Chapter 4

Sr$_2$Ti$_9$O$_{20}$ and Ca$_2$Ti$_9$O$_{20}$ Filled PTFE Composite Laminates

4.1. Introduction

The reduction of circuit size using PTFE laminates having high dielectric constant is studied meticulously in chapter 3. Realization of such materials leads to an increase in circuit density and hence miniaturization of devices. But as the circuit density increases, there is a chance for cross talking to happen and hence the integrity of the signals will be lost. This problem can be overcome by using materials with low loss tangent. A decrease in loss tangent of substrate material will reduce the rate of deterioration in amplitude of the propagating electromagnetic waves. So, substrates having high dielectric constant together with low loss tangent are preferred to fulfill the needs of modern communication systems.

In chapter 2, it is demonstrated that dimensionally stable filled PTFE substrates having a dielectric constant up to 10.2 can be developed through SMECH process using rutile grade titania as particulate fillers. In chapter 3, the dielectric constant of the composite has been improved to 13.1, wherein SrTiO$_3$ is used as the particulate filler. CaTiO$_3$ filled PTFE is also resulted in a composite having dielectric constant as high as 11.9. Since the loss tangent of SrTiO$_3$ is relatively higher, the filled composites also exhibit higher loss tangent. Although the loss tangent of CaTiO$_3$ filled composites are low, they suffer from high moisture absorption and brittleness. In order to satisfy the need for rapidly advancing microwave integrated technology, novel substrate materials having high dielectric constant, low loss tangent and better dimensional stability are inevitable. To accomplish this task, high dielectric and ultra low loss ceramic materials have to be identified as particulate fillers. It is to be noted that only very few materials having
dielectric constant greater than 100 together with low dielectric loss are reported so far in the open literature [15, 205-210]. Table 1 summarizes examples of materials having dielectric constant greater than 100 with reasonably good quality factor.

Table 4.1 Dielectric properties of materials having dielectric constant >100

<table>
<thead>
<tr>
<th>Material</th>
<th>$\varepsilon_r$</th>
<th>$Q \times f$ (GHz)</th>
<th>$\tau_f$ (ppm/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$<em>{1.3}$Nd$</em>{2x/3}$TiO$_3$ (x=0.3)</td>
<td>107</td>
<td>6590</td>
<td>316</td>
</tr>
<tr>
<td>Sr$_2$Ce$_2$Ti$<em>5$O$</em>{16}$</td>
<td>113</td>
<td>8000</td>
<td>306</td>
</tr>
<tr>
<td>Ca(Zr$<em>{0.4}$Ti$</em>{0.6}$)O$_3$</td>
<td>118</td>
<td>6400</td>
<td>*</td>
</tr>
<tr>
<td>Ca$<em>{1.2}$Sm$</em>{2x/3}$TiO$_3$</td>
<td>119</td>
<td>12330</td>
<td>*</td>
</tr>
<tr>
<td>Sr$<em>{0.8}$Ca$</em>{0.2}$TiO$_3$</td>
<td>145</td>
<td>4050</td>
<td>1534</td>
</tr>
</tbody>
</table>

* $\tau_f$ is not reported in the literature

Lead (Pb) and Bismuth (Bi) containing dielectric resonator materials is reported with high dielectric constant and relatively high quality factor but these important properties are mostly governed by the amount of these volatile elements [211-213]. In addition, the microstructure formed during sintering process also has decisive role in controlling the end properties of such materials. Because of the above mentioned reasons, mostly such materials are not preferred as particulate fillers in PTFE based systems. Solid solutions containing Li, Na, and Fe etc. are also reported as high dielectric constant microwave ceramic materials [214, 215]. However these materials have relatively low quality factor. Hence, there is a perceived need to develop novel high dielectric constant and low loss microwave ceramic compositions as particulate fillers to tailor the end performance of PTFE based substrates.

Ba$_2$Ti$_6$O$_{20}$ is the most widely used dielectric resonator material from the perovskite family. It has a dielectric constant around 38 with a quality factor greater than 9000 at 4 GHz [216, 217]. Many efforts have been done so far to tailor the dielectric constant and dielectric loss through A site substitution in Ba$_2$Ti$_6$O$_{20}$. An increase in dielectric constant by successive replacement of Ba by Sr ions has been reported by Sreemoolanadhan et al. [218]. They could achieve a permittivity of 160 and a quality
factor of 3000 at microwave frequency while replacing Ba completely by Sr. However, a
detailed structural analysis of these materials is not reported so far to the best of our
knowledge. In addition there is no literature available on the substitution of Ca$^{2+}$ ions in
the A site and associated changes in the microwave dielectric properties. Hence it is
decided to prepare the solid solution of both Sr$_2$Ti$_9$O$_{20}$ and Ca$_2$Ti$_9$O$_{20}$ and study their
structural morphological and microwave dielectric properties in detail.

The basic objective of this study is to develop high dielectric and low loss ceramic
filled PTFE composites using Sr$_2$Ti$_9$O$_{20}$ and Ca$_2$Ti$_9$O$_{20}$ particulates. The effect of filler
loading on the dielectric, mechanical and thermal properties of the composite system has
been studied. The observed effective dielectric constant of the composite system is
compared with different theoretical models.

