization (position of Ti^{4+} ions) for $BaTiO_3$ type ceramics can be easily reversed with application of external electric field. The characteristics of having spontaneous polarization, and ability to reverse the direction of polarization with external electric field are specifically called ferroelectricity.

<Mechanism of aging>

$BaTiO_3$ ceramics are an aggregation of polycrystalline having sub-μm diameter as shown in Figure 3. These crystalline are called grains, and their structures are neatly aligned as shown in Figures 1 and 2. Those grains are divided into many domains at temperatures below the Curie point. Within each domain, the direction of crystal axis is the same, therefore the direction of spontaneous polarization is the same as well.

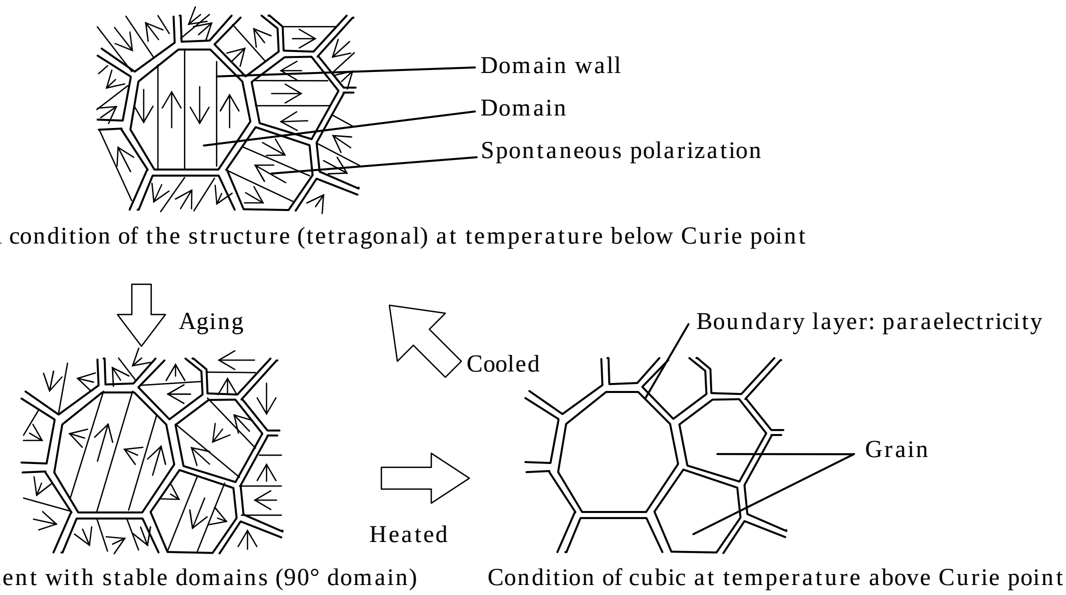


Figure 3　Micro structure of $BaTiO_3$ type ceramics

When $BaTiO_3$ type ceramics is heated above the Curie point, the crystalline structure goes through a phase transition from tetragonal to cubic. With this, spontaneous polarization the domains also disappear. When cooled below the Curie point, phase transition from cubic to tetragonal takes place near Curie point, and the C axis stretches by about 1% in the axial direction. The other axes shrink slightly to form spontaneous polarization and domains. Simultaneously, grains receive stress from the distortion of its surroundings.

At this point, several small domains in grains are generated, and spontaneous polarization of each domain can be easily reversed with a low electric field. Since relative dielectric constant corresponds with the reversal of spontaneous polarization per unit volume, it is measured as higher capacitance. When the capacitor is left without load at the temperature below the Curie point, domains that faced random directions gradually realign themselves with the passage of time to become a larger and stable shape in terms of energy (Figure 3. 90° domain), releasing the stress caused by crystal distortion. In addition, space charge of the boundary layer (slow moving ions and lattice vacancies) migrates, causing space charge polarization. Space charge polarization prevents spontaneous polarization from becoming reversed.

