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## INTRODUCTION

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### 1.1 Dielectric materials and their technological importance *in modern industry*

Electrical insulator materials which will prevent the flow of current in an electrical circuit are being used since from the beginning of the science and technology of electrical phenomena. Dielectrics are insulating materials that exhibit the property of electrical polarization, thereby they modify the dielectric function of the vacuum.

The first capacitor was constructed by Cunaeus and Mussachenbroek in 1745 which was known as Leyden jar [1]. But there were no studies about the properties of insulating materials until 1837. Faraday published the first numerical measurements on these materials, which he called dielectrics [2]. *He* has found that the capacity of a condenser was dependent on the nature of the material separating the conducting surface. This discovery encouraged further empirical studies of insulating materials aiming at maximizing the amount of charge that can be stored by a capacitor. Throughout most of the 19<sup>th</sup> century, scientists searching for insulating materials for specific applications have become increasingly concerned with the detailed physical mechanism governing the behavior of these materials. In contrast *to* the insulation aspect, the dielectric phenomena have become more general and fundamental, as it has the origin with the dielectric polarization.

Mossotti [3, 4] and Clausius [5] have done a systematic investigation about the dielectric properties of materials. They attempted to correlate the specific inductive capacity, a macroscopic characteristic of the insulator introduced by Faraday [2] which is now popularly termed as dielectric constant with the microscopic structure of the material. Following Faraday in considering the dielectrics to be composed of conducting spheres in a non-conducting medium, Clausius and Mossotti succeeded in deriving a relation between the real part of the dielectric constant  $\epsilon_r$  and the volume fraction occupied by the conducting particles in the dielectric.

In the begning of 20<sup>th</sup> century, Debye [6] realized that some molecules had permanent electric dipole moments associated with them, and this molecular dipole moment is responsible for the macroscopic dielectric properties of such materials. Debye succeeded in extending the Clausius -Mossotti theory to take into account the permanent

moments of the molecules, which allowed him and others to calculate the molecular dipole moment from the measurement of dielectric constant. His theory was later extended by Onsager [7] and Kirkwood [8, 9] and is in excellent agreement with experimental results for most of the polar liquids. Debye's other major contribution to the theory of dielectrics is his application of the concept of molecular permanent dipole moment to explain the anomalous dispersion of the dielectric constant observed by Drude [10]. For an alternating field, Debye deduced that the time lag between the average orientation of moments and the field becomes noticeable when the frequency of the field is within the same order of magnitude as the reciprocal relaxation time. This way the molecular relaxation process leads to the macroscopic phenomena of dielectric relaxation, i.e., the anomalous dispersion of the dielectric constant and the accompanying absorption of electromagnetic energy over certain range of frequencies.

Debye's theory shows excellent agreement with the experiments for the polar liquids while the dielectric behaviour for solids was found to be deviating considerably. Several modifications and extensions of Debye's theory have been proposed to correct this. There are two major approaches in the extension of Debye's theory. The first approach, pioneered by Cole [11], Davidson [12] and Williams [13], interprets the non-Debye relaxation behavior of the material in terms of the superposition of an exponentially relaxing process, which then leads to a distribution of relaxation times. The second approach by Joncher [14] proposes that the relaxation behaviour at the molecular level is intrinsically non-Debye-like due to the cooperative molecular motions.

After more than eighty years of development, the theory of dielectrics is still a active area for research. Understanding the behaviour of dielectric materials with the variations of field, temperature and frequency is of particular importance for present day electronics. Modern day electronics demand dielectric materials with narrowly defined properties tailored for particular applications. The scaling of metal-oxide-semiconductor (MOS) devices for ultra large-scale integration (ULSI) applications has been placing an ever-increasing burden upon the performance of gate dielectrics [15]. Durability has become an issue as the dielectric thickness is decreased leading to a search for dielectrics with better properties than the conventional SiO<sub>2</sub> dielectric. The gallium arsenide (GaAs) based metal - insulator- semiconductor field effect transistor (MISFET) is still largely unavailable due to the lack of a suitable dielectric material for the insulation layer [16]. Recent advances in wireless communication technologies have elevated the interest in materials with the unusual combination of properties like high dielectric constant, low

dielectric loss and low values of temperature dependence of dielectric constant [17]. The constant need for miniaturization provides a continuing driving force for the discovery and the development of increasingly sophisticated materials to perform the same or improved function with decreased size and weight. The dielectric materials mentioned above are used as the basis for resonators and filterers for the microwaves carrying the desired information [18]. These materials are presently employed as bulk ceramics in microwave communication devices. They are not integrated into the microelectronics but are being used as discrete components. The need for better dielectrics with improved properties suitable for modern integrated manufacturing needs is the motivation behind the present study.

## 1.2 Theory of dielectrics

This section presents a brief description of the atomic interpretation of the dielectric and optical properties of insulator materials on the basis of classical theory. This section is essentially concerned with the static dielectric constant, the frequency dependence of dielectric constant and dielectric losses.

### 1.2.1 Electric susceptibility and permittivity

It was Michael Faraday who first noticed that when a capacitor of value  $C_0$  under vacuum is filled with a dielectric material, its charge storage capacity (capacitance) increases to a value of  $C$ . The ratio  $\chi'$  of the increase of capacitance  $\Delta C = C - C_0$  to its initial capacitance-  $C_0$ ,

$$\chi' = \frac{C - C_0}{C} = \frac{\Delta C}{C_0} \quad (1.1)$$

$\chi'$  is called the electrical susceptibility of the dielectric. The most often used terminology is the dielectric permittivity or dielectric constant instead of susceptibility, which is defined as the ratio of the capacitance  $C$  of the capacitor filled with a dielectric to the value  $C_0$  of the same capacitor under vacuum.

$$\epsilon_r = \frac{C}{C_0} \quad (1.2)$$

From the above equations the relationship between the electric susceptibility and the dielectric permittivity is given as:

$$\chi' = \epsilon_r - 1 \quad (1.3)$$

Thus, by definition, the electric susceptibility and permittivity are non-dimensional real quantities. The dielectric constant or permittivity of a material is a measure of the extent to which the electric charge distribution in the material can be distorted or polarized by the application of an electric field.

### 1.2.2 Mechanism of electric polarization

At the atomic level, all matter consists ultimately of positively and negatively charged particles whose charges balance each other macroscopically in the absence of an electric field giving rise to overall charge neutrality. Once the electric field is applied, the balances of charges are perturbed by the following four basic polarization mechanisms [19].

**Electronic polarization:** It occurs in neutral atoms when an electric field displaces the nucleus with respect to the negative charge. Thus electronic polarization is an induced polarization effect.

**Atomic/ionic polarization:** It is observed when different atoms that comprise a molecule share their electrons asymmetrically, and cause the electron cloud to be shifted towards the stronger binding atom, the atoms acquire charges of opposite polarity and an external field acting on these net charges will tend to change the equilibrium positions of the atoms themselves, leading to the atomic polarization.

**Dipolar/orientational polarization:** When an ionic bond is formed between two molecules by the transfer of some valence electrons, a permanent dipole moment will originate in them. This permanent dipole moment is equal to the product of the charges of the transferred valence electrons and the inter-atomic distance between them. In the presence of an electric field  $E$ , the molecules carrying a permanent dipole moment will orient to align along the direction of the electric field  $E$ . This process is called the dipolar or orientational polarization. This occurs only in dipolar materials possessing permanent dipole moments.

**Space charge polarization:** It is present in dielectric materials which contain charge carriers that can migrate for some distance through the bulk of the material (via diffusion, fast ionic conduction or hopping, etc.) thus creating a macroscopic field distortion. Such a distortion appears to an outside observer as an increase in the capacitance of the sample and may be indistinguishable from the real rise of the dielectric permittivity. Space charge polarization is the only type of electrical polarization that is accompanied by macroscopic charge transport (and in the case when the migrating charge carriers are ions a macroscopic mass transport as well). In general, the space charge polarization can be

grouped into hopping polarization and interfacial polarization. In dielectric materials, localized charges (ions and vacancies, or electrons and holes) can hop from one site to another site, which creates the hopping polarization. Similarly the separation of the mobile positive and negative charges under an electric field can produce an interfacial polarization.

### 1.2.3 Polarization and dielectric constant

The ability of a dielectric material to store electric energy under the influence of an electric field, results from the field-induced separation and alignment of electric charges. Polarization occurs when the electric field causes a separation of the positive and negative charges in the material. The larger the dipole moment arms of this charge separation in the direction of a field and the larger the number of these dipoles, the higher the material's dielectric permittivity.

In the presence of electronic, ionic and dipolar polarization mechanisms, the average induced dipole moment per molecule  $P_{av}$  will be the sum of all the contributions in terms of the local field (effective field) acting on each individual molecule.

$$P_{av} = \alpha_e E_{loc} + \alpha_i E_{loc} + \alpha_d E_{loc} \quad (1.4)$$

Here,  $\alpha_e$ ,  $\alpha_i$ ,  $\alpha_d$  are the electronic, ionic and dipolar polarizabilities.  $E_{loc}$  is the local field or the effective field at the site of an individual molecule that causes the individual polarization. Each effect adds linearly to the net dipole moment of the molecule. Interfacial polarization cannot be simply added to the total polarization as  $\alpha_{ij}E_{loc}$  because it occurs at the interfaces and cannot be put into an average polarization per molecule in bulk. Moreover, the fields are not well defined at the interfaces.