4.2 Experimental

4.2.1 Filler preparation and characterization

The Ba$_{2-x}$Sr$_x$Ti$_9$O$_{20}$ (0≤x≤2) and Ca$_2$Ti$_9$O$_{20}$ ceramic compositions were prepared
through solid state ceramic route. Stoichiometric amount of SrCO$_3$ (99%, Sigma Aldrich,
USA), BaCO$_3$ (99%, Sigma Aldrich, USA), CaCO$_3$ (99%, Sigma Aldrich, USA) and TiO$_2$
(99%, Sigma Aldrich, USA) were used as the starting materials. After mixing well in an
agate mortar with double distilled water as solvent, the chemicals were calcined at 1100
to 1200 °C for 4 h. The calcined powders were taken out and binder (PVA) was added.
Green compacts having 11 mm diameter and 9 mm height were made out of the powder
through uniaxial pressing at a pressure of ~200 MPa for microwave characterization. 1
mm thick and 11 mm diameter green compacts were made through uniaxial pressing for
low frequency measurements. The compacts were sintered at different temperatures
between 1300 to 1400 °C. The sintered pellets were powdered and the phase formation
was studied using powder X-ray diffraction studies. Density of the sintered pellets was
measured using dimensional method. The resonators were mirror polished using different
grades of fine emery paper for getting better properties at microwave frequency range.
Pellets were measured at 1MHz as well as at microwave frequency region. The
temperature variation of resonant frequency ($\tau_f$) was also measured in the temperature
range of 25-100 °C.
Powder X-ray diffraction patterns of Ba$_{2-x}$Sr$_x$Ti$_9$O$_{20}$ are shown in figure 4.1. It is interesting to note that a structural change is noticed on successive replacement of Ba by Sr. The change is more pronounced for compositions with Sr substitution more than x=1. A close examination of the XRD pattern with standard JCPDS files infers that Sr$_2$Ti$_9$O$_{20}$ is a mixture of SrTiO$_3$ and TiO$_2$. The respective peaks of both SrTiO$_3$ (without *) and TiO$_2$ (with *) are indexed and shown separately in figure 4.2.
Figure 4.2 Powder X-ray diffraction pattern of Sr$_2$Ti$_9$O$_{20}$ calcined at 1200 °C for 4h.

Figure 4.3 Laser Raman Spectra of SrTiO$_3$, TiO$_2$ and Sr$_2$Ti$_9$O$_{20}$ powders

Although XRD pattern clearly shows the presence of both SrTiO$_3$ and TiO$_2$ phases, further studies on the phase formation of Sr$_2$Ti$_9$O$_{20}$ was conducted using Laser Raman spectroscopy. In addition to the Raman spectrum of Sr$_2$Ti$_9$O$_{20}$, the spectra of TiO$_2$ and SrTiO$_3$ are also given for comparison in figure 4.3. Interestingly, the Raman spectrum of Sr$_2$Ti$_9$O$_{20}$ resembles closely with that of TiO$_2$. The fundamental TiO$_6$
vibrations $A_{1g}$ ($610 \text{ cm}^{-1}$) and $E_{g}$ ($447 \text{ cm}^{-1}$) are clearly seen from the Raman spectrum of $\text{Sr}_2\text{Ti}_9\text{O}_{20}$. Moreover, no shift in fundamental vibrational modes is observed in the Raman spectrum of $\text{Sr}_2\text{Ti}_9\text{O}_{20}$ compared to $\text{TiO}_2$. No bands correspond to $\text{SrTiO}_3$ are seen in the Raman spectrum of $\text{Sr}_2\text{Ti}_9\text{O}_{20}$. One of the reasons for this may be due to the diffuse Raman peaks of $\text{SrTiO}_3$ since first order modes are Raman inactive [201].

Pellets of $\text{Sr}_2\text{Ti}_9\text{O}_{20}$ sintered at 1370 $^\circ\text{C}$ are polished well using fine emery paper and subsequently thermally etched at 1300 $^\circ\text{C}$. The thermally etched pellets were used for SEM studies. The SEM micrographs are shown in figure 4.4. There are two types of grains seen in the microstructure of $\text{Sr}_2\text{Ti}_9\text{O}_{20}$. In addition to the columnar grains having length of around 7 to 9 $\mu\text{m}$, hexagonal grains are also seen in the SEM picture.

![SEM images](image)

(a) (b)

Figure 4.4 (a) Secondary electron and (b) Back scattered electron SEM images of $\text{Sr}_2\text{Ti}_9\text{O}_{20}$ ceramics

In addition to $\text{Sr}_2\text{Ti}_9\text{O}_{20}$, solid solution of $\text{Ca}_2\text{Ti}_9\text{O}_{20}$ is also prepared. There are no reports available on the preparation, structural and dielectric properties of $\text{Ca}_2\text{Ti}_9\text{O}_{20}$ so far. The phase formation of the composition was studied using powder X-ray diffraction technique. The diffraction pattern shows close matching with that of rutile $\text{TiO}_2$ (JCPDS No. 21-1276) and $\text{CaTiO}_3$ (JCPDS No. 42-423). The peaks corresponds to rutile were indexed with ‘*’ mark and that corresponds to $\text{CaTiO}_3$ were indexed without ‘*’ (figure 4.5). Form the figure, it is inferred that as in the case of $\text{Sr}_2\text{Ti}_9\text{O}_{20}$, $\text{Ca}_2\text{Ti}_9\text{O}_{20}$ is also multiphase in nature comprising of both $\text{CaTiO}_3$ and rutile.
Figure 4.5 Powder X-ray diffraction pattern of Ca$_2$Ti$_9$O$_{20}$ calcined at 1100 °C

Figure 4.6 Laser Raman spectra of CaTiO$_3$, TiO$_2$ and Ca$_2$Ti$_9$O$_{20}$ powders

As in the case of Sr$_2$Ti$_9$O$_{20}$, the Raman spectrum of Ca$_2$Ti$_9$O$_{20}$ is also recorded and given in figure 4.6 together with the spectra of TiO$_2$ and CaTiO$_3$ for comparison. In the present case also, the Raman spectrum of Ca$_2$Ti$_9$O$_{20}$ resembles more with TiO$_2$ except a small broad peak near 248 cm$^{-1}$. The fundamental stretching and bending vibrations of CaTiO$_3$ is intercalated with the strong vibrational modes of TiO$_2$. 

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Pellets of $\text{Ca}_2\text{Ti}_9\text{O}_{20}$ sintered at 1370 °C are well polished using fine emery paper and thermally etched at 1300 °C for 30 min. The SEM micrographs of thermally etched $\text{Ca}_2\text{Ti}_9\text{O}_{20}$ ceramics are shown in figure 4.7. There are two types of grains seen in the microstructure of $\text{Ca}_2\text{Ti}_9\text{O}_{20}$. The columnar grains have length around 7 to 9 µm. In addition to the columnar grains hexagonal grains are also seen in the SEM picture.

