1.1 Microwaves

Electromagnetic spectrum is an ordered arrangement of electromagnetic signals ranging from radio frequency to gamma ray in the order of increase in frequency (figure 1.1). In the electromagnetic spectrum, frequencies ranging from 300 MHz to 300 GHz are known as microwaves since in this region wavelength can be measured in microns [1]. The first detection of radiofrequency wave was done by Henrich Hertz in 1897. The name ‘microwave’ was coined by Arrora in 1932 to represent the shorter waves in electromagnetic
spectrum [2]. James Clark Maxwell was the first to make a systematic study of the behavior of electromagnetic signals during 1880s. His conclusions were comprehended into four well known equations called Maxwell’s equations [1, 2]. The first experimental set up to transmit and receive electromagnetic signals was done by Marcony. He succeeded to send radio frequency signals to a distance greater than one mile and was able to receive at the other end. This invention revolutionized the communication sector and following this, the electromagnetic signals were extensively exploited to transfer data from one end to the other [3]. During World War II, the communication sector using electromagnetic radiation reach new heights and as a result higher frequencies other than radio waves were explored to suit the requirement. Most of the present day communication including both civil and military purpose are catered with microwave frequencies. They found applications in satellite communications, RADAR, mobile phones, Global Positioning Systems (GPS), General Pocket Radio Services (GPRS), Bluetooth etc.

Table 1.1 IEEE Microwave frequency bands

<table>
<thead>
<tr>
<th>Designation</th>
<th>Frequency range (GHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UHF</td>
<td>0.300-1.000</td>
</tr>
<tr>
<td>L band</td>
<td>1.000-2.000</td>
</tr>
<tr>
<td>S band</td>
<td>2.000-4.000</td>
</tr>
<tr>
<td>C band</td>
<td>4.000-8.000</td>
</tr>
<tr>
<td>X band</td>
<td>8.000-12.000</td>
</tr>
<tr>
<td>Ku band</td>
<td>12.000-18.000</td>
</tr>
<tr>
<td>K band</td>
<td>18.000-27.000</td>
</tr>
<tr>
<td>Ka band</td>
<td>27.000-40.000</td>
</tr>
<tr>
<td>Millimeter</td>
<td>40.000-300.000</td>
</tr>
<tr>
<td>Submillimeter</td>
<td>&gt;300.000</td>
</tr>
</tbody>
</table>
Institute of Electrical and Electronic Engineers (IEEE) categorized the entire microwave spectrum into different bands and are shown in table 1.1 [1]. Each band has its own specified applications such as L and S-bands are for satellite communication and K and Ka-bands are for military applications. In addition to communication sector, microwave finds applications in domestic cooking also. The domestic microwave oven works at 2.45 GHz. During 1980s microwave assisted preparation is emerged as a main processing route for various organic as well as inorganic materials. Microwave assisted processing is conducted in open vessel as well as closed vessel (hydrothermal) conditions [4]. Loss tangent and dielectric constant of the material as well as the solvent are the important parameters for microwave assisted synthesis. Microwave assisted processing is time saving as well as cost effective method for material preparation [5, 6].

1.2 Interaction of electromagnetic radiation with matter

Interaction of microwaves with materials depends on the dielectric constant and loss tangent of the materials and wavelength of the microwave signal. Dielectric constant determines the signal speed because the velocity of light through a medium is inversely proportional to the square root of the dielectric constant of the material [7]. The lower the dielectric constant, the faster the signal travels through the material. Every polar material consists of electric dipoles, which may either permanent or induced. When an electric field is applied to an ideal dielectric material there is no longer transport of charge but only a limited rearrangement such that the dielectric acquires a dipole moment and is said to be polarized. When dielectric is subjected to an external field \( E \), dipole moment is induced inside the material. The dielectric can act as storage device for electrical energy through the generation of electric dipoles and the ability of a material to store its electrical energy is determined by dielectric constant. The dielectric polarization \( P \) is equal to the total dipole moment induced in the material by electric field. Then, \( P = N_1 \mu_1 \) where \( N_1 \) is the number of dipoles and \( \mu_1 \) is the average dipole moment [7, 8].
1.2.1 Types of polarization

There are four types of polarizations such as electronic, ionic, orientation and space charge polarizations occur in dielectrics while subjected to electromagnetic field. Polarization occurs due to different mechanisms as shown in figure 1.2. Electronic polarization is the result of the displacement of the positively charged nucleus and the electrons of an atom in opposite directions on application of an electric field. On applying a field, the electron cloud around the nucleus readily shifts towards the positive end of the field. Such a shift results in a dipole moment within the atom as the nucleus and the center of the electron cloud are separated by a certain distance (figure 1.2a). At very high frequencies, ie, around $10^{15}$ Hz, only electronic polarization is prevalent. During chemical bonding, the atoms may acquire excess negative or positive charge and form an ionic bond. When an electric field is applied to ionic solid, cations and anions get displaced in opposite
directions (figure 1.2b) which results in ionic polarization. The ionic polarisability is due to this shift of the ions relative to other oppositely charged ions. Ionic polarization is responsible for the dielectric properties exhibited by materials at microwave frequency region. Certain molecules carry dipole moment even in the absence of an electric field. When an electric field is applied on such molecules, they tend to align themselves in the applied field. The polarization due to this alignment is called orientation polarization. With increasing temperature, the thermal energy tends to randomize the alignment (figure 1.2c). The fourth type of polarization is called the space charge polarization. It occurs due to the accumulation of charges at the electrodes or at the interfaces. The ions diffuse over appreciable in response to the applied field, giving rise to a redistribution of charges in the dielectric medium (figure 1.2d). The frequency dependence of the different polarization mechanisms is shown in figure 1.3 [7-11].

Figure 1.3 Frequency dependence of polarization
1.2.2 Dielectric constant

The dielectrics not only obstruct electrical conduction but can also act as a storage device for electrical energy through the generation of electric dipoles. The ability of a material to store electrical energy is determined by its dielectric constant, which is simply the ratio of dielectric constant of the material to the dielectric constant of vacuum [7]. In the presence of an electric field, the displacement vector can be written as

\[ D = \varepsilon_0 E + P \]  \hspace{1cm} (1.1)

where \( \varepsilon_0 = 8.85 \times 10^{-12} \text{ Nm}^2 /\text{C}^2 \) is the dielectric constant of free space and \( P \) is the polarization vector and

\[ P = \chi_e \varepsilon_0 E \]  \hspace{1cm} (1.2)

Hence equation 1.1 becomes

\[ D = \varepsilon_0 E + \chi_e \varepsilon_0 E = (1 + \chi_e)\varepsilon_0 E \]  \hspace{1cm} (1.3)

Since \( D \) is equivalent to total charge density \( \sigma_t \), equation 1.3 can be written as

\[ \frac{Q_t}{A} = (1 + \chi_e)\varepsilon_0 \frac{A}{h} \]  \hspace{1cm} (1.4)

where \( Q_t \) is the total charge, \( A \) is the area and \( h \) is the thickness of the dielectric material. Therefore the capacitance of the material is

\[ C = \frac{Q_t}{V} = (1 + \chi_e)\varepsilon_0 \frac{A}{h} \]  \hspace{1cm} (1.5)

where \( V \) is the applied voltage. Since vacuum has zero susceptibility, the capacitance of an empty parallel plate capacitor can be written as

\[ C_0 = \varepsilon_0 \frac{A}{h} \]

If there is a material having susceptibility \( \chi_e \) then the capacitance will be increased by a factor \( (1 + \chi_e) \)

Hence the dielectric constant \( \varepsilon \) of a dielectric can be defined as

\[ \varepsilon = \varepsilon_0 (1 + \chi_e) \]

\[ \frac{\varepsilon}{\varepsilon_0} = (1 + \chi_e) = \varepsilon' \]  \hspace{1cm} (1.6)
\( \varepsilon_r \) is the relative dielectric constant of the material.

Dielectric constant of a material is a function of frequency of the applied electromagnetic radiation and the operating temperature. On application of an electric field, polarization occurs, as a function of time

\[
P(t) = P \left(1 - e^{-t/t_r}\right)
\]

(1.7)

where \( P \) is the maximum polarization attained and \( t_r \) is the relaxation time for polarization process.

The relaxation time \( t_r \) is a measure of time scale of a polarization process. It is the time taken for a polarization process to reach 0.63 of the maximum value (when \( t = t_r \) in equation 1.7) [7, 11]. Electronic polarization is extremely rapid. When the applied frequency is very large electronic polarization occurs. Ionic polarization is slower than electronic polarization, as the displacement involved here is that of much heavier ion, as compared to electron cloud. If the frequency of the applied voltage is less than \( 10^{13} \) Hz, the ions have enough time to respond during each cycle. Orientation polarization is even slower than the ionic polarization. Space charge polarization is the slowest process; as it involves the diffusion of ions over several interatomic distances. Generally space charge polarization occurs in the low frequency range but in the case of polymer/ceramic composites it seems to be extended up to MHz region. Figure 1.3 gives the frequency dependence of polarization. As the frequency increases, space charge, orientation and ionic polarization become inoperative in that order. When several polarization processes occur in a material, it follows that the dielectric constant decreases with increase in frequency of the applied voltage [7, 12].

The effect of temperature on the relative dielectric constant of a material can be two fold. In orientation polarization the randomizing action of thermal energy decreases the tendency for permanent dipoles to align themselves in the applied field and results in a decrease of \( \varepsilon_r \).
The other effect of temperature is to facilitate the diffusion of ions in space charge polarization. Thermal energy may also aid in overcoming the activation barrier for the orientation of polar molecules in the direction of field. For example, the relatively large polar molecule nitrobenzene is not able to reorient themselves in the solid state under an applied field and therefore does not exhibit orientation polarization. However on melting, the molecules have sufficient thermal energy to orient themselves in the applied field and therefore \( \varepsilon' \) will increases. When temperature increases due to thermal expansion of matter the ratio of the number of molecule to the effective length of the dielectric diminishes. Therefore the dielectric constant should also diminish. Temperature does not affect the process of electronic polarization in non polar dielectrics [12].

1.2.3 Loss tangent

When an electric field acts on any matter, the matter dissipates a certain quantity of electric energy that transfers as heat energy. This phenomenon is known as power loss. The amount of power loss in a dielectric under the action of voltage applied is known as dielectric loss [7]. The dissipation of power in a dielectric depends on the voltage, frequency and also on the nature of dielectric material. A dielectric material placed in an alternating voltage as a parallel plate capacitor, the current \( V_0 \omega \cos(\omega t) \) leads the voltage \( V_0 \sin(\omega t) \) by 90°. The phaser diagram shown in figure 1.4 is an instantaneous snapshot of the voltage and current vectors as they rotate in an anti clockwise direction with angular frequency \( \omega \), with a constant phase difference of 90°. If there is a net power extraction from the source, the component \( I_v \) of the vector \( I \) along \( V \) leads to the power loss whereas the \( I_c \) does not. Therefore the time average of power loss is

\[
\bar{P} = \frac{1}{T} \int_0^T V I dt
\]

\[
= \frac{1}{T} \int_0^T V_0 \sin(\omega t) I_0 \cos(\omega t - \delta) dt
\]

Integrating equation 1.8

\[
\bar{P} = \frac{1}{2} V_0 I_0 \sin \delta
\]
Since $I_0 = I_c / \cos \delta$ and $I_c = \omega V_0 C$

\[ P = \frac{1}{2} V_0 I_c \tan \delta = \frac{1}{2} V_0^2 \omega C \tan \delta \]  

(1.10)

Form equation (1.9), it can be seen that $\sin \delta$ represents the fraction of the current voltage product which is dissipated as heat and is called as the power factor.

