Chapter 1

Introduction and Literature Review

1 Introduction

Today electronic industry is developing at a very fast pace. With this development, miniaturization of electronic devices has become a prime objective of engineers and scientists working in electronics industry. Need for high permittivity (ε') material is also driven by the constant demand of modern electronics industry for miniaturization of the electronic devices.

Electronic systems are generally composed of active and passive components. Passive components are attracting lot of interest because these are steadily growing in number as the electronics industry is progressing toward higher functionality [Tummala (1999)]. For example, the ratio of the passive to active components in a mobile cellular phone is over 20 [Lau (1994)]. Next generation technology demands the passive components such as capacitors (C), resistors (R) and inductors (L) to be integrated as a thin film into the substrate rather than being mounted on the surface of the substrate as discrete components. The passive components integrated into the substrate are called integral passives or embedded ones. Embedded passives are more advantageous than discrete components and play a crucial role in the microelectronics. Among all the passive components, capacitors outnumber the active components in almost all industrial applications and occupy a significant space in a circuit board. Fig. 1.1 shows the market shares of the capacitors, resistors and inductors in the United States. As capacitors are widely employed in electronic devices, integration of the capacitors is very important.

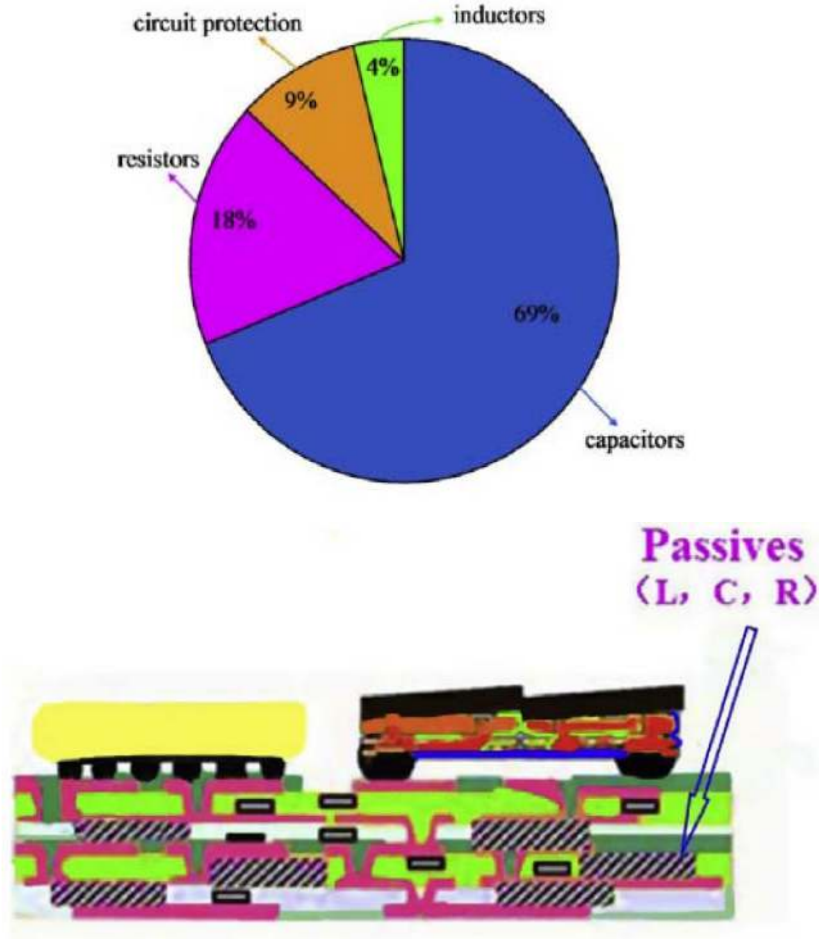
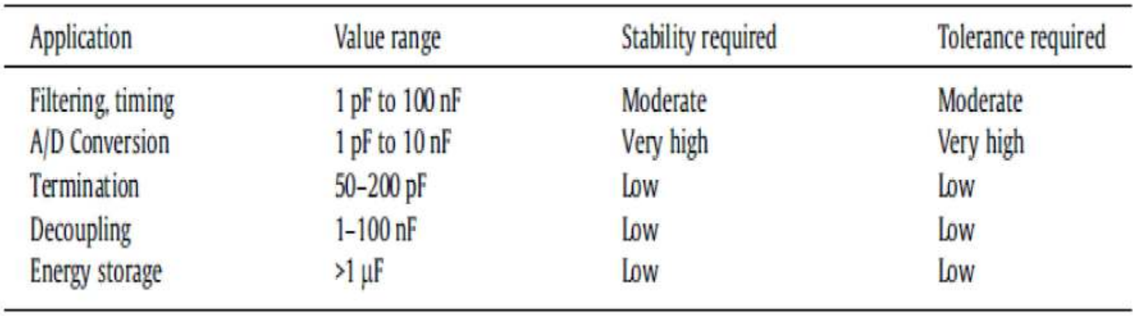


Figure 1.1 (a) Market shares of capacitors, resistors, and inductors [Kapadia et al (1999)]. (b) a schematic image of embedded passive substrate, the arrow showing position of passive components [Kakimoto et al 2006].

Capacitors have many applications, as listed in Table 1.1. These can be used for filtering, timing, alternating/direct (A/D) current conversion, termination, decoupling and energy storage. Particularly, the development of microelectronics needs decoupling capacitors with higher capacitance and shorter distance from its serving devices [Kapadia et al (1999)].

Table 1.1 Applications of capacitors in industry [Dang et al (2011)]



Application	Value range	Stability required	Tolerance required
Filtering, timing	1 pF to 100 nF	Moderate	Moderate
A/D Conversion	1 pF to 10 nF	Very high	Very high
Termination	50–200 pF	Low	Low
Decoupling	1–100 nF	Low	Low
Energy storage	>1 μF	Low	Low

Apart from electronic industry, high ε' materials are also used in many military and civilian applications like active vibrations control, aerospace, underwater navigation and surveillance, hydrophones, biomedical imaging, non-destructive testing and air imaging microphones (Fig 1.2) [Bar-Cohen (2002) and Uchino (1997)]. Capacitor is one such component that enables the reduction of the circuit size and can realize tera-bit density static/dynamic random access memory [Tummala (1999)]. For example, high ε' elastic rubber–matrix composites are now a days widely used as potential functional materials for cable accessories in electrical engineering because these can balance the distribution of electric field of the cable terminal to prevent the cable from failure.

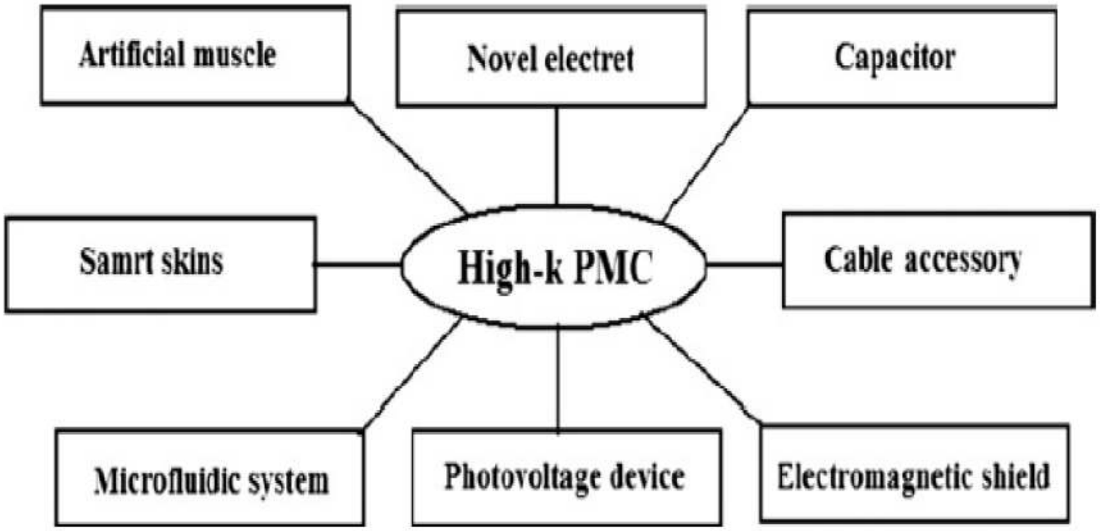


Figure 1.2 Outlook for applications of the high k polymer composites [Uchino (1997)].

1.1 Fundamental aspects of high ε' composites

1.1.1 Fundamentals of Dielectrics

A dielectric material is a substance that is a poor conductor of electricity but an efficient supporter of electrostatic fields. If the flow of current between opposite electric charge poles is kept to a minimum while the electrostatic lines of flux are not impeded or interrupted, an electrostatic field can store energy. This property is useful in capacitors, especially at radio frequencies. Dielectric materials are also used in the construction of radio-frequency transmission lines.

In practice, most dielectric materials are solid. Examples include porcelain (ceramic), mica, glass, plastics, and the oxides of various metals. Some liquids and gases can serve as good dielectric materials. Dry air is an excellent dielectric and is used in variable capacitors and some types of transmission lines. Distilled water is a fair dielectric. A vacuum is an exceptionally efficient dielectric.

The dielectric constant is the ratio of the permittivity of a substance to the permittivity of free space. It is an expression of the extent to which a material concentrates electric flux and is the electrical equivalent of relative magnetic permeability.

As the dielectric constant increases, the electric flux density increases, if all other factors remain unchanged. This enables objects of a given size such as sets of metal plates to hold their electric charge for long periods of time and/or to hold large quantities of charge. Materials with high ε' are useful in the manufacture of high-value capacitors.

A high ε' is not always desirable, it depends on the application. Generally, substances with high ε' break down more easily when subjected to intense electric fields than do materials with low ε'. For example, dry air has a low ε', but it makes an excellent dielectric material for capacitors used in high power radio-frequency (RF) transmitters. Even if air does undergo dielectric breakdown (a condition in which the dielectric suddenly begins to conduct current), the breakdown is not permanent. When the excessive electric field is removed, air returns to its normal dielectric state. Solid dielectric substances such as polyethylene or glass, however, well undergo permanent damage.

In engineering applications, permittivity is often expressed in relative, rather than in absolute, terms. Physically it means that greater the polarization developed by a material in an applied field of given strength, the greater will be the dielectric permittivity. If ε_o represents the permittivity of free space (that is, 8.85 x 10^{-12} F/m) and ε represents the permittivity of the substance in question (also specified in farads per meter), then the relative permittivity, also called the dielectric constant ε' , is given by:

$$\varepsilon' = \frac{\varepsilon}{\varepsilon_0} \qquad (1.1)$$

Various substances have dielectric constants ε' greater than 1. These substances are generally called dielectric materials, or simply dielectrics. Commonly used dielectrics include glass, paper, mica, various ceramics, polyethylene, and certain metal oxides. Dielectrics are used in capacitors and transmission lines in alternating current (AC), audio frequency (AF) and radio frequency (RF) applications. It should be pointed out that the symbol 'ε'' for dielectric permittivity is mostly used in the microelectronic field. In electrical engineering and other fields, the symbol 'k' is commonly employed. ε_r is also used to represent relative dielectric permittivity. In this thesis, the symbol 'ε'' is used throughout.

Based on the applications, there are different needs for dielectric materials. For some applications, such as insulation materials of integrated circuit, dielectrics with a low dielectric permittivity (i.e., low ε' materials) are required. For applications, such as capacitors and transistors, materials with a high ε' are desired. A high permittivity material can store more electric energy than the one with a low value. As a result, its use in the electronic devices improves their efficiency as well as the quality. Traditionally dielectric materials are made from inorganic substances eg. mica and silicon dioxide. Dielectrics used under a high electric field generally require high dielectric breakdown strength (E_b) with a low loss at the applied electric field.