Table 4.2 The sintering temperature, bulk density and dielectric properties of $\text{Ba}_{2-x}\text{Sr}_x\text{Ti}_9\text{O}_{20}$ at 1 MHz

<table>
<thead>
<tr>
<th>Value of $x$</th>
<th>Sintering Temp. (°C/3h)</th>
<th>Bulk Density (g/cc)</th>
<th>Dielectric constant</th>
<th>Loss tangent</th>
<th>$\tau_{\varepsilon}^* (\text{ppm/°C})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1370</td>
<td>4.07</td>
<td>38.1</td>
<td>0.0016</td>
<td>-4</td>
</tr>
<tr>
<td>1.00</td>
<td>1360</td>
<td>4.36</td>
<td>73.7</td>
<td>0.0048</td>
<td>-738</td>
</tr>
<tr>
<td>2.00</td>
<td>1370</td>
<td>4.38</td>
<td>160.7</td>
<td>0.0024</td>
<td>-1708</td>
</tr>
</tbody>
</table>

The $\text{Ba}_{2-x}\text{Sr}_x\text{Ti}_9\text{O}_{20}$ ($x=0$, 1 and 2) are sintered in the temperature range of 1350 to 1400 °C. The bulk density, dielectric constant, loss tangent and temperature coefficient of dielectric constant are shown in table 4.2. The dielectric constant values were measured at 1 MHz. Form the table it is clear that there is a definite increase in dielectric constant with respect to Sr substitution in the A site. $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ has a dielectric constant around 38 whereas complete replacement of $\text{Ba}^{2+}$ with $\text{Sr}^{2+}$ ($\text{Sr}_2\text{Ti}_9\text{O}_{20}$) results in a dielectric constant ∼160 with comparatively low loss tangent. Dielectric resonators are made using
Sr$_2$Ti$_9$O$_{20}$ are characterized at microwave frequency region through Hakki and Coleman post resonator technique [120] and the results are shown in table 4.3. Sr$_2$Ti$_9$O$_{20}$ has a dielectric constant of 158 with unloaded quality factor of 2000 at 3.2 GHz. The newly developed ceramic system Ca$_2$Ti$_9$O$_{20}$ is also characterized at microwave frequency region. The sharp TE$_{011}$ resonant mode of Ca$_2$Ti$_9$O$_{20}$ measured at 3.591 GHz at 100 MHz span is shown in figure 4.8. It is interesting to note that Ca$_2$Ti$_9$O$_{20}$ has a dielectric constant of 117 with unloaded quality factor greater than 5000. The temperature coefficient of resonant frequency is at the higher side (∼540 ppm/°C). The results are compiled in table 4.3.

Table 4.3: Density, dielectric constant, unloaded quality factor and temperature coefficient of resonant frequency for A$_2$Ti$_9$O$_{20}$ (A=Ca,Sr)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Sintering temperature (°C)</th>
<th>Bulk Density (g/cc)</th>
<th>$\varepsilon_r$</th>
<th>$Q_u$</th>
<th>$Q \times f$ (GHz)</th>
<th>$\tau_f$ (ppm/°C)</th>
<th>$\tau_{\varepsilon_r}$ (ppm/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr$_2$Ti$<em>9$O$</em>{20}$</td>
<td>1370</td>
<td>4.38</td>
<td>158</td>
<td>3800</td>
<td>12,160</td>
<td>+920</td>
<td>-1800</td>
</tr>
<tr>
<td>Ca$_2$Ti$<em>9$O$</em>{20}$</td>
<td>1370</td>
<td>3.94</td>
<td>117</td>
<td>5920</td>
<td>21,260</td>
<td>+540</td>
<td>-1100</td>
</tr>
</tbody>
</table>

Figure 4.8 TE$_{011}$ resonant mode of Ca$_2$Ti$_9$O$_{20}$ measured at 100 MHz span
The end performance of ceramic filled PTFE flexible substrates are decided by the dielectric properties of the particulate ceramic filler materials. In order to have reproducible end properties, the filler materials should have very consistent properties. Batch wise variations in the dielectric properties of the ceramic filler are not admissible. A small batch wise change in dielectric property can detrimentally affect the end properties of the composite substrates. Moreover, the physical properties of particulate fillers such as size, distribution and morphology will also have profound influence on the end properties of filled composites. Hence ceramic compositions need to be precisely screened before put in to use as particulate filler in PTFE matrix. This is particularly true with multiphase compositions because the slight variations in phase formation during calcination stage may adversely affect the final properties of the formed composites and hence hamper the reproducibility of the same during industrial production. In the present system also, there exists a chance to vary the amount of the individual phases; TiO$_2$ and SrTiO$_3$ during formation stage. The phase formation is mainly depends on the reactivity of the initial raw materials as well as the calcination temperatures. Hence it is essential to ensure the reproducibility of the final properties of the formed composites by optimizing appropriate calcination temperature of the particulate fillers. To accomplish this objective, Sr$_2$Ti$_9$O$_{20}$ composition is calcined at three different temperatures 1150, 1200 and 1250 °C for 4h each. The powder XRD patterns of the well ground ceramic compositions are taken using CuK$\alpha$ radiations and are shown in figure 4.9. The powder XRD patterns of all the three calcined powders are exactly the same. However the calcined powders obtained at 1200 °C is found to be agglomerate free and free flowing. Whereas the powder calcined beyond 1250 °C appeared to be coarse in nature. Hence for composite preparation the composition calcined at 1200 °C is used.
Since vibrational spectroscopy is sensitive to molecular level, a further study on the phase formation with respect to calcination temperature of these compositions is done using Laser Raman Spectroscopy. The Raman spectra of the powders calcined at three different temperatures (1150, 1200 and 1250 °C) are shown in figure 4.10. The stretching as well as bending vibrations of TiO$_6$ octahedra are found to be at same wave numbers in all the three compositions. The symmetric stretching vibrations of TiO$_6$ octahedra is observed at 610 cm$^{-1}$ as a strong band in all the three compositions. Similarly the symmetric bending vibrations are also observed at same wavenumbers (450 cm$^{-1}$). Apart from the fundamental vibrational modes of TiO$_6$ octahedra, no other vibrations are observed in the internal mode region which rules out the possibility of any unreacted phase in the compositions calcined in the range 1150 to 1250 °C. The peaks observed below 400 cm$^{-1}$, lattice mode region, are also appeared to be similar in nature which corresponds to the rotational and translational vibrations of TiO$_6$ octahedra and Sr-O stretching modes. The unequivocal assignment of modes in the lattice mode region is always difficult.
Similar to Sr$_2$Ti$_9$O$_{20}$ the phase purity of Ca$_2$Ti$_9$O$_{20}$ is also studied in detail with respect to calcination temperature. Since the reactivity of Ca$_2$Ti$_9$O$_{20}$ is comparatively higher than that of Sr$_2$Ti$_9$O$_{20}$, the calcination studies were performed at 1050, 1100 and 1150 °C for 4h. Further, the calcined powders have been thoroughly analyzed using powder X-ray diffraction and Laser Raman studies. The powder XRD patterns of the calcined samples are shown in figure 4.11. It is interesting to note from figure 4.11 that the powders calcined at three different temperatures have almost identical XRD patterns. Although Ca$_2$Ti$_9$O$_{20}$ is a mixture of TiO$_2$ and CaTiO$_3$, there is no significant variation in the XRD patterns with respect to calcination temperatures. However, the powder calcined at 1150 °C seems to be over calcined and hence further attempts to increase the calcination temperature was avoided. Coarser and agglomerated ceramic fillers are not preferred as particulate fillers since it induces dielectric anisotropy due to non uniform filler distribution. So, in the case of Ca$_2$Ti$_9$O$_{20}$, the powders calcined at 1100 °C for 4h has been used as particulate filler for composite preparation.
Laser Raman studies have been conducted on calcined Ca$_2$Ti$_9$O$_{20}$ samples in order to study the effect of calcination temperature on its phase formation. The Raman spectra (figure 4.12) show that, as in the case of Sr$_2$Ti$_9$O$_{20}$, the vibrational modes of Ca$_2$Ti$_9$O$_{20}$ calcined at three different temperatures are similar in nature and hence the formation of any secondary phase with respect to calcination temperature can be ruled out.
In addition to the phase purity, particle size and size distribution of the calcined powder also have decisive role while making filled composites. The particle size of $\text{Sr}_2\text{Ti}_9\text{O}_{20}$ and $\text{Ca}_2\text{Ti}_9\text{O}_{20}$ calcined powders has been measured using M/s. Microtrack X100, USA make particle size analyzer and the results are shown in figure 4.13. As can be seen in figure 4.13 (a) that the calcined powder of $\text{Sr}_2\text{Ti}_9\text{O}_{20}$ has wider particle size distribution compared to $\text{Ca}_2\text{Ti}_9\text{O}_{20}$, which is ranging from 0.5 to 100 $\mu$m. The $D_{50}$ values of both the compositions are comparable and observed to be around 3 to 4 $\mu$m.