![Diagram of current components](image)

Figure 1.4 Capacitative and loss components of total current $I$

For a complex relative dielectric constant $\varepsilon^* = \varepsilon'_r - j \varepsilon''_r$, where $\varepsilon'_r$ is the real and $\varepsilon''_r$ is the imaginary parts of relative dielectric constant. It follows that

\[ I = j \omega \varepsilon'_r C_0 V \]  

(1.11)

\[ = j \omega \varepsilon'_r C_0 V + \omega \varepsilon''_r C_0 V \]  

(1.12)

The current is made up of two components, one is capacitative and lossless component and the other is in-phase with voltage and is lossy. From figure 1.4 it can be seen that

\[ \frac{\varepsilon''_r}{\varepsilon'_r} = \tan \delta \]  

(1.13)
1.3 Microwave materials

Microwave communication has turned out to be one of the most rapidly growing fields of information society [13]. Wireless communication based on individual handsets has revealed breathtaking growth rates with a dramatic increase of transferred data rates and number of subscribers. In particular, wireless multimedia applications are considered to enforce a dramatic increase of wireless system capability in the near future. In order to overcome the intrinsic bandwidth limitations of microwave communication systems, modern systems have to utilize the available bandwidth most efficiently. Current system specifications including those for the 3rd generation mobile telephone systems are based on the available performance of the current devices and subsystems. However, novel devices with improved performance are likely to increase the capacity of the systems or may become even a necessity in order to operate a system properly under any circumstances. The increasing requirements for the development of high speed, high frequency circuits and systems require novel materials, which can function at microwave frequencies. Dielectric constant, loss tangent, temperature stability, dielectric tunability etc. are the key parameters, which decide the applicability of a material at microwave frequency region [13-16].

Both paraelectric and ferroelectric materials have its own importance in microwave materials spectrum depending on the requirement at the user end. Ceramics, polymers, glass ceramics, ceramic-ceramic composites and polymer-ceramic composites with variety of physical properties found suitable applications as microwave materials [13]. Ceramics and its composites with tailored electrical, thermal and mechanical properties are most commonly used to fabricate passive microwave components. Most of the materials used for microwave applications have perovskite or perovskite related crystal structure. Mostly, linear dielectric materials are used to fabricate microwave dielectric resonators, filters, oscillators and substrates whereas ferroelectric materials are used for tunable dielectric applications [17].
1.3.1 Dielectric resonators

Dielectric resonators are ceramic compacts with comparatively high dielectric constant ($\varepsilon_r$>25), high quality factor (Qu>2000) and near zero temperature coefficient of resonant frequency ($\tau_f$~0 ppm/$^\circ$C) used to confine electromagnetic energy in the microwave region. For narrow bandwidth applications, low loss, temperature stable ceramics are used for frequency selectivity. Single mode dielectric resonators are cylindrical pucks, which work using the principle of total internal reflection first suggested by Richtmyer in 1930 [18]. The electric and magnetic field lines of electromagnetic radiation with such pucks are shown in figure 1.5. The dimension and dielectric properties of the pucks are in such a way that standing wave are formed within the body for a particular frequency and may therefore act as either a filter or a transmitting resonator. Multimode resonators are fabricated with unusual geometries to induce several microwave resonant modes within the body at a time. Even though ceramic resonators are simple in concept and design, a slight difference in batch wise or within a batch variation during production may alter their resonant frequency and temperature stability [19].

Figure 1.5 Electric and magnetic field lines associated with a cylindrical ceramic resonator
The key properties of a dielectric resonator/filter are dielectric constant, quality factor and temperature coefficient of dielectric constant. The dielectric constant $\varepsilon_r > 20$ for circuit miniaturization as can be seen from equation (1.14).

$$f_0 \approx \frac{c}{\lambda_d \sqrt{\varepsilon_r}} \approx \frac{c}{D \sqrt{\varepsilon_r}}$$

(1.14)

where $c$ is the speed of light in vacuum, $f_0$ is the resonant frequency and $\lambda_d$ is the wavelength of the standing wave formed in the dielectric resonator of diameter $D$. If the dielectric constant of the resonator is increased, the size may decrease to retain the specific resonant frequency. This implies that materials with high dielectric constant enable circuit miniaturization [13]. Quality factor (Q) is another important parameter that determines the performance of a DR. In any resonant circuit the efficiency is expressed by the Q factor.

$$Q = 2 \pi \frac{\text{Energy stored per cycle}}{\text{Energy dissipated per cycle}}$$

(1.15)

The sharpness of tuning at resonance depends on quality factor. The higher is Q, the lower is the damping and sharper is the resonance [20]. The dissipation of the power in a dielectric depends on the voltage, frequency and the nature of the dielectric material. The power dissipated in a dielectric is proportional to its frequency. This explains the demand for low loss factor dielectric for high frequency application. High loss factor dielectric for high frequencies cannot be tolerated; partly because excessive power dissipation can lead to unacceptable rises in temperature, and partly, and more importantly, because the resonance in tuned circuits becomes less sharp so that the precise selection of well defined frequency bands is not possible. The quality factor is approximately the inverse of loss tangent (tanδ) and should be greater than 2000 depending on the application. Quality factor can be determined by dividing the resonant frequency $f_o$ with the bandwidth $\Delta f$ at 3dB below the maximum height at resonance. A high quality factor keeps the signal integrity and reduce the risk of cross talk within a given frequency region [21]. Dielectric resonators used in the mobile base station require very high quality factor (Qxf) $> 250000$ GHz, where as in the hand sets Qxf $> 2000$ GHz is sufficient.
Temperature coefficient of resonant frequency ($\tau_f$) measures the drift in resonant frequency with respect to temperature. $\tau_f < \pm 2 \text{ ppm/}^\circ\text{C}$ is very much essential to maintain the resonant frequency of the resonator even if the temperature of the working environment changes. $\tau_f$ can be defined as

$$\tau_f = -\left(\frac{1}{2} \tau_e + \alpha_L\right)$$  \hspace{1cm} (1.16)

where $\tau_e$ is the temperature coefficient of dielectric constant and $\alpha_L$ is the linear expansion coefficient. For practical applications, a small non-zero value of $\tau_f$ is required for dielectric resonators to compensate for thermal expansion of the metallic microwave packages.

In the early stages of microwave communication, Invar/Copper cavities were used for oscillator/filter design. Metallic cavity resonators offer high quality factor but suffer from bulky size, high cost and high temperature coefficient of dielectric constant. Ceramic resonators are better alternatives with temperature stable properties and high dielectric constant values. Rutile was the first material in this kind with quality factor greater than 10,000. In 1980s first generation ceramic resonators such as (Mg,Ca)TiO$_3$, ZrTiO$_4$ and BaTi$_4$O$_9$ were extensively used in microwave communication systems [22-26]. As the overcrowding of lower end of microwave spectrum, materials with very high quality factor are needed to fabricate resonators/filters used in the base station applications. Ba(Mg$_{1/3}$Ta$_{2/3}$)O$_3$ and Ba(Zn$_{1/3}$Ta$_{2/3}$)O$_3$ are the examples of such high Q materials which can be used for base station applications [27, 28]. Some of the commercially available high quality factor, temperature stable microwave resonators are shown in Table 1.2 [13]. From the table it is clear that the perovskites are of particular interest for microwave applications because they can be fabricated with exceptionally high quality factors at microwave frequencies.
Table 1.2 List of commercially available ceramic resonators [13].

<table>
<thead>
<tr>
<th>Material</th>
<th>Abbreviation</th>
<th>$\varepsilon_r$</th>
<th>Q x f (GHz)</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba(Mg\textsubscript{1/3}Ta\textsubscript{2/3})O\textsubscript{3}</td>
<td>BMT</td>
<td>24</td>
<td>250 000</td>
<td>Comp. Perov.</td>
</tr>
<tr>
<td>Ba(Zn\textsubscript{1/3}Ta\textsubscript{2/3})O\textsubscript{3}</td>
<td>BZN</td>
<td>29</td>
<td>150 000</td>
<td>Comp. Perov.</td>
</tr>
<tr>
<td>Ba(Co,Zn)\textsubscript{1/3}Ta\textsubscript{2/3}O\textsubscript{3}</td>
<td>BCZN</td>
<td>34</td>
<td>90 000</td>
<td>Comp. Perov.</td>
</tr>
<tr>
<td>SrTiO\textsubscript{3}-LaAlO\textsubscript{3}</td>
<td>STLA</td>
<td>39</td>
<td>60 000</td>
<td>Simp. Perov.</td>
</tr>
<tr>
<td>CaTiO\textsubscript{3}-NdAlO\textsubscript{3}</td>
<td>CTNA</td>
<td>45</td>
<td>48 000</td>
<td>Simp. Perov.</td>
</tr>
<tr>
<td>ZrTiO\textsubscript{4}-ZnNb\textsubscript{2}O\textsubscript{6}</td>
<td>ZTN</td>
<td>44</td>
<td>48 000</td>
<td>$\alpha$ PbO\textsubscript{2}</td>
</tr>
<tr>
<td>Ba\textsubscript{4}Nd\textsubscript{0.33}Tu\textsubscript{1.6}O\textsubscript{5.4}</td>
<td>BNT</td>
<td>80</td>
<td>10 000</td>
<td>Perov./TTB</td>
</tr>
<tr>
<td>Ba\textsubscript{2}TiO\textsubscript{20}</td>
<td>BT</td>
<td>39</td>
<td>12000</td>
<td>Comp. Perov.</td>
</tr>
<tr>
<td>Zr\textsubscript{0.8}Sn\textsubscript{0.2}TiO\textsubscript{4}</td>
<td>ZST</td>
<td>38</td>
<td>8400</td>
<td>$\alpha$ PbO\textsubscript{2}</td>
</tr>
</tbody>
</table>

Comp: Complex, Simp: Simple, Perov: Perovskite, TTB: Tetragonal Tungsten Bronze

1.3.2 Ferroelectric microwave materials

Ferroelectric materials usually have high dielectric constant and they depend highly on frequency, temperature and external fields. The piezoelectric and pyroelectric properties of ferroelectric materials are mostly exploited until the invention of ferroelectric random access memories. Besides, ferroelectric materials were also used for the development of tunable microwave devices which is used in satellites as well as terrestrial communication sector where the frequencies are higher than which Silicon can support. Ferroelectric materials exhibit a hysteresis effect of polarization with an applied field (figure 1.6). Even after the removal of the electric field some polarization remains in the ferroelectric material called remanent polarization. For ferroelectric materials there is a particular temperature called Curie temperature where the materials show ferroelectric behavior below Curie temperature and above it is in paraelectric state. The dielectric constant of a ferroelectric material can be represented as derivative if the electric field dependent polarization (eqn. 1.17) [29-33].
This change in dielectric constant with respect to external DC field is called dielectric tunability and can be exploited for the development of tunable microwave devices. The tunability can often be represented as equation (1.18).

\[
\text{Tunability} \% = \frac{\varepsilon_{r0} - \varepsilon_r}{\varepsilon_{r0}} \times 100
\]

(1.18)

where $\varepsilon_{r0}$ is the dielectric constant without electric field and $\varepsilon_r$ is the dielectric constant with external DC field. The figure of merit $K$ ($K=\text{Tunability}/\tan\delta$) of the material is often used to indicate the quality of the ferroelectric material wherein $\tan\delta$ at zero external fields is used for calculations.

Tunable circuits including filters, matching networks and phase shifters offer the flexibility to adapt changes in operating conditions such as frequency, impedance environment or RF drive level. Thin film ferroelectrics are receiving increased attention because of their potential in producing tunable RF and microwave circuits. Ba$_{1-x}$Sr$_x$TiO$_3$ (BST) is the one of the most studied material systems exhibiting dielectric tunability. In
addition to BST, AgTa$_3$Nb$_{1-x}$O$_3$ and Na$_x$K$_{1-x}$NbO$_3$ are the other two well known material systems showing tunable dielectric properties in the microwave frequency range [34, 35].

1.3.3 Microwave absorbers

Microwave absorbers are used in both military and civil applications for the past many years to reduce radar signature and to reduce electromagnetic wave pollution. Usage of suitable microwave absorbing materials in electronic equipments will help to control the excessive self emission of electromagnetic wave and ensure the undisturbed functioning of the equipment in the presence of external electromagnetic interference. In stealth technology also a microwave absorbing coating over the exterior surface of aircrafts were made for an effective countermeasure against radar surveillance. Microwave absorbing materials were prepared in polycrystalline form, which can be used as paints as well as filled in various polymer matrices. Most of the polymers are transparent to microwaves and the microwave absorption in the composites mainly achieved by filling it with particulate filler materials. The absorbers being resonant type, the sample thickness and complex dielectric constant are the important parameters [36, 37].