The use of high ε' materials has extended beyond electronics and has triggered the development of other high ε' materials including polymer matrix composites (PMC). Although high ε' PMC cannot be considered as gate dielectrics due to some well-known disadvantages, yet these are widely used for embedded capacitor applications in electronic devices and many other applications. Moreover, their mechanical flexibility and tunable properties make them appealing for high ε' materials.

1.1.2. Capacitance and storage of electrical energy in materials

Two conducting electrodes separated by a dielectric constitute a capacitor (formerly called a condenser) (Fig 1.3).

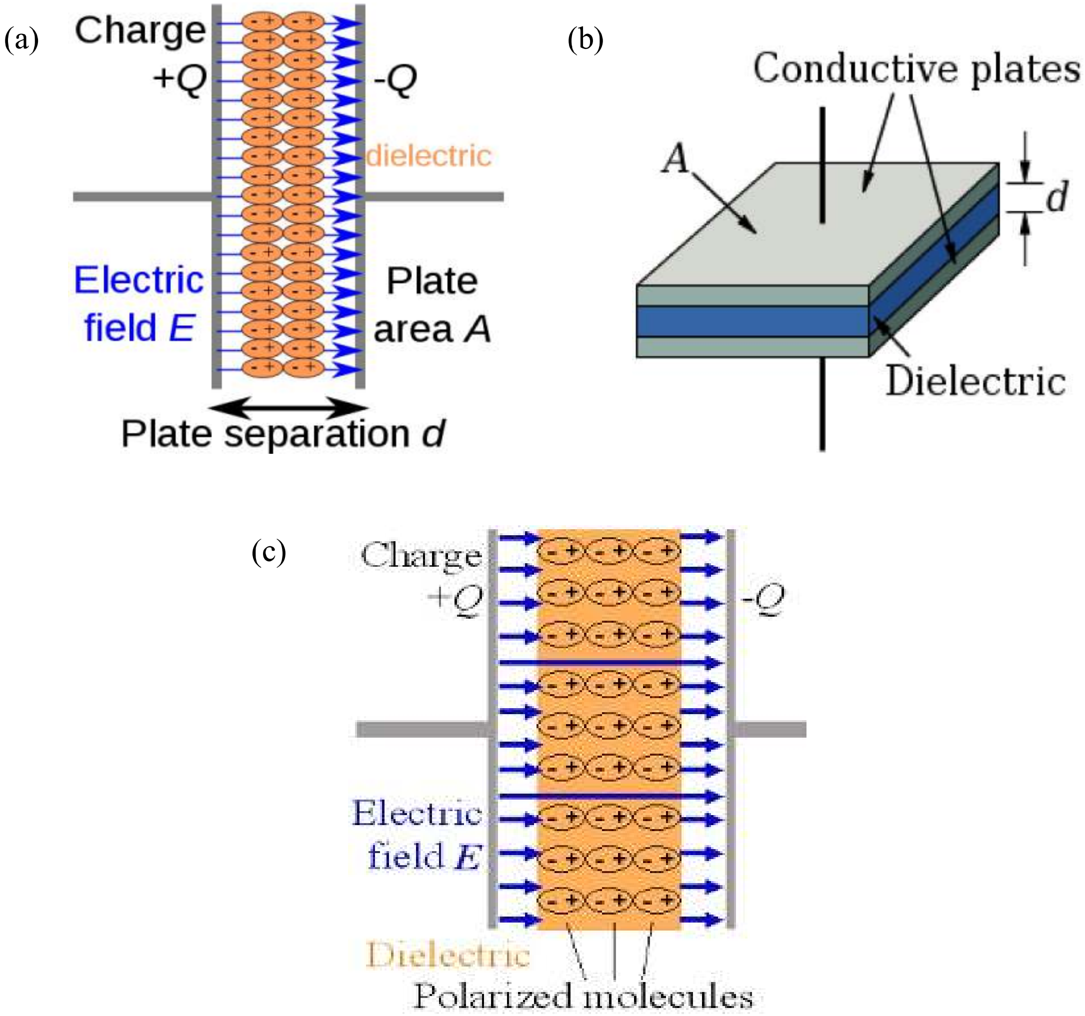


Figure 1.3 (a) Charge separation in a parallel plate capacitor (b) dielectric capacitor (c) Effect of electric field on the dielectric (www.physicsforums.com)

If a battery of potential difference (V) is connected across the electrodes then the capacitor can store electrical charge (Q), expressed in coulombs, which is directly proportional to the applied voltage, expressed in volts (V), according to the following equation:

$$Q=CV \qquad (1.2)$$

where C is the capacitance expressed in farad (F). Hence the capacitance value is defined as 1 F when the electrical potential difference across the capacitor is 1 V and a charging current of 1 A flows for 1 s. A farad is a very large unit and is not encountered in practice. Therefore submultiples of the farad are commonly encountered. In decreasing order of use, these are the picofarad (pF), the nanofarad (nF), and the microfarad (mF). The simplest arrangement of a capacitor consists of two parallel electrodes of area A separated by a distance d. If a material with permittivity ε_a ($\varepsilon_a = \varepsilon_o\varepsilon'$ where ε_a is the absolute permittivity) is inserted between the electrodes, the capacitance can be written as:

$$C=\varepsilon'\varepsilon_o\frac{A}{d} \qquad (1.3)$$

where ε_0 is the dielectric permittivity of vacuum and is 8.854 pF/m, ε' is the permittivity. If the medium is a macroscopic material, it is often called the dielectric permittivity of the material. Hence the dielectric permittivity (ε') is defined by the equation $\varepsilon' = \varepsilon_0\varepsilon_r$. Eq. (1.3) shows when an electric field is applied to a capacitive material; electric energy can be stored in it.

Based on the above eq (1.3), it is possible to increase the capacitance of a device in several ways, such as:

- increasing the electrode area;
- decreasing the distance between the electrodes and
- Inserting a dielectric material with high permittivity.

As demanded by electronic industry, from one generation to the next one, capacitors should have the desired capacitance in a reduced geometry. So, increasing the electrode area, and consequently the device size, is not a good idea. Besides, decreasing the spacing between electrodes limits the maximum voltage which can be applied across the capacitor by the dielectric strength of the vacuum or material.

Obviously, it limits the capacitor use. So, the best way to produce a small device with high capacitance is by using materials with high ε'. In a simplest way, this is the reason why high (or giant) dielectric permittivity materials are so important from the technological point of view. Besides, most of them can also be used as memory devices, for a wide range of applications.

1.1.3. Mechanism of Polarization

The dielectric response, P, in a dielectric material may originate from different mechanisms. For a homogeneous material, the dielectric responses have, in general, four mechanisms (as illustrated in Figure 1.4) [Barsoum (1997); Taylor (1984)].

(i) Electronic polarization: The electric field causes the displacement of the outer electron cloud from the inner positive nucleus. This polarization has a response time of 10^{-14}~10^{-16} s and is independent of temperature.

(ii) Ionic polarization: Ions response to an electric field with a change in the relative distance between the ions. The response time is about 10^{-12}~10^{-13} s and is almost independent of temperature.

(iii) Orientational Polarization: If there are dipoles existing in a material, the electric field E would generate a torque on each dipole and the torque would cause the dipoles to align along the electric field direction. The response time is about 1~10^{-8} s and is strongly dependent on temperature.

(iv) Space charge polarization: When on application of an electric field, E the positive and negative charges separate over considerable distances and are restricted to move at the interface of two or more materials, space charge polarization is produced. The response time may be more than 1 second.

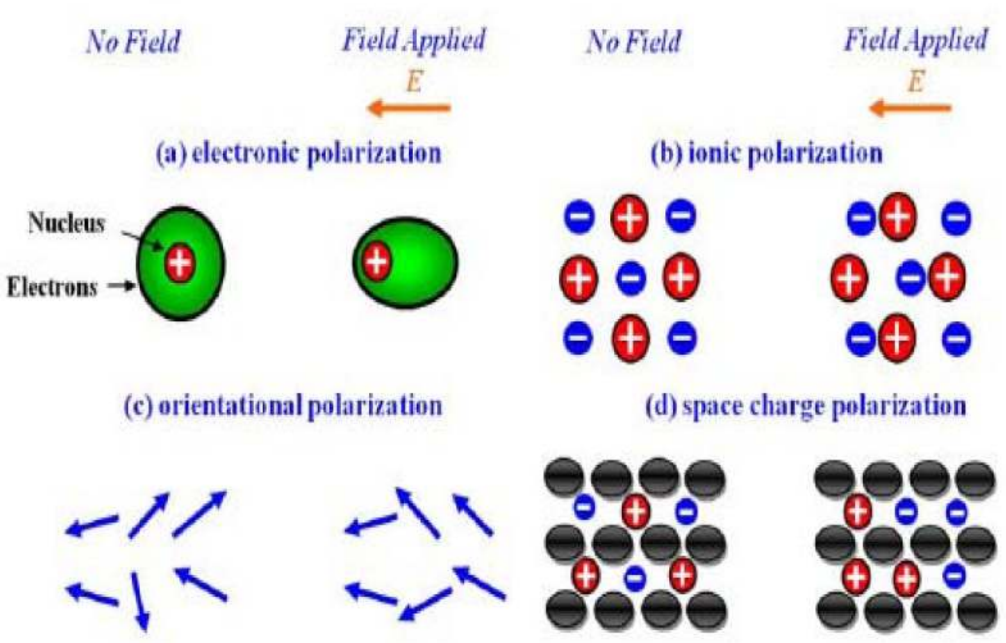


Figure1.4 Schematic of (a) electronic polarization, (b) ionic polarization, (c) orientational polarization, (d) space charge polarization [Taylor (1984)].

The dielectric response of each polarization mechanism changes with frequency *f*, but with different patterns. The electronic and ionic polarization result in a resonance, while the response of the orientational and space charge polarization is relaxation.

1.2 Dielectric Materials

Now a days several dielectrics such as gases, liquids and solids, are widely used for various industrial applications based on their different and unique dielectric properties. Classification of the dielectric materials is generally based on either structure or composition. In the classification category of structure, polar and non polar materials come. A polar material is a material possessing a permanent dipole moment which is associated with its molecule or unit cell while a non polar material is a material whose molecule or unit cell does not possess a permanent dipole moment. Some polar materials, show strong interaction among their dipoles and these dipoles align along the same direction which results in a spontaneous polarization *Ps* (i.e. the material has a polarization without an electric field applied on it). These materials are named as pyroelectric materials. The pyroelectric materials have a critical temperature (i.e. Curie temperature). In physics and materials science, the Curie temperature (T_c), or Curie point, is the temperature where a material's permanent polarization changes to induced polarization or material's intrinsic dipole moments change direction. Below Curie temperature, the material is pyroelectric, while above the Curie temperature, the material is paraelectric (PE). If the *Ps* in a pyroelectric material switches in the presence of external electric field, then it is called a ferroelectric (FE) material (Fig 1.5). Since the electric field can switch the Ps in a ferroelectric, FE materials usually exhibit a very high ε', especially at temperature around the FE-to-PE phase transition temperature [Kittel (1976); Damjanovic (1998); Jonker (1983)]. On the basis of the composition, dielectrics can be classified into inorganic and organic materials. In solid dielectrics, both organic and inorganic compounds are vastly used. In general, the polymers have a low processing temperature, are flexible and exhibit a high breakdown field but have a low ε'. Inorganic dielectrics exhibit a high dielectric permittivity, but require a high processing temperature and are brittle with a lower breakdown field. All of these materials are suitable and of interest for different applications.