![Figure 4.13 Particle size distribution](image)

Figures 4.14 a&b show the SEM images of $\text{Sr}_2\text{Ti}_9\text{O}_{20}$ and $\text{Ca}_2\text{Ti}_9\text{O}_{20}$ ceramic particulates respectively. From the SEM pictures it is clear that the powders have an average particle size $\sim$3 $\mu$m together with a wide particle size distribution. In addition, $\text{Sr}_2\text{Ti}_9\text{O}_{20}$ powder shows comparatively better particle size distribution than $\text{Ca}_2\text{Ti}_9\text{O}_{20}$. 

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This further confirms the results obtained from particle size analysis. The SEM pictures of both Sr$_2$Ti$_9$O$_{20}$ and Ca$_2$Ti$_9$O$_{20}$ powder show regular particle morphology.

![SEM images of Sr$_2$Ti$_9$O$_{20}$ and Ca$_2$Ti$_9$O$_{20}$ powder](image)

Figure 4.14 SEM images of (a) Sr$_2$Ti$_9$O$_{20}$ calcined at 1200 $^\circ$C/4h and (b) Ca$_2$Ti$_9$O$_{20}$ calcined at 1100 $^\circ$C/4h

4.2.2 Composite preparation and characterization

PTFE based flexible substrates were prepared through SMECH process as discussed earlier. Calcined, well ground and silane coated powders of Sr$_2$Ti$_9$O$_{20}$ and Ca$_2$Ti$_9$O$_{20}$ are used as particulate filler materials in the PTFE matrix. 10 to 70 wt% of the ceramic particulates are used to fill in the PTFE matrix. As explained in 2.2.2.3.4, 2 wt% short E-glass fiber was used in both Sr$_2$Ti$_9$O$_{20}$ and Ca$_2$Ti$_9$O$_{20}$ filled composites to increase the mechanical strength as well as fine control over the surface properties.

To study the effect of secondary fillers on the microwave dielectric properties of PTFE composites, SrTiO$_3$ and rutile TiO$_2$ are filled in 2:7 ratio and substrates were prepared using SMECH process as explained above. Similarly CaTiO$_3$ and rutile TiO$_2$ were also filled in the PTFE matrix in 2:7 molar ratios.

The hot pressed composite substrates were subjected to electrical, mechanical and thermal characterizations as explained in 1.7. The results and discussion of the composite systems under study are explained in the following sections.
4.3 Results and Discussion

Since substrates with high dielectric constant and low loss are needed to increase the circuit density, the low loss dielectric resonator compositions, Sr$_2$Ti$_9$O$_{20}$ ($\varepsilon'_r$=158) and Ca$_2$Ti$_9$O$_{20}$ ($\varepsilon'_r$=117) are used to fill in the PTFE matrix. Although Sr$_2$Ti$_9$O$_{20}$ and Ca$_2$Ti$_9$O$_{20}$ compositions have excellent microwave dielectric properties, the usefulness of these ceramic compositions as particulate fillers need to be ascertained thoroughly through experimental iterations since these compositions are multiphase in nature. Generally multiphase compositions are not preferred as dielectric resonators because small variations in compositional inhomogenities can detrimentally affect the operating frequency of circuits utilizing such materials. This is particularly true since operating frequency of microwave devices are decided by the dielectric constant of ceramic resonators. The dielectric constant and temperature coefficient of dielectric constant of dielectric resonator can vary with respect to compositional changes. On the contrary, heterogeneous compositions are attempted as particulate fillers in the polymer matrix to control the temperature stability of the resulting composite systems. Recently L.M Walpita et al. has demonstrated that high dielectric constant polyphenylene sulphide (PPS) composites can be realized using SrTiO$_3$ as the primary filler and mica as the secondary filler. The same approach has been extended in CaZrO$_3$/PPS composites to get medium dielectric constant composites by L.M Walpita and M.R.Ahern [84,85]. The dielectric anisotropy of such composite will be higher due to the uneven distribution caused by the difference in rheological factors of individual fillers. The difference in bulk density of the fillers can also introduce uneven distribution. In the present work, the intricacies of using secondary fillers have been dealt with by using a solid solution of two different fillers in composition form. To ascertain the utility of such compositions, composites are prepared using single solid solution as well as mixture of individual ceramic compositions. For example a solid solution of Sr$_2$Ti$_9$O$_{20}$ as well as a mixture of SrTiO$_3$ and TiO$_2$ in 2:7 ratios is filled in PTFE matrix to study the distribution of fillers and associated changes in the microwave dielectric properties. The compositional homogeneity of these solid solutions is ensured by optimizing the calcination temperature.
4.3.1 \( \text{Sr}_2\text{Ti}_9\text{O}_{20} \) filled PTFE composites