The radar absorbing materials (RAM) work based on the interactive loss process of molecules or ions within the material. When microwave absorbing materials are subjected to external electromagnetic field, several dipoles were formed and aligned in the direction of applied field. On the alteration of the field the dipoles are aligned in the opposite direction and some amount of energy will be dissipated as heat. The microwave absorption is not an instantaneous process but the signal attenuation can happen by heat dissipation, due to ohmic losses and spin inversions, and multiple reflections. The total incident energy ($E_i$) can be split into three components via $E_a$ the absorbed energy, $E_t$ is the transmitted energy and $E_r$ is the energy reflected back (equation 1.19).

$$E_i = E_a + E_t + E_r$$  \hspace{1cm} (1.19)

The attenuation can be represented as

$$Attenuation\ (dB) = 10\log\frac{E_r}{E_i}$$  \hspace{1cm} (1.20)
1.3.4 Microwave substrates

Microwave substrates are the integral part of the circuits which they support whereas in the case of low frequency circuit, with low data rates, the function of a substrate is only to support components and get current flow from one point to another. It is judicious to select the type of substrate material depending on the frequency of operation and more particularly on the end performance of the device fabricated out of that. Microwave packaging technology demands substrate materials with high frequency compatibility, minimal dielectric loss, low coefficient of thermal expansion, high thermal conductivity etc. [38]. Dielectric constant is a critical parameter since signal transmission rate and impedance of the circuit largely depends on substrate dielectric constant. In microwave packages, neighbouring signal traces couple through their mutual inductance and capacitance and thereby inducts noise into the circuit. Such noise is referred as crosstalk and is prominent in high density packages. This is increased with the dielectric constant of the base material. Hence for realizing high density packages, high dielectric constant with low loss tangent is essential. In order to cater these requirements special materials having stringent dielectric properties together with improved thermal stability are needed [38, 39].

There is no ultimate material for every microwave circuit designs but varies depending on the application and the expected performance limit of the device. Dielectric constant, dielectric thickness and loss tangent are the critical parameters considered during microwave circuit fabrication. The width of the circuit pattern (w) fabricated over a substrate is inversely proportional to the square root of dielectric constant ($\varepsilon_r$) at a specific impedance (generally 50Ω) for substrate having fixed thickness. Dielectric constant, width of the circuit pattern and impedance of the circuit ($z_o$) are related by equation (1.21) [38].

$$z_o\sqrt{\varepsilon_r} = 60\ln\left(\frac{4h}{\pi w}\right)$$  \hspace{1cm} (1.21)

The width of the circuit pattern can be reduced and hence the circuit density can be increased by increasing the dielectric constant of the base material. For example, to fabricate a strip
line of 50 Ω impedance with a working frequency of 2 GHz over two ½ x ½ inch size substrates having dielectric constant of 2.1 and 10.2, the wavelength should be \( \lambda = 4.07 \) inch and \( \lambda = 1.08 \) inch respectively. This indicates that it is possible to fabricate a stripline for full wavelength in substrates with \( \varepsilon_r = 10.2 \) whereas strip line for 0.45 \( \lambda \) itself will take entire surface of substrates with \( \varepsilon_r = 2.1 \). In the same way loss tangent and dielectric thickness also vary depending on application. This indicates that selection of a particular substrate for specific requirement is solely depends on the user requirements [38].

\[
\lambda = \frac{c}{f \sqrt{\varepsilon_r}}
\]  

Microwave substrates are usually metallised with either copper or gold on at least one surface before put into application. Copper is the cheapest conducting layer and is cladded on the substrate surface through electroless coating followed by electroplating as well as vacuum lamination of oxygen free copper foils. The circuit patterns for microwave applications are photo etched on the substrates, which are generally known as the microwave artwork. Design and fabrication of microwave artwork involves three steps 1) the initial drawing 2) the lay out and 3) the photo process. After photo etching the unwanted metal layer will be etched out from the substrate surface and only the required circuit pattern will remains. Figure 1.7 shows the schematic of a substrate with microwave artwork. The next step in microwave circuit fabrication is the attachment of components to the circuit, interconnecting substrates and attaching the substrates to a case called microwave packaging. The attachment of microwave chips and resonator materials in to the base material is done using non-conductive bonding materials. In addition, good electrical contacts between metallic parts are made using solder, epoxy, thermocompression bonding, thermosonic bonding etc. The connectors used in microwave circuits are attached to the base substrate generally through soldering and the solder used in microwave application are called soft solder due to its low melting point [38, 40].
Figure 1.7 Microwave substrate with conducting patterns.

The selection of package is also very important for microwave circuit since it is an integral part which influences the performance of the final microwave device. Three methods used for microwave transmission such as microstrip, stripline and suspended substrates with casing are shown in figure 1.8 [38]. Figure 1.8a is a packaged microstrip where substrate having dielectric thickness ‘h’ is placed directly on the case floor. The distance between substrate and top casing ‘H’ has significant influence on the performance of microstrips since the effective dielectric constant \( \varepsilon_{\text{eff}} \) of the substrate depends on ‘H’.

\[
\varepsilon_{\text{eff}} = \frac{\varepsilon_r + 1}{2} + q \frac{\varepsilon_r - 1}{2}
\]  

(1.23)

where \( \varepsilon_r \) is the relative dielectric constant and \( q \) is the filling factor, which compensates for the two dielectric constant of microstrip, air and solid dielectric of the circuit.

\[
q = (q_\infty - q_t)q_c
\]

where in

\[
q_t = \frac{2 \ln 2}{\pi} \frac{t}{h} \left(\frac{w}{h}\right)^{1/2}, \text{ the correction factor for a finite conductor thickness}
\]

\[
q_c = \tanh(1.043 + 0.121(H/h) - \frac{1.164}{(H/h)}), \text{ correction factor for non infinite shielding}
\]
\[ q_v = \left(1 + \frac{10h}{w}\right)^j \], the filling factor for an infinite cover height and \( j = \frac{a(w/h)h(\varepsilon_r)}{t} \), \( t \) is the thickness and \( w \) is the width of the conducting pattern.

In microstrip packages, chances for the generation of unwanted modes based on the case height also should be controlled. Figure 1.8b shows a stripline package wherein the conducting pattern is sandwiched between two dielectric substrates. Unlike microstrip packages where two dielectric media decide the circuit performance, i.e., substrate and air, design consideration of stripline packages restricts to dielectric material alone. This can eliminate unwanted mode generation. In the case of suspended substrates (figure 1.8c) the outer case itself will act as the bottom conducting layer. The shape and size of the casing is depend on the application.

![Figure 1.8 Microwave transmission mediums in metallic cases.](image)
After World War II only a large number of materials were attempted as base material for high frequency communication circuitries. Based on the composition and physical properties, microwave substrates are broadly classified into hard and soft substrates. Hard substrates are made out of sintered ceramic materials whereas soft substrates are fabricated using ceramic or glass fiber filled polymer composite substrates [38, 41, 42].

1.3.4.1 Hard microwave substrates

Hard substrates include ceramics such as alumina, aluminum nitride, beryllium oxide etc. having desirable dielectric properties at microwave frequency region. Ceramics possess a combination of electrical, mechanical, thermal and dimensional properties unmatched to other group of materials. For instance, ceramics have coefficient of thermal expansion of silicon which is matching to that of copper or silver and have thermal conductivity higher than that of aluminium metal (220 W/m/K). Another desirable property of ceramic substrates is their high temperature stability, which helps the circuits to perform at higher temperatures. Ceramic substrates are better choice for circuits where hermeticity is required. Hard substrates have another advantage of isotropic dielectric properties throughout the material medium. Some of the important materials used as the base substrates in microwave frequency region are shown in table 1.3 [40, 43, 44].

Table 1.3 Examples of hard microwave substrates

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (g/cc)</th>
<th>Dielectric constant</th>
<th>Loss tangent</th>
<th>Coefficient of thermal expansion (ppm/°C)</th>
<th>Thermal conductivity (W/m/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>99.6%Alumina(Al₂O₃)</td>
<td>3.97</td>
<td>9.8</td>
<td>0.0001</td>
<td>8.2</td>
<td>35</td>
</tr>
<tr>
<td>Aluminum nitride(AlN)</td>
<td>3.80</td>
<td>8.9</td>
<td>0.0005</td>
<td>4.4</td>
<td>260</td>
</tr>
<tr>
<td>Beryllium Oxide(BeO)</td>
<td>-</td>
<td>6.7</td>
<td>0.003</td>
<td>6.05</td>
<td>250</td>
</tr>
<tr>
<td>Gallium Arsenide(GaAs)</td>
<td>5.32</td>
<td>12.88</td>
<td>0.0004</td>
<td>6.86</td>
<td>46</td>
</tr>
<tr>
<td>Quartz</td>
<td>2.2</td>
<td>3.8</td>
<td>0.0001</td>
<td>0.6</td>
<td>5</td>
</tr>
<tr>
<td>Silicon Carbide (SiC)</td>
<td>3.2</td>
<td>10.8</td>
<td>0.002</td>
<td>3.1</td>
<td>350</td>
</tr>
</tbody>
</table>

Alumina with greater than 99.6% purity is the widely used ceramic material for high frequency packaging applications. Alumina has a dielectric constant of 10 with very high
quality factor. The dielectric properties of this material are highly depending on the sintered density and its microstructure. The sintered density depends on the amount of constituent phase, such as $\alpha$-alumina and $\theta$-alumina and the sintering aids. Sintered alumina samples with relative density around 99.49% at 1400 °C for 8h have been reported by Huang et al. A dielectric constant of 10 and $Q_{\tau f}$ value of 6,34,000 at 14 GHz with $\tau\sim40$ ppm/°C was obtained for these authors [45]. Reports are also available for high quality factor alumina substrates with Titanium dioxide as the sintering aid [46].

Aluminium nitride is another important packaging material with superior thermal conductivity than alumina. It has a dielectric constant less than alumina with thermal expansion coefficient comparable to that of silicon. Aluminium nitride has been reported with a number of additives to improve sinterability or to modify the microstructure [47,48]. SiC is an electrically insulating substrate with very high thermal conductivity with CTE very close to that of silicon. The sintering temperature of SiC is still very high (2100 °C) even after the addition of BeO as sintering aid. The enhanced thermal conductivity of SiC may be due to the segregation of BeO in the grain boundaries which restricts the grain growth and forming a resistive network on the grain boundaries as a result of purity of SiC grains. Fused silica and cordierite are the other materials used as base substrates having dielectric constant of 3.78 and 4.5 respectively [40, 49].

Eventhough ceramic substrates are the best packaging materials at microwave frequencies they have some drawbacks. They require higher processing temperature than plastics, making them more expensive. For example 99.6% pure alumina can be sintered only at temperature $>$1400 °C in high temperature furnaces wherein MoSi$_2$ heating elements were used. Controlling microstructure and avoiding warpage is also difficult at high temperature processing. Ceramics are brittle in nature, which makes them prone to catastrophic failure and sensitive to stress corrosion. Ceramic microwave substrates have only specific dielectric constant values and hence the circuit designers have limited choice to select base materials. In addition, for very high performance applications, ceramics cannot compete with polymer packages, wherein very low dielectric constant together with high packaging density is needed [38, 40, 42].
1.3.4.2 Soft microwave substrates

Soft substrates are polymer based materials wherein polymers are filled with either ceramic particulates or woven glass materials. Soft substrates are advantageous over hard substrates in low temperature processing, flexibility, low cost conducting patterns, easy machinability etc. [38, 42]. Wide range of dielectric constant can be realized in soft substrates by controlling the filler content in the polymer matrix. Soft substrates for the high frequency applications are divided into two categories, thermoplastic and thermoset materials. Thermoplastic materials are those have melt temperature associated with them, while dimensional behavior of thermosets were characterized by its glass transition temperature Tg. In the last few years the growth of wireless market and the recent advances in high speed digital technology have brought about the introduction of new thermoset as well as thermoplastic materials with superior electrical performance to address these needs [50, 51].

Most common base substrate used for microwave circuit fabrication is the Epoxy/Glass substrate (FR-4) having dielectric constant of 4.4 with loss tangent 0.05 at 800 MHz. FR-4 is fabricated through hot pressing of woven fabric/brominated epoxy composites [63]. But the usage of FR-4 substrates at high frequencies (>1 GHz) were restricted due to their higher loss tangent [52, 53]. Polystyrene is a low loss material and hence can be used for high frequency applications. Alumina filled Polystyrene composites were reported as substrate material for microwave applications. But the low service temperature and crack formation make polystyrene unfavorable in commercial use [54].