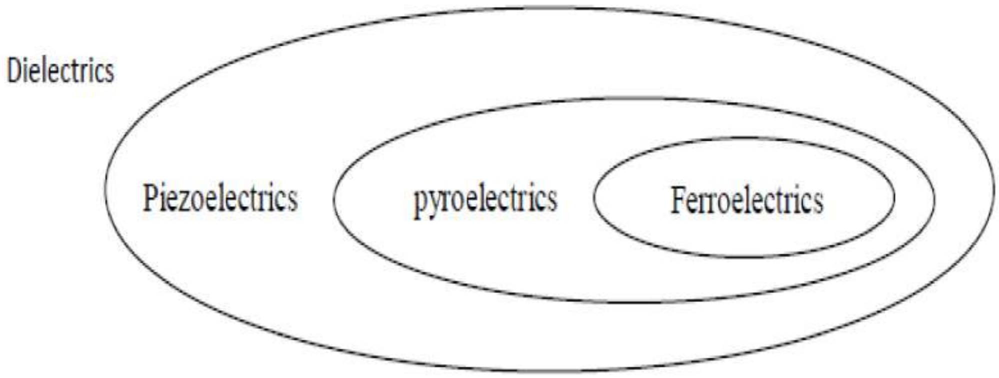


Figure 1.5 Venn diagram showing the relationship between ferroelectrics, pyroelectrics and piezoelectrics [Damjanovic (1998)].

1.2.1. Inorganic Dielectric Materials

A nonpolar material is defined as a material containing no permanent dipole moments. Their ε' is relatively small, such as silicon≈3.7, diamond≈5.5~10, paraffin≈1.9~2.5 and carbon tetrachloride≈2.0.

The polar inorganic materials such as the ferroelectric ceramics and crystals, usually exhibit a high ε' (~10^3). For example, the widely studied/used ferroelectric $BaTiO_3$ (BT) exhibits a ε' of 1500. The ε' of other ceramics $Pb(Mg_{1/3}Nb_{2/3})O_3$(PMN) and $Pb(Zr_{0.52}Ti_{0.48})O_3$(PZT) at 1 kHz are larger than 1000, such as ε_{PMN}=5500, ε_{PZT}=1300, etc [Patterson et al (2005); Yu et al (2008); Chiodelli et al (2004)]. Although these ferroelectrics exhibit a high ε', but their ε' is strongly dependent on temperature. For example, their ε' shows a maximum at the FE-to-PE phase transition temperature.

Some ferroelectric based solid solution ceramics/crystals, such as PMN, exhibit a so-called relaxor ferroelectric behavior. The relaxor ferroelectrics (RFEs) have a weaker temperature dependence of the ε' than the ferroelectrics at temperatures around their Curie temperature. RFEs exhibit a very high ε' over a broad temperature range. However, the ε' of the relaxor ferroelectrics is still strongly dependent on the temperature and more importantly, this is strongly frequency dependent.

During the last 15 years, some inorganic non-ferroelectric materials with very high ε' (~10^4) have been developed, such as $CaCu_3Ti_4O_{12}$ (CCTO), $Bi_{2/3}Cu_3Ti_4O_{12}$ or in the $ACu_3Ti_4O_{12}$ family. These materials are very interesting for dielectric study and applications. Among these materials, CCTO is of interest since it exhibits a high ε' that is nearly independent of the temperature over a broad temperature range from 100 to 400 K at frequencies below 1 MHz [Subramanian et al. (2000); Rai et al (2011); Hong et al (2007); Jesurani et al (2013)].

1.2.2. Dielectric Polymers

Various polymers, such as epoxy, polyethylene (PE), polyester (PS), poly(methyl methacrylate) (PMMA), poly(vinyl chloride) (PVC), polyurethanes (PU) and Polytetrafluoroethylene (PTFE) have been studied as dielectrics based on their processibility, flexibility, dielectric response, dielectric strength, melting temperature and glass transition temperature for different applications. The non-polar polymers exhibit a small ε'. For example, ε_{epoxy}=4, ε_{PE}=2.2~2.4, ε_{PS}=2.8~4.5, ε_{PTFE}=2.1, etc [Pothukuchi et al (2004); Immergut et al (2008); Qi et al (2005)].

To achieve a high ε' in polymers, polar polymers have been widely studied and used as dielectrics. Vinylidene fluoride (VDF) is a monomer with CF_2=CH_2 formula, which can polymerize alone or with other co-monomers, some of the most commonly used being trifluoroethylene (TrFE) and hexafluoroethylene (HFP), to form VDF based polymers.

Ferroelectric poly(vinylidene fluoride) (PVDF) is the most studied polar polymer. PVDF homopolymer and PVDF-based copolymers and terpolymers such as poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)], poly(vinylidene fluoride-chlorotrifluoroethylene) [P(VDF-CTFE)], poly(vinylidene fluoride-hexafluoropropylene) [P(VDF-HFP)] and P(VDF-TrFE-CFE), have been developed and studied as dielectrics [Nalwa (1995); Dario et al (2000); Dang et al (2002); Qi et al (2005); Lu et al (2006)]. All these polymers exhibit a ε' in the range 5-10 at room temperature and this can be as high as ~70 at their FE-to-PE phase transition temperature. The ferroelectricity in polymers originates from the dipole associated with the configuration of polymer chain, such as (-CH_2-CF_2-) in PVDF has a dipole moment of about 7.06×10^{-30} Cm. For PVDF-based copolymers, TrFE and CTFE are very interesting since these copolymers exhibit a high electromechanical response and have a high energy storage capability. The difference and similarity among VDF, TrFE, and CTFE monomers are shown in Figure 1.6.

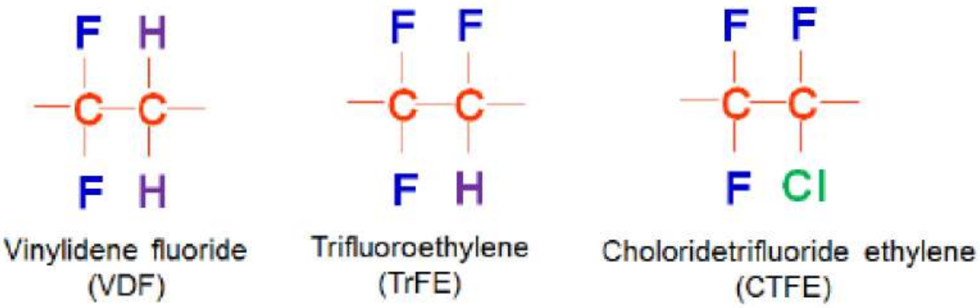
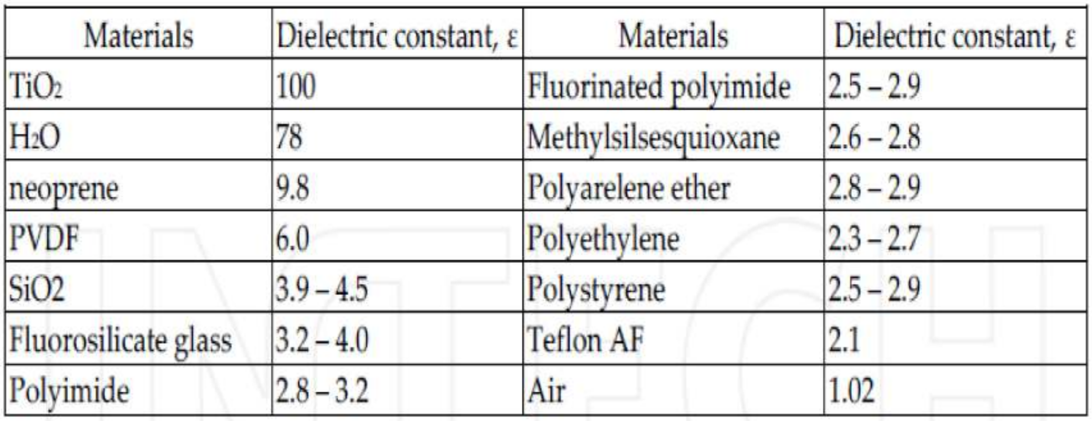


Figure 1.6 The chemical units of VDF, TrFE and CTFE [Dario et al (2000)].

However polymers are gaining wider use as dielectric materials. This is due to the easier processing, flexibility, ability to be tailor made for specific use and better resistance to chemical attack. As early as mid-60’s polymers eg polyvinyl fluoride [Milton et al (1967)] and aromatic-containing polymers [Alfred et al (1966)] are used as dielectric materials in capacitors. Further improvement in the organic films fabrication was established as revealed in US Patent 4153925. Polymers can be easily processed into thin film by various techniques such as solution casting and spin coating, extrusion method and compression molding, immersion in organic substrate, electron or UV radiation and glow discharge methods. Lower processing temperature can be attributed to inferior thermal properties such as glass transition and melting temperature. Their solubility is controllable without offsetting their intrinsic properties. In the case of inorganic materials and ceramics, they need very high processing temperature due to their slow nature of thermochemical reaction controlled by temperature. On the other hand, polymers cannot bear high temperature. As compared to ceramics, the polymer have high coefficient of thermal expansion, which makes them susceptible to atmospheric and hydrolytic degradation. Table 1.2 shows the values of dielectric properties of several polymers and comparisons with several inorganic materials. Inorganic/ceramics materials have higher ε' than polymers. Air having a ε' of 1.02, is taken as reference dielectric. Water has a relatively high ε'. This is quite cumbersome as any traces of moisture trapped or absorbed will dramatically alter the desired dielectric properties. Inorganic materials generally possess higher ε' compared to polymeric materials.

Table1.2 Dielectric permittivity of several polymers and inorganic materials [Lu et al (2006)].



Materials	Dielectric constant, ε	Materials	Dielectric constant, ε
TiO_2	100	Fluorinated polyimide	2.5 – 2.9
H_2O	78	Methylsilsesquioxane	2.6 – 2.8
neoprene	9.8	Polyarelene ether	2.8 – 2.9
PVDF	6.0	Polyethylene	2.3 – 2.7
SiO2	3.9 – 4.5	Polystyrene	2.5 – 2.9
Fluorosilicate glass	3.2 – 4.0	Teflon AF	2.1
Polyimide	2.8 – 3.2	Air	1.02

1.2.3. Dielectric composites

Synthesis and characterizations of the high dielectric materials have been studied by many investigators. The most promising materials, like ferroelectric oxides such as $BaTiO_3$ or relaxors such as $(Bi,Sr)TiO_3$ [Ang et al (1999)], exhibit high dielectric permittivity. But their dielectric permittivity show strong temperature dependence which is detrimental for microelectronic devices. This limits their applications in electronics instruments. So search for high dielectric permittivity materials is motivated, by special properties such as almost temperature and frequency independent dielectric permittivity and low dielectric loss. In recent years, many materials have been searched including perovskites and others, aiming to achieve nearly temperature independent high dielectric permittivity materials for practical applications. Recently Ba/Pb-free, giant (or colossal) dielectric ceramics with good thermal stability have gained much importance due to their wide applications in microelectronics. Oxides with the perovskite structure are well known for their nearly temperature independent high dielectric permittivity. The $ACu_3Ti_4O_{12}$ family of compounds has been known since 1967 [Deschanvres et al (1967)]. This family was expanded and accurate structures were determined in 1979 [Bochu et al (1979)]. Subramanian et al. [Subramanian et al. (2000)] reported a class of compounds with a pervoskite structure which have dielectric properties very different from those of ferroelectrics or relaxors.