For simple dielectrics ( eg. gases) one can take the local field to be the same as the macroscopic field. This means that  $E_{loc}=E$  the applied field and therefore the polarization is,

$$P = \chi_e \epsilon_e E = (\epsilon_r - 1) \epsilon_0 E \quad (1.5)$$

$P = N \cdot P_{av}$  where  $N$  is the number of atoms or molecule per unit volume [20].

$$\epsilon_r = 1 + N\alpha/\epsilon_0 \quad (1.6)$$

$\alpha$  is the polarizability of the molecule.

### 1.2.4 Clausius and Mossotti relation for dielectric permittivity

Consider a molecule of a dielectric medium situated in a uniform electric field  $E$ . The total electric field acting on this molecule  $E_{loc}$  will have three main components-  $E_1$ ,  $E_2$ , and  $E_3$ . Here  $E_1$  is the applied electric field  $E$ ,  $E_2$  is the field from the free ends of the dipole chain and  $E_3$  is the near field arising from the individual molecular interactions. In solids we have to consider the actual effective field acting on a molecule in order to estimate the dielectric permittivity. For electronic and ionic polarization, the local field for cubic crystals and isotropic liquids can be given by the Lorentz field, given by

$$E_{loc} = \frac{1}{3\epsilon_0} P \quad (1.7)$$

By assuming the near field  $E_3$  is zero, Clausius and Mossotti derived a relation for the dielectric constant of a material under electronic and ionic polarization [21].

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{1}{3\epsilon_0} (N_i \alpha_i + N_e \alpha_e) \quad (1.8)$$

Here,  $\epsilon_r$  is the relative permittivity at low frequencies,  $\alpha_i$  is the effective ionic polarizability per ion pair,  $N_i$  is the number of ions pair per unit volume,  $\alpha_e$  is the electronic polarizability and  $N_e$  is the number of ions (or atoms) per unit volume exhibiting electronic polarization. The atomic/ionic polarizability  $\alpha_i$  and the electronic polarizability  $\alpha_e$  cannot be separated at low frequencies and hence they are together represented as the induced polarizability  $\alpha_{ind}$

Hence equation 1.8 can be written as:

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{1}{3\epsilon_0} (N_m \alpha_{ind}) \quad (1.9)$$

This is known as the clausius –Mossotti equation for non polar dielectrics.

Above the frequencies of ionic polarization relaxation, only electronic polarization will contribute to the relative permittivity, which will be lowered to  $\epsilon_{r\infty}$  (relative permittivity at optical frequencies).

$$\frac{\epsilon_{r\infty} - 1}{\epsilon_{r\infty} + 2} = \frac{N_e \alpha_e}{3\epsilon_0} \quad (1.10)$$

By using the Maxwell relation for a lossless (non-absorbing), non magnetic medium,

$$n^2 = \epsilon_{r\infty} \quad (1.11)$$

where  $n$  is the index of refraction of the material, equation (1.10) can be rewritten as:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{N_e \alpha_e}{3\epsilon_0} \quad (1.12)$$

In this form, it is known as Lorentz-Lorenz equation. It can be used to approximate the static dielectric constant  $\epsilon_r$  of non polar and non magnetic materials from their optical properties. In the case of dipolar materials we cannot use the simple Lorentz field approximation and hence the Clausius–Mossotti equation cannot be used in the case of dipolar materials.

### 1.2.5 Debye theory for polar dielectrics

In addition to the induced polarization present in all dielectrics, the polar dielectrics possess an orientational polarization that exists even in the absence of an applied electric field. It should be noted that the polarizability  $\alpha_o$  corresponding to the orientational polarization is related to the orientation of the molecules which are heavier than that of atoms or electrons that are involved in induced polarization. Hence the  $\alpha_o$  contributes to the total molecular polarizability  $\alpha$  at much lower frequencies than  $\alpha_{ind}$  does. So the dielectric constant that remains after the relaxation of orientational polarization (the dielectric constant due to the induced polarization) can be designated separately and it is usually represented by  $\epsilon_\infty$  in the case of dipolar dielectrics. So the equation (1.9) can be written as:

$$\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \frac{N_m}{3\epsilon_0} \alpha_{ind} \quad (1.13)$$

To account for the orientational contribution to the dielectric constant, Debye [22] used classical Boltzmann statistics and the Langevin function  $L(y) = \coth y - \frac{1}{y}$  from the theory of paramagnetism, to estimate the temperature dependence of permanent dipole orientation. Assuming that these dipoles do not interact with each other, Debye derived the following equation for the orientational polarizability.

$$\alpha_o = \frac{\mu^2}{3KT} \quad (1.14)$$

Using Clausius-Mosotti's internal field argument discussed above, this additional polarization contributes to the static dielectric constant according to the following formulae:

$$\frac{\varepsilon^1 - 1}{\varepsilon^1 + 2} = \frac{N_m}{3\varepsilon_0} \alpha_{ind} + \frac{N_d}{3\varepsilon_0} \alpha_o \quad (1.15)$$

Here  $N_d$  is the number of dipolar molecules per unit volume which is same as  $N_m$ .

This equation can be rewritten in the following form using equation (1.13).

$$\frac{\varepsilon^1 - 1}{\varepsilon^1 + 2} - \frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} = \frac{N_d \mu^2}{9\varepsilon_0 KT} \quad (1.16)$$

This result, from Debye [23], has been used successfully to predict the static dielectric constant of many polar gases and polar liquids. However, when applied to the condensed state of matter, Debye's theory breaks down while predicting the infinite dielectric susceptibility (Mosotti catastrophe). The reason for this breakdown lies in the assumption that is made in the expression for the Clausius-Mosotti local field. The near field in this case is assumed to be zero. In the condensed phase, permanent dipoles tend to lose their individual freedom of orientation through association and steric hindrance. Their interaction with their surroundings has to be taken into account and the near field cannot be neglected.

### 1.2.6 Onsager theory

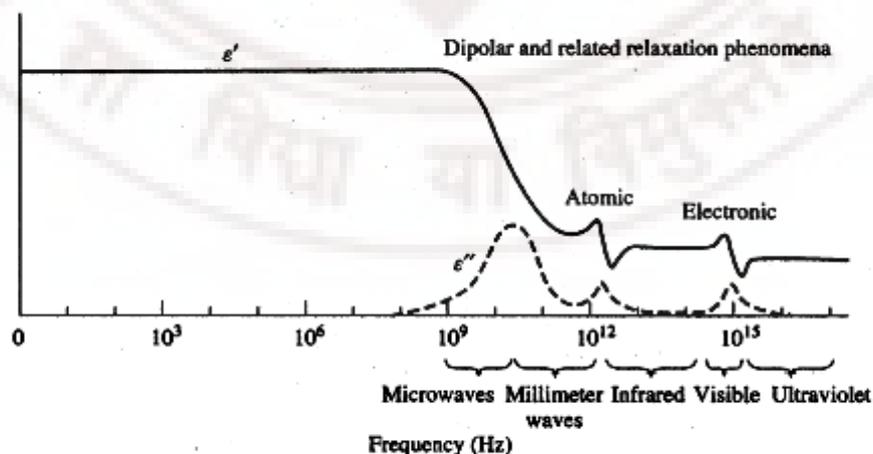
To avoid the Mosotti catastrophe, Onsager modified the Debye theory by introducing a cavity. In his new approach to the problem, the electric field was represented by the sum of a 'cavity field' and a 'reaction field'. If the surroundings of each molecule are considered to be a homogeneous continuum having the macroscopic properties of the substance, then the 'cavity field' is the field inside a cavity of molecular dimensions due to a uniform external field. This cavity field is the field in the cavity resulting from the polarization induced in the surrounding medium by the molecule in the cavity. This part of the field exerts no torque on the molecule. Onsager's molecular model consisted of a sphere with a permanent dipole moment and an isotropic polarizability. Based on this model he arrives at the following expression, linking the molecular dipole moment with the static dielectric constant:

$$\frac{\varepsilon^1 - 1}{\varepsilon^1 + 2} - \frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} = \frac{3\varepsilon^1(\varepsilon_\infty + 2)}{(2\varepsilon^1 + \varepsilon_\infty)(\varepsilon^1 + 2)} \frac{N_d \mu^2}{9\varepsilon_0 KT} \quad (1.17)$$

Onsager's relation is quite well satisfied for non associated polar liquids [24, 25] and can also be applied to weakly bound Van der Waals solids. In general, most of the solid dielectrics do not obey any of the local field expressions at sufficiently low frequencies due to the charge carriers present in these materials, mostly ions, but possibly also electrons. This renders any meaningful measurement of the low frequency dielectric permittivity very difficult, making the comparison with local field theory rather doubtful.