Several materials based on thermosetting polymer matrix are available for high frequency applications. Thermosetting polyimide is one of the most preferred matrices for fabricating such substrates. Rogers Corporation, USA, is the main manufacturers of these type of substrate materials. Rogers RO4000 series materials are another class of thermoset hydrocarbon based materials having dielectric constant 3.38, 3.48 and 3.17 respectively for RO 4000, RO 4350B and RO 4403 but suffer from comparatively high loss tangent. One of the most common PCBs for high frequency application is filled poly (1, 2-butadiene)
composites [55]. These composites exhibit low porosity content even at filler loading of 60 volume%. Poly (1, 2-butadiene) based substrates having dielectric constant 3.27, 4.5, 6, 9.2 and 9.8 with loss tangent <0.0025 at 10 GHz are commercially available. Table 1.4 shows the properties of some of the poly (1, 2-butadiene) based high frequency substrate materials, which are commercially available. Laminates based on thermoset polymers need only ordinary processing techniques but suffer from high moisture absorption content and low tensile strength. Long term exposure of these thermoset matrix substrates to highly oxidative environment may lead to change in the dielectric properties of hydrocarbons and hence the substrates. It is difficult to use this class of materials in the extreme chemical environment [56-58].

Table 1.4 Properties of some thermoset polymer based microwave substrates

<table>
<thead>
<tr>
<th>Properties</th>
<th>TMM3</th>
<th>TMM4</th>
<th>TMM6</th>
<th>TMM10</th>
<th>TMM10i</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dielectric constant</td>
<td>3.27±0.03</td>
<td>4.5±0.04</td>
<td>6.0±0.08</td>
<td>9.2±0.23</td>
<td>9.8±0.24</td>
</tr>
<tr>
<td>Loss tangent</td>
<td>0.002</td>
<td>0.002</td>
<td>0.0023</td>
<td>0.0022</td>
<td>0.002</td>
</tr>
<tr>
<td>$\tau_{\varepsilon}$ (ppm/°C)</td>
<td>+37</td>
<td>+15</td>
<td>-11</td>
<td>-38</td>
<td>-43</td>
</tr>
<tr>
<td>CTE (ppm/°C)</td>
<td>23</td>
<td>21</td>
<td>26</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Moisture absorption(%)</td>
<td>0.12</td>
<td>0.18</td>
<td>0.2</td>
<td>0.2</td>
<td>0.13</td>
</tr>
<tr>
<td>Thermal conductivity(W/m/K)</td>
<td>0.70</td>
<td>0.70</td>
<td>0.72</td>
<td>0.76</td>
<td>0.76</td>
</tr>
<tr>
<td>Glass Transition temp. (°C)</td>
<td>425</td>
<td>425</td>
<td>425</td>
<td>425</td>
<td>425</td>
</tr>
</tbody>
</table>

TMM is the registered trade mark of poly (1, 2-butadiene) based substrates

Thermoplastic materials have advantages over thermoset matrices in their chemical inertness and high service temperature. Various thermoplastics having low loss tangent are used as the matrix for making flexible microwave substrates. Poly(tetrafluoroethylene) (PTFE), Polyphenylene Oxide (PPO), Polyetherimide (PEI) etc are the major thermoplastic polymer matrices having stable dielectric properties in the microwave frequency region [59]. In late 1960s, Polyphenylene oxide (PPO) was introduced as an ideal material for microwave application with uniform and reproducible dielectric properties. NorClad laminates manufactured by Polyflon Company, USA are made using thermoplastic Polyphenylene
Oxide and having a dielectric constant of 2.54 (Table 1.5). The PPO based PCB is chemically weak and appeared to be sticky after chemical etching. Fine cracks are developed after the circuit had been patterned and the device has been fabricated. Irradiated high density polyolefin and Polyetherimide (PEI) are two thermoplastics which are used to fabricate high frequency laminates. Polyguide and ULTEM are the two commercially available substrates fabricated using Polyolefin and Polyetherimide matrices respectively. The physical properties of these substrates are shown in Table 1.5. The main drawback of thermoplastic matrix laminates is their high coefficient of thermal expansion along Z-axis. Large mismatch in CTE exists between the base substrate and the conducting layer and hence make them difficult to use during temperature cycling. In addition, these thermoplastic materials show high loss tangent at very high frequencies [38, 60-62].

Table 1.5 Properties of some thermoplastic polymer based microwave substrates

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>NorClad</th>
<th>POLYGUIDE</th>
<th>ULTEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dielectric constant (3 GHz)</td>
<td>2.55</td>
<td>2.32</td>
<td>3.05</td>
</tr>
<tr>
<td>Loss tangent (3GHz)</td>
<td>0.0011</td>
<td>0.0005</td>
<td>0.0033</td>
</tr>
<tr>
<td>Density (g/cc)</td>
<td>1.12</td>
<td>0.95</td>
<td>1.27</td>
</tr>
<tr>
<td>CTE (ppm/°C)</td>
<td>53</td>
<td>108</td>
<td>56</td>
</tr>
<tr>
<td>Moisture absorption (%)</td>
<td>0.06</td>
<td>0.01</td>
<td>0.25</td>
</tr>
<tr>
<td>Thermal conductivity (W/m/K)</td>
<td>0.23</td>
<td>0.51</td>
<td>0.22</td>
</tr>
<tr>
<td>Max. Operating temperature (°C)</td>
<td>&lt;175</td>
<td>&lt;125</td>
<td>&lt;225</td>
</tr>
</tbody>
</table>

PTFE based substrates are ideal choice to fabricate microwave integrated circuits for high performance applications. PTFE has extremely low loss tangent due to its non polar molecular structure. PTFE as such cannot be used for circuit fabrication due its high linear coefficient of thermal expansion (CTE~ +109 ppm/°C), very low thermal conductivity (TC~0.25 W/m/K), poor machinability etc. [63]. However, these problems can be surmounted by incorporating particulate ceramics or woven/non woven glass materials in to it and accordingly the CTE of PTFE can be reduced to match with that of copper conducting.
layer and the lead soldering. A better stress relief during circuit fabrication can be achieved in PTFE composites than that of virgin PTFE due to comparable CTE with that of conducting layer as well as lead soldering. The thermal conductivity of PTFE can also be improved by ceramic or woven/non woven glass filler content [38, 42].

By early 1950s itself, PTFE filled with glass cloth laminates having dielectric constant 2.55 were identified to replace polystyrene based substrates. Later on several attempts have been made to tailor the dielectric properties of PTFE using woven as well as non woven glass. PTFE/glass laminates have low dielectric constant, low loss tangent, low moisture absorption and low CTE compared to thermoplastic matrix laminates. They have been in use for civil as well as military applications and having some standard designations. The standard designations used for PTFE/glass laminates are shown in table 1.6 [38].

Table 1.6 Standard designation of microwave laminates

<table>
<thead>
<tr>
<th>Designation</th>
<th>Systems</th>
</tr>
</thead>
<tbody>
<tr>
<td>GP</td>
<td>Non woven glass fabric base, PTFE resin, flame resistant</td>
</tr>
<tr>
<td>GR</td>
<td>Non woven glass fabric base, PTFE resin, flame resistant</td>
</tr>
<tr>
<td>GT</td>
<td>Woven glass fabric base, PTFE resin, flame resistant</td>
</tr>
<tr>
<td>GX</td>
<td>Woven glass fabric base, PTFE resin, flame resistant</td>
</tr>
<tr>
<td>GI</td>
<td>Glass fabric base, Polyimide resin</td>
</tr>
<tr>
<td>GY</td>
<td>Woven glass fabric base, PTFE resin, flame resistant</td>
</tr>
</tbody>
</table>

After developing PTFE/glass laminates having dielectric constant 2.55, the amount of glass content in the matrix is reduced to make ‘GX’ type product having MIL-P-13949 specifications (military specifications) with dielectric constant 2.45 [38]. Later microfiber glass filled PTFE laminates were introduced with superior mechanical properties. A dielectric constant of 2.2 with loss tangent 0.0009 was obtained for such laminates. Including this, a range of materials has been realized in PTFE/glass system with dielectric constant
varying from 2.17 to 2.55. The loss tangent also increases with respect to glass content in the PTFE matrix. In PTFE/woven glass material, the woven pattern of fiber glass strands was embedded into PTFE material. This uniform and consistent construction results in better consistency in dielectric parameters and gives better machinability. Whereas, in the case of PTFE/microfiber glass laminates, individual glass microfibers are encapsulated with PTFE and dispersed uniformly throughout the matrix with random orientation. These materials are softer than PTFE/woven glass laminates and hence require precautions during processing [38]. M/s Rogers corporation, USA, is the main manufacturer of PTFE/glass microwave laminates. RT/Duroid 5880 and RT/Duroid 5870 are the two main flexible PTFE/glass fibre laminates having dielectric constant 2.2 and 2.33 and loss tangent of 0.0009 and 0.0012 respectively. The temperature coefficient of dielectric constant of RT/Duroid 5880 and RT/Duroid 5870 is -125 and -115 ppm/°C respectively and they possess very low moisture absorption characteristics (<0.06%). These materials possess high tensile strength and through hole reliability. Even though PTFE/glass laminates have excellent microwave dielectric and mechanical properties, they suffer from severe drawback viz. dielectric anisotropy [38, 64].

Figure 1.9 Dielectric anisotropy versus dielectric constant

An important parameter, the dielectric anisotropy (the difference in dielectric constant of the laminate measured in the XY plane to that in the Z direction), is comparatively higher in the case of PTFE/glass laminates due to its particular structure.
Among PTFE/glass laminates, PTFE/woven glass laminates show comparatively higher dielectric anisotropy (figure 1.9). The anisotropy is observed to increase with glass content also. On the other hand ceramic filled PTFE composite substrates have various advantages over PTFE/glass composites mainly due to its nearly isotropic dielectric constant and ease of achieving higher dielectric constant values. Ceramic oxides with low loss tangent can be used as particulate filler in PTFE matrix at appropriate filling fraction to fabricate planar substrates with higher dielectric constant and acceptable loss tangent [38, 65].

Ceramic filled PTFE composites are widely used as base material for high frequency circuits where very stringent circuit performance is needed. Silica and rutile grade titania are used as particulate fillers for making low and high dielectric constant substrates respectively. The main advantages of ceramic filled PTFE substrates are their nearly isotropic dielectric constant compared to PTFE/woven glass substrates. Through proper process modification uniform dielectric constant can be achieved in the X, Y and Z directions. The CTE can be reduced and the thermal conductivity can be increased by proper filler loading in the PTFE matrix. Ceramic filled PTFE substrates having various thicknesses were produced commercially without much dielectric anisotropy. But in the case of woven glass filled PTFE, the dielectric anisotropy increases with respect to substrate thickness. The ceramic fillers may distribute uniformly in the X-Y and Z directions and there by reduce the dielectric anisotropy [38, 42].

M/s. Rogers Corporation, USA, is the main manufacturer of ceramic filled PTFE microwave substrates and their products are known under the trade name RT/Duroid 6002, RT/Duroid 6006 and RT/Duroid 6010. Among commercially available ceramic filled PTFE substrates, RT/Duroid 6010 has the highest dielectric constant, 10.2±0.25, RT/Duroid 6002 has the lowest dielectric constant of 2.94±0.04 and RT/Duroid 6006±0.15 has medium dielectric constant of 6.15 together with loss tangents of 0.0022, 0.0019 and 0.0027 respectively [66, 67]. The temperature coefficient of dielectric constant of RT/Duroid 6010 and RT/Duroid 6006 are on the higher side, -425 ppm/°C and -410 ppm/°C respectively. The important properties of RT/Duroid 6000 series microwave substrates are shown in table 1.7. This is one of the main disadvantages of these classes of materials since the high temperature
coefficient of dielectric constant affects the operating frequency during outdoor wireless applications. All the three substrates based on PTFE ceramic system have low CTE, which is comparable to that of copper conducting patterns. In addition, low moisture absorption and high chemical inertness are the common characteristics for ceramic filled PTFE substrates. Ceramic filled PTFE substrates are widely used for the fabrication of patch antenna, RADAR and various other high frequency circuitries owing to its unique electrical and mechanical properties [68, 69].