One advantage of these compounds is that their high ε' show only a small dependence on temperature. Among all the compounds studied by Subramanian et al. [Subramanian et al (2000)] the CCTO (A = Ca) shows the maximum dielectric permittivity (10,000 for polycrystalline ceramic and over 100,000 for single crystals) becoming an interesting material to be deeply analyzed (Fig 1.7). Several series of dielectric materials have been studied for improving dielectric properties, e.g. (M, N)-doped NiO (M = Li, Na, K and N = Ti, Al, Si, Ta) ($\varepsilon' \sim 10^4 – 10^5$), CuO ($\varepsilon' = 10^4$), $A_{2/3}Cu_3Ti_4O_{12}$ (A = trivalent rare-earth or Bi), Fe-containing complex perovskite $A(Fe_{1/2}B_{1/2})O_3$ (A = Ba, Sr, Ca and B = Nb, Ta, Sb) and $BaTi_{1-x}(Ni_{1/2}W_{1/2})_xO_3$. Because $CaCu_3Ti_4O_{12}$ (CCTO) possesses exceptional high dielectric permittivity, this material is more explored [Rai et al (2011); Hong et al (2007); Jesurani et al (2013); Parkash et al (2008)].

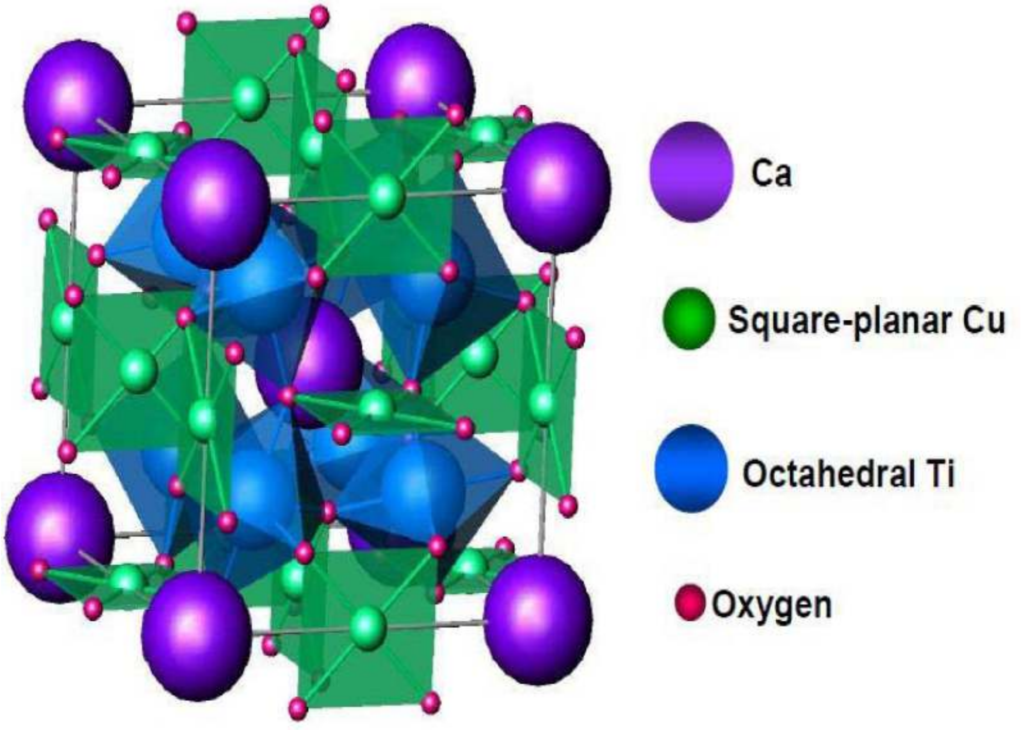


Figure1.7 $CaCu_3Ti_4O_{12}$: A strongly distorted, A-site ordered double-perovskite structure [Subramanian et al (2000)].

To design small electronic circuits, materials with high ε_r are needed. Therefore CCTO is considered as a very potential material for applications in microelectronics, especially in the capacitive components and varistors. It finds important applications in microelectronics and memory devices as static dielectric permittivity of a material ultimately decides the degree of miniaturization. It may be widely used in the electronic industries to manufacture electronic components such as multilayer capacitor (MLCC), DRAMs (Dynamic Random Access Memory), microwave devices, electronic devices in automobiles and aircrafts.

Partial substitution of appropriate cations in CCTO is considered as an effective method to improve its dielectric properties. For successful partial substitution, radius, valancy and co-ordination number of an element are important parameters to determine the site it occupies in the parent compound [Liu et al (2007); Hutagalung et al (2008); Cai et al (2007)]. Despite the fact that much research work has been done to reveal the nature and origin of the giant dielectric permittivity of CCTO ceramics, it still remains controversial and unsolved to date. At present, a possible explanation that an internal barrier layer capacitance (IBLC) model between the insulating grain boundaries and semiconducting grains is widely accepted by the researchers. High permittivity values may be attributed to [Thomas et al (2008); West et al (2004); Grubbs et al (2005)]:

1. The barrier layer capacitance arising at twin boundaries
2. Disparity in electrical properties between grains interior and grain boundaries
3. Space charge at interfaces between the sample and the electrode contacts
4. Polarizability contributions from the lattice distortions
5. Differences in the electrical properties due to internal domains
6. Dipolar contributions from oxygen vacancies
7. The role of Cu off-stoichiometry in modifying the polarization mechanisms
8. Cation disorder induced planer defects and associated inhomogeneity.

1.2.4 Advantage of $CaCu_3Ti_4O_{12}$ over $BaTiO_3$

In the cubic perovskite structure encountered in $BaTiO_3$ above 120^0C, the Ti^{4+} cation is in a site of full cubic symmetry. With decreasing temperature, Ti^{4+} displaces toward one, then two and finally three oxygen anions, to produce, respectively, the tetragonal, orthorhombic and rhombohedral ferroelectric structures. The site symmetry for Ti^{4+} in $CaCu_3Ti_4O_{12}$ is much lower than that in cubic $BaTiO_3$; this greatly reduces the possibility of a ferroelectric phase transition based on the displacement of Ti^{4+} from the center of its octahedron. For example, the lack of a fourfold axis in the *Im3* space group for $CaCu_3Ti_4O_{12}$ eliminates the possibility of a transition to a tetragonal ferroelectric structure. Ti^{4+}cations could displace off center, along their one threefold axis. However, this could not be a pure ferroelectric transition because the displacements would actually occur along four different directions. Thus, we have in $CaCu_3Ti_4O_{12}$ a perovskite-type structure where the polarizability and dielectric permittivity are enhanced by tension on the Ti-O bonds but where a transition to a ferroelectric state is frustrated by the TiO_6 octahedra tilt structure that accommodates the square planar coordination of Cu^{2+}.

1.2.5. Various types of synthesis technique of $CaCu_3Ti_4O_{12}$

Synthesis of ceramic powder is very important in the field of materials science. The basic idea is that synthesis technique should give uniformity in the microstructure of a single phase ceramic for better properties. With a view to obtain high dielectric permittivity and low loss tangent calcium copper titanate, Ca, Cu and Ti exchange was studied by many research groups. Numerous techniques are available in the literature for the synthesis of the ceramic samples. Selection of the synthesis route is crucial to control the composition, structure, and morphology of a chosen material. There are mainly two approaches for synthesis of ceramic powder. One is the chemical method and the other one is the mechanical method. Mechanical methods are (a) dry method or mixed oxide process or solid state reaction process and (b) high energy ball milling (ball mill, planetary ball mill, rotator ball mill, etc.). The chemical methods of synthesis of ceramic powders are sol-gel method, co-precipitation method, hydrothermal method, combustion method, molten salts, liquid-phase and gas-phase reactions, polymer pyrolysis, Pechini method, citrate gel methods, aerosols and emulsions etc. [Liu et al (2007); Jin et al (2007); Jhu et al (2009)]. The chemical method gives a better product as compared to the mechanical method due to the absence of secondary phase, chemically, structurally and morphologically homogeneous sample. But the disadvantages of chemical method are it is time consuming, reaction procedures are complex and requirement of costly ingredients. The initial product obtained from chemical method is also calcined at temperatures 500^0C to 1000^0C depending on the material which is the same as in solid state reaction route. The chemical precursors taken in chemical method are hydrophobic, unstable at room temperature, hence react with other materials. The disadvantage of solid state reaction is that the synthesized powder has imperfect surface structure, non-uniform strain and coarse particle size due to prolonged heating at high temperature. Still the solid state reaction route method is well used for a large-scale production of bulk ceramic powders. It requires low cost precursors which are readily available and needs easier preparation technique.

Solid-state reaction or Dry method: The perovskite oxides are generally synthesized by conventional solid-state route [Hutagalung et al (2008); Mu et al (2009)] or dry method. Solid state synthesis is a technique used to produce materials by the reactions carried out at high temperature and pressure. This method is generally used for the mass production of unique, advanced structures for dielectrics and piezoelectrics. It is a conventional method for preparing ceramics and includes several successive steps of intimate grinding and sintering of the stoichiometric mixture of starting materials. In this route, oxides or salts of various cations are mixed in stoichiometric ratio using a suitable liquid (acetone or ethanol) and ground to fine powder using a mortar pestle. Dried mixed powder is calcined at a particular temperature for a certain period of time to decompose any salt to give fine oxide for further reaction. The calcined powder is again ground to convert it into fine powder. An optimum amount of a suitable binder, e.g polyvinyl alcohol (PVA) is added to the powder and mixed uniformly and then it is pressed into a suitable shape. The resulting product is first heated slowly to a particular temperature to remove the binder and then the temperature of the sample is increased to a suitable temperature and maintained there for certain duration for sintering. After sintering, the sample is cooled under controlled rate of cooling. The final resulting product forms by diffusion of metal ions at high temperature.

The solid state synthesis of CCTO powders typically starts with the mixing of precursors by ball milling or other techniques. The most commonly used precursors are $CaCO_3$, CuO and TiO_2 of high purity. However, other precursors can also be used in the form of acetates, oxalates etc. Generally, the solid state method cannot produce CCTO powders in nanometer scale because of high temperature employed during calcination and sintering. However, by modifying this method and processing parameters it can give the CCTO powders with an average particle size of around 500 nm.

Sol-gel process [Masingboon et al (2009)] use metal alkoxides as the starting materials which are very expensive and extremely sensitive to the environmental conditions such as moisture, light and heat. Moisture sensitivity makes it necessary to conduct the experiment in dry boxes or clean rooms and also this method needs long heat-treatment times. Co-precipitation processes involve repeated washing in order to eliminate the anions coming from the precursor salts used, making the process complicated and very time consuming. Every synthesis route has its own advantages and disadvantages.

Semi wet method: This route is modified sol-gel technique [Singh et al (2009)]. It is also named as citrate-nitrate gel chemical method which is a type of combustion synthesis technique. Combustion synthesis is generally used to obtain multi-component single phase material. The combustion technique is based on redox reaction between a fuel and an oxidant present in the precursor solution. Generally, citric acid, urea, ethylene glycol etc. are used as fuels and nitrates of different metals are used as an oxidant. The chelating agents like EDTA, acetic acid etc. can form complex with metal ions present in the precursor solution and act as fuel. This complex on dehydration produces a viscous gel which on further heating self-ignites with the evolution of huge amount of gases. This leads to the development of porous floppy ash. Fine phase pure powder can be obtained on further calcination of the ash at high temperature.