### 1.2.7 Dielectric loss

The permittivity of a dielectric material has both real and imaginary mathematical representations. The imaginary part of permittivity is represented in mathematical equations as  $\epsilon''$ . This imaginary part of permittivity describes the energy loss from an AC signal as it passes through the dielectric. The real part of permittivity,  $\epsilon'$  is also called the dielectric constant and relative permittivity. The permittivity of a material describes the relationship between an AC signal's transmission speed and the dielectric material's capacitance. When the word "relative" is used in front of permittivity, the implication is that the number is reported relative to the dielectric properties of a vacuum. The imaginary part of the dielectric permittivity which is a measure of how much field is lost as heat during the polarization of a material by an applied alternating electric field is also termed as dielectric loss. The characteristic orientation of the dipoles in an electric field results in a frequency variation of dielectric constant and loss over a broad band of frequencies. The typical behavior of real and imaginary part of the permittivity as a function of frequency is shown in Figure 1.1 [26].



**Figure 1.1** Frequency dependence of dielectric permittivity for an ideal dielectric material.

The relative permittivity of material is related to a variety of physical phenomena that contribute to the polarization of the dielectric material. In the low frequency range the  $\epsilon''$  is dominated by the influence of ion conductivity. The variation of permittivity in the microwave range is mainly caused by dipolar relaxation, and the absorption peaks in the infrared region and above, are mainly due to atomic and electronic polarizations.

The dielectric properties of solid dielectrics at microwave and radio frequencies are highly influenced by the ionic positions and changes caused by the lattice vibrations. Two types of dielectric losses are identified in crystalline solids at high frequencies, namely intrinsic losses and extrinsic losses. The dielectric dispersion in solids depends on the factors such as ionic masses, electric charge/valence state of the ions, spring constant of the bond, lattice imperfections etc. The dielectric losses close to the lattice vibration frequencies are generally estimated in terms of the anharmonicity of lattice vibrations. The low frequency phonons are responsible for the intrinsic dielectric losses in solid dielectrics. The intrinsic loss mechanism occurs due to the interaction between the phonons and the microwave field or due to the relaxation of the phonon distribution function. The lattice phonon modes will determine intrinsic limits of the high frequency dielectric losses in crystalline solids. The extrinsic losses are occurred due to the interaction between the charged defects and the microwave fields.

### 1.2.8 Complex dielectric permittivity and Maxwell equations

In case of dielectric polarization, the polarization of the material is related to the electric field by:

$$P = \epsilon_0 \chi_e E \quad (1.18)$$

This leads to:

$$D = \epsilon_0 (1 + \chi_e) E = \epsilon_0 \epsilon_r E \quad (1.19)$$

For real materials D can be described as[27]:

$$D = (\epsilon - j\epsilon_p) E \quad (1.20)$$

Here,  $\epsilon = \epsilon_0 \epsilon_r$ , the real part of permittivity, and  $\epsilon_p = \epsilon_0 \epsilon''$  is a factor describing the dielectric (polarization) losses.

For a region filled with homogeneous isotropic material, the first Maxwell equation can be written as:

$$\nabla \times H = \frac{\partial D}{\partial t} + \sigma E \quad (1.21)$$

Here,  $\sigma$  is the conductivity of the material. Substituting for D from equation [1.20] the equation (1.21) becomes:

$$\nabla \times H = i\omega(\epsilon - i(\epsilon_p + \sigma / \omega))E \quad (1.22)$$

The complex dielectric constant is defined as below:

$$\epsilon^* = \epsilon - i(\epsilon_p + \sigma / \omega) \quad (1.23)$$

Here,  $\epsilon$  is the real part of the permittivity and is defined as:

$$\epsilon = \epsilon_r \epsilon_0 \quad (1.24)$$

Here  $\epsilon_r$  is known as the relative permittivity or dielectric constant and  $\epsilon_0$  is the permittivity of free space. Here the first and second term in the imaginary part of the complex permittivity represent the dielectric and ohmic losses respectively [28].

The loss tangent is given as:

$$\tan \delta = \frac{\epsilon''}{\epsilon'} \quad (1.25)$$

In this thesis  $\epsilon_r$  is used throughout to represent relative permittivity of the materials and  $\tan \delta$  is used to represent a measure for the dielectric loss.

### 1.3 Classification of Dielectric materials

Dielectric materials can be classified into two major categories: Linear (normal dielectric) materials and non linear dielectric materials. The linear dielectric materials can be again subdivided into three classes based on the mechanism of electric polarization as non polar and dipolar materials.

#### 1.3.1 Linear dielectric materials

The dielectric materials which are exhibiting a linear relationship between the polarization and applied electric field are known as linear dielectrics. This class of materials gets polarized with the application of the field and gets depolarized on the

removal of field. Based on the nature of the polarization mechanism, the linear dielectrics can be grouped as follows [29]:

**Non polar materials:** In materials of this class, an electric field can cause only elastic displacement of the electron cloud (mainly the valence electron cloud). So they have only electronic polarization. Such materials are generally referred to as elemental materials.

**Polar materials:** In materials of this class an electric field can cause only elastic displacement of electron clouds as well as elastic displacement of the relative positions of ions. These materials have both electronic and ionic polarization. The material may be composed of molecules and each of the molecules is made of more than one kind of atom without any permanent dipole moment. Examples of such materials are ionic crystals; in this case the total polarizability is the sum of the ionic and electronic polarizabilities.

$$\alpha = \alpha_e + \alpha_i \quad (1.26)$$

**Dipolar materials:** The materials of this class have all three fundamental polarizations: electronic, ionic and orientation. Thus the total polarizability for them is

$$\alpha = \alpha_e + \alpha_i + \alpha_o \quad (1.27)$$

Materials, whose molecules possess a permanent dipole moment, belong to this class examples are water, methyl alcohol.

### 1.3.2 Non linear dielectric materials

The materials which have got a spontaneous polarization even in the absence of an external field are grouped into the class of non linear dielectrics. The spontaneous polarization appears in these class of materials due to its crystal structure. A necessary condition for a solid to fall in the class of non linear dielectrics is the absence of a center of symmetry. Among the 32 crystal classes, 11 of them have a center of symmetry and hence they won't exhibit spontaneous polarization. Out of the remaining 21 classes of crystals without a centre of symmetry, 20 of them are piezoelectric, ie these crystals can be polarized under the influence of an external stress. Ten out of the 20 piezoelectric crystals exhibit the pyroelectric effect, ie the polarization of these classes of materials can be changed with the change of temperature. The ferroelectric materials discussed below are part of the spontaneously polarized pyroelectrics.

### **1.3.3 Ferroelectric Materials:**

A ferroelectric material is a non-linear dielectric that exhibits a remanent polarization in the absence of an external electric field and its direction can be switched by an applied electric field [30]. The name ferroelectricity comes from the similarities between polarizations of ferroelectric materials with the magnetization of ferromagnetic materials. Ferroelectric materials display a hysteresis effect of polarization with an applied field. The hysteresis loop is caused by the existence of permanent electric dipoles in the material. When the external electric field is initially increased from zero value, the polarization increases as more of the dipoles are lined up along the direction of the field. When the field is strong enough, all dipoles are lined up with the field, so the material is in a saturation state. If the applied electric field decreases from the saturation point, the polarization also decreases. However, when the external electric field reaches zero, the polarization does not reach zero. The polarization at the zero fields is called the remanent polarization. When the direction of the electric field is reversed, the polarization decreases. When the reverse field reaches a certain value, called the coercive field, the polarization becomes zero. By further increasing the field in this reverse direction, the reverse saturation can be reached. When the field is decreased from this saturation point, the sequence just reverses itself.

In a ferroelectric material a transition occurs from a centro symmetric to a non-centro symmetric unit cell at the Curie point  $T_c$ . The shift in structural symmetry affects both the structural and physical properties of the crystal. Ferroelectricity can be maintained only below the Curie temperature. When the temperature is higher than  $T_c$ , a ferroelectric material is in its paraelectric state. Ferroelectric materials have great application potential in developing smart electromagnetic materials, structures, and devices, including miniature capacitors, electrically tunable capacitors, filters and phase shifters in recent years. Their application in the microwave frequencies are still under intensive investigations.

### **1.4 Tunable dielectrics**

The dielectric materials, which have a voltage-dependent dielectric constant, are termed as tunable dielectric materials [31]. Generally this class of materials exhibits a large change in dielectric constant with an applied DC electric field. The major classes of materials being considered for tunable dielectric applications are ferroelectrics in their paraelectric state. The ferroelectric materials (FE) have been investigated in the microwave range since the 1950s. Only recently, monolithically compatible processing of

certain ferroelectric thin-film compounds become possible, and has generated great interest and promises for designing a new class of tunable microwave devices. For a microwave engineer the main attraction of a tunable material is the strong dependence of their dielectric permittivity  $\varepsilon$  on the applied bias electric field  $E_0$ . This characteristic is commonly described by a parameter named tunability  $n$ , defined as the ratio of the permittivity of the material at zero electric field  $\varepsilon(0)$  to its permittivity at some non-zero electric field  $\varepsilon(E)$  as given by equation (1.28). The relative tunability  $n_r$  is defined by equation (1.29) [31].

$$n = \frac{\varepsilon(0)}{\varepsilon(E)} \quad (1.28)$$

$$n_r = \frac{\varepsilon(0) - \varepsilon(E)}{\varepsilon(0)} \quad (1.29)$$

The dielectric loss of a tunable dielectric material is also dependent on the applied DC electric field. Experiments show that a ferroelectric material with higher loss tangent usually has larger tunability. Since the loss tangent of a material is an important factor affecting the performances of the electric circuit, in the development of electrically tunable ferroelectric microwave devices, a figure of merit  $K$  ( $K$ -factor), defined by  $K = \text{Tunability} / \tan \delta$

$$K = \frac{\varepsilon(0) - \varepsilon(E)}{\varepsilon(0)} \times \frac{1}{\tan \delta} \quad (1.30)$$

is often used to indicate the quality of the tunable dielectric materials. Usually, in the calculation of  $K$ , the loss tangent at the maximum external DC electric field is used [32].