Table 1.7 Properties of PTFE/Ceramic microwave substrates

<table>
<thead>
<tr>
<th>Properties</th>
<th>RT/Duroid 6002</th>
<th>RT/Duroid 6006</th>
<th>RT/Duroid 6010</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dielectric constant</td>
<td>2.94</td>
<td>6.15</td>
<td>10.2</td>
</tr>
<tr>
<td>Loss tangent</td>
<td>0.0019</td>
<td>0.0027</td>
<td>0.0022</td>
</tr>
<tr>
<td>$\varepsilon_r$ (ppm/°C)</td>
<td>+12</td>
<td>-410</td>
<td>-425</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>17</td>
<td>20</td>
<td>17</td>
</tr>
<tr>
<td>CTE (ppm/°C)</td>
<td>20</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>Moisture absorption (%)</td>
<td>&lt;0.1</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
</tbody>
</table>

Even though ceramic filled PTFE substrates are the ideal choice for high frequency circuit applications, their cost is on the higher side compared to ordinary epoxy/glass (FR-4) based materials. This is because special processing techniques are needed for the fabrication of PTFE/ceramic substrates. As explained earlier, it is difficult to disperse ceramic particulates uniformly throughout the PTFE matrix due to its very high melt viscosity. Hence special processing techniques are needed for achieving uniform filler distribution in PTFE matrix which in turn increases the cost of the final product. In figure 1.10 the performance and cost of PTFE based microwave laminates were compared with other soft microwave substrate materials. All the soft microwave substrates explained are heterogeneous systems consists of more than one component wherein one component is a polymer matrix. It is to be noted from the figure that the cost of substrates depends on the loss tangent. Filled PTFE
substrates have the lowest loss tangent and hence relatively high cost due to processing difficulties.

Figure 1.10 PTFE based materials with other soft microwave substrates

1.4 Polymer/Ceramic composites

A composite material is the one which is composed of at least two components working together to produce material properties that are different to the properties of those elements on their own. In practice most composites consist of a bulk material (the matrix) and a reinforcement of some kind added primarily to increase the strength and stiffness of the matrix. It is typically consists of one or more fillers in a certain matrix. The matrix is usually a polymer, a metal, a carbon, a ceramic or a combination of different materials. Except for sandwich composites, the matrix is three-dimensionally continuous, whereas the filler can be three-dimensionally discontinuous or continuous. Depending up on the matrix, composites are classified as polymer matrix composites, metal matrix composites and ceramic matrix composites. Among these, polymer matrix composites are easier to fabricate. These composites have higher strength than traditional materials due to aligned fibers carrying the load. They are stiffer than conventional materials of the same weight due to their adaptive nature and fibers can be aligned in the direction to carry the load. Polymer composites are
lighter than the traditional materials due to their tailor ability that can be designed to minimum weight without sacrificing strength.

Polymer matrix composites can be classified in to two categories depending on the nature of the matrix used, ie. thermoset or thermoplastic. Among them, thermoset matrix composites are most common while the thermoplastic composites are under rapid development. The main advantage of thermoplastic matrix composites compared with thermoset matrix composites are unlimited shelf life, does not require curing, possibility of reproducing, most of them are chemically inert, lower moisture absorption, thermal processibility and higher service temperature etc. In addition, they also have high environmental tolerance. But still processing difficulties and relatively high viscosity are some drawbacks [69-74].

1.5 Literature review

Even though PTFE based substrates are common in use for the last few decades, only handful of open literature are available regarding the fabrication of these commercially and technologically important class of materials. Most of the research works in this line are protected by patent laws [75, 76]. One of the earliest patents in this direction appeared in 1982 which discloses the fabrication of PTFE/rutile composite. An aqueous polymeric dispersion of PTFE is used for the preparation of composites wherein short microfiber glass is used as reinforcing agent to increase the mechanical strength of the composites. An electrical circuit board is prepared by the authors, over a conductive foil, which is supported on a substrate of a hot-melt resin in accordance with the desired circuit pattern is described here in. The resin may be applied by screen printing and, after curing, functions as a resist coating for the conductive material during subsequent chemical removal of the foil from unprotected areas to form the individual conductor patterns. During subsequent connection of the circuit to other components, contact areas on the individual conductors may be exposed by contacting the resin coating with molten solder [76].
In US patent 4633035, circuit boards useful in microwave frequency applications, are formed from a laminate consisting initially of an insulator sandwiched between a copper foil and an aluminium plate is disclosed [77]. The boards are provided with through-hole connections by means of a procedure which includes drilling through the board to form through-holes, anodizing all exposed surfaces of the aluminium, electroplating copper over all anodized aluminium surfaces, sodium or plasma etching to alter the surfaces of the walls of the holes in the insulator to allow them to be wet, and electroless copper plating the entire board to form a continuous upper coating over the copper foil, the copper plate and the walls of the through holes [77]. In another invention, PTFE filled with fused silica and small amount of microfiber glass for microwave circuit application was disclosed. Here the particulate filler was coated with silane coupling agents to preclude the moisture absorption. Further, different surface modifiers such as zirconate and titanate coupling agents were tried to improve the surface properties of the particulate fillers [78].

Later on several modifications have been attempted to improve the electrical and mechanical properties of filled PTFE composites and to find improved substrate materials for microwave applications [79]. A high capacitance flexible dielectric sheet having dielectric material comprised of a monolayer of multilayer or single layer high dielectric chips or pellets of relatively small area and thickness which are arranged in a planar array is revealed in US patent 4908258. These high dielectric constant chips are spaced apart by a small distance. The spaces between the chips are then filled with a flexible polymer/adhesive to define a cohesive sheet with the polymer bonding the array of high dielectric chips together. The opposite planar surfaces of the array are electroless plated or electroded by vacuum metal deposition, or sputtering to define opposed metallized surfaces. The end result is a relatively flexible high capacitance film or sheet material, which is drillable, platable, printable, etchable, laminable and reliable [79]. Arthur et al. prepared PTFE/silica composites having improved mechanical properties whereas the particulate silica filler is coated with rubbery elastomeric polymeric material to improve the adhesion between filler and the matrix [80].
US patent 5358775 discloses the fabrication of PTFE/ceramic composites having Class1 capacitor materials as the primary filler and alumina or silica as the secondary filler to control the temperature induced shift in dielectric constant [81]. A thermoplastic composite material is presented in US patent 5384181, which comprises of a thermoplastic matrix, which is highly filled with coated ceramic filler. In an important feature of this invention, the ceramic filler has been coated with a rubbery polymer that bonds to the filler. In a preferred embodiment, thermoplastic matrix comprises of a fluoropolymer, preferably a chlorofluoropolymer and the ceramic filler is fused amorphous silica coated with a rubbery polymeric material [82]. Horn III disclosed the preparation of filled PTFE composites with temperature stable dielectric properties in USP 5552210 [83]. Ceramic fillers having temperature coefficient of dielectric constant >-300 ppm/°C and \( \tau_{\varepsilon} > 0 \) are used for the fabrication of such composites. PTFE/ceramic composites having dielectric constant > 5 with \( \tau_{\varepsilon} < 200 \) ppm/°C was realized by these authors.

Apart from these, Walpita et al. disclosed temperature stable filled Polyphenyl sulphide (PPS) composites for printed wiring board applications in US patent 5739193. They introduced temperature stable high dielectric constant thermoplastic polymer composites and copper laminated sheets made out of them for microwave circuits. The design, fabrication and properties of the composites are discussed in detail. The effect of temperature on the resonant frequency of a patch antenna made out of the copper laminated high dielectric constant composite sheets is also discussed. Polyphenyle sulphide of loss tangent 0.002 at 1 GHz is taken as the polymer matrix. Temperature stability of dielectric constant was achieved by incorporating two ceramic fillers whereas first filler has a high negative temperature coefficient of dielectric constant and the second filler has a positive temperature coefficient of dielectric constant. SrTiO\(_3\) ceramic with high negative temperature coefficient of dielectric constant is the first filler and alumina and silica were used as the secondary fillers. These authors succeeded in controlling the temperature coefficient of dielectric constant change of 1% by using mica as the secondary filler. The patch antenna made using this substrate shows <0.5% variation in dielectric constant in the -40 to 100 °C temperature range. The main problem anticipated while using secondary filler is the non-uniform filler distribution due to difference in density and morphology of the secondary fillers. The non-
uniform filler distribution causes dielectric anisotropy and thereby produces fringing capacitance while operation [84, 85].

Apart from patent literature, most of the literature dealing with PTFE substrates concentrate on the behavior of commercially available RT/Duroid printed circuit boards and components fabricated out of it. Tonkin and Hosking studied the dielectric constant and thermal expansion of RT/Duroid substrates at low temperatures -283 to 30 °C [67]. A microstrip in the form of a ring resonator was fabricated over a substrate of thickness 0.25 mm with 17.5 µm thick copper cladding, to study its low temperature dielectric constant and thermal expansion at microwave frequencies. Dielectric constant shows increasing trend with decreasing temperature. A comparative study on the dielectric behavior of FR4 materials with RT/Duroid materials at high frequency has been conducted by R Aguilar et al. It is reported that RT/Duroid materials perform well over FR4 materials at high frequency region [86]. L. J. Matienzo and D. Farquhar studied the effectiveness of PTFE base substrates in multilayer printed wiring boards. This paper reports the use of a model system comprising of pure PTFE film and Cr-coated copper surfaces to optimize the bonding process through lamination conditions for a fluoropolymer composite and chromium-coated copper surfaces and to study both the interface mechanics and its chemistry as a function of processing parameters. Rogers RO series materials were used for comparative studies [87]. E.L Yang studied the static contact characteristics of PTFE on to stainless steel (AISI 316) and silicon wafers at a temperature range of 21-300 °C. It is inferred that the amount of transferred PTFE depend on the relative amount of amorphous phase in the PTFE contact area [88]. Dielectric properties of pure PTFE are measured at very low temperature by Mohan Jacob et al. A loss tangent of 2x10^-6 was reported for PTFE and suggested to be suitable for fabricating high Q microwave devices at cryogenic temperatures [89].

Recently many researchers showed renewed interest in ceramic filled PTFE composites and a couple of research papers are appeared. Most of the works are basic studies discussing the effect of filler loading on the dielectric properties of PTFE/ceramic composites. PTFE/BZN composites reported by Xiang et al. exhibit high dielectric constant (ε'_r=13 at 800 MHz) but too lossy (tan δ=0.014 at 800 MHz) to be used at higher frequencies
The effect of filler content on the dielectric, thermal and mechanical properties of PTFE/SiO$_2$ composites was studied by Chen et al. Chen et al. have studied PTFE reinforced with tetraethoxysilane (TEOS) derived SiO$_2$ prepared through sol-gel process and the composite is fabricated through two roll milling followed by pressureless sintering. These researchers reported that the water absorption and dielectric loss of PTFE/SiO$_2$ hybrid have significantly improved with silylation agent. The silylation process replaced SiO-OH with SiOCH$_3$ on the surface of the TEOS-derived silica colloidal particle. Nitrogen-absorption techniques are used to characterize the modified and unmodified PTFE/SiO$_2$ hybrids. The microstructure of SiO$_2$ in the matrix is also evaluated with scanning electron microscopy and transmission electron microscopy. Their results show that the silylated sol–gel derived PTFE/SiO$_2$ hybrids have exhibited high porosity (53.7%) with nanosize pores (10–40 nm) and nanosize colloidal particles (20–50 nm) [91].

Preparation of SiO$_2$ reinforced PTFE composites using PTFE suspension and silica powders (5 µm and 25 µm SiO$_2$) through dispersion mixing, rolling followed by pressureless sintering have been reported by the same authors. Their results reveal that the composite filled with 25 µm SiO$_2$ at 60 wt% filler content has the highest modulus, lowest CTE along Z-direction and acceptable dielectric properties [92]. Composites with different sizes of filler show a similar trend of decreasing tensile strength and CTE, and increasing tensile modulus, water absorption and dielectric properties as the filler content increases. Furthermore, the composites filled with filler having lower size show higher water absorption and dielectric loss properties due to the presence of higher SiO$_2$ surface area. Poor adhesion between filler and matrix is projected as the primary cause for low tensile properties and lack of increase in thermal stability, which is confirmed by fracture surface analysis through scanning electron microscopy. It is also observed that experimental values of dielectric constant and CTE along Z-direction agree with the theoretically calculated values using equations from literature. It is also found that the modified Nicolais-Narkis equation provides a good estimation for the tensile strength of composites [91].

In another work from the same research group, the effect of phenyltrimethoxysilane coupling agents on the thermal properties, dielectric properties, tensile strength and
morphology of PTFE/Silica composites has been studied. 60 wt% fused silica filled PTFE composite were prepared following the same materials and method published earlier [93].