It is well known that the dielectric properties of CCTO are strongly dependent on the processing condition as well as on doping [Subramanian et al (2000); Yu et al (2008)]. A lot of research work has been done on the partial substitution of Ca, Cu and Ti ions in CCTO ceramic in order to improve the dielectric permittivity and decrease dielectric loss [Ni et al (2010); Chiodelli et al (2004)]. In the previous works, various substitutions were made on different sites such as Ca, Cu and Ti of CCTO to study the effect of substitution on dielectric properties [Singh et al (2013); Zhao et al (2012); Jesurani et al (2013)]. In the present work, $CaCu_3Ti_4O_{12}$ (CCTO) and La, Nb, Sn and Zr cations doped calcium copper titanate, CCTO, at higher concentration level (5 mol% and 10 mol%), were synthesized by the semi wet route and solid state method.

Feng et al (2006) prepared Ceramic samples of $Ca_{1-x}La_xCu_3Ti_4O_{12}$ (x = 0, 0.1, 0.2, 0.3 and 0.4) by a conventional solid-state reaction. They reported dielectric permittivity greater than 3000 and dissipation factor below 0.015 at 10 kHz from 180 K to 300 K for $Ca_{0.8}La_{0.2}Cu_3Ti_4O_{12}$. The impedance spectroscopy analysis confirms that the decrease of dielectric loss is mainly due to the increase of conductivity in the CCTO grain/subgrain.

Hong et al (2007) synthesized pure and Nb-substituted $CaCu_3Ti_{4-x}Nb_xO_{12+x/2}$ (CCTO, x= 0, 0.02, 0.1, 0.2, 0.4) ceramics by a conventional solid-state sintering and their electric and dielectric properties were investigated using an impedance analyzer. A single-phase CCTO was obtained up to x = 0.2 Nb substitution The dielectric permittivity increased with Nb substitution, and the highest value of 420000 was observed in the x = 0.2 Nb-substituted specimen at 10 kHz. The obtained electric and dielectric properties in Nb substituted CCTO were explained on the basis of internal barrier layer capacitor model, particularly focusing on a ratio of thickness of the grain boundary region to grain size.

Jin et al (2009) synthesized $Ca_{1-x}La_{2x/3}Cu_3Ti_4O_{12}$ (x = 0.00, 0.05, 0.10, 0.15 and 0.20) powders by the sol–gel method. They reported room-temperature dielectric permittivity of the $Ca_{1-x}La_{2x/3}Cu_3Ti_4O_{12}$ of the order of 10^3–10^4 for x=0.05 value. Compared with $CaCu_3Ti_4O_{12}$, La^{3+}doped $CaCu_3Ti_4O_{12}$ showed a flatter dielectric permittivity vs frequency plot. It was found that the loss tangent of the $Ca_{1-x}La_{2x/3}Cu_3Ti_4O_{12}$ ceramics was less than 0.20 in ~600–10^5 Hz frequency range, which rapidly decreased to a minimum value of 0.03 by La^{3+}doping with x = 0.05.

Sulaiman et al (2010) prepared Nb doped $CaCu_3Ti_4O_{12}$ (CCTO) electroceramic using the solid state reaction method. Dielectric properties were measured in the frequency range of 1 MHz to 1 GHz. It was found that CCTO doped with 1 mol% Nb gave the highest dielectric permittivity of 18,000 at 1 MHz. Meanwhile, the lowest dielectric loss (0.31) at 1 MHz was given by CCTO doped with 10 mol% Nb. The dielectric permittivity between 10 MHz and 1 GHz was almost stable with values at around 500.

Kumar et al. (2011) synthesized the nano-particles of $CaCu_3Ti_4O_{12}$ by sol–gel route sintered at 1025°C with reduced sintering time and obtained CCTO samples with high dielectric permittivity ε~5000 and tanδ~0.37 at 10 Hz. The TEM images of the as calcined powder at 700°C showed large agglomeration of nano-particles. The average particle size was in the 50–150 nm range. The agglomeration may be due to strong inter-particle forces between the particles.

Omar et al (2012) synthesized $CaCu_3Ti_4O_{12}$ (CCTO) by conventional solid-state reaction technique. Dielectric permittivity of CCTO ceramic sintered at 1090 °C showed weak frequency dependence in the range of 100 Hz to 1 MHz and gave a value of 10^4 measured at room temperature and 100 Hz. While the samples sintered at 1140°C showed significant frequency dependence and gave a value of 10^5 for ε'. The dielectric loss was about 0.3 for the sample sintered at 1090 °C while it was close to 1 for the sample sintered at 1140 °C.

Kim et al (2013) studied the effect of doping Sn on the microstructure and dielectric properties of $CaCu_3Ti_{4-x}Sn_xO_{12}$. Samples were produced by a conventional solid-state reaction method. Sintering was carried out at 1115°C for 2-16 h in air. The formation of coarse grains with a reduced thickness of the boundary brought about an enhanced dielectric permittivity and a lower dielectric loss below ~1 kHz. Dielectric permittivity improved in the doped sample relative to the pure sample. At 1 kHz, the measured dielectric permittivity was around 71,300 for the pure sample, while for the doped sample it was about three times greater than that in the pure sample.

Jesurani et al. (2013) successfully prepared the giant dielectric permittivity Zr substituted CaCu3Ti4-xZrxO12 (CCTZO) with x = 0.00, 0.02, 0.10, 0.20 and 0.50 mol% nano powder by sol–gel technique with lower processing temperature from the metal nitrate solutions, titanium isoproxide and zirconium oxy chloride. XRD analysis confirmed the formation of a single phase material in the ceramics calcined at 800°C for 3 h. Formation of the barrier layers and presence of interfacial polarization gave rise to increased value of the dielectric permittivity. The effect of doping Zr [x = 0.02, 0.1, 0.2 and0.5 mol%] on the dielectric permittivity of the samples sintered at1020°C and 1040°C was studied. The high dielectric permittivities of these samples are 2960, 4190, 4610 and 6770 and the corresponding values of dielectric loss are 0.5, 1.0, 1.0 and 1.0. The results show that the highest dielectric permittivity at 50 Hz is achieved when the dopant concentration is 0.5 mol%. In the case of ceramic sintered at 1040°C, the value of x is 0.1.

Till now, many mechanisms have been put forward to explain the high dielectric permittivity of CCTO. Among these, the internal-boundary-layer-capacitor (IBLC) model is the most widely accepted one [Subramanian et al (2000); Hong and Kim (2007)]. According to the IBLC model, CCTO ceramic can be considered as a composite material composed of the n-type semiconducting grains connected by the insulating grain boundaries and the electrons in grain are inhibited by a depletion layer at the grain boundary. This induces a large polarization and results in high dielectric permittivity. The conducting electrons in the grain are mainly because of the formation and ionization of oxygen vacancies. In this process, the electrons re-leased from neutral oxygen vacancies will be accepted by Ti^{4+}, to produce Ti^{3+} ions [Subramanian et al (2000); Hong and Kim (2007)]. Therefore, the change in the concentration of oxygen vacancies may greatly influence the dielectric and electrical properties of CCTO. According to semiconductor physics, the concentration of oxygen vacancies and the electronic structure can be altered by replacing some ions by other ones having different valence states. Moreover, the effective dielectric permittivity is suggested to depend on the microstructure of the materials and is usually determined by the following relation:

$$\varepsilon_{eff} = \frac{\varepsilon_{gb}\, t_g}{t_{gb}} \qquad (1.4)$$

where ε_{gb} is the grain boundary permittivity and t_g and t_{gb} are the thickness of the grain and grain boundary respectively [Subramanian et al (2000); Grubbs et al (2005)]]. So doping significantly modifies the grain boundaries and results in increase in the dielectric permittivity and decrease in dielectric loss.

Most of the ceramics possess high stiffness, excellent thermal stability as well as high permittivity. But their brittleness, high density and challenging processing conditions creates limits in their use for practical applications. The polymers have advantages over ceramics because of their easy processing, mechanical flexibility and low cost.

Moreover, integration of capacitors into the internal structure of printed wiring boards (PWB), or, directly into integrated circuits packaging requires materials compatible with electronic circuits and should have adhesive properties. The polymers possesses these properties while the ceramics do not [Chahal et al (1998), Bhattacharya et al (2000), Prymark et al (2001),Ulrich et al (2003)]. Polymer matrix composites (PMC) get lot of attention because of their mechanical flexibility and tunable properties. Polymer matrix composites (PMC) also find so many applications in electromechanical devices as transducers to convert electrical energy to mechanical energy or vice versa. These devices can be used as smart skins for drag reduction, artificial muscles, actuators for active noise and vibration control and micro fluidic systems for drug delivery and micro-reactors [Bar-Cohen et al (2011); Zhang et al (2000); Nalwa et al (1995); Dario et al (2000)].

Low dielectric permittivity of polymers, in the range of 2–5 [Immergut et al 2008], impede their use in high ε' materials applications despite their excellent physical properties. Thus a key issue is to substantially enhance the dielectric permittivity of the polymers while retaining their excellent mechanical properties. Day by day, new strategies are being adopted to improve the dielectric permittivity of PMC. The most common one is the dispersion of high ε' fillers in polymers to make composites. The most common materials used for dispersion in polymers to make composites are metals [Popielarz et al (2001); Rao et al (2004); Pothukuchi et al (2004); Dang et al (2003); Lu et al (2006); Dang et al (2008); Li et al (2006)], ceramics [Ang et al (2003); Devara et al (2006); Bai et al (2000); Dias et al (1996); Bidstrup-Allen et al (2002); Cho et al (2004);], carbon based materials [Fan et al (2006); Moniruzzaman et al (2006); He et al (2009); Wang et al (2005); Dang et al (2007); Yao et al (2008); Jiang et al (2007); Xu et al (2007)] and organic fillers such as semiconducting olligomer [Achar et al (1982); Zhang et al (2002); Wang et al (2004); Huang et al (2005); Bobnar et al (2006)] and conducting polymers [Huang et al (2003); Li et al (2004); Wang et al (2008); Yuan et al (2008); Yuan et al (2010)].

By using conductive particles, high dielectric permittivity percolative polymer composites can be made in the vicinity of the percolation threshold. For example, polymer composites with high dielectric permittivity have been developed using highly conducting fillers such as metals and carbon nanotubes on the basis of percolation [Popielarz et al (2001); Pothukuchi et al (2004); Dang et al (2003); Zhang et al (2002); Wang et al (2004); Huang et al (2005); Li et al (2004); Yuan et al (2008)]. A permittivity value of 2000 has been reported for silver flakes-doped epoxy systems [Rao et al (2010)]. Dang et al. reported a value of 400 in Ni/PVDF composites [Dang et al (2003); Dang et al (2002)]. In using conductive fillers this drastic increase in dielectric permittivity, is always associated with significant increases in the electrical conductivity and dielectric loss due to the ‘insulator–conductor’ transition occurring at the percolation threshold (Fig 1.8). This transition also makes dielectric permittivity very sensitive to the content of the conductive fillers.

