

Chapter 1

Introduction



1.1 Background

Dielectric can be defined as a material with high electrical resistivity that used in the form of a capacitor. Ceramic capacitors can fulfil various functions in electronic circuits including blocking, coupling and decoupling, filtering, AC-DC separation and energy storage (1). As compared in 1987 consumption rate, the consumption of ceramic capacitors is projected to grow at an average 6% a year. Dielectric ceramics are produced in wide range compositions and shapes to cover all those applications.

In the early days, steatite, glass, mica, and aluminous porcelain were used in electronic system, but they had a low dielectric constant. Dielectric with high dielectric constant of rutite ($k' > 10$) was first produced commercially in 1930s and barium titanate ($k' > 1000$) in 1974. For dielectric based on titanates the composition with rare earth revealed low loss and high dielectric constant. Nevertheless, they had high temperature coefficients. This problem can be modified by altering the chemical composition and controlling ceramic textures to optimize the required properties.

The properties of dielectric materials which should be considered are as follows:

1. Dielectric constant or relative permittivity; this measures the response of the dielectric polarization mechanisms to an electric field.
2. Dissipation factor or loss factor; this measures the net inefficiency of the polarization process.

3. Insulation resistance, determining the efficiency of DC blocking.

The capabilities of the various capacitor types are compared with the characteristics described below.

1. Volume efficiency

Volume efficiency is a measure of the material ability to store charges so called capacitance, which depends on a size of capacitor. As shown in the following equation, the capacitance of a parallel-plate capacitor of area A and electrode separation h

$$C = \epsilon_0 k' \frac{A}{h}$$

where ϵ_0 = permittivity of free space.

k' = relative permittivity or relative dielectric constant.

and the volume efficiency C/V can be define as

$$\frac{C}{V} = \frac{\epsilon_0 k'}{h^2}$$

The volume efficiency can be represented as the charge storage efficiency of the capacitor.

2. DC resistance

Ideally, the DC resistance is infinite, but in practice it will have a finite value, R_L . In the case of a parallel-plate capacitor as defined

$$R_L = \rho \frac{h}{A}$$

where R_L = the DC resistance.

ρ = the resistivity of the dielectric.

h = the thickness of dielectric material.

A = the area of electrode.

From the volume efficiency and resistance, the size effects these two. As the thickness decreases, the volume efficiency increases but the DC resistance decreases. So the improvement in the ability of capacitor can be made by increasing k' and ρ which are the characteristics of the materials depending on composition.

1.2 Ferroelectric Properties

The principle effects determining properties of dielectric ceramic are:

1. Cation ratio

The capacitive compositions are usually complex mixture prepared from binary solid solution; such as the BaO-TiO₂ system. Cation ratio is the ratio of the total number of ions on A site to those on B site in the perovskite structure (ABO₃). Although several investigators (2,3,4) have studied the phase relation in the system BaO-TiO₂, it was found that with excess BaO and excess TiO₂ a second phase appeared at the grain boundaries and triple-point region, whereas no second phase was observed in samples having Ba/Ti = 1.000. The effect of a second phase on the dielectric constant and the temperature coefficient was discussed (5). With excess BaO the maximum dielectric constant moved to lower temperatures and it greatly reduced. Also, its temperature coefficient was reduced with an increase in TiO₂.

2. Substituents

The Curie point of ferroelectrics can generally be adjusted over a wide temperature range by altering the cation composition. For example, the effect of the cation composition on the phase transition of BaTiO₃ is shown in figure 1.1. The divalent ions forming solid solutions by partially substituting barium ions are lead, strontium and calcium. For titanium, zirconium and tin can be used. Lead is the

only cation that raises the curie point, calcium has little effect and strontium lowers it. However, with calcium the broad phase transition can be observed and the dielectric constant of BaTiO_3 decreases. Zirconium and tin lower the Curie point.