A study on PTFE reinforced with silica having 5 \( \mu \)m and 20 nm size is described by S-I Huang et al. In this study, the amount of micron size silica filler is replaced with nano silica in 2 wt% interval keeping the total filler concentration at 35 wt%. It is found that the composites filled with 2 wt% nanosize silica (20 nm) and 33 wt% micron-size silica (5 \( \mu \)m) have the best modulus. The Z-direction coefficient of thermal expansion decreases with the increasing concentration of nano-sized silica in the composites. The higher content of nanosized silica added in the PTFE results in porous morphology, and lowers the dielectric constant. However, the authors have not mentioned about the loss tangent of the composite as a result of nano silica content [94]. These authors studied the effect of silylation agent on porosity, hydophobicity, thermal resistance, dielectric, microstructure and mechanical properties of PTFE/SiO\(_2\) hybrids. Invariably in all these works, colloidal PTFE which contains non-ionic surfactants (Triton X-100) was used for the preparation of the composites. In order to get better composite properties, non-ionic surfactant has to be completely removed through extensive ion-free water washing before sintering process.

To avoid the presence of harmful impurities such as Triton X-100, recently researchers are paying more attention to use granular PTFE powder for making composites for electronic applications. One such effort in this direction was done by G. Subodh et al. using \( \text{Sr}_2\text{Ce}_2\text{Ti}_5\text{O}_{16} \) ceramic fillers in PTFE matrix through powder processing route [95]. The effect of TeO\(_2\) filler loading on the microwave dielectric properties of PTFE composite has also been studied by the same authors [96]. 60 vol% TeO\(_2\) loading in PTFE matrix results in a composite having a dielectric constant \( \varepsilon'_r \sim 6 \) and a loss tangent of 0.0055 [96]. Recently P. S. Anjana et al. prepared PTFE/CeO\(_2\) composites through powder processing technique. Dielectric constant of 5 with loss tangent 0.0064 at 7 GHz was measured by these authors at 60 vol% filler loading [97]. In another report, S. Thomas el al. discusses the fabrication of PTFE/ZnAl\(_2\)O\(_4\)–TiO\(_2\) composites through the powder processing route and its dielectric properties at microwave frequency region [98]. Although the processing route is simple and uniform filler distribution is achieved through this process, yet the final density of
the composites are rather poor. The high amount of porosity will determinately affect the moisture absorption as well as microwave dielectric properties of composite substrates while put in to use for circuit applications [81]. Hence an alternate method is essentially needed for the fabrication of dimensionally stable PTFE composite substrates with bare minimum porosity.

1.6 Objective of the present work

It is clear from the foregoing discussions that PTFE is the ideal matrix to fabricate flexible laminates for microwave circuit applications. PTFE possesses the lowest loss tangent (0.0003 at 10GHz) and stable dielectric constant among polymers because of the symmetrical conformation of the polymer backbone, which effectively neutralizes the dipole forces of the carbon fluorine bonds. In addition to its extraordinary dielectric properties, PTFE also has advantages like high chemical inertness, low moisture absorption, and high operating temperature (<250°C) as a result of its unique structure. However PTFE as such can not be used for microwave substrate application because of its high coefficient of thermal expansion (CTE ~109 ppm/°C) and poor dimensional stability. Hence PTFE is often filled with either glass fiber or ceramic particulates to circumvent these problems. Among these, ceramic filled PTFE substrates are widely accepted for microwave packaging applications because of its nearly isotropic microwave dielectric properties, low coefficient of thermal expansion and better machinability. However, processing of filled PTFE substrates are severely impeded through conventional techniques because of the extremely high melt viscosity of PTFE (10^{11} Pa.s). Because of these processing difficulties, PTFE based microwave substrates are produced only by handful of industries and the research outcomes are protected by patent laws. More over the PTFE/ceramic substrates available from commercial market are restricted to three different classes with dielectric constant only up to 10.2. For further circuit miniaturization, dielectric constant needs to be increased. Hence there is a perceived need to develop a novel processing methodology for the fabrication of filled PTFE substrates which can deliver dimensionally stable and nearly isotropic planar substrates with wide range of dielectric constant to meet present and future requirements. To the best of our knowledge, no
open literature is available regarding the fabrication of planar PTFE substrates for microwave circuit applications.

Hence in the present work, an attempt has been made to prepare planar filled PTFE substrates and evaluate its properties. The effect of particle size, morphology of the filler and the loading fraction in the PTFE matrix was studied. The ceramic fillers were treated with silane coupling agent in order to preclude its moisture absorption. Ceramics having high dielectric constant such as rutile, SrTiO$_3$, CaTiO$_3$, Sr$_2$Ti$_9$O$_{20}$ and Ca$_2$Ti$_9$O$_{20}$ were filled in the PTFE matrix to realize high dielectric and low loss planar circuit laminates.

In addition, different modeling schemes have been attempted to predict the effective dielectric constant of the filled PTFE substrates. Such precise modeling approaches are expected to yield composite substrates having predefined dielectric properties.

Precise determination of microwave dielectric properties of filled PTFE substrates are also of vital importance since circuit design is done based on the effective dielectric constant and thickness of the base substrates. Further, coefficient of thermal expansion, moisture absorption and tensile properties are also important for better functioning of the microwave circuitry at extreme conditions.

In short, the main objectives of the present research work concentrates on the following important factors of microwave substrate materials and how best these properties can be tailored.
1) Development of a novel process methodology for the fabrication of PTFE based composites for microwave substrate applications.
2) Precise theoretical modeling approaches to predict effective dielectric constant.
3) Preparation of ceramic filled PTFE laminates having high dielectric constant.
4) Achieving temperature stability in high dielectric PTFE laminates.
5) Microwave dielectric, thermal and mechanical characterization of filled PTFE substrates.
6) The role of filler size, morphology and distribution characteristics on the end properties of filled PTFE substrates.
1.7 Characterization techniques

In order to accomplish the above-mentioned objectives, the dielectric, thermal and mechanical properties of the polymer ceramic composites need to be thoroughly evaluated. In the present study, ceramic filler materials and the filled composite substrates are extensively evaluated using different characterization techniques. The basic principle and methodology of different characterization techniques adopted in the present work is discussed in the following sections.

1.7.1 Powder X-ray Diffraction technique

X-ray Diffraction (XRD) is an analytical technique with very broad range of applications in Physics, Materials Science, Geology, Mineralogy, Ceramics, etc. X-ray diffraction can be explained in simple terms by diffraction of an X-ray beam from a stack of parallel equidistant atomic planes. A small portion of the beam can be considered to be reflected at each atomic plane. If those reflected beams emerge from the crystal in such a way that they do not cancel each other by interference, a diffracted beam can be observed. The condition where the reflected beams interfere positively to give a strong diffracted beam is represented by Bragg's law and is given by \(2d\sin\theta = n\lambda\), where \(n\) is an integral number describing the order of reflection, \(\lambda\) is the wavelength of X-rays, \(d\) is the interplanar spacing and \(\theta\) is the Bragg's angle at which a maximum in diffracted intensity occurs. If the material under investigation is crystalline, then well-defined peaks will be observed while non-crystalline or amorphous systems show hallow instead of well defined peaks.

X-ray diffraction technique is widely accepted for the characterization of micron and nano particles. Width and shape of the measured diffraction lines are characteristic of the crystallite size as well as the lattice strain. Very small crystallites can be considered to be domains, which are diffracting incoherently with respect to one another, resulting in a Lorentzian line broadening. Line profile analysis of XRD data is well suited for the determination of the crystallite size distribution. If the line broadening is caused only by small crystallite size, the crystallite size can be estimated from the Scherrer’s equation
\[ D = \frac{k\lambda}{\beta \cos \theta} \]  

(1.24)

where \( \theta \) is the Bragg angle, \( \lambda \) is the wavelength of the X-rays, \( D \) is the mean dimension of the crystallite size. For the powder sample \( \beta \) is the full width at half maximum of the pure diffraction profile on the 2\( \theta \) scale in radians. \( k \) is a constant approximately equal to unity. In the determination of particle size by this method, it must be realized that instrumental effects might also increase the width of reflection and correction for instrumental broadening must be applied [99, 100].

X-ray diffraction studies for the present investigation were performed using an AXS Bruker D5005 X-ray diffractometer (Germany) with a vertical goniometer. X-ray generator was operated at 40 kV and 30 mA. CuK\(_\alpha\) (\( \lambda = 1.5418 \) Å) radiation was used with Ni filter.

1.7.2 Scanning Electron Microscopy

Scanning Electron Microscope (SEM) is used primarily for the study of surface morphology of solid specimens and to get images that have a high visual impact. SEM has been applied to the study of fibrous materials, ceramics, composites, metals etc. Information may be obtained by examination of both natural surface of materials and that exposed by either fracture or sectioning. Rough topographic features, void content and particle agglomerates are easily revealed as well as phase differences within a material.

In SEM, an electron beam passes through an evacuated column, which is focused by electromagnetic lenses onto the specimen surface. The beam is then rastered over the specimen in synchronism with the beam of a cathode ray tube display screen. Inelastically scattered secondary electrons are emitted from the sample surfaces and collected by a scintillator, and the signal from which is used to modulate the brightness of the cathode ray tube. In this way, the secondary electron emission from the sample is used to form an image on the cathode ray tube display screen. Differences in the secondary emission result from changes in surface topography. If elastically back scattered electron beam are collected to form the image, contrast result from compositional differences [101, 102]. Cameras are
provided to record the images on the display screen. In the present study, we used a Philips XL-30 Model (The Netherlands) SEM machine for analyzing the morphology of the samples.

1.7.3 Transmission Electron Microscopy

Theoretically the maximum resolution that one can obtain with a light microscope has been limited by the wavelength of the photons that are being used to probe the sample and the numerical aperture of the system. Electrons have both wave and particle properties and their wave-like properties mean that a beam of electrons can be made to behave like a beam of electromagnetic radiation. Since electron beam can have wavelength 100,000 times less than that of visible light and hence can be focused up to few nanometers. Transmission Electron Microscopy is one of the most powerful microscopic techniques, which utilize the wave nature of electrons for the visualization and characterization of fine particles.

TEM technique involves a high voltage electron beam (~100 kV) which is derived by cathode emission. This beam is focused by electrostatic and electromagnetic lenses (condenser system) and transmitted through a specimen that, depending on the spatial amount of staining reagent (negative staining TEM) or sample embedded in vitreous ice (cryo-TEM), is partially transparent to electrons. Consequently, the electron beam carries information about the structure of the specimen and is subsequently transferred to the imaging system of the microscope. There, the image is magnified by a series of electromagnetic lenses (projective system) until it is recorded by hitting a fluorescent screen, photographic plate, or light sensitive sensor such as a CCD (Charge-Coupled Device) camera [103, 104]. A Hitachi H600, Japan make transmission electron microscope was used in the present study.

1.7.4 Particle Size Analysis

Particle size and distribution play a critical role in determining the filler loading fraction in polymer/ceramic composites. Particle size analysis has been done using laser diffractometry. The powder samples to be analysed is suspended in an appropriate liquid
medium. This suspension is pumped through a measuring cell and illuminated by a laser beam. The scattered light is collected by a detector and the size distribution of the particles can be calculated from the diffraction pattern. When particles of different sizes pass through a laser beam, they cause the laser light to be scattered at angles that are inversely proportional to the particle size. There are several techniques based on different principles to determine the particle size distribution, each giving its own results. The irregularity effects are ignored during measurements [105, 106].

The possible errors during measurements can come from the inhomogeneity of the sample, agglomeration effects and large differences in particle size and particle shape. The technique should not be applied to highly magnetic materials. In the present study Microtrack X100 (USA) make particle size analyzer has been used for the measurement of particle size and size distribution.

1.7.5 Infrared spectroscopy

Infrared (IR) spectroscopy is one of the most popular analytical techniques used to characterize ceramic samples in their different stages especially in sol-gel preparation route of silica. The IR region of electromagnetic spectrum is divided into three regions such as near IR (14000-4000 cm\(^{-1}\)), used to excite overtones and harmonic vibrations, mid IR (4000-400 cm\(^{-1}\)) used to study the fundamental vibrations associated with rotational vibrational structure and far IR (400-10 cm\(^{-1}\)) used for rotational spectroscopy. IR spectroscopy exploits the fact that molecules have specific frequencies at which they rotate or vibrate corresponding to discrete energy levels (vibrational modes). These resonant frequencies are determined by the shape of the molecular potential energy surface, the masses of the atoms associated and by the associated vibronic coupling. In order for a vibrational mode in a molecule to be IR active, it must possess a change in the permanent dipole. In particular, when the molecular Hamiltonian corresponding to the electronic ground state can be approximated by normal modes corresponds to the molecular electronic ground state potential energy surface [107, 108].
The IR spectrum of a sample is collected by passing a beam of IR light through the sample. Examination of the transmitted light reveals how much energy was absorbed at each wavelength. This can be done by a monochromatic beam which changes in wavelength or time or by using a Fourier transform instrument to measure all wavelength at once. From this transmittance or absorbance spectrum can be produced showing at which IR wavelength the sample will absorb. Analysis of these absorption characteristics reveals detail about the molecular structure of the sample. The powder sample to which the IR spectrum should be taken is grind well with purified potassium bromide (KBr) to avoid the scattering effect from the large crystals and then placed inside a cuvet through which IR can pass.