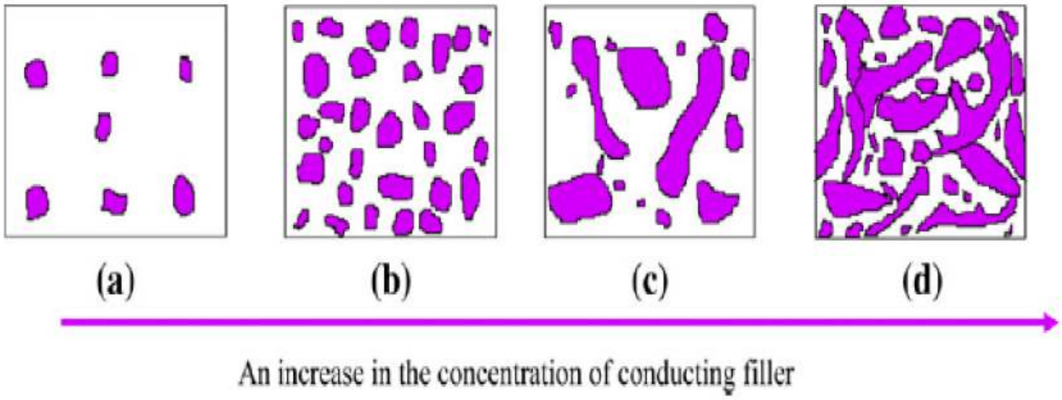


Figure1.8 Schemes showing the formation of a percolation-like clusters structure with an increase in the concentration of conducting fillers in the composite. (a) randomly dispersed grain structure; (b) uniformly dispersed grain structure; (c) aggregated grain structure; (d) percolation-like clusters structure [Nan (1993); Bruggeman (1935)].

In other words, a small deviation in the percolation threshold results in serious drop in the dielectric permittivity. This makes it very difficult to control the processing parameters. The issues mentioned above are considered as drawbacks for conducting fillers/polymer composite systems.

Now a days nanotubes also offer exciting opportunities for new high ε' polymer composites. Due to their superior electrical and mechanical properties, high ε' PMC can be developed at a very low filler content [Pothukuchi et al (2004); Dang et al (2003)]. Their superior dielectric properties can be attributed to higher surface area and larger aspect ratios they possess.

As a milestone, superior electrical properties of nanotubes possess superior electrical properties and offer exciting opportunities for new high ε' polymer composites. Apart from electrical properties, nanotubes also exhibit better mechanical strength [Pothukuchi et al (2004); Dang et al (2003)]. Superior dielectric properties of nanotubes composites can be attributed to their higher surface area and larger aspect ratios. Despite several good properties, agglomeration of nanotubes and their compatibility with the polymer matrices are prime concern for researchers in this field. Although several strategies are being adopted like modifications of the nanotubes to overcome these difficulties, yet it remains a challenge.

In general, polymer-ceramic composites are the most favored one. They are prepared by adding high permittivity ceramic fillers in polymer matrices [Ang et al (2003); Devara et al (2006); Bai et al (2000); Dang et al (2005); Dias et al (1996); Bidstrup-Allen et al (2002); Cho et al (2004); Dang et al (2006); Dang et al (2007);]. The advantages of these composites are high dielectric permittivity, relatively low dielectric loss and easy fabrication [Dang et al (2002); Bai et al (2000); Dang et al (2005); Dang et al (2008)]. So, polymer ceramic composites with high permittivity, low dielectric loss, good adhesive properties and good process compatibility have become promising candidates as dielectric materials for embedded capacitor applications. This is because high permittivity polymer ceramic composites provide an ideal solution to combine the dielectric and electrical properties of the ceramics and easy processability and mechanical flexibility of the polymer matrix [Popielarz et al (2001); Rao et al (2004); Pothukuchi et al (2004); Dang et al (2003); Ang et al (2003); Devara et al (2006); Bai et al (2000)]. Furthermore, good adhesive properties are additional advantage of PMCs over ceramics for their use in the embedded capacitor applications. However, a few drawbacks associated with polymer- ceramic composites are deterioration of mechanical and processing properties at higher concentration of rigid ceramic particles in the flexible polymer matrix.

To increase the dielectric permittivity of polymers, the several inorganic fillers are dispersed in the matrix. The dielectric permittivity of inorganic fillers, such as ceramics powders, $BaTiO_3$, $PbTiO_3$, $Pb(Zr,Ti)O_3$ (PZT), and $Pb(Mg1/3Nb2/3)O_3$–$PbTiO_3$ (PMN–PT) is very high. However, in most cases, even at very high filler concentrations the dielectric permittivity of the polymers could not exceed above 50. For embedded capacitor technology, polymer ceramic composites should have a dielectric permittivity of 50–200 to make layout area small enough for embedded capacitors in many cases such as for decoupling. To achieve dielectric permittivity above 50, high filler loadings more than 50 vol% are required, which drastically deteriorates the peel adhesion strength and thermal stress reliability of these composites, inhibiting their real application as an embedded capacitor. To make the high-ε composites useful, lower volume filler loading has to be used but this decreases the dielectric permittivity of the composites. Therefore, fundamental understanding of the adhesion and thermal stress reliability of these composites needs to be addressed in order to obtain high dielectric permittivity ($\varepsilon_r > 50$) embedded capacitor dielectrics which can successfully pass the adhesion, thermal stress reliability and mechanical tests [Bai et al (2000); Banno et al (1989); Daben et al (1990); Ngoma et al (1990); Das-Gupta et al (1991); Wei et al (1994); Chan et al (2001)]. Low dielectric permittivity of the composites with ceramic fillers at high loading can be attributed to the weak interfacial interaction, agglomeration and pores in the composites [Bai et al (2000); Kuo et al (2001); Gregorio et al (1996); Chan et al (1998); Dias et al (1996)]. In addition, mechanical properties of the composites deteriorate if the concentration of the fillers employed is high. Therefore, a new way must be developed to improve the dielectric permittivity of composites while maintaining the content of ceramic low.

Properties of PMCs, depend on the type of filler, type of matrix, as well as the way they are coupled. Coupling or bonding is called connectivity and was first introduced by Newnham [Newnham et al (1978)]. In case of two phase system, if a phase is self-connected in two directions, its connectivity is termed as 2, if a phase is self-connected in three directions, its connectivity is termed as 3 and so on. A binary composite connectivity is defined by combination of the terms m–n. Here m is for the connectivity of the active phase (filler) while n is for the connectivity of the inactive one (matrix). On the basis of connectivity, 10 different types of composites exist: 0–0, 0–1, 0–2, 0–3, 1–1, 1–2, 1–3, 2–2, 2–3, and 3–3.

Herein, the 0–0, 0–1, 0–2, and 0–3 connectivity patterns in Fig.1.9 are the dispersed grain structures in which the 0–0 pattern is equivalent to the dispersed grain structure and the 0–1, 0–2, and 0–3 patterns correspond to the dispersed grain structure. The 1–2, 2–3, and 1–3 connectivity patterns in Fig. 1.5 correspond to the aggregated grain structure in which the minor phase grains in the 1–3 pattern are aggregated in the form of single chain-like clusters and those grains in the 1–2 and 2–3 patterns are aggregated in the form of close-packed clusters. Similarly the 1–1 and 2–2 connectivity patterns are specific cases of aggregated grain structures in which the grains are aggregated along a definite direction as laminated structures. The 3–3 connectivity pattern stands for the percolation-like cluster structure in which the two phases form interpenetrating three-dimensional networks (percolation cluster). In the present work, the 0–3 [Wei et al (2007); Dasgupta and Doughty (1998); Arbatti et al (2007); Garner et al (2005); McLachlan et al (1990)] connectivity patterns are used to fabricate filler/polymer matrix composites.

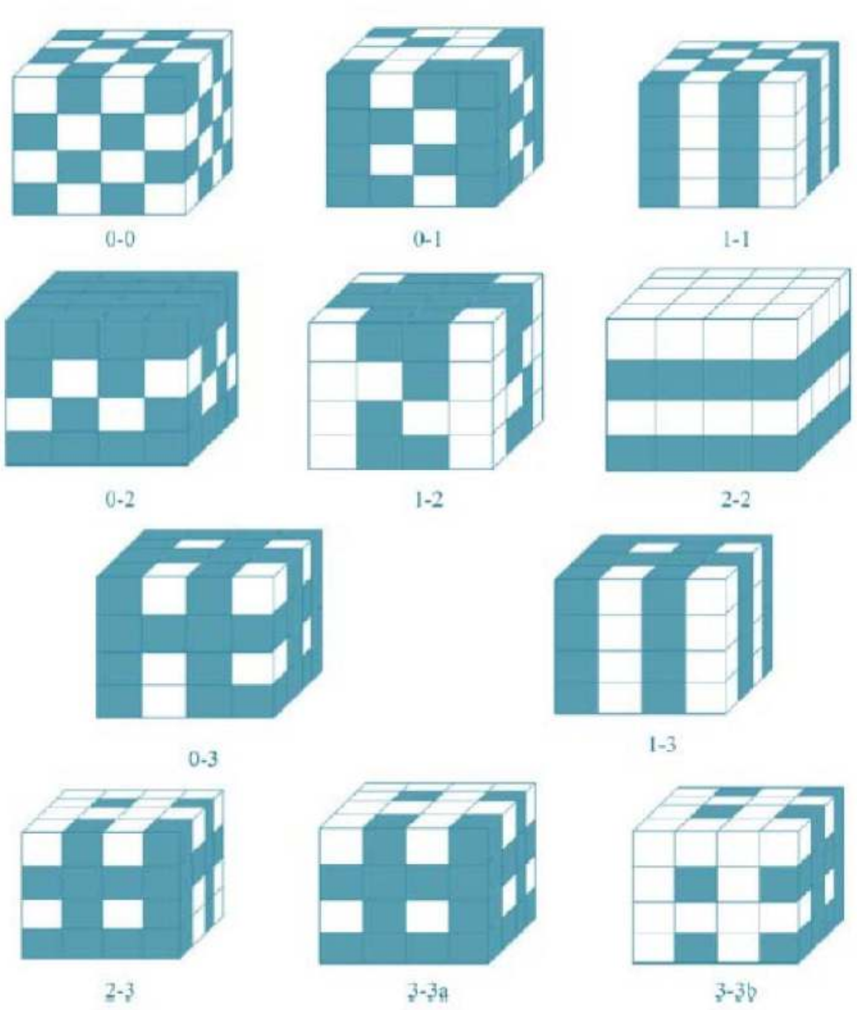


Figure 1.9 Ten connectivity patterns for two-phase composites [Nan (1993); Newnham et al (1978)].

Basically, a composite with 0-3 connectivity consists of particles connected in zero dimensions and a three dimensionally interconnected polymer matrix as shown in Figure 1.10. By the use of the right proportion of the constituent materials, the composite with 0-3 configuration can be fabricated with ease.