The \( \text{Sr}_2\text{Ti}_9\text{O}_{20} \) ceramic particulate is filled in the composite from 10 to 70 wt%. Since \( \text{Sr}_2\text{Ti}_9\text{O}_{20} \) has higher dielectric constant and a comparatively low loss tangent, it is expected that the resulting composite substrate must have a higher dielectric constant with reasonably good dielectric loss. The results obtained were discussed in the following sections.

4.3.1.1 Density of the composites

Variation of density with respect to filler loading in the PTFE matrix is shown in figure 4.15. Theoretical density of the composites has been calculated using rule of mixtures (Eq. 2.1). The theoretical density of PTFE is 2.17 g/cc and that of short E-glass fibre is 2.56 g/cc. Since the theoretical density of \( \text{Sr}_2\text{Ti}_9\text{O}_{20} \) is not available in the literature, the optimized bulk density of the ceramic compact, which is 4.38 g/cc, is taken for calculations. From figure 4.15 it can be seen that the experimental density of the composites increases with an increase in ceramic loading in the polymer matrix. It is to be noted that the experimental density of the composite is always less than that of the calculated density. In this case also it is worth noticing the decrease in experimental density beyond 60 wt% as a result of porosity.

![Figure 4.15 Variation of density with filler loading](image-url)
4.3.1.2 Dielectric properties of the composites

The variation of dielectric constant with respect to Sr$_2$Ti$_9$O$_{20}$ loading in the PTFE matrix is shown in figure 4.16. It can be seen from figure that the dielectric constant measured at 1 MHz increases as a result of particulate filler loading (Sr$_2$Ti$_9$O$_{20}$) in the PTFE matrix. We could obtain a dielectric constant as high as 17 at 1 MHz while loading 70 wt% of Sr$_2$Ti$_9$O$_{20}$. The loss tangent also increases linearly with filler loading since the filler material is lossy than the matrix (figure 4.17). In addition, higher filler loading leads to more ceramic polymer interfaces which also contributes to the loss tangent of the composite system.

![Graph showing dielectric constant and loss tangent vs Sr$_2$Ti$_9$O$_{20}$ loading at 1 MHz](image)

Figure 4.16 Variation of dielectric constant and dielectric loss with Sr$_2$Ti$_9$O$_{20}$ loading at 1 MHz

Since these composite materials has to be used at microwave frequencies for circuit fabrication, the microwave dielectric properties of filled composites have been carefully measured in the 8.2 to 12.4 GHz (X-band) frequency region using waveguide cavity perturbation technique. Both dielectric constant and loss tangent increase with the loading of more polarizable ceramic filler and due to the increase in interface region. Although the dielectric constant increases linearly with respect to filler loading the change in dielectric constant is more at higher loading. As can be seen from figure 4.17 the difference in dielectric constant is only 1.15 for filler loading from 20 to 30 wt% whereas it is around 2.83 for 50 to 60 wt% loading. This may be due to the fact that at higher filler loading the ceramic to ceramic connectivity increases and as a result the
depolarization factor decreases which in turn enhances the dielectric constant of the composites.

![Graph showing variation of dielectric constant and dielectric loss with Sr2Ti9O20 loading at X-band.](image)

**Figure 4.17** Variation of dielectric constant and dielectric loss with Sr2Ti9O20 loading at X-band

The loss tangent also increases with filler loading (figure 4.17). This is expected since ceramic filler has higher loss tangent compared to PTFE matrix. In the case of loss tangent also the rate of increase is high while loading from 50 to 70 wt%. At very high filler fractions the interface effect is more pronounced due to better connectivity between ceramic particulates. The increase in interface region together with void formation can induce high loss tangent at very high filler loading. The loss tangent obtained for 70 wt% loading is 0.0074 whereas it is 0.0041 at 60 wt%. The dielectric constant and loss tangent of 60 and 70 wt% Sr2Ti9O20 filled composites are very different possibly due to increase in porosity as a result of filler loading. From these results it can be inferred that the optimum loading level possible in PTFE/Sr2Ti9O20 composites lie between 60 and 70 wt%.

As in the case of other composite systems, there is an observable difference in dielectric constant measured at low frequency as well as that measured at microwave frequency region for these composites. A comparison between the dielectric constant of Sr2Ti9O20 filled PTFE composites at 1 MHz and that at 9.8 GHz are shown in figure 4.18. When measurements were carried out at microwave frequency, there is a definite reduction in dielectric constant compared with that at 1 MHz. The difference is significant.
at higher filling fraction. The increase in dielectric constant at 1 MHz compared to that at X-band region could be due to the contribution from interfacial polarization mechanism.

Figure 4.18 Comparison of dielectric constant measured at 1 MHz and X-band

![Dielectric constant graph](image)

Figure 4.19 Variation of dielectric constant and loss tangent with Sr$_2$Ti$_9$O$_{20}$ loading (57 to 71 wt%)

In order to find out the optimum filler loading, fine tuning was done by loading ceramic particulate from 57 to 69 wt% in the polymer matrix. Dielectric properties of the thin laminates have been measured at microwave frequency region and the results are shown in figure 4.19. Fine tuning results show that the dielectric constant as well as density decreases after a filler loading of 67 wt%. From the above results, it can be inferred that the optimum filler loading possible with less than 3 μm Sr$_2$Ti$_9$O$_{20}$ in PTFE
matrix is 67 wt%. Optimized PTFE/Sr$_2$Ti$_9$O$_{20}$ composite has a dielectric constant of 14.4 with a loss tangent of 0.0057 at X-band.