In the present study the IR spectrum was taken using Shimadzu 8400, Japan, make FTIR spectrometer in the mid IR region.

1.7.6 Laser Raman spectroscopy

The inelastic scattering of light by vibrational excitation takes the name of Raman scattering. If a phonon is created, then the scattering is referred as Stokes process \( (\omega_S = \omega_L + \omega_K) \) and if a phonon is annihilated then the process is an anti Stokes process \( (\omega_S = \omega_L - \omega_K) \). In order to be Raman active a molecular rotation or vibration must cause some change in a component of the molecular polarizability. A change in polarizability is reflected by a change in either the magnitude or the direction of the polarizability ellipsoid. Raman spectroscopy generally applied in the wavelength limit of 50 to 1000 cm\(^{-1}\). Raman and IR vibrations are related by rule of mutual exclusion. Rule of mutual exclusion states that, if a molecule has centre of symmetry then Raman active vibrations are IR inactive and vice versa. If there is no centre of symmetry then some (but not necessarily all) vibrations may be both Raman and infrared active.

Raman spectrometers were revolutionized by the invention of lasers and its subsequent applicability in Raman spectroscopy. The laser is an ideal source for Raman experiment; it can give very narrow, highly monochromatic, coherent beam, which can be focused very finely into a sample. The plane polarized laser beam is passed through a cell
usual a narrow glass or quartz tube filled with sample. Light scattered sideways from the sample is collected by lenses and passed in to a grating monochromator. The signal is measured after passing through a photomultiplier and then plots the Raman spectrum. Raman spectroscopy has several advantages over IR spectroscopy mainly in the case of sample cells, small quantity of samples and usability in aqueous samples because the sample signal is not absorbed by the solvent [109, 110].

In the present work Bruker, RFS 1001s spectrophotometer with Nd:YAG laser of wavelength 1064 nm and Ge target was used for the measurement.

1.7.7 Thermal analyses

Thermal method of analyses exists as an imperative tool in materials characterization for the last five decades. In thermal analysis, the physical parameter of a system is determined as a function of temperature. Among the different thermal analyses, thermomechanical analysis (TMA) and thermogravimetry (TG) are discussed in length due to its relevance in the present work [111, 112].

1.7.7.1 Thermomechanical analysis

The determination of the change in length or volume of a sample as a function of temperature is called thermo mechanical analysis (TMA). Dilatometry has been used in ceramics and metallurgy for last many years and only recently this technique has been applied to characterize polymers. In the case of polymer, besides measuring the length or volume change, softening point, glass transitions, heat distortion under load and tensile modulus etc. can also be measured using this technique. Due to variety of applications, TMA is used instead of dilatometry in a board sense. The variation in length of a sample can be expressed as function of temperature as shown in equation (1.40).

\[ L = L_0(1 + \alpha T) \]  

(1.40)
where $L$ is the sample length at temperature $T\,^\circ\text{C}$ and $L_0$ is the sample length at 0 °C, $\alpha$ is the linear coefficient of thermal expansion. In TMA, $L$ is recorded as a function of temperature and will be a straight line with slope $\alpha$ with the assumption that $\alpha$ is a constant and there is no glass transition in the temperature range [111, 112].

The instrumentation used in TMA is very simple. Changes in volume or length of a sample is detected by mechanical, optical or electrical transducers and recorded as a function of temperature or time. In commonly used TMA apparatus the change in length of a sample is detected via a pushrod by a linear variable differential transformer (LVDT). The transformer armature is attached directly to the pushrod, and the displacement of it results in an output voltage, which is proportional to the linear displacement.

Perkin-Elmer TMA-7, USA make Thermo Mechanical Alayzer was used for the CTE measurements in the present study.

1.7.7.2 Thermogravimetric analysis

Thermogravimetry (TG) is a thermal analysis in which the change in mass of the sample is recorded as a function of temperature. There are three modes of thermogravimetry (a) isothermal or static thermogravimetry in which the sample mass is recorded as function of time at constant temperature, (b) quasistatic thermogravimetry in which the sample is heated to a constant mass at each of a series of increasing temperature and (c) dynamic thermogravimetry in which the sample is heated in an environment whose temperature is changing in a predetermined manner. In the present study we used dynamic thermogravimetry for the analysis of sample prepared. The thermogravimetric curve or the thermogram gives information regarding the thermal stability and composition of initial samples as well as intermediate products, the composition of the residue and volatile products formed during heating. The first thermobalance was developed by Honda in 1915 but it was successfully used for thermogravimetric analysis of inorganic samples by Duval in 1947. Some of the factors affecting the thermogravimetric analysis are furnace heating rate,
recording speed, sensitivity of the machine, amount of the sample, solubility of evolved gas, thermal conductivity of the sample etc. [111].

It should be noted that in many cases only a single thermal analysis may not provide sufficient information about a given system. Complimentary or supplementary techniques like Differential Thermal Analysis (DTA) or Differential Scanning Calorimetry (DSC) should also be used along with Thermogravimetric Analysis (TGA). In DTA the temperature of the sample is compared with the temperature of thermally inert materials recorded as a function of the sample, inert material or furnace temperature as the sample is heated or cooled in a uniform rate. The temperature changes in the sample are due to exothermic or endothermic phase changes, fusion, crystalline structure inversion, boiling, oxidation, decomposition etc. In DSC the sample and the reference material were maintained isothermally to each other by the proper application of electrical energy as they were heated or cooled in a linear rate. The curve obtained is a record of the heat flow, \( \Delta H/\Delta t \) in mcal/s as a function of temperature. In DTA and DSC, the area enclosed by the DSC/DTA curve peak is directly proportional to the enthalpy change.

\[
\text{Area} = k\Delta Hm
\]  
(1.41)

In the present study TA SDT Q 600, USA make thermal analyzer was used for the simultaneous DSC/TG analysis.

1.7.8 Brunauer- Emmett-Teller (BET) surface area analysis

The most widely used and studied technique for surface area determination is that of gas sorption. The amount of gas adsorbed by a solid as a function of pressure is determined either gravimetrically or volumetrically and the surface area calculated from the adsorption isotherm by the method of Brunauer et al. (1938). BET is the acronym derived from the authors Brunauer, Emmett and Teller who formulated an equation that allows the determination of superficial specific surface area of solids. BET uses the principle of the physical inert gas adsorption (nitrogen) to vary of the relationship between the partial
pressure of nitrogen and its vapor pressure to the temperature of liquid nitrogen. The technique can be carried out in static or dynamic conditions.

The famous BET equation is given as Equation (1.42).

\[
\frac{1}{v \left( \frac{P}{P_0} \right) - 1} = c \left( \frac{P}{P_0} \right) \frac{1}{v_m c} + \frac{1}{v_m c}
\]  

where \( P \) and \( P_0 \) are the equilibrium and saturation pressure of the adsorbate at the temperature of adsorption, \( v \) is the adsorbed gas volume, \( v_m \) is the monolayer adsorbed gas quantity and \( c \) is the BET constant shown in equation 1.43 where \( E_1 \) is the heat of adsorption of the first monolayer and \( E_L \) is the heat of liquefaction [112, 113].

\[
c = \exp \left( \frac{E_1 - E_L}{RT} \right)
\]  

Equation (1.42) is an adsorption isotherm and can be plotted as a straight line with \( 1 / (v \left( \frac{P}{P_0} \right) - 1) \) on the Y-axis and \( \varphi = \frac{P}{P_0} \) on the X-axis according to experimental results. This plot is called a BET plot. The linear relationship of this equation is maintained only in the range of \( 0.05 < \frac{P}{P_0} < 0.35 \). The value of the slope ‘A’ and the Y-intercept ‘I’ of the line are used to calculate the monolayer adsorbed gas.

\[
v_m = \frac{1}{A + I}
\]

Then specific surface area

\[
SA = \frac{v_m N_s}{V_{aw}}
\]

where \( N \) is the Avogadro’s number, \( s \) is the adsorption cross section (16.1 Å for \( N_2 \)), \( V \) is the molar volume of adsorbed gas, ‘a’ is the molecular weight of adsorbed gas and \( w \) is the sample weight.

The average particle size can be estimated by assuming that all the particles have the same spherical shape and size. The average particle diameter, \( D \), expressed in nm is given by:
\[ D = \left( \frac{6}{\rho \times S.A.} \right)^{1000} \] (1.45)

In the present work Quantachrome USA make Nova1200 model BET surface area analyzer was used to measure the specific surface area of ceramic powders.

1.7.9 Mercury porosimetry

Porosity refers to the pore volume in a material. Pores are classified according to the size into three categories; micropores (pore diameter less than 2 nm), mesopores (pore diameter in between 2-50 nm) and macropores (pore diameter greater than 50 nm). In mercury porosimetry, gas is evacuated from the sample cell and then mercury is transferred to the sample cell under vacuum and pressure is then applied to force mercury into the sample. During measurement, applied pressure \( P \) and intruded volume of mercury, \( V \), are registered. As a result of analysis, an intrusion-extrusion curve is obtained. Parameters describing the pore structure of the sample can be calculated from the data obtained. Mercury porosimetry is based on the Washburn equation (Eqn 1.46) where \( p \) is the pressure, \( r \) is the radius of the pore where mercury intrudes, \( \gamma \) surface tension of mercury and \( \theta \) is the contact angle of the mercury on the surface of a solid sample. Generally used values for surface tension and contact angle of mercury are 480 mNm\(^{-1}\) and 140° respectively.

\[ p \times r = -2 \gamma \cos \theta \] (1.46)

Mercury porosimetry is a relatively rapid method, with which a wide pore diameter ranges (3 nm - 200 µm) and variety of porosity parameters can be determined. Using the method, only pores that reach the surface of the sample can be determined. The sample must be dry because mercury cannot intrude into the sample when voids are filled with another liquid [114, 115].

CE instruments (Pascal 440), UK make mercury porosimeter is used in the present work. It can apply pressure up to 400 kPa and provides extremely high resolution that is 2500 data point per analysis.
1.7.10 Mechanical properties

Measurement of mechanical properties is very much important for microwave substrates since substrates have to withstand at extreme conditions. Lots of studies have already been done in the tribological as well as wear properties of filled PTFE composites. For substrate applications tensile properties holds more importance because the flexibility and shock resistance capacity are mainly depends on it. Hence in the present work Ultimate Tensile Strength (UTS) and strain of the substrate samples are measured.

There are three typical definitions for the stress at which plastics get deformed. First one is yield strength, the stress at which material strain changes from elastic deformation to plastic deformation, causing it to deform permanently, second one is the ultimate strength, The maximum stress a material can withstand when subjected to tension, compression or shearing and it is the maximum stress on the stress-strain curve and third one is the breaking strength, the stress coordinate on the stress-strain curve at the point of rupture (figure 1.11).