In other words, as time passes after spontaneous polarization occurs, it is realigned to a more stable condition, while space charge polarization occurs in the boundary layer preventing reversal of spontaneous polarization. In this state, we need a higher electric field to reverse spontaneous polarization of domains. This means fewer domains reverse under low electric field and capacitance decreases. This is considered to be the mechanism for aging.

The Micro structure of crystals will return to the initial state when heated to temperature above Curie point, and when cooled, the aging process starts again.

<Aging characteristics of Murata products>

Generally, the capacitance of high dielectric constant type monolithic ceramic capacitors decreases practically linearly on the logarithmic time graph with the value at 24 hours after the heat treatment over 125 °C as the standard. Please refer to the appendix indicating typical examples of aging characteristics in the capacitance of Murata products. Capacitance decreases from aging will recover by being heated during the soldering process, etc.

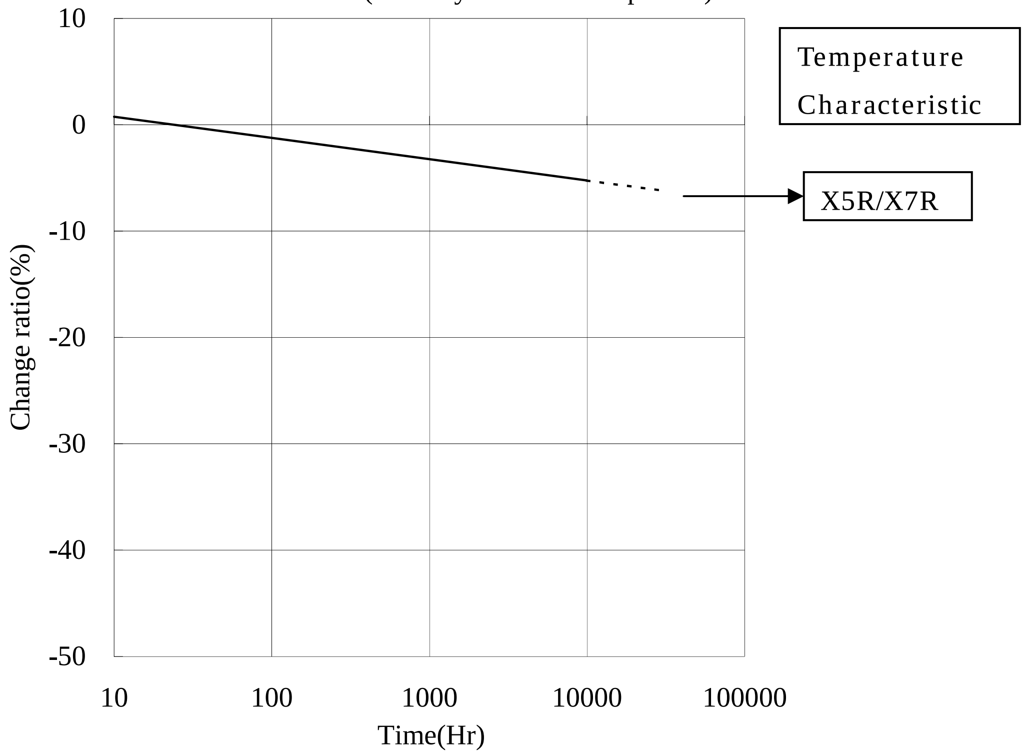
The capacitance of a ceramic capacitor is expected to maintain a value within spec when built onto the circuit. We have determined the capacitance range based on the reasons above. No aging phenomenon is observed with temperature compensating type capacitors.

<Handling care>

Aging phenomenon is a basic characteristic of high dielectric constant type ($BaTiO_3$) ceramic capacitors, and the degree of change in capacitance from aging varies depending on the type of ceramic material used. Also, when DC bias is applied on an actual circuit, the degree of capacitance aging varies depending on the level of DC bias voltage. Therefore, when using high dielectric constant type ceramic capacitors, change in capacitance from the aging phenomenon should be taken into consideration, and especially when the stability of capacitance is important, it should be verified on the actual circuit.

<Appendix>

1. Capacitance Change according to Aging
(Multilayer Ceramic Capacitor)



2. Capacitance Change according to Aging
(Multilayer Ceramic Capacitor)