For study the reproducibility of microwave dielectric properties at optimum filler loading, the PTFE/Sr$_2$Ti$_9$O$_{20}$ composites have been prepared at five different batches. The results obtained are plotted in figure 4.20. It is clear that the dielectric constant and loss tangent are quite reproducible at microwave frequency region, while preparing the composites at similar experimental conditions.

![Figure 4.20 Variation of dielectric constant and loss tangent with repetition of experiments at 67 wt% filler loading](image)

4.3.1.3 Temperature coefficient of dielectric constant

Temperature coefficient of dielectric constant ($\tau_{\varepsilon_r}$) of Sr$_2$Ti$_9$O$_{20}$ filled PTFE substrates are studied in the temperature range 0 to 100 °C. The variation of $\tau_{\varepsilon_r}$ with filler loading is shown in figure 4.21. When PTFE is filled with Sr$_2$Ti$_9$O$_{20}$, the coefficient of thermal expansion of the matrix, which is around +109 ppm/°C, will be negated with that of $\tau_{\varepsilon_r}$ of the filler. Since the $\tau_{\varepsilon_r}$ of the filler is a high negative value (~ -1800 ppm/°C), the temperature coefficient of dielectric constant of composite system also changes to the negative direction.
4.3.1.4 Theoretical modeling of PTFE/Sr$_2$Ti$_9$O$_{20}$ composites

Figure 4.22 Comparison of experimental and theoretically predicted dielectric constant values for PTFE/Sr$_2$Ti$_9$O$_{20}$ composites

The effective dielectric constant of composite is compared with different theoretical approaches and the results are shown in figure 4.22. Lichtenecker model (Eq. 2.19), Maxwell Garnett model (Eq. 2.20) and Modified Lichtenecker Model (Eq. 2.21) were used for the prediction of effective dielectric constant. The experimental curve follows the same trend as that of the values predicted by different theoretical models. The theoretically obtained dielectric constant values using Maxwell Garnett model show
Dielectric constant values of PTFE/Sr$_2$Ti$_9$O$_{20}$ composites match with experimental results up to 30 wt% of the filler loading, beyond which the experimental curve deviates from the theoretical curve. For the present PTFE/Sr$_2$Ti$_9$O$_{20}$ composite system, theoretically predicted values using modified form of Lichtenecker model with fitting factor $k=0.3$ deviate from the experimental dielectric constant. To obtain accurate results the fitting factor needs to be modified by accounting the morphology of the filler.

![Figure 4.23 Comparison of porosity corrected dielectric constant values of PTFE/Sr$_2$Ti$_9$O$_{20}$ composites with Lichtenecker model](image)

To account for the difference in dielectric constant between experimental and predicted values, porosity correction was applied in experimentally obtained dielectric constant, as done in chapter 2, and is plotted in figure 4.23. This is the maximum dielectric constant achievable in PTFE/Sr$_2$Ti$_9$O$_{20}$ composite systems. From figure 4.23 it is clear that even if porosity correction is applied to the experimental results, there is a slight deviation in the experimental curves from the values predicted using Lichtenecker model at higher loading fractions. In addition to porosity, other factors like interface effect will also have to be taken into account at higher filler fractions.

4.3.1.5 Effect of calcination temperature of filler

As explained earlier, the calcination temperature needs to be optimized for the reproducibility of final properties, since the filler material is multiphase in nature. Composite samples with fillers calcined at three different temperatures have been studied.
in order to find out the effect of calcination temperature of the $\text{Sr}_2\text{Ti}_9\text{O}_{20}$ ceramic composition on the microwave dielectric properties of filled composites (figure 4.24). Dielectric constant is observed to be same for the three calcination temperatures. This indicates that there is no variation of microwave dielectric properties with respect to calcination temperature in the range 1150 to 1250 °C.

![Figure 4.24 Variation of dielectric constant of the composites with calcination temperature of filler](image)

4.3.1.6 Morphology of the composites

Figure 4.25 shows the SEM pictures of $\text{Sr}_2\text{Ti}_9\text{O}_{20}$ filled PTFE composites. The SEM pictures of both planar and fractured surfaces were taken. Figure 4.25a is the cross sectional view of 67 wt% ceramic loaded PTFE composite at a lower magnification. The short E-glass fibers are oriented in the calendered direction. While breaking the sample at liquid nitrogen for cross sectional studies, the oriented microfibers are broken which created pits and are clearly visible in the microstructure. It is clear from the cross sectional and planar SEM images of PTFE/$\text{Sr}_2\text{Ti}_9\text{O}_{20}$ composites that the particulate fillers are observed to be uniformly distributed in the PTFE matrix from figure 4.25b (cross sectional image) and from figure 4.25c (planar image). In order to get an idea about the distribution of fillers and its connectivity, over filled composites are also subjected to SEM studies. From figure 4.25d, it is clear that the over filled composites (70 wt%) clearly show the presence of porosity. In addition, the poor adhesion between the matrix
and the filler is also evident from the magnified image of cross sectional picture (figure 4.25e). Although fillers of uniform particle size (3 µm) are visible, the 0-3 connectivity of the composite is completely lost. Hence an optimum filler loading is always preferable to make a dimensionally stable composite with good surface texture and bare minimum porosity.

Figure 4.25  a,b) cross sectional and c) planar images of 67 wt% loaded and d& e) are the planar and cross sectional images of 70 wt% loaded PTFE/Sr$_2$Ti$_9$O$_{20}$ composites
4.3.1.7 Moisture absorption characteristics

The moisture absorption characteristics of composites have been studied as per IPC-TM-650 2.6.2.1 standards and the results are shown in figure 4.26. Composite shows comparatively high moisture absorption percentage than that of rutile filled composites. The water absorption of optimized composites (67 wt% filled) was also measured and found to be < 0.03%.