Tensile strength measures the force required to pull something such as rope, wire, or a structural beam to the point where it breaks. The UTS is the maximum resistance to fracture. It is equivalent to the maximum load that can be carried by one square inch of cross-sectional area when the load is applied as simple tension (equation 1.47). It is expressed in pounds per square inch.

\[
UTS = \frac{\text{Maximum load}}{\text{Area of original cross section}} \text{ psi} \tag{1.47}
\]

If the complete engineering stress-strain curve is available, the ultimate tensile strength appears as the stress coordinate value of the highest point on the curve. Materials that elongate greatly before breaking undergo such a large reduction of cross-sectional area that the material will carry less load in the final stages of the test. A marked decrease in cross-section is called "necking." UTS is often shortened to "tensile strength" or even to "the ultimate." "Ultimate strength" is sometimes used but can be misleading and, therefore, is not used in some disciplines.
1.7.11 Dielectric property measurements

Dielectric property measurement is very much important in this investigation since the materials are prepared with an objective to use for high frequency electronic applications. The dielectric constant and loss tangent of the samples have been measured up to 13 MHz frequency as well as at microwave frequency region. Parallel plate capacitor method is used for low frequency measurements where as Hakki and Coleman technique, TE\textsubscript{01δ} cavity method and waveguide cavity perturbation technique were used to evaluate dielectric properties at microwave frequency region.
1.7.11.1 Low frequency dielectric property measurements

Dielectric measurements were carried out using HP 4192A LF Impedance Analyzer in the frequency up to 13 MHz. Dielectric constant, loss tangent and temperature coefficient of dielectric constant of the samples are measured by parallel plate capacitor method. Parallel plate capacitor method is the most common and the simplest technique for the measurement of dielectric constant of dielectric materials. The material to be measured is placed in between two conducting parallel plates and dielectric constant is measured using the equation (1.48) given below [118].

\[
C = \frac{\varepsilon_r \varepsilon_0 A}{d}
\]  

(1.48)

where \( C \) is the capacitance, \( \varepsilon_r \) is the relative dielectric constant of the material and \( \varepsilon_0 \) is the dielectric constant of the free space, \( A \) is the area of the plates and \( d \) is the plate separation. The most general approximation in this technique is that the dielectric material fills the void between the two conducting plates and the effective dielectric thickness is equal to the plate separation. The relation between capacitance and inverse dielectric thickness is linear in nature but in some cases it will deviate from the linearity due to the trapped air. For higher value of inverse dielectric thickness the non linearity is observed to be increased and hence it is difficult to measure small capacitors using this technique. In addition to that stray parallel capacitance and resistance from the lead also could appear as error in the capacitance measurements.

In the present study, thin parallel samples were cut from the substrates for making parallel plate capacitors. The capacitors were fabricated using room temperature silver paste and copper leads. Dielectric measurements were carried out with a HP 4192A LF Impedance Analyzer in the frequency range up to 13 MHz. Both capacitance and dielectric loss tangent of the samples were measured as a function of frequency. Dielectric constant was calculated using the thickness and area of the samples using equation (1.48).

Temperature coefficient of dielectric constant (\( \tau_{\varepsilon_r} \)) of the samples is measured using HP 4192A LF Impedance Analyzer coupled with a hot and cold chamber (Clitech, India).
The sample to be measured is placed inside the hot and cold chamber and is connected to the impedance analyzer using an one meter standard cable provided by HP. The temperature inside the hot and cold chamber is varied from 0-100 °C with an accuracy of ±1 °C and the temperature very near to the sample has been measured. The dielectric constant of the sample is measured at every 10 °C interval and a graph is plotted. Temperature coefficient of dielectric constant is calculated using equation (1.49)

\[
\tau_{\varepsilon'} = \frac{1}{\varepsilon'_{r30}} \frac{\Delta \varepsilon'_r}{\Delta T}
\]

where \(\Delta \varepsilon'_r/\Delta T\) is the change in dielectric constant with respect to temperature.

1.7.11.2 Microwave dielectric property measurements

Since the materials used in the present work and the resulting composites developed find application in microwave frequency region, characterization of the initial raw materials used and the composites developed out of this need to be characterized precisely in the microwave frequency region.

1.7.11.2.1 Hakki and Coleman method

In 1959 Karpova proposed an exact resonance method with an accuracy of ± 0.1% wherein a circular disc of the material to be measured is inserted in the gap of a resonant cavity of known dimension [119]. Later, this method was modified by B.W. Hakki and P.D. Coleman in 1960 by using an open boundary resonant structure of the material to be measured has been placed between two mathematically infinite conducting plates [120]. They used an iris coupling from a waveguide to couple microwave to the test sample. Further modification on this method by using two horizontally oriented E-field probe for coupling the microwave energy to the sample was done by Courtney in 1970 [121] wherein the sample is placed between two conducting plates as shown in figure 1.12.
The characteristic equation for the TE_{0m} modes in a dielectric rod resonant structure can be written as

\[
\frac{J_\alpha(\alpha)}{J_1(\alpha)} = -\beta \frac{K_\alpha(\beta)}{K_1(\beta)}
\]  

(1.50)

Where \( J_\alpha(\alpha) \) and \( J_1(\alpha) \) are the Bessel functions of first kind of orders zero and one respectively, \( K_\alpha(\beta) \) and \( K_1(\beta) \) are the modified Bessel functions of the second kind of the orders of zero and one respectively. The parameters \( \alpha \) and \( \beta \) depend on the geometry, the resonant wavelength and dielectric properties of the resonant structures.

\[
\alpha = \frac{2\pi a}{\lambda_o} \left[ \varepsilon_r - \left( \frac{c}{v_p} \right)^2 \right]^{1/2}
\]  

(1.51)

\[
\beta = \frac{2\pi a}{\lambda_o} \left[ \left( \frac{c}{v_p} \right)^2 - 1 \right]^{1/2}
\]  

(1.52)

‘c’ is the velocity of light and \( v_p \) the phase velocity in the structure so that

\[
\frac{c}{v_p} = \left( \frac{1\lambda_o}{2L} \right)
\]  

(1.53)
Where \( l \) is the number of longitudinal vibrations of the field along the axis and \( \lambda_0 \) is the free space resonant wavelength. By solving equation (1.51) and (1.52) using (1.53) we get

\[
\varepsilon_r' = 1 + \left( \frac{c}{2 \pi \alpha f_0} \right)^2 \left( \alpha_i^2 + \beta_i^2 \right)
\]  

(1.54)

Hakki and Coleman used a graphical solution to solve the characteristic equations 1.51 and 1.52. The mode chart showing the variation of \( \alpha \) as a function of \( \beta \) is given in figure 1.13. The main difficulty in this measurement technique is the accurate determination of \( TE_{0nl} \) mode. \( TE_{011} \) mode is chosen for measurements because for this mode only azimuthal component of electric field exists and the error due to air gap is practically eliminated [122]. The measurements are performed by using Agilent PNA E8362B Vector Network Analyzer.

Figure 1.13 Mode chart for the calculation of \( \alpha_n \)
1.7.11.2.2 TE\textsubscript{018} mode dielectric resonator method

![Figure 1.14 The cavity setup for the measurement of Q-factor](image)

Quality factor ‘Q’ is one of the very important parameters for dielectric resonator materials since it determines the selectivity of the device. When the Q of a dielectric resonator is measured through Hakki and Coleman technique, it is affected by conductor and radiation losses [13]. Instead, as proposed by Krupka, the DR material is placed at the exact centre of a metallic cavity having the same aspect ratio as that of the resonator[132]. A low loss material such as quartz or teflon is used as the support material as shown in the figure 1.14. The microwave energy is coupled to the DR through two coupling loops. To get maximum separation between modes and to avoid interference between modes a D/L (diameter/length) ratio of 2-2.5 is generally used. Since the field confinement is not complete in the Z direction TE\textsubscript{011} mode is designated as TE\textsubscript{018} mode. After identifying the TE\textsubscript{018} mode, the resonant frequency and 3 dB bandwidth are determined by a Network Analyzer. Loaded quality factor is the ratio of the resonant frequency to the -3dB bandwidth. The coupling coefficients $\beta c_1$ ($\beta c_1 = (1-S_{11})/(S_{11}+S_{22})$) and $\beta c_2$ ($\beta c_2=(1-S_{22})/(S_{11}+S_{22})$) were calculated using the scattering parameters $S_{11}$ and $S_{22}$. From the measured loaded quality factor $Q_L$, the unloaded quality factor can be calculated using equation 1.54.

$$\frac{1}{Q_u} = \frac{1}{Q_L} \left( 1 + \beta c_1 + \beta c_2 \right)$$

(1.54)

In addition to this, microstrip excited cavity method and Whispering Gallery Mode (WGM) technique were also used for quality factor evaluation of dielectric resonators[124, 125].
1.7.11.2.3 Temperature coefficient of resonant frequency ($\tau_f$)

Temperature coefficient of resonant frequency measures the shift in operating frequency with respect to temperature.

By definition

$$\tau_f = \frac{1}{f_o} \frac{\Delta f}{\Delta T} \quad (1.55)$$

$\Delta f$ and $\Delta T$ are the change in resonant frequency with respect to temperature. For the measurement of $\tau_f$ the resonator is placed inside an aluminum cavity of dimension around twice the aspect ratio of the sample. The cavity is closed at the bottom and opens at the top and an E-field probe is used for microwave coupling using Agilent PNA E8362B Vector Network Analyzer. The dielectric resonator sample is loosely coupled to the probe so that the tuning effects due to expansion can be minimized. The setup is then heated slowly using a hot plate in the 25-100 °C temperature range. The shift in frequency with respect to temperature is noted and from this coefficient of temperature variation of resonant frequency has been calculated [13,19].

1.7.11.2.4 Waveguide cavity perturbation technique

Waveguide cavity perturbation technique is most widely used characterization technique to find the dielectric constant of thin sheet samples having low and medium dielectric loss [126]. In the cavity perturbation technique, a small piece of material usually in the form of sheet is placed in a metallic cavity operating in a known mode. The cavity resonator is constructed from a portion of a waveguide with two of its ends closed. Transmission type studies are conducted in cavity perturbation technique. The basic principle in this method is that the field inside the cavity is perturbed while introducing the sample inside the cavity. But the perturbation applied should be minimum. The dielectric parameters can be determined from the cavity parameters such as resonance frequency and quality factor. There is a coupling device called iris, which couples microwave power to the resonator and from the resonator to the coaxial cable. The cavity resonator is connected with
the two ports of a S-parameter test set up and is excited in the TE\textsubscript{01P} mode. The number of resonant frequencies of the cavity is determined by the cavity length [126, 127].

When a dielectric material is introduced in a cavity the field perturbation due to the sample at the position of maximum electric field is given by

\[ -\frac{d\Omega}{\Omega} = \frac{(\bar{\varepsilon}_r - 1)\int_{\Omega_s} E E_0 \, dV}{\int_{\Omega_c} |E_0|^2 \, dV} \] (1.56)

where \(d\Omega\) is the complex frequency shift, \(E_0\) is the electric field inside the unperturbed cavity and \(E\) is the field in the perturbed state, \(\bar{\varepsilon}_r\) is the relative complex dielectric constant of the sample. But \(\varepsilon^* = \varepsilon' - \varepsilon''\), where \(\varepsilon'\) is the real and \(\varepsilon''\) is the imaginary part of dielectric constant. The imaginary part is associated with dielectric loss. \(V_s\) and \(V_c\) are the volume of the sample and cavity respectively.

Complex frequency shift is related to the quality factor as

\[ \frac{d\Omega}{\Omega} = \frac{d\omega}{\omega} + j\left(\frac{1}{Q_s} - \frac{1}{Q_c}\right) \] (1.57)

\(Q_s\) and \(Q_c\) are the quality factors with and without samples. \(Q\) is given by \(Q = \frac{f}{\Delta f}\), \(f\) is the resonant frequency and \(\Delta f\) is the corresponding band width at 3 dB. For small perturbations it is assumed that \(E = E_0\)

For dominant TE\textsubscript{01P} mode in rectangular wave guide

\[ E_0 = E_{0\text{max}} \sin \frac{\pi x}{a} \sin \frac{p \pi Z}{d}, \quad p=1,2,3\ldots \] (1.58)

\(E_{0\text{max}}\) is the peak value of \(E_0\), \(a\) and \(b\) are the breadth and length of the waveguide cavity resonator respectively.

From equations (1.56), (1.57) & (1.58)

\[ \varepsilon'_r - 1 = \frac{f_c - f_s}{2f_s} \left(\frac{V_c}{V_s}\right) \] (1.59)
\[
\varepsilon^* = \frac{V_c}{4V_s} \left( \frac{Q_s - Q_c}{Q_c Q_s} \right) \tag{1.60}
\]

loss tangent \(\tan\delta\) is given by the expression

\[
\tan\delta = \frac{\varepsilon''}{\varepsilon'} \tag{1.61}
\]

Figure 1.15 (a) An X-band waveguide cavity and (b) the resonant modes with and without samples

A standard X-band waveguide has five resonant modes 8.4, 9.1, 9.8, 10.6 and 11.5 GHz between 8.2 to 12.4 GHz. The frequency \(f_c\) and quality factor \(Q_c\) of each resonant modes of the empty cavity was measured first. Then the sample was introduced in to the cavity and each resonant mode was perturbed. The sample inside the cavity is moved inside the cavity to get maximum deflection of the resonant mode from the initial position. The resonant frequency \(f_s\) and quality factor \(Q_s\) at maximum perturbed position was noted. Using these values the real an imaginary parts of dielectric constant has been calculated.