#### 1.4.1 Tunable materials for microwave devices

Microwave materials have been widely used in a variety of applications ranging from communication devices to satellite services, and the study of their properties at microwave frequencies and the development of functional microwave materials have always been among the most active areas of solid-state physics, materials science, and electrical and electronic engineering. In recent years, the increasing requirements for the development of high speed and high frequency circuits and systems made a thorough understanding of the properties of materials at microwave frequencies a necessity [33].

The wireless systems operating in the microwave region is required to be lightweight, compact and of low cost, which could be addressed by miniaturization and integration. Meanwhile, the need of frequency agile applications demands the use of low loss, and highly tunable devices to allow multi-bandwidth operation with little impact on the component count. Microwave tunable passive devices mainly include filters, phase shifters, delay lines and matching circuits in connection with applications such as reconfigurable antennas, software defined radios, etc [34, 35]. Implementing several separate transceiver circuits in a single hardware device increases the component count and hence the overall cost. Therefore in terms of RF front end circuitry, significant cost saving can be achieved by using electronically tunable components. In this scenario a single tunable component is employed to replace several fixed components. For example, a band pass filter (BPF) with a tunable pass band could replace several fixed filters or a tunable delay line could replace a set of fixed delay lines in the beam-forming network of a phased array antenna [36].

Electronically tunable capacitors known as varactors can be used to fabricate reconfigurable components for RF and microwave applications [37]. The established technology for microwave varactors is based on semiconductors typically employing GaAs or silicon technology. The varactor diodes are now a proven technology for tunable microwave devices [38]. Another advantage of varactor diodes fabricated on silicon substrates is that they are easily incorporated in the standard complementary metal oxide semiconductor (CMOS) integrated circuit processes. However the semiconductor varactor diodes have smaller power handling capability and the silicon based varactors are more lossy above 10GHz frequency [39].

Micro electro mechanical system (MEMS) technology can also be used to fabricate varactors [40]. The advantage of MEMS varactors include high power handling and low inter modulation distortion. However MEMS devices require a careful packaging and reliability is an issue due to mechanical moving parts. Further, MEMS devices have a lower tuning speed than semiconductor varactors.

The ferroelectric material Barium strontium titanate (BST) is of particular interest for tunable microwave devices since it has a high dielectric constant that can be tuned by applying an electric field, and it exhibits relatively low losses at microwave frequencies [41]. The high dielectric constant is useful for minimizing the size of the component fabricated from BST, leading to higher integration. Another useful property of BST is that the microwave dielectric properties can be tailored for specific application by controlling

the ratios of barium and strontium according to the formula  $Ba_xSr_{1-x}TiO_3$ . BST is being explored as a tunable dielectric material for varactor fabrications. BST varactors have some important advantages over semiconductor varactors including higher power handling and lower cost. It has been shown that BST varactors have lower device losses than silicon based varactors at frequencies above 10GHz [42].

There are several ferroelectric materials that have been considered as possible candidates for tunable microwave devices. The most attention has been paid to  $SrTiO_3$  and its solid solutions with  $BaTiO_3$  and  $PbTiO_3$  [43]. The bulk form of  $SrTiO_3$  exhibits large tunabilities at cryogenic temperatures while at room temperature a large electric field is required for its tuning [44]. Voltage tunable  $(Ba,Sr)TiO_3$  thin films and ceramics have been extensively investigated due to their high power handling capacity and large tunability over a wide frequency range. Thin films of BST type materials are desirable, because they can be easily integrated with standard IC processing procedures and can therefore be scaled for mass production [45]. In addition to barium strontium titanate (BST), lead strontium titanate (PST) has been proposed as a potential candidate material for high frequency tunable devices [46]. Ferroelectric sodium potassium niobium oxide  $Na_xK_{(1-x)}NbO_3$  is another candidate material considered for the tunable applications[47]. It is a continuous solid solution of  $KNbO_3$  and  $NaNbO_3$ , having a perovskite structure for  $x < 0.97$ . The dielectric properties of these ceramics were well studied by many researchers. The NKN thin films deposited on various oxide substrates have shown high dielectric permittivity and voltage tunability. Because of their excellent crystallinity and electrical properties, NKN films were studied for memory and tunable microwave device applications.

#### **1.4.2 Tunable devices based on BST**

BST is essentially a solid solution of  $BaTiO_3$  and  $SrTiO_3$ .  $BaTiO_3$  is in the ferroelectric (polar) phase at room temperature, and has a ferroelectric to paraelectric transition temperature (Curie point) of  $130 \pm \text{ }^\circ\text{C}$ , while  $SrTiO_3$  is a paraelectric (non-polar) down to zero Kelvin [48]. For microwave applications, it is generally suggested that BST thin films should be in the paraelectric phase at room temperature. In the paraelectric phase, BST has simultaneously high tunability and relatively low dielectric loss at microwave frequencies [31]. At room temperature the paraelectric phase can be achieved by adjusting the chemical composition so that  $x = 0.5$  in  $Ba_xSr_{1-x}TiO_3$ . In the ferroelectric polar phase, BST is also piezoelectric, and dielectric losses in this phase are

associated with mechanical damping caused by domain wall motion [48]. This results in high dielectric loss at microwave frequencies. Many research groups implemented tunable filters and phase shifters based on BST thin films over the past 10 years.

At NASA, Glenn centre, Subramanyam et al [49,50] have fabricated a YBCO/SrTiO<sub>3</sub> thin film based K-band tunable band pass filter on lanthanum aluminates substrate. The two-pole filter had a center frequency of 19 GHz and a bandwidth of 4%. Tunability was achieved through the nonlinear temperature dependence as well as the electric field dependence of dielectric constant of SrTiO<sub>3</sub> thin films. BST thin film based low pass and band pass filters were reported by Tombak et al[51]. These circuits have used lumped inductors and tunable BST capacitors. Jayesh Nath et al[52] reported a tunable third order combline band pass filter using BST varactors fabricated on sapphire substrates. The application of a 0-200V DC bias varied the center frequency of the filter from 2.44 to 2.88 GHz (16% tuning) with 1 dB bandwidth of 400 MHz. The insertion loss varied from 5.1 dB at zero bias to 3.3 dB at full bias. An electronically tunable impedance transformer and matching network were fabricated using BST capacitors on sapphire substrates by Chen et al [53]. The impedance transformer was able to vary electronically from a 4:1 to 2:1 transformation in a 50 ohm environment. BST based microwave filters have already been commercialized. Paratek Microwave Inc has commercialized two types of BST based band pass filters [54]. Filters based on hybrid microstripline configuration ( $f \sim 2\text{GHz}$ ) and finline waveguide resonator configurations ( $f \sim 22.5\text{GHz}$ ) both employing BST thin films have been reported. The first device is a 4 pole microstrip combline band pass filter with tunable BST capacitors.

The first phase shifter using BST was reported by Flaviis in 1997[55]. Bulk BST with thickness of 0.1 to 0.15 mm was used in the microstripline circuits. In 1999 Van Keuls et al[56] reported a thirteen segment Ku band coupled microstrip phase shifters, in which BST based interdigitated capacitors were used as the series coupling components. S.Lee et al[57] demonstrated an X-band loaded transmission line type phase shifter by using BST thin films. The phase shifter consisted of coplanar waveguide (CPW) lines that are periodically loaded with voltage tunable BST varactors. The voltage tunable BST varactors showed a large dielectric tunability of 69% and a quality factor of 29.5 at a frequency of 10 GHz. The most comprehensive work on phase shifters based on ferroelectric thin films has been carried out by York et al [58, 59] at the University of California, Santa Barbara. They have reported several phase shifters using parallel plate and interdigital BST capacitors. Moon et al [60] fabricated a phased array antenna using

four element ferroelectric phase shifters with CPW transmission line structures based on BST thin films. This X-band phased array antenna system with the ferroelectric BST phase shifters was capable of having a beam steering of  $15^\circ$  in either direction.

#### **1.4.3 Need for non ferroelectric tunable materials**

Till date, almost exclusively, BST and  $\text{SrTiO}_3$  have been investigated for tunable microwave application. Most of the literature on RF applications of tunable dielectrics has focused on the  $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$  (BST) thin films, and numerous devices and circuit demonstrations have been reported [61,62]. A promising RF performance has been achieved but in general, the RF losses of BST-based devices are high. All these tunable dielectric materials investigated till date fall under the group of ferroelectrics and they exhibit temperature dependent structure and dielectric properties. They also exhibit the phenomena of hysteresis in their ferroelectric state. The dielectric properties of ferroelectric thin films are found to be highly thickness dependent. All these things put together make such materials lossier at microwave frequencies. If one can employ a non ferroelectric material for tunable microwave application, one can avoid the loss originating from the coupling of the soft modes with electromagnetic fields which is a characteristic feature of all ferroelectrics. Also, ferroelectric thin films are vulnerable to the process related strain and impurities, which in effect would increase the dielectric losses in these thin films [31]. These limitations of the ferroelectric thin films enhance the search for non ferroelectric tunable materials having low loss at the microwave frequencies, even if the tunability is relatively lower since the low losses could lead to higher K factor.