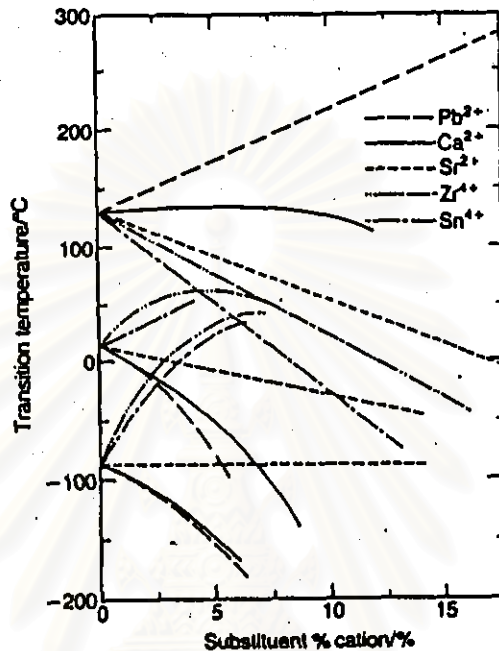


Fig. 1.1 Transition temperature versus concentration of isovalent substituents in BaTiO_3 (1)

3. Effect of crystal size

The grain size of a ferroelectric BaTiO_3 has a marked effect on the permittivity for the size range 1-50 μm (6) as shown in figure 1.2. An important factor leading to this behaviour is the variation in the stress within the grain. As the grain size decreases, the number of domain per grain become larger. This result is an increase in stress which is accompanied by an increase in permittivity(6). But the grain size below about 1 μm the permittivity usually falls with decreasing grain size.

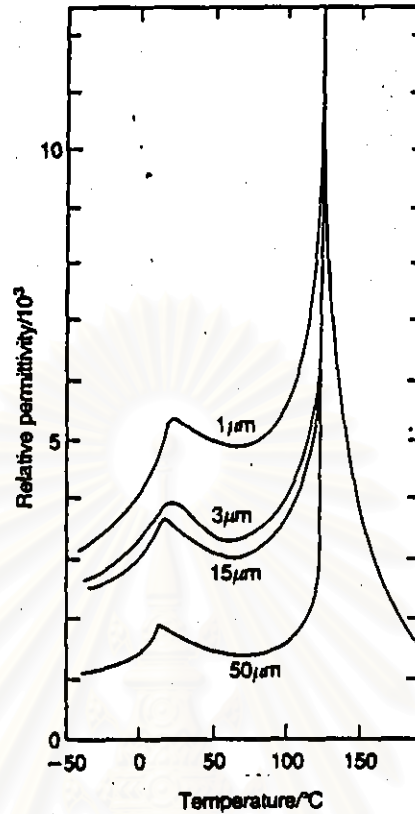


Fig. 1.2 The effect of grain size on the permittivity of a BaTiO₃ ceramic (6)

Ceramic capacitive components typically must have high permittivity for volumetric efficiency. In addition, their temperature coefficient of capacitance should be low. Therefore the modification of a new dielectric ceramic for capacitors should concentrate on:

1. high dielectric constant (k'); commonly found in lead-based perovskite.
2. diffuse or broad phase transition; easily modified by adding dopants to broaden temperature dependence of dielectric constant.

Modified by adding cation as dopants, the temperature of the peak permittivity can be shifted as required and distributed to the transition peaks thus k' is expected to be broad.

1.3 Background of BaTiO₃

Barium titanate (BT) was discovered in the 1940s. It was a complex compound with the perovskite structure (ABO₃). The crystal structure and crystallographic transformation of BaTiO₃ were discussed as a function of temperature (7). Above 120°C its structure is cubic perovskite. Below this temperature, the oxygen and titanium ions shift relative to the barium ions to form a tetragonal structure corresponding to the maximum dielectric constant. At this phase transition, a paraelectric cubic change to a ferroelectric tetragonal. Below 0°C there is a further shift to the ions in the unit cell and the structure changes to orthorhombic structure. Moreover, an orthorhombic ferroelectric changes to a monoclinic ferroelectric at -90°C.

In 1950 the lattice constant was found to be a definite function of the percentage content and position of the constituents by Durst et al. (8). From X-ray diffraction its structure was cubic having the lattice constant $a=4.071$ (7). For the phase transition from cubic to tetragonal structure, the ionic displacements also resulted in a change in lattice constants, $a=3.9903 \text{ \AA}$ and $c=4.0319 \text{ \AA}$ (9).