![Figure 4.26 Moisture absorption characteristics of Sr$_2$Ti$_9$O$_{20}$ filled PTFE composites](image)

4.3.1.8 Tensile properties of the composites

The tensile strength of Sr$_2$Ti$_9$O$_{20}$ filled PTFE composites has been studied and the results obtained are shown in figure 4.27. The ultimate tensile strength shows a decreasing trend while increasing the filler loading. As explained earlier as the ceramic loading increases the interface region will also increases. Hence the three dimensional connectivity of the polymer matrix decreases which in turn decreases the deformation area in the matrix decreases. As a result, the tensile strength of the composites decreases with increasing filler loading.
4.3.1.9 Coefficient of thermal expansion

Figure 4.28 shows the variation of coefficient of thermal expansion with filler loading. The measurement was carried out from room temperature to 180 °C. The CTE of the composites loaded with 0, 20, 40 and 60 wt% of Sr$_2$Ti$_9$O$_{20}$ were taken for measurement. A significant difference is not observed in CTE between 20 and 40 wt% loaded composites. But when PTFE is loaded with 60 wt% ceramic, a significant reduction in the slope of the curve is noticed. A remarkable decrease in CTE is observed for samples loaded beyond 60 wt% compared to that of 40 wt%. CTE of 67 wt% Sr$_2$Ti$_9$O$_{20}$ loaded PTFE composite is ~20 ppm/°C in room temperature to 180 °C temperature range.
4.3.2 Characterization of \( \text{Ca}_2\text{Ti}_9\text{O}_{20} \) filled PTFE composites

4.3.2.1 Density of the composites

Variation of density with respect to ceramic loading is shown in figure 4.29. In the present case also the experimental density of the composites increases as a result of filler loading. The theoretical density of the composites is also calculated and compared with the experimental values (figure 4.29). As in the case of \( \text{Sr}_2\text{Ti}_9\text{O}_{20} \), here also the theoretical density of \( \text{Ca}_2\text{Ti}_9\text{O}_{20} \) is not reported. So the optimized bulk density of the ceramic is taken for calculations. The bulk density obtained is 3.94 g/cc when the pellet is sintered at 1370 °C for 3h. As observed in the case of other composite systems, the experimental density decreases beyond a ceramic loading of 60 wt% due to void formation.

![Figure 4.29 Variation of density with \( \text{Ca}_2\text{Ti}_9\text{O}_{20} \) loading](image)

4.3.2.2 Dielectric properties of composites

\( \text{Ca}_2\text{Ti}_9\text{O}_{20} \) filled PTFE composites are prepared through SMECH process. The amount of filler is varied from 10 to 70 weight percentage. Dielectric properties of the composite samples in the low frequency region have been measured by parallel plate capacitor method. Figure 4.30 shows the variation of dielectric constant and loss tangent with respect to filler loading measured at 1 MHz. It is evident from the figure that the relative dielectric constant of the composite increases with an increase in the amount of
ceramic particulate as a result of an increase in the effective polarisability of the composite system. Loss tangent also shows an increase with increase in filler content.

![Graph showing Variation of dielectric constant and dielectric loss with filler loading](image)

Figure 4.30 Variation of dielectric constant and dielectric loss with filler loading

The composite samples were characterized in the X-band frequency region using waveguide cavity perturbation technique as explained in section 1.7.11.2.4. Variation in dielectric properties of the composites at X-band region with respect to filler loading from 10 to 70 wt% is shown in figure 4.31. Dielectric constant increases with respect to filler loading up to 70 wt%. As expected, the percentage of variation is high while the filler content increases from 60 to 70 wt%. As noticed in the case of low frequency measurements, the loss tangent shows a rapid change from 0.0035 to 0.0061 in the microwave frequency region also, when the amount of ceramic particulate increases from 60 to 70 wt%. This indicates that at very high ceramic loading ceramic-ceramic connectivity increases which is more prominent in the case of over-filled composites. These results further confirm the importance of optimum filled composites for reproducible dielectric as well as mechanical properties.
Figure 4. 31 Variation of dielectric constant and dielectric loss with Ca$_2$Ti$_9$O$_{20}$ loading

Figure 4.32 shows a comparison of the effective dielectric constant measured at 1 MHz as well as that at microwave frequency region. The trend in variation of the dielectric constant is same for both measurements up to a filler loading of 60 wt%. Beyond that there is a definite reduction in dielectric constant while measuring the samples in the microwave frequency region compared with that measured at 1 MHz. The effect of interface polarization at low frequency dielectric measurement is clear in this case also.

Figure 4.32 Comparison of dielectric constant measured at 1MHz and X-band
Figure 4.33 Variation of dielectric constant and loss tangent at optimum filler loading

Fine tuning of the filler loading has been done in order to have composites with optimum microwave dielectric properties. It is clear from figure 4.33 that the dielectric constant and loss tangent increase with increasing ceramic content as in the case of Sr₂Ti₉O₂₀ filled composites. But dielectric constant decreases beyond 67 wt% of the ceramic loading. This indicates void formation in the composite system beyond optimum filler fraction. It is to be noted that as porosity increases beyond a filler fraction, although the volume remains the same, the effective dielectric constant decreases because of porosity since air has a dielectric constant of unity. Microwave frequency measurements show that 67 wt% is the optimum filling fraction for Ca₂Ti₉O₂₀ with a particle size less than 5 μm in PTFE matrix. Figure 4.33 shows that PTFE/Ca₂Ti₉O₂₀ composite has a dielectric constant of 12.9 with a loss tangent of 0.004 at X-band at optimum loading.

PTFE/Ca₂Ti₉O₂₀ composites have been prepared at optimum filler loading using Ca₂Ti₉O₂₀ prepared at five different batches to study the reproducibility of microwave dielectric properties. The results obtained are shown in figure 4.34 from which it is clear that reproducible microwave dielectric properties can be arrived at, while preparing the composites at similar experimental conditions.
Figure 4.34 Variation of dielectric constant and loss tangent with repetition of experiments at 67 wt% filler loading

4.3.2.3 Temperature coefficient of dielectric constant

Temperature coefficient of dielectric constant \( (\tau_{\varepsilon_r}) \) of Ca\(_2\)Ti\(_9\)O\(_{20}\) filled PTFE substrates are studied in the temperature range 0 to 100 \(^\circ\)C. The variation of \( \tau_{\varepsilon_r} \) with filler loading is shown in figure 4.35. When PTFE is filled with Ca\(_2\)Ti\(_9\)O\(_{20}\), the coefficient of thermal expansion of the matrix, which is around +109 ppm/\(^\circ\)C, will be negated with that of \( \tau_{\varepsilon_r} \) of the filler. Since the \( \tau_{\varepsilon_r} \) of the filler is a high negative value (~ -1100 ppm/\(^\circ\)C), the temperature coefficient of dielectric constant of composite system also changes to the negative direction.
4.3.2.4 Theoretical modeling of PTFE/\(\text{Ca}_2\text{Ti}_9\text{O}_{20}\) composites