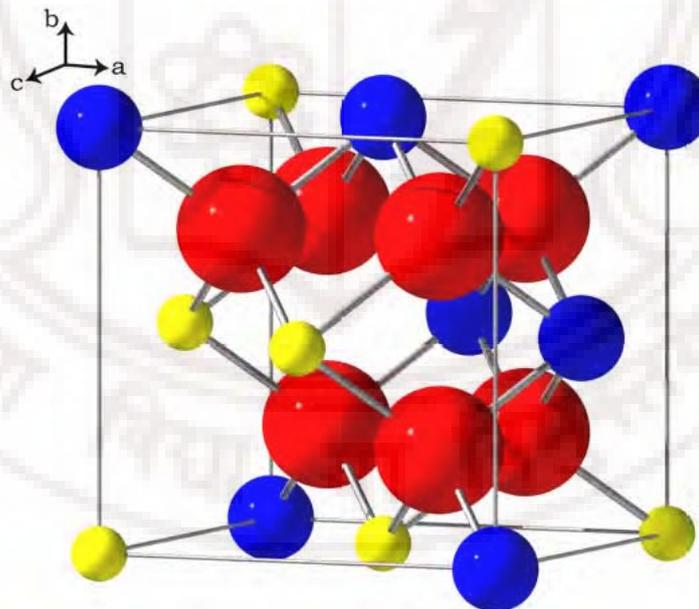
#### **1.4.4 Bismuth Zinc Niobate as a possible non ferroelectric tunable material**

Bismuth based pyrochlore ceramics were discovered in the early 1970s and have attracted additional study during the last 10 years due to their possible applications in high frequency capacitors and microwave resonators [63]. Recently, researchers are showing much interest in the ternary oxides of the  $\text{Bi}_2\text{O}_3\text{-ZnO-Nb}_2\text{O}_5$  (BZN) system which exhibit a high dielectric permittivity ( $\epsilon_r$ ), relatively low dielectric loss ( $\tan\delta$ ), and a compositionally tunable temperature coefficient of capacitance ( $\tau_c$ ) [64]. These properties, combined with lower sintering temperatures (less than  $950^\circ\text{C}$ ), make these materials attractive candidates for high frequency filter applications and in multilayered capacitors based on co-fired ceramic structures [65]. There are two main phases in the  $\text{Bi}_2\text{O}_3\text{-ZnO-Nb}_2\text{O}_5$  system:  $\text{Bi}_{1.5}\text{Zn}_{1.0}\text{Nb}_{1.5}\text{O}_7$  (c-BZN) with cubic pyrochlore structure, in

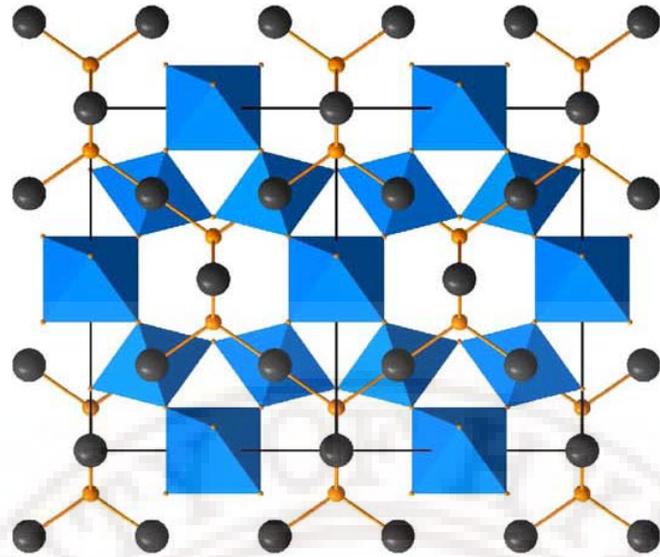
which at least some Zn atoms occupy A site positions with  $\epsilon_r \sim 160$  at room temperatures and  $\text{Bi}_2\text{Zn}_{2/3}\text{Nb}_{4/3}\text{O}_7$  (m-BZN) which has  $\epsilon_r \sim 80$  with a monoclinic zirconolite like structure.  $\text{Bi}_2\text{O}_3$ -  $\text{ZnO}$ - $\text{Nb}_2\text{O}_5$  based pyrochlore ceramics are presently being considered as smart microwave material because of their unique dielectric properties in the microwave range. It is one of the few non ferroelectric material known today exhibiting voltage dependent dielectric permittivity. Because of being non ferroelectric, this material exhibits low loss and high figure of merit in the microwave frequency region.

#### 1.4.5 Crystal chemistry of BZN

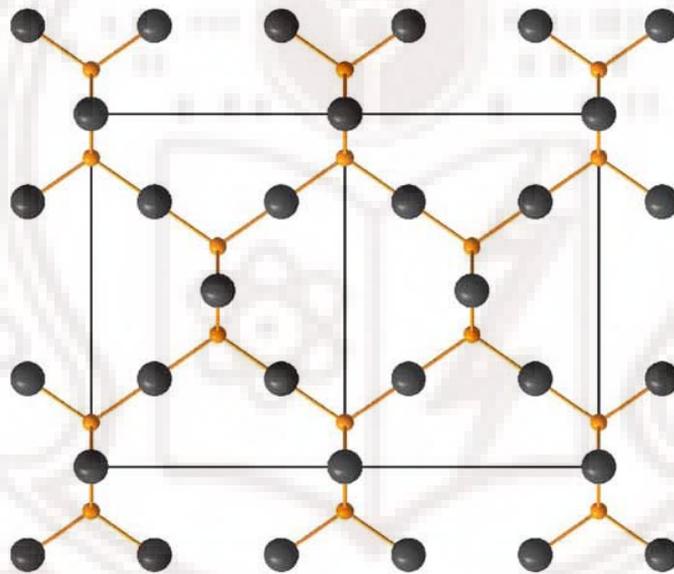
The bismuth zinc niobate has got the pyrochlore structure. The pyrochlore structure belongs to one of the oxygen octahedron based families. The general formulae for the oxide pyrochlores can be written as  $\text{A}_2\text{B}_2\text{O}_7$ . The A cations are eight coordinated and the B cations are six coordinated [67]. In spite of the immense flexibility of chemical composition in the pyrochlore system, a cubic structure with eight molecules per unit cell ( $Z=8$ ) and space group  $\text{Fd}\bar{3}\text{m}$  is the predominant phase.



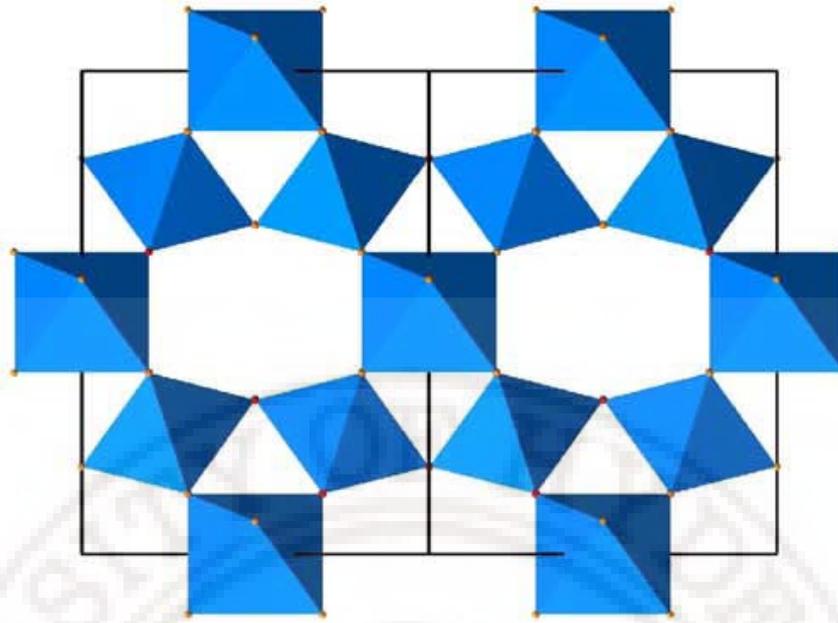
**Figure 1.2** The Pyrochlore structure (1/8 unit cell). Large blue spheres are ' $\text{A}^{3+}$ ' ions, small yellow spheres are ' $\text{B}^{4+}$ ' ions, and large red spheres are ' $\text{O}^{2-}$ ' ions.



**Figure 1.3** Ideal pyrochlore  $A_2B_2O_6O'$  crystal structure in the  $Fd\bar{3}m$  space group [77] showing black A atoms, orange  $O'$  and the network of corner-connected  $BO_6$  octahedra (blue).