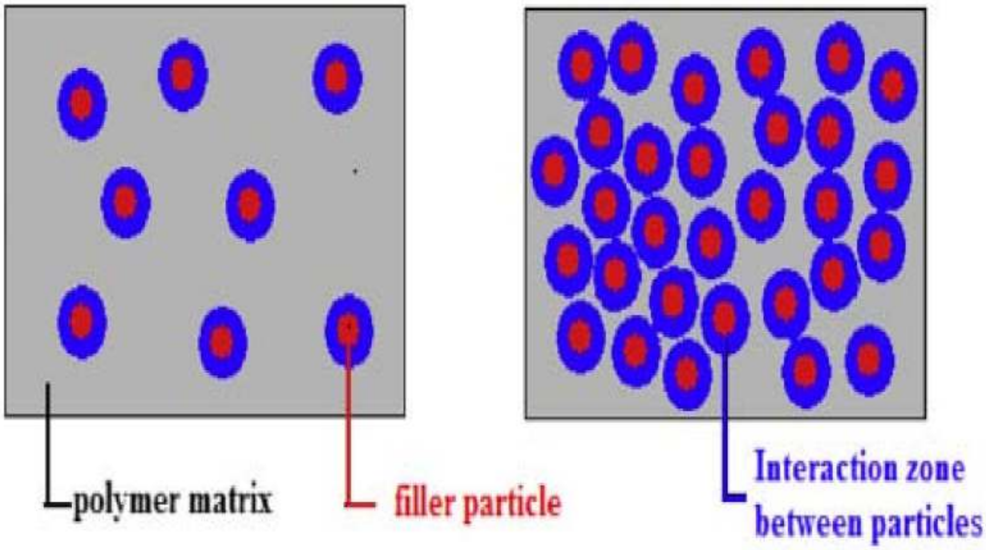
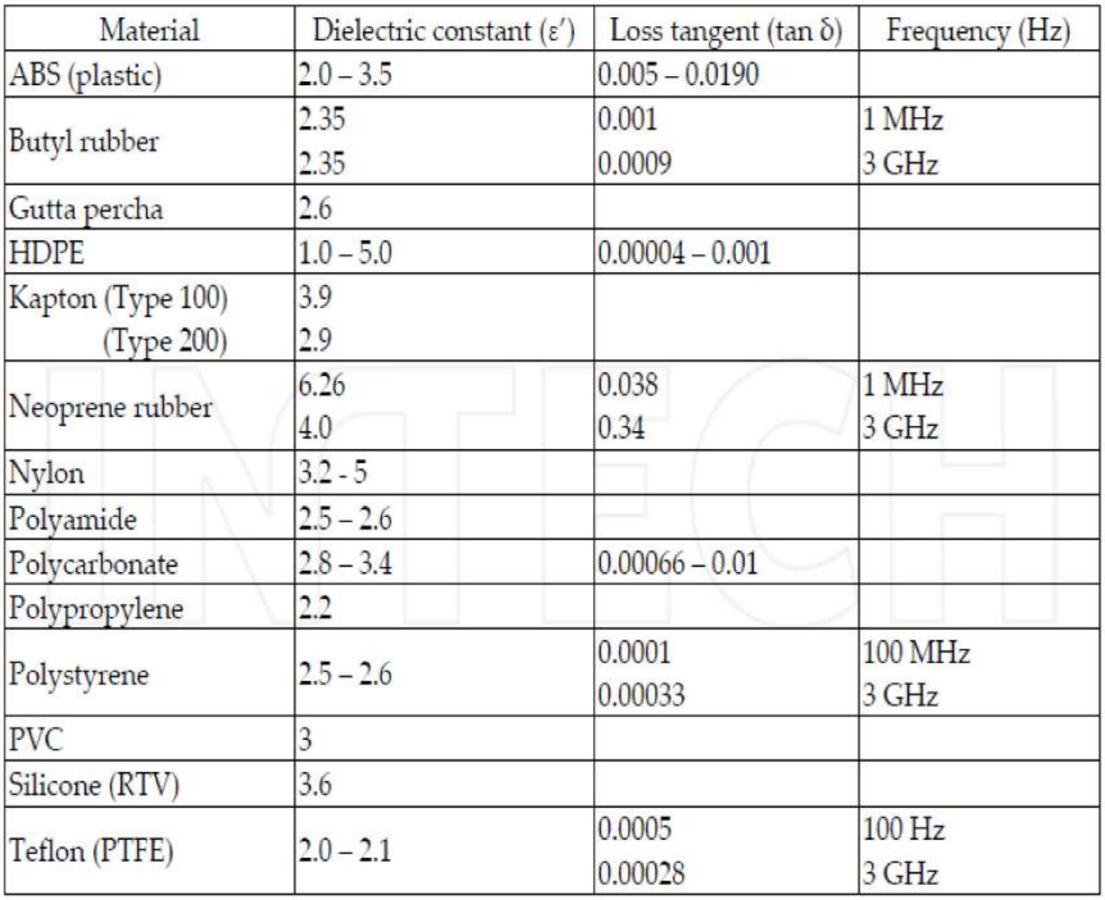


Figure 1.10 Composite with 0-3 configuration pattern [Dang et al (2012)].

Like fillers, different types of polymer matrices are also used. Choice of polymer matrix depends upon the type of application of the final product. Thermoplastic, thermoset [Dang et al (2008); Cho et al (2004); Dang et al (2008); Dang et al (2009)] and elastomer [Jiang et al (2007); Dang et al (2009)] are all good candidates to be used as matrix materials. Polyvinylidene fluoride (PVDF) is a semi-crystalline thermoplastic having remarkable thermal stability, high melting temperature, good chemical resistance, unique piezoelectric and pyroelectric characteristics. PVDF and PVDF copolymers show widespread technological applications in transducers, transistors, capacitors, and pipes for caustic chemicals. Furthermore, PVDF is an attractive polymer matrix for micro- and nanocomposites with superior mechanical and electrical properties [Xu et al (2007); Bar-Cohen (2001); Zhang et al (2000)]. The following Table 1.3 presents the dielectric permittivity and loss of some commercially used polymers.

Table 1.3 Dielectric parameters for some polymers at various frequencies [Dang et al (2008)].



Material	Dielectric constant (ε′)	Loss tangent (tan δ)	Frequency (Hz)
ABS (plastic)	2.0 – 3.5	0.005 – 0.0190	
Butyl rubber	2.35 2.35	0.001 0.0009	1 MHz 3 GHz
Gutta percha	2.6		
HDPE	1.0 – 5.0	0.00004 – 0.001	
Kapton (Type 100) (Type 200)	3.9 2.9		
Neoprene rubber	6.26 4.0	0.038 0.34	1 MHz 3 GHz
Nylon	3.2 - 5		
Polyamide	2.5 – 2.6		
Polycarbonate	2.8 – 3.4	0.00066 – 0.01	
Polypropylene	2.2		
Polystyrene	2.5 – 2.6	0.0001 0.00033	100 MHz 3 GHz
PVC	3		
Silicone (RTV)	3.6		
Teflon (PTFE)	2.0 – 2.1	0.0005 0.00028	100 Hz 3 GHz

In these composites filler concentration is very important parameter to control the dielectric permittivity. Several models like Maxwell's model [Maxwell 1954], Clausius-Mossotti model [Frolich 1949], Lichtenker rule [Nalwa 1995], effective medium theory (EMT) model [Rao et al (2000)] have been proposed to explain the dielectric behavior of ferroelectric ceramics and organic fillers dispersed polymer composites.

To predict the effective dielectric permittivity of the composites various models are used. The dielectric property of a diphasic dielectric mixture comprising of spherical crystallites with high dielectric permittivity dispersed in a matrix of low dielectric permittivity could be well described by Maxwell's model [Maxwell 1954]. According to this model, the effective dielectric permittivity of the composite is given by.

$$\varepsilon_{\text{eff}} = \frac{\delta_{\text{p}}\ \varepsilon_{p}\left({}^{2}/_{3} + {}^{\varepsilon_c}/_{3\varepsilon_p}\right) + \delta_c\ \varepsilon_c}{\delta_{\text{p}}\left({}^{2}/_{3} + {}^{\varepsilon_c}/_{3\varepsilon_p}\right) + \delta_c} \qquad (1.5)$$

where, ε_c, ε_p, δ_c and δ_p are the dielectric permittivity of ceramic, polymer, the volume fraction of the ceramic and the polymer respectively.

In the case of Clausius-Mossotti model [Frolich 1949], it is assumed that the mixture of dielectric is composed of spherical crystallites dispersed in a continuous medium. The effective dielectric permittivity (ε_{eff}) of the composite is given by the following equation.

$$\varepsilon_{eff} = \varepsilon_p\ [1 + 3\delta\left(\frac{(\varepsilon_c - \varepsilon_p)}{\varepsilon_c + 2\varepsilon_p}\right)] \qquad (1.6)$$

Lichtenecker's or logarithmic mixture rule is also used to predict the effective dielectric permittivity value [Nalwa 1995]

$$\text{Log}\ \varepsilon_{eff} = \delta_1 log\varepsilon_1 + \delta_2 log\varepsilon_2 \qquad (1.7)$$

The effective medium theory (EMT) model [Rao et al (2000)] has been developed taking into account the morphology of the particles. According to this model, the ε_{eff} is given by

$$\varepsilon_{eff} = \varepsilon_p[1 + \frac{f_c(\varepsilon_c - \varepsilon_p)}{\varepsilon_p + n(1 - f_c)(\varepsilon_c - \varepsilon_p)}] \qquad (1.8)$$

where f_c is the volume fraction of the ceramic dispersed, ε_c, ε_p and n are the dielectric permittivity of the ceramic, polymer and the ceramic morphology fitting factor respectively.

Chanmal et al (2008) prepared $BaTiO_3$ (10–30% by wt %) dispersed PVDF nanocomposites using simple melt mixing method. Dielectric permittivity of PVDF/ BaTiO3 nanocomposites increases with the increase in BaTiO3 content. It was found that dielectric permittivity measured at lower frequency is always greater than that of higher frequency. With the increasing frequency, dielectric permittivity decreases. In the studied frequency range 10^{-02} to 10^{+07} Hz, the decrease in dielectric permittivity of

PVDF/$BaTiO_3$ nanocomposites with increase in frequency is similar to that of PVDF. The frequency dependence of dielectric study indicates that introduction of $BaTiO_3$ increases the dielectric permittivity of the PVDF from about 11 to 25 at 30 wt% of $BaTiO_3$ content. In dielectric permittivity study, two relaxation processes are identified corresponding to the crystalline, glass transition in the PVDF/$BaTiO_3$ nanocomposites. The peaks shift to higher frequencies as the temperature is increased. In M'' spectra, two peaks are observed only at high temperature and low frequency whereas a single relaxation peak appears at low temperatures. The single relaxation peak appearing at low temperatures is the α_c relaxation attributed to crystalline chain relaxation in PVDF and the second relaxation peak which appears only at high temperatures and at a frequency lower than α_c relaxation is identified as MWS relaxation.

Ramajo et al (2008) studied the dielectric behavior of composite materials (epoxy resin – barium titanate and epoxy – CCTO) as a function of ceramic amount. Composites were prepared by mixing the components and pouring them into suitable moulds. Dielectric measurements were performed from 20 Hz to 1 MHz and 30 to 120 °C. It was demonstrated that the epoxy – CCTO composites possessed higher permittivity than the classic epoxy – $BaTiO_3$ composites. Dielectric permittivity of CCTO composites was higher than the ones of $BaTiO_3$ / epoxy composites. Values of $\varepsilon' = 10$ was obtained for 15 vol (%) of CCTO particles. Dielectric permittivity increased with the temperature due to the higher mobility of polymer chains.

Dang et al (2009) synthesized CCTO/Polyimide (PI) hybrid films by in situ polymerization. They reported dielectric permittivity value of 49 when the concentration of CCTO filler reaches 40 vol% at 10^2 Hz, which is 14 times larger than that of a pure PI matrix, while the film is still flexible and has good thermal stability. They compared their results with $BaTiO_3$/PI film with 40 vol% $BaTiO_3$ loading. Dielectric permittivity of the $BaTiO_3$/PI film with 40 vol% $BaTiO_3$ loading is only 18.6 at 10^2 Hz. Improvement of dielectric permittivity of the CCTO/PI hybrid films is more significant than that of the $BaTiO_3$/PI films. The dependence of the dielectric permittivity of the CCTO/PI hybrid films on frequency at room temperature is very less upto 20 vol%, when the concentration of CCTO is 30 vol%, the permittivity has a weak frequency dependency. But when the concentration of CCTO is more than 40 vol% strong frequency dependence of the dielectric permittivity was observed. Namely, the permittivity decreases dramatically with an increase in frequency. However, in comparison with composites loaded with conductive fillers, the decrease of the permittivity with the change of frequency here is less. This phenomenon was attributed to the semiconductive characteristic of the CCTO filler.