The change of lattice parameters of BaTiO₃ single crystal had been shown from the thermal expansion (7). Above the Curie temperature the expansion of the polycrystalline material is nearly identical with the change in lattice parameter of crystal, the expansion coefficient being about $15 \times 10^{-6} / ^\circ\text{C}$. Below this point, the behavior of BaTiO₃ ceramic is complicated by the fact that expansion occurs in one direction while contraction in the others. Hence, no definite value can be given for the expansion coefficient in this region.

Since 1940s, the effects of impurities on electrical solid-state of BaTiO_3 have been studied. They found that lattice defects or imperfections due to impurities caused three basic changes in ferroelectrics; 1) charge mobilization, 2) local changes in the potential barrier, and 3) changes in crystal growth habit (10). Isovalent cation substitution is the replacement of cations having the same charge. For example, Ba^{2+} can be replaced by Sr^{2+} and Pb^{2+} or Ti^{4+} can be replaced by Zr^{4+} , Hf^{4+} and Sn^{4+} .

The substituents such as SrO , PbO , MgO , CaO , ZrO_2 , and La_2O_3 can modify the ferroelectric properties of BaTiO_3 by controlling grain size and by suppressing or broadening the Curie peak.

Barium titanate solid solution with other titanate

-Barium Strontium Titanate

Strontium titanate can form a complete range of solid solution with barium titanate. Additions with strontium shift the Curie point to lower temperatures. In addition, the size of the unit cell for this system decreases linearly with the amount of strontium titanate (11). This is because the size of strontium is smaller than that of barium.

-Barium Lead Titanate

The addition of lead titanate lowers the room temperature dielectric constant and raises the temperature at which the maximum dielectric constant occurs. The maximum value of the dielectric constant decreases as lead is added (11). The DC resistivity and the activation energy decrease with increasing amounts of lead. Also, the thermal expansion of the solid solution up to the Curie point decreases as the lead content is increased, becoming highly negative for high lead titanate compositions (11).

-Barium Calcium Titanate (8,11,12)

Calcium titanate can form a solid solution with barium titanate up to above 25 mole percent and barium titanate dissolves in calcium titanate to about the same extent. The barium-rich phase has the tetragonal perovskite structure, the unit cell size decreasing with addition of calcium due to the smaller size of calcium. The calcium-rich phase has the orthorhombic perovskite modification, the unit cell size increasing with addition of barium. The addition of calcium to barium titanate lowers the room temperature dielectric constant. It does not shift the 120°C transition appreciably but shift the 0°C transition to lower temperatures.

-Barium Magnesium Titanate

The main effect of the magnesium titanate is to act as a diluent, lowering the dielectric constant at all temperatures (11).

-Barium Zirconium Titanate

The effect of ZrO₂ is to increase the second transition temperature in BaTiO₃. But it decreases the Curie temperature. Small addition of ZrO₂ enhanced microstructural uniformity of BaTiO₃ and inhibited grain growth depending on sintering temperature (13). Dielectric losses decrease with addition of ZrO₂. This can be modified by controlling grain size and broadening the Curie peak (15).

-Lanthanum doped barium titanate

Lanthanum also acts as grain growth inhibitor and shifts the Curie point to lower temperature with increasing lanthanum (15).

In 1996, (16) Ganesh and Goo studied the microstructure and dielectric properties of the (Pb_xBa_{0.5-x}Sr_{0.5})TiO₃ system. It was found that this system formed a solid solution in the entire composition range (0.0<x<0.5). The x= 0, 0.1 and 0.2

compositions showed a cubic form. With other compositions tetragonal was more stable. The paraelectric-ferroelectric for $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ transition occurred nearly -41°C and its maximum dielectric constant was approximately 12000. For the composition with $x=0.1$, the Curie temperature occurred nearly 90°C and the maximum k' decreased to 1700. These results showed that Pb effected not only the maximum dielectric constant but also the transition temperature.

1.4 Objective of this thesis

BaTiO_3 - SrTiO_3 system has a high dielectric constant at all temperatures. Most studies on this material and its modification have focused on capacitor applications. The aim of this work are to select the best composition of BaTiO_3 - SrTiO_3 that giving the highest maximum dielectric constant and to study the effect of lead on the dielectric properties. To explain how lead affects the dielectric properties, the microstructure of this system is also investigated. With regard to this aim, it is designed to make the system useful as a wide-range temperature and high dielectric capacitor.

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