**Figure1.4** A view of the tetrahedral  $A_2O'$  sub lattice [77]



**Figure 1.5.** A view of the  $B_2O_6$  sub lattice [77].

The  $A_2B_2O_7$  pyrochlore structure is often described by the formula  $B_2O_6.A_2O'$  (where  $O'$  is the oxygen atom attached only to the A cations) which emphasises that the structure is built of two interpenetrating networks:  $BO_6$  octahedra sharing the vertices from a three dimensional network resulting in large cavities which contain the  $O'$  and A atoms in an  $A_2O'$  tetrahedral net, as shown in figures 1.2-1.5. The A cations are randomly displaced by  $\sim 0.39\text{\AA}$  from the ideal eightfold coordinated positions. The displacement occurs along the six  $\langle 122 \rangle$  directions perpendicular to the  $O'-A-O'$  links. In addition, the  $O'$  ions are randomly displaced by  $\sim 0.46\text{\AA}$  along all twelve  $110$  directions. In the compound with the pyrochlore structure, noncubic symmetry occurs frequently in the case when A cations are with inert lone pairs of electron such as  $Bi^{3+}$ ,  $Pb^{2+}$  and so on [66]. The BZN family is one of the large and rapidly growing group of inherently disordered cubic  $A_2B_2O_7$  cubic pyrochlore. Apart from the cubic structure, the BZN pyrochlore can also exist in a monoclinic zirconolite-like structure with four molecules per unit cell ( $z=4$ ) with  $C2/c$  space group. The cubic pyrochlore phase that has the chemical composition  $Bi_{1.5}ZnNb_{1.5}O_7$  is termed as c-BZN and a monoclinic zirconolite-like pyrochlore that has the chemical composition  $Bi_2Zn_{2/3}Nb_{4/3}O_7$  is termed as m-BZN. Many research groups have actively studied the structure and dielectric properties of the BZN ceramics. A brief overview of some of the important studies on the BZN ceramics reported by various research groups is given below.

X.Wang et al [67] have investigated the structure, phase transformation and dielectric properties of  $\text{Bi}_2\text{O}_3\text{-ZnO-Nb}_2\text{O}_5$  systems. They have identified two-distinct phases in this system having the composition  $\text{Bi}_{1.5}\text{Zn}_{1.0}\text{Nb}_{1.5}\text{O}_7$  (c-BZN) and  $\text{Bi}_2\text{Zn}_{2/3}\text{Nb}_{4/3}\text{O}_7$  (m-BZN) respectively. The c-BZN has got a cubic pyrochlore structure with a unit cell volume of  $1117\text{\AA}^3$  and a theoretical density of  $7.11\text{g/cm}^3$ . The m-BZN ceramic has got a monoclinic structure with a cell volume of  $583\text{\AA}^3$  and a theoretical density of  $7.94\text{g/cm}^3$ . The c-BZN ceramics had a dielectric constant about 170,  $\tan\delta < 0.0004$  and a temperature coefficient of capacitance  $T_c -400\text{ppm/}^\circ\text{C}$ . The m-BZN ceramics had a dielectric constant of 80,  $\tan\delta < 0.0004$  and a temperature coefficient of capacitance about  $+150\text{ppm/}^\circ\text{C}$ . The local symmetry of the c-BZN ceramics as well as the  $\text{Sn}^{4+}, \text{Ti}^{4+}$  substituted BZN ceramics was studied by Liue et al [68]. The structural properties of the B site substituted c-BZN ceramics are found to be remarkably similar to that of c-BZN ceramics it self. The underlying crystal chemistry of BZN and BZN related pyrochlore is shown to result from strong local Bi/Zn ordering rules and associated large amplitude structural relaxation. Frequency dispersion associated with the dielectric relaxation phenomena in polycrystalline c-BZN ceramics was analyzed by Nino et al [69]. Measurements at cryogenic temperatures and at high frequencies reveal a broad distribution of relaxation times in these ceramics. The dielectric loss data could be modeled using a function convoluting the Vogel-Fulcher law and Gaussian distribution.

The complex dielectric responses of the c-BZN [70] ceramics were investigated between 100Hz to 100 THz by Kamba et al. They have observed a dielectric relaxation over a wide frequency and temperature range. The dielectric permittivity and loss maxima shift to the higher temperature values as the frequency increases. The relaxation is assigned to the local hopping of atoms in the A and  $\text{O}^1$  positions of the pyrochlore structure among the several potential minima. Temperature dependence of the reflectance of the cubic bismuth pyrochlores  $\text{Bi}_{3/2}\text{ZnTa}_{3/2}\text{O}_7$ ,  $\text{Bi}_{3/2}\text{MgNb}_{3/2}\text{O}_7$ , and  $\text{Bi}_{3/2}\text{ZnNb}_{3/2}\text{O}_7$  were investigated by Chen et al [71]. The spectra were collected from 30 to  $3300\text{cm}^{-1}$  between 50 and 300K and the optical constants were estimated by Kramers-Kroning analysis and classical dispersion theory. In addition, BZN was studied from the tera hertz frequencies to lower frequencies. Infrared-active phonon modes have been assigned to specific bending and stretching vibrational modes. The splitting of the B-O stretching phonon modes and O-B-O bending modes are assigned to mixed cation occupancy.

c-BZN ceramics with 0-1.5 mole percentage titanium content in the B site were synthesized and investigated by Wang et al [72] between 100Hz to 100 THz by means of broadband dielectric spectroscopy, infrared reflectivity spectroscopy and Raman spectroscopy. c-BZN ceramics were found to be exhibiting a microwave relaxation which slows down and broadens remarkably on cooling. They also reported that the relaxation originates from the hopping of disordered Bi and a part of Zn atoms being in the A sites of the pyrochlore structure. Substitution of Ti atoms in the B site results in an increase of dielectric permittivity. Du et al [73] studied the relaxation behavior of c-BZN ceramics substituted with Ti at the B site. They have observed a relaxor type behavior at cryogenic temperatures in this system.

Hong Wang et al [74] studied the impact of ion substitution at the A site of the monoclinic bismuth zinc niobate (m-BZN) ceramics. They have shown that the structure and permittivity of the m-BZN ceramics with various ion substitutions in the A site is almost equal to that of pure m-BZN ceramics. The barium substituted compound was having higher dielectric permittivity due to a multiphase structure. The higher microwave quality factor with lower sintering temperature makes these materials suitable for LTCC application.

c-BZN –Ag composites were prepared by Sebastian et al using the conventional solid state reaction technique [75]. These composites were able to get sintered at a temperature of 850°C. The dielectric constant of these composites is found to be increased with the increase of silver content. They have reported a dielectric constant of 2350 for the composites with 0.14 volume fraction of silver and a large dielectric constant  $\epsilon_r \approx 10^5$  for the composites with 15 volume percentage of silver.

The displacive disorder in the bismuth oxide based pyrochlores was studied by Seshadri et al [76]. They have found that the A and O' sites split due to the displacement from their ideal positions. Each O' site can be split into 12 different sites through the displacement from the ideal positions and each A site is split into six different sites through displacements. The local displacements in the A and O' sites are responsible for the higher dielectric constant in these materials. They have also found that the static displacement in the pyrochlore structure is as large as 20% or more of the typical bond length. In general, for the crystals with such a large extent of disorder to be stable they should be in the proximity of a phase transition. But the BZN pyrochlores are found to remain in their cubic phase till the lowest temperatures. This behaviour is thought to be

due to the intrinsic difficulty of distorting the cubic ice like lattice of the pyrochlore in a coherent fashion [77].

#### **1.4.6 Review of tunable dielectric properties of BZN thin films**

This section provides a review of existing research into the BZN thin films for various microwave and electronics applications. It also presents the advantages of amorphous fused silica as a substrate material for BZN deposition. Most of the BZN thin films prepared as part of this thesis work were deposited on amorphous fused silica substrates. Finally, based on the existing work, opportunities for further investigations are identified.

c-BZN and m- BZN pyrochlore thin films were prepared on platinised Si substrates by the metal organic deposition technique by Ren et al [78]. They have studied the dielectric properties of these thin films in detail with respect to the processing conditions. The c- BZN thin films were having a dielectric constant of 150 and the m- BZN thin films were having a dielectric constant of 80. The dielectric loss tangents of both these films were less than that of 0.008. The c-BZN thin films were highly tunable with a tunability of 16% where as the m- BZN thin films were having a nearly field independent dielectric constant. Jiang et al [79] investigated the dielectric properties of pulsed laser deposited c-BZN thin films on Pt/SiO<sub>2</sub>/Si substrate. They have observed that the c-BZN thin films had pure cubic pyrochlore structure in the deposition temperature range of 500°C-650°C. The thin films were having a low loss tangent and a maximum voltage tunability of 6%.

A detailed investigation of composition, structure and crystallinity of c-BZN thin films deposited using RF magnetron sputtering was done by Lu et al [80]. They could obtain a crystalline phase for the films deposited at 400°C or above and the complete crystallinity was obtained for the films deposited at 750°C. The films were grown on platinised silicon substrate as well as on platinised sapphire substrates. The crystalline films deposited at 400°C were having a dielectric constant of 49 and the films deposited at 750°C were having a dielectric constant of 170. The increase in dielectric constant with temperature was attributed to the increase in crystallinity. The dielectric constant started degrading for higher annealing temperatures and it was attributed to the loss of volatile components. The films deposited on platinised silicon exhibited a tunability of 29.6% whereas the films deposited on platinised sapphire were having a dielectric tunability of 23%. The dielectric loss tangent of these films is about 0.002.