Thomas et al (2010) prepared Poly(vinylidene fluoride)/$CaCu_3Ti_4O_{12}$ (CCTO) nanocrystal composite films (thickness = 85 µm) by the solution casting followed by spin coating technique with relatively high dielectric permittivity (90 at 100Hz). The structural, the microstructural and the dielectric properties of the composites were studied using X-ray diffraction, Scanning Electron Microscope and Impedance analyzer respectively. The effective dielectric permittivity (ε_{eff}) of the composite increased with increase in the volume fraction of CCTO at all the frequencies (100 Hz to 1MHz) under investigation. The room temperature dielectric permittivity which is around 90 at 100 Hz, increased to about 290 at 125°C (100Hz). The PVDF+CCTO-30% nanocomposite showed higher dielectric permittivity than that of pure PVDF and the other composites under study. The relaxation processes associated with these composites were attributed to the interfacial polarization or MWS effect. Though there is an improvement in the dielectric permittivity, the decrease in dielectric breakdown strength may limit its use for high voltage applications. These results may be exploited in the development of high energy density capacitors.

Zak et al (2011) prepared poly(vinylidene fluoride) / lead zirconate titanate nanocomposite (PVDF/PZT-NPs) by mixing fine $Pb(Zr_{0.52},Ti_{0.48})O_3$ nanoparticles (PZT-NPs) with PVDF solution under ultrasonication. The nanocomposites exhibited good dielectric stability over a wide frequency range. The effective dielectric permittivity (ε) increased at all frequency as the PZT-NPs were added to the matrix under study. The effective dielectric permittivity obtained was higher than that of pure PVDF but much lower than that of the pure PZT-NPs. Dielectric permittivity obtained for PVDF/ PZT-NPs composite was 11.10 at 100 Hz and room temperature.

Thomas et al (2011) prepared polymer–ceramic composite by incorporating the giant dielectric permittivity material, $CaCu_3Ti_4O_{12}$ (CCTO) in Poly(vinylidene fluoride) (PVDF) polymer matrix by melt mixing and hot pressing process. The effective dielectric permittivity (ε_{eff}) of the composite increased with increase in the volume fraction of CCTO at all the frequencies (100 Hz–1 MHz) under study. The dielectric loss did not show any variation up to 40% loading of CCTO but showed an increasing trend beyond 40%. The room temperature dielectric permittivity as high as 95 at 100 Hz has been realized for the composite with 55 vol.% of CCTO which has increased to about 190 at 150^0 C. Theoretical models like Maxwell's, Clausius–Mossotti, Effective medium theory, logarithmic law and Yamada were employed to rationalize the dielectric behaviour of the composite and discussed. Among the various models used for rationalizing the dielectric behaviour, experimental ε_{eff} at higher volume fractions regime is comparable with those obtained with the models like EMT (n = 0.11) and Yamada (n = 9.3) and the difference between the experimental data and the predicted value is less than 10%.

Yang et al (2011) investigated the microstructure and dielectric properties of composites comprising polyvinylidene fluoride (PVDF) and calcium copper titanate (CCTO). Nano- and microsized CCTO were employed separately and investigated comparatively. The effective dielectric permittivity (ε') of the composite containing 40 vol.% nanosized CCTO filler is over 10^6 at 10^2 Hz and room temperature, which is substantially higher than that of the composite containing microsized CCTO, of which the ε_r value is 35.7 (with 4 0 vol.%). The ε', and loss tangent ($\tan\delta$) decrease with temperature for the composite containing nanosized CCTO, while the one with microsized CCTO shows the opposite tendency. For the composite with nanosized CCTO, the conductivity decreases sharply with increasing temperature in the low frequency range (10^0–10^4 Hz) and slightly increases in the high frequency range while the conductivity of the composite with microsized CCTO is nearly independent of temperature. Theoretical analysis also shows that the dielectric performance of the composite with nanosized CCTO does not follow the conventional mixing rules and the giant dielectric permittivity comes mainly from the interfacial polarization. The dielectric properties of the composite containing microsized CCTO matches well with the Maxwell–Garnett and effective medium theory models indicating insulating interfaces between the fillers and the matrix. The results obtained in this study indicate that the composite containing microsized CCTO may be suitable for embedded device applications, while the one with nanosized CCTO may find a new application as a temperature sensor.

Thomas et al (2012) fabricated poly (methyl methacrylate) (PMMA)/ $CaCu_3Ti_4O_{12}$ (CCTO) composite by melt mixing followed by hot pressing. The solid state reaction route was adopted for synthesizing CCTO ceramic. Structural, morphological and dielectric properties were characterized. The dielectric permittivity recorded for CCTO at 10 kHz is 2500 and the loss is 0.04 respectively. ε' of the composites increased when the CCTO content increased in the PMMA matrix. The dielectric permittivity of PMMA is around 4.9 at 100Hz which increased to 15.7 at 100Hz when the ceramic content increased to 40 vol %. At low frequencies, space charge polarization is dominant. The loss value obtained at 100 Hz for PMMA+CCTO-40 vol % composite is around 0.094 and it has decreased to 0.0094 at 10MHz.

Zhang et al (2012) fabricated nanocomposite thin film, in which nanosized $CaCu_3Ti_4O_{12}$ (CCTO) particles are used as filler and P(VDF–TrFE) 55/45 mol % copolymer was used as polymer matrix. The contents of CCTO in the nanocomposites range from 0% to 50 vol%. The dielectric property of these nanocomposites was characterized at frequencies ranging from 100 Hz to 1 MHz and at temperatures ranging from 200 K to 370 K. A dielectric permittivity of 62 with a loss of 0.05 was obtained in the nanocomposite with 50 vol% CCTO at room temperature at 1 kHz. At the phase transition temperature (~340 K) of the copolymer, a dielectric permittivity of 150 with a loss less than 0.1 was obtained in this nanocomposite. It was found that the dielectric loss of the nanocomposites was dominated by the polymer which had a relaxation process. As compared to composites made using microsized CCTO, the nanocomposites exhibit a much lower dielectric loss and a lower dielectric permittivity. This indicates that the nanosized CCTO particles have a lower dielectric permittivity than the microsized CCTO particles.

Goyal et al (2013) prepared barium titanate ($BaTiO_3$) filled polymethylmethacrylate (PMMA) composites using the simple solution method followed by hot pressing. The content of $BaTiO_3$ was varied from 0 to 65 vol. %. Scanning electron microscopy showed good dispersion and adhesion of $BaTiO_3$ with the PMMA matrix. The dielectric permittivity of the composites increased with increasing content of $BaTiO_3$. The dielectric permittivity and dissipation factor of 45 vol.% composite measured at 1 MHz were 27.3 and 0.0296, respectively. The microhardness increased approximately 4.7-fold for 65 vol % of the filler. Dielectric permittivity of the composites measured at 1 MHz increased approximately to 69 for 65 vol% of $BaTiO_3$. Dissipation factor of the composites varied between 0.021 and 0.029, but it increased abruptly to a value of 0.0528 for 65 vol.% composite.

Su et al (2013) prepared $Na_{0.5}Bi_{0.5}Cu_3Ti_4O_{12}$ (NBCTO)/poly(vinylidene fluoride) (PVDF) composites with various NBCTO volume fractions via solution mixing and hot pressing process. The structure, morphology, and dielectric properties of the composites were characterized. The dielectric permittivity (ε) and dielectric loss ($\tan \delta$) of the composites were both found to increase with increasing NBCTO volume fraction within the frequency range of $1–10^6$ Hz at room temperature. Relatively high dielectric permittivity of 79.8 and low loss of 0.21 at 1 kHz were obtained for the NBCTO/PVDF composite with 50 vol% NBCTO. Additionally, theoretical models like Logarithmic mixture rule, Maxwell–Garnet, Effective medium theory, and Yamada model were also employed to predict the dielectric permittivity of these composites. The values obtained by the EMT model are in close agreement with the experimental values.

Luo et al (2014) prepared calcium barium zirconate titanate ($Ba_{0.95}Ca_{0.05}Zr_{0.15}Ti_{0.85}O_3$, BCZT) ceramic particles by a conventional solid-state method. BCZT powders were modified by dopamine through a chemical coating method. The composite flexible films based on dopamine BCZT and polyvinylidene fluoride were fabricated via a solution casting method. The dielectric permittivity increased with the increase of BCZT contents, while the loss tangent remained constant in the frequency range of 10^3 to 10^5 Hz. The dielectric permittivity and the loss of dopamine at BCZT/PVDF composite films as a function of the BCZT content were measured over the frequency range of 40 Hz to 10 MHz at room temperature. It was found that the dielectric permittivity increased with the increase of dopamine BCZT contents and slightly decreased with the increase of frequency. When the loading of BCZT particles was over 41 vol%, the dielectric permittivity increased rapidly with the increasing dopamine BCZT contents. With the increasing frequency from 40 Hz to 10 MHz, the dielectric permittivity of composites decreases yet it could remain above 20 even at a high frequency of 10 MHz. The dielectric permittivity of the samples with 61 vol% BCZT at 1000 Hz increased to 100 from that of the neat PVDF samples which is 4. Meanwhile, the dielectric loss tangent remained quite low in the frequency range from 1000 Hz to 10^5 Hz. It is also observed that the dielectric loss of the 52 vol % and 61 vol% dopamine BCZT/PVDF composites decreased compared with that of the dopamine BCZT/PVDF composites at 4 and 22 vol%. It could be explained by the fact that dopamine reduced the concentration and mobility of ionizable hydroxyl groups on the surface of BCZT particles resulting in the decrease of the leakage current. The dielectric loss tangent in the frequency range from 40 to 100 Hz was high confirming the existence of interfacial polarization.

Roy et al (2014) prepared $(Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO_3$-polyvenylidene fluoride (BNBT06-PVDF) 0-3 composite samples by solution cast method at an elevated temperature having 10, 20 and 30 volume percentage of BNBT06 powder. They studied effective complex relative permittivity and ac conductivity of these composites. SEM micrographs of the fractured surfaces showed that the particle distribution in the grains is not strictly homogeneous. Some areas of agglomeration of particles in the grains are also seen in the micrographs. The resulting data for room temperature real and imaginary parts of relative permittivity as well as real part of ac conductivity showed an increasing trend with increasing volume fraction of the ceramic filler. The 30 vol. % of BNBT06-PVDF composite had the highest dielectric permittivity of 75.3 and loss tangent ~0.08.

From the literature survey it has been found that lot of work has been done on $BaTiO_3$ and pure $CaCu_3Ti_4O_{12}$ dispersed polymer composites, but not much work has been done on modified CCTO. There were few problems associated with these composites.

- In the case of $BaTiO_3$ dispersed polymer composites dielectric permittivity could not be increased beyond 50, even at a very high content of loading.
- In the case of pure CCTO dispersed polymer composites, high dielectric permittivity has been achieved, but at a very high content of loading i.e. 55 or 60 vol %.
- Higher content of ceramic loading results in the deterioration of mechanical properties, due to agglomeration and porosity.
- It has been reported that increasing content of ceramic, adversely affects the adhesive properties of PMCs.
- To achieve dielectric permittivity above 50, high filler loadings more than 50 vol% are used to be done, which drastically deteriorates the peel adhesion strength of these composites, inhibiting their real application as an embedded capacitor.
- As ceramics are mostly hydrophilic in nature, at high content of ceramic in the composites remain hydrophilic, this is not good for electronics instruments. Any trace of moisture trapped or absorbed will dramatically alter the desired dielectric properties.
- It has also been reported that with the increase in CCTO content, dielectric permittivity of the composites start showing frequency dependence due to the semiconductive characteristic of the CCTO filler.
- Earlier studies on these polymer ceramic composites were confined to dielectric properties and lacked study of their mechanical properties.