Yan et al [81] investigated the microwave dielectric properties of c-BZN-BST composite thin films deposited on SrTiO<sub>3</sub> and MgO substrates via pulsed laser deposition technique. The thin films on STO and MgO substrates showed a dielectric constant of 435 and 401, a dielectric loss tangent of 0.0043 and 0.0037 and dielectric tunability of 6% and 5.7% respectively. This study showed that the dielectric loss tangent of this composite thin film is considerably low compared to that of BST thin films. W.Fu et al [82] investigated the dielectric properties of BZN-Mn-doped Ba<sub>0.5</sub>Sr<sub>0.5</sub>TiO<sub>3</sub> hetero layered films grown by the pulsed laser deposition technique on Nb doped SrTiO<sub>3</sub> substrate. These heterolayered films were found to possess a medium permittivity of around 200, low loss tangent of 0.0025 and a relatively high tunability up to 25%. They have proposed a maximum tunability of about 40% based on the layer structure model developed by them. H.Wang et al [83] investigated the dielectric and C-V characteristics of the BST-BZN composite thin films deposited on platinised silicon substrates by pulsed laser deposition. The dielectric constant and loss tangent for these thin films were found to be 200 and 0.001 respectively, at room temperature. The measured in plane tunability for these films were greater than 50-60%.

Cheng et al [84] investigated the effect of laser annealing on the crystallization temperature of the c-BZN thin films. The c-BZN thin films got crystallized at a substrate temperature of 400°C when they are initially annealed at a laser fluence of energy density 27mJ/cm<sup>2</sup>. The films were having a dielectric permittivity of 156 and a tunability of 33%. The low crystallization temperature obtained for c-BZN thin films by this process makes them suitable to integrate with polymeric substrates.

Effects of substrate heating on the structure and dielectric properties of the c-BZN thin films were investigated by Ha et al [85]. The films were deposited on platinised silicon substrate by RF magnetron sputtering at various substrate temperatures. The films deposited at 550°C followed by a post deposition annealing of 800 °C show a tunability of 26.5% at 1 MHz. The dielectric constant of the films was about 160 and the loss tangent was about 0.002.

Y.P Hong et al [86] investigated the voltage tunable dielectric properties of c-BZN thin films deposited on platinised Si substrates by RF magnetron sputtering. The prepared dielectric thin films were found to exhibit a dielectric constant of 153, tanδ of 0.003 and a maximum tunability of 14% when measured at a frequency of 1 MHz. Cao et al [87] deposited c- BZN thin films with different thickness and preferred orientations on

Nb doped SrTiO<sub>3</sub> substrates by pulsed laser deposition. They found that the dielectric constant increases and the loss tangent decreases with the increase in thickness. Tunability was found to be independent of the film thickness. They also observed that the (111) oriented films exhibited higher dielectric loss compared to (100) oriented films. c-axis oriented c-BZN thin films were grown on Nb doped SrTiO<sub>3</sub> substrates by W.Y.Fu et al by pulsed laser deposition [88]. They obtained the dielectric permittivity of 187, loss tangent of 0.002 with a tunability of 6% for the c axis oriented films. The effect of thermal strain on the dielectric properties of c.BZN thin films was studied by Funakubo et al [89]. They have found that the c.BZN thin films have high stability of dielectric constant and tunability against thermal strain when compared to BST thin films. They have attributed this high dielectric stability against thermal strain to the smaller electrostrictive coefficient of c-BZN thin films.

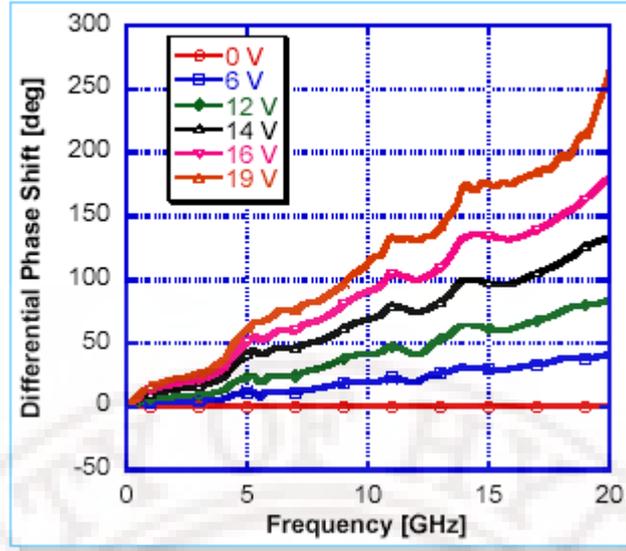
Recently Park et al [90] demonstrated the fabrication of metal insulator metal capacitors on a polymeric substrate using c-BZN thin films by pulsed laser deposition. The c-BZN thin films were deposited at ambient and annealed at 150°C. The films were having a dielectric constant of 70 even though it was in an amorphous state. This was one of the highest dielectric constant reported for thin films processed below 200°C. Choi et al [91] fabricated a low voltage organic thin film transistor (OTFT) using c-BZN thin film for gate dielectric. The c-BZN based OTFT was having an operating voltage less than 2V because of the high permittivity and the low leakage characteristics of c-BZN thin films processed at low temperatures.

A monolithic Ku-band phase shifter employing a voltage tunable c-BZN thin film parallel plate capacitor is reported by Jaehoon Park et al [92]. They have designed a nine section distributed coplanar waveguide loaded line phase shifter as shown figure 1.6.



**Figure1.6** Photograph of the BZN phase shifter fabricated by Jaehoon Park et al

These phase shifters were reported to have a differential phase shift of 175° with a maximum insertion loss of 3.5 dB at 15 GHz. This reported insertion loss is significantly better than that of the BST 5 based phase shifters using a similar design.



**Figure 1.7** Differential phase shifts with applied DC bias of c-BZN based phase shifter fabricated by Jaehoon Park et al [92].

The BST phase shifter was having an insertion loss of 3dB at 10 GHz [93] whereas the BZN phase shifter was having an insertion loss of only 1.8dB at 10 GHz. This shows that the BZN thin film devices maintain relatively low losses well into the microwave frequency region.

#### 1.4.7 Physics of tunability in c- BZN independent of ferroelectric origin.

Till date, large dielectric tunabilities have only been observed in ferroelectric materials. c-BZN is not a ferroelectric material. To have a better understanding about the nature of tunability in these materials certain models were reported. Dielectric tunability is believed to be related to the off-centering of ions in the cubic pyrochlore structure and the hopping of ions between the energetically equivalent positions. Under an applied field, off-centered ions can hop between energetically equivalent sites. A simple model based on the electric field  $E$  as a function of Temperature  $T$  which is needed to achieve a given tunability  $n$  can be expressed as [94]

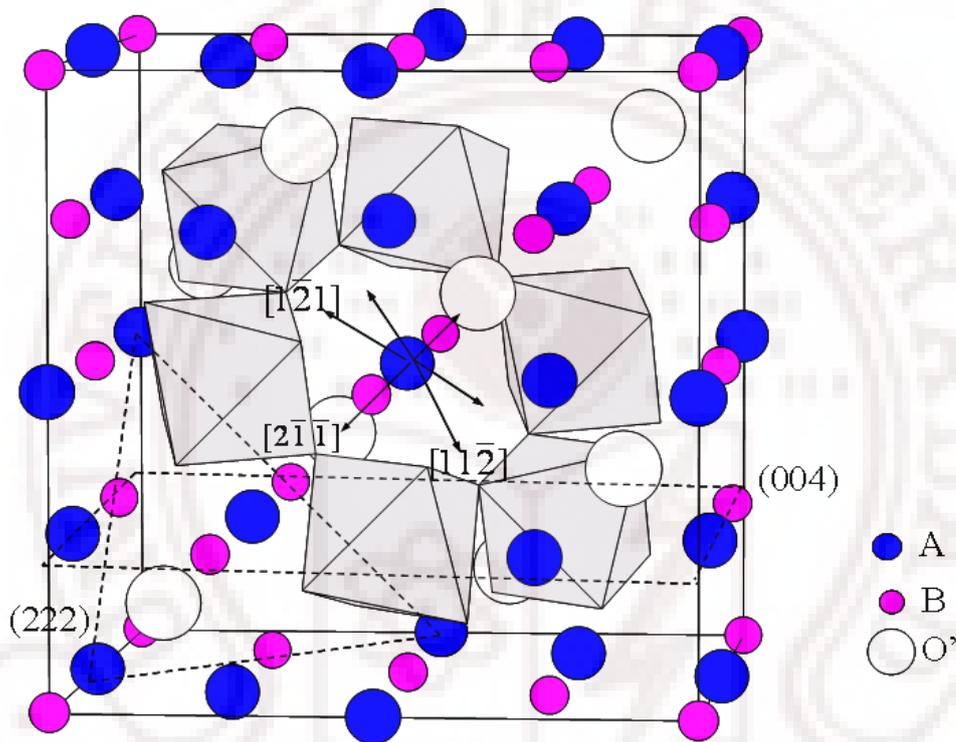
$$E_n = \frac{kT}{p_0} \ln(\sqrt{n} + \sqrt{n-1}) \quad (1.31)$$

Here,  $p_0$  is the dipole moment.

This model could not explain the experimental data that have been obtained for c-BZN. A better model has been developed based on the idea of hopping dipoles under the influence of a random field in the structure which is given below.

$$E_n = \frac{kT}{p_0} \ln \left( \sqrt{1 + (n-1) \cosh^2(p_0 E_r / kT)} + \sqrt{(n-1) \cosh^2(p_0 E_r / kT)} \right) \quad (1.32)$$

A cubic pyrochlore structure with random off-centering of ions hopping between the off-centered positions is the physical basis of the model used to describe the tunability  $n$ . The random fields in the crystal structure are thought to be originating from the random substitution of Zn on the Bi-sites. A schematic diagram of the cation hopping in c-BZN pyrochlores is shown in figure 1.8



**Figure 1.8** Schematic diagram of A site cation hopping in c-BZN pyrochlores

Recently Seshadri et al [77] found that the A and O' sites are split due to the displacement from their ideal positions. The O' sites can split in to the 12 different sites through the displacement from the ideal positions and each A site is split in to six different sites through displacement. Hopping of the A and O' ions in these equivalent states is considered to be responsible for the tunability in these materials.

### 1.5 Research objectives

In summary, the ternary oxides in the  $\text{Bi}_2\text{O}_3\text{-ZnO-Nb}_2\text{O}_5$  (BZN) system exhibit high values of dielectric constants ( $\epsilon_r$ ), relatively low dielectric losses, and a compositionally tunable temperature coefficient of capacitance ( $\tau_c$ ). Such properties, combined with sintering temperatures of less than  $950^\circ\text{C}$ , render these materials as

attractive candidates for multilayer capacitors and low temperature co-fired ceramics (LTCC) for many technological applications [95]. The two members of this family that have received most of the attention  $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$  (c-BZN) ( $\epsilon_r \approx 145, \tau_c \approx -400 \text{ ppm}/^\circ\text{C}$ ) and  $\text{Bi}_2\text{Zn}_{2/3}\text{Nb}_{4/3}\text{O}_7$  (m-BZN) ( $\epsilon_r \approx 80, \tau_c \approx +200 \text{ ppm}/^\circ\text{C}$ ), were shown to adopt cubic and monoclinic zirconolite-like stoichiometric pyrochlore structures. Thin films of these materials may have the advantage of lower crystallization temperatures and smaller device size than bulk ceramics and could get potentially integrated in to microelectronic devices .

The cubic pyrochlore  $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$  (c- BZN) ceramics are presently being considered as a smart microwave material because of the unique dielectric properties in the microwave frequency range [89]. It is one of the few non-ferroelectric materials known today exhibiting a voltage dependent dielectric permittivity. Recently numerous investigations have focused on integration of c-BZN thin films for use in microwave devices for communication purposes, taking advantage of its voltage dependent dielectric constant. More over the c-BZN thin films based microwave devices are having low dielectric loss and high figure of merit than the ferroelectric based tunable devices. Although the bulk dielectric properties of the c- BZN and m-BZN are reasonably studied, thin films of these materials are not well understood in the microwave range.

For the effective microwave application of these thin films, the choice of the substrate is an important factor. Most of the previous works are on the growth of polycrystalline BZN films on single crystal substrates such as sapphire and lanthanum aluminate [78]. The growth of these films on a low cost, low loss and low dielectric permittivity substrate is important for the microwave application of these thin films. Fused silica is one of the ideal substrates for the growth of thin films meant for microwave applications, because it satisfies these requirements. Its dielectric characteristics permit the design of transmission lines of high impedance and matched impedance as per the requirements. Its low losses make it possible to obtain overall low losses for the device at a given impedance. The integration of these thin films appropriately to the existing silicon technology is a very attractive area of research. The tunable thin films have been earlier deposited directly on to silicon wafers for this purpose. However the low resistivity of the silicon limits the realization of low loss microwave transmission lines and other passive components on these thin films. The other possible alternative explored was high resistive silicon which also found to loose its

high resistivity due to the high temperature processing required for these thin films. An alternate technology coming up for integration of these thin films is silicon on sapphire (SoS) technology where thick layer of silicon will be deposited on sapphire substrates and appropriate active and passive circuits were incorporated in the same wafer. This technology could provide high isolation and higher operating speed but the high cost of the sapphire substrate has become a limiting factor for the wide spread use of this technology.

However if these films could grow on fused silica (amorphous  $\text{SiO}_2$ ) substrates, it opens an easy and cost-effective way for the integration of these materials with the existing silicon technology. Already, industrially compatible fabrication processes are available for Si and  $\text{SiO}_2$ . The  $\text{SiO}_2$  can be directly deposited on Si substrates or it can be produced by the surface oxidization of the Si substrates. The tunable dielectric films can be grown directly on the  $\text{SiO}_2$  layer and the required passive circuits can be fabricated. The active circuits can also be incorporated in the same wafer by exposing Si substrates through the selective etching of the  $\text{SiO}_2$  layer. Thus the tunable thin films on  $\text{SiO}_2/\text{Si}$  substrates will lead to a cost effective way of integration of microwave tunable circuits in to the existing silicon technology. Hence a study on the growth of BZN thin films on amorphous  $\text{SiO}_2$  (fused silica) substrates and the impact of thermal treatments on them will be an important milestone to develop the process technologies for the BZN thin films compatible with Si technology. However, growing crystalline thin films of these materials on amorphous fused silica substrates is challenging and requires serious process optimization.

An important focus of this thesis is on understanding the relationship between the material and microwave properties of c-BZN and m-BZN thin films on amorphous fused silica substrate. The influences of the deposition condition on the structure, microstructure and microwave dielectric properties were also investigated. From these studies a set of deposition conditions which provide a high dielectric constant, low dielectric loss and high tunability (for c-BZN thin films) can be determined. Establishing these conditions is important since the relationship between the deposition conditions and microwave properties of BZN thin films grown directly on these substrates especially on amorphous fused silica has not been systematically studied. For achieving this major objective a series of intermediate objectives have to be set and achieved. The first

objective was the identification of a suitable deposition method for fabrication of thin films.

Out of many techniques available for the deposition of thin films, the Pulsed Laser Deposition (PLD) technique has been selected to deposit c-BZN and m-BZN thin films in the current study. It provides excellent control of the stoichiometric composition of oxide films with many components, which is especially necessary for BZN thin films due to the high volatility of Zn and Bi. As composition is the key factor that determines the crystal structure and dielectric properties of BZN thin films, PLD is expected to provide the attractive advantage of control to realize the cubic and monoclinic pyrochlore structure of the BZN thin films.

Preparation of the high-density ceramic targets of c-BZN and m-BZN for pulsed laser deposition has become an intermediate objective in this study. It is desirable to have a fair knowledge about the structural and electrical properties of these bulk ceramics before making them in the thin film form. So the preparation and characterization of the bulk m-BZN and c-BZN ceramics become an essential objective in the present work.

The second major objective of this study was the development of suitable techniques for the characterization of these thin films at the microwave frequency range. Currently most of these materials are characterized at much lower frequencies compared to the frequency of operation of the devices in which they are a part. Unambiguous measurement of dielectric constant and loss of dielectric thin films on insulating substrates in the microwave region has long been an important objective in micro/nano-electronics. The difficulty lies in the predominant response of the dielectric substrate submerging the response of the film or the requirement of a metallised circuit layer over the film thereby losing information about the as-deposited state of the film. So the development of various characterization techniques to measure the dielectric constant, loss tangent and tunability at microwave frequency regions becomes the most challenging objective of the present investigation.

For the microwave characterization of these thin films, various test structures have to be fabricated. Hence demonstrating a suitable micro fabrication process flow suitable for BZN thin films has become an important objective of this study. A lift-off based photolithographic process, which allowed the fabrication of CPW lines circular patch capacitors and IDC structures, has to be established. Using this process flow one could be able to pattern small feature sizes in the order of 8-10  $\mu\text{m}$ .

It is also interesting to know the low frequency dielectric properties and electrical properties of c-BZN and m-BZN thin films grown on different substrates. So the characterization of the leakage conduction mechanisms and dielectric properties at low frequencies are also an objective of the present study.

The present investigation also aims to understand the voltage dependent dielectric properties of c-BZN thin films deposited on platinised silicon substrates as well as amorphous fused silica substrates. The dielectric properties of both c-BZN and m-BZN thin films on fused silica substrates are studied in comparison to that of the films grown on single crystal substrates such as LAO, ALO and MgO.

As stated earlier, BZN films are mainly being considered for microwave dielectric applications. However, the optical properties of these thin films are also interesting for a number of reasons, including identifying the electronic component of polarisability and monitoring the film growth and degradation processes. Optical properties such as refractive index and band gap are good indicators of the growth patterns of the dielectric films and can be effectively used to monitor their growth.

A major issue in thin film dielectrics is the difference between the thin film properties and those of the corresponding bulk materials. Since the dielectric properties and lattice dynamics are closely related, Raman spectroscopy provides a potentially valuable technique for the study of dielectric materials. It is highly sensitive to local structure and local symmetry. Moreover, it is a nondestructive technique, which does not require any special treatment of samples. Owing to the technological importance of BZN thin films, we present the Raman spectral analysis of these films to have a better understanding of their dielectric behavior.

Lastly the basic element of a tunable device in the microwave frequencies is a varactor. Hence fabrication and testing of the planar and parallel plate varactors using BZN thin films becomes the final objective of this work.

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