The effective dielectric constant of composite is compared with different theoretical approaches and the results are shown in figure 4.36. Lichtenecker model (Eq 2.19), Maxwell Garnett model (Eq 2.20) and Modified Lichtenecker Model (Eq 2.21) were used for the prediction of effective dielectric constant. The experimental curve follows the same trend as that of the values predicted by different theoretical models. In
the case of PTFE/Ca$_2$Ti$_9$O$_{20}$ composites also experimental dielectric constant matches with Maxwell Garnett model at lower filling fraction (up to 30 wt%). Modified form of Lichtenecker model with fitting factor $k=0.3$ deviates from the experimental dielectric constant for the present PTFE/Ca$_2$Ti$_9$O$_{20}$ composite system.

![Figure 4.37 Comparison of experimental and porosity corrected dielectric constant with that of Lichtenecker model](image)

Lichtenecker model shows comparatively better correlation with the experimental results than the other two models. Still the experimental values are found to be less than that of the predicted dielectric constant. The porosity corrected dielectric constant of the composite system using equation (2.22) is shown in figure 4.37. The optimum dielectric constant achievable in PTFE/Ca$_2$Ti$_9$O$_{20}$ composite systems without porosity shows a slight deviation from the Lichtenecker model at higher loading fractions.

4.3.2.5 Effect of calcination temperature of filler on the dielectric properties of the composites

In order to study the effect of calcination temperature on the microwave dielectric properties of filled composites, Ca$_2$Ti$_9$O$_{20}$ compositions have been calcined at 1050, 1100 and 1150 °C for 4 h each. Although the Raman and XRD results did not show any change in structure with respect to the calcination temperature, a slight variation in dielectric constant is noticed for the composite prepared using powder calcined at 1050 °C (figure 4.38). But the dielectric constant values are the same for the compositions calcined from
1075 to 1100 °C. Beyond 1100 °C, the calcined powder is coarse and hence can not be used as particulate filler.

![Diagram showing the effect of calcination temperature on dielectric constant.](image)

Figure 4.38. Effect of calcination temperature of the filler on the dielectric properties of the composites.

4.3.2.6 Morphology of the composites

Distribution of particulate filler inside the polymer matrix and the morphology of the composite are studied using SEM technique. The SEM pictures of both planar and fractured surface were taken. Figure 4.39 (a) is the cross sectional view of 60 wt% ceramic loaded PTFE composite at lower magnification. The composite is observed as a single entity without any delamination. Cross sectional view of 67 wt% ceramic loaded composite shows good interface between filler and polymer matrix. The filler are observed to be distributed evenly in the polymer matrix (figure 4.39 (b)). The SEM micrograph of 67 wt% ceramic loaded composite has been taken from the planar surface (figure 4.39 (c)). A good surface texture with evenly distributed particles of size less than 5 µm is clearly observed. On further increase in filler loading (70 wt %), the pores start to appear on the surface of the composite (figure 4.39 (d)). So an optimum filler loading is always preferred to get a composite with good surface texture together with bare minimum porosity. From the SEM results it can be confirmed that the decrease in density
as well as dielectric constant of PTFE/Ca$_2$Ti$_9$O$_{20}$ composites are due to the occurrence of porosity caused by over filling beyond 67 wt%.

![SEM micrographs of a) crosssection of 60 wt%, b) cross section of 67 wt%, c) planar view of 67 wt% and d) planar view of 70 wt% Ca$_2$Ti$_9$O$_{20}$ filled PTFE composites](image)

4.3.2.7 Moisture absorption characteristics

The moisture absorption characteristics of composites have been studied and the results are shown in figure 4.40. Composite shows comparatively high moisture absorption percentage. The moisture absorption of optimized composite (67 wt% filled) is also measured and found to be < 0.03%.
4.3.2.8 Tensile properties of the composites

The tensile strength of Ca$_2$Ti$_9$O$_{20}$ filled PTFE composites has been studied and the results obtained are shown in figure 4.41. The ultimate tensile strength shows a decreasing trend while increasing the filler loading. As explained earlier, as the ceramic loading increases, the interface region increases and hence the three dimensional connectivity of the polymer matrix decreases. When PTFE is loaded with more and more inorganic fillers, the deformation area in the matrix decreases which in turn reduces the tensile strength.
4.3.2.9 Coefficient of thermal expansion

![Coefficient of thermal expansion graph](image)

Figure 4.42 Variation of coefficient of thermal expansion with filler loading

As in the case of Sr$_2$Ti$_9$O$_{20}$ filled composites, coefficient of thermal expansion of PTFE/Ca$_2$Ti$_9$O$_{20}$ composite is also measured at different filler loading. The variation in CTE with respect to filler loading measured up to 180 °C is shown in figure 4.42. Here also significant changes in PLC are noticed when filler loading is increased from 40 to 60 wt%. This may be due to the fact that there is a threshold value for filler content beyond which the filler sufficiently restricts the polymer from expanding during heating. The CTE of optimized composition (67 wt %) is also measured and is around 18 ppm/°C, which is comparable with copper conducting pattern.

4.3.3 Two filler composites

Since Sr$_2$Ti$_9$O$_{20}$ is a multiphase composition of SrTi$_3$ and TiO$_2$ in the ratio 2:7, a composite is prepared at optimum filler loading (67 wt%) with a mixture of SrTi$_3$ and TiO$_2$ in 2:7 ratio. SMECH process is employed to fill both SrTi$_3$ and TiO$_2$ together in the PTFE matrix. The composite has a dielectric constant of 12.1 with loss tangent of 0.01 at X-band. It is clear that the dielectric properties were deteriorated while filling SrTi$_3$ and TiO$_2$ separately in the matrix than using as a single composition. It can be inferred that while preparing Sr$_2$Ti$_9$O$_{20}$ ceramics, the surface properties after calcination are extremely different from that of a mixture of SrTi$_3$ and TiO$_2$. In addition, CaTiO$_3$ and TiO$_2$ were also filled independently in the PTFE matrix in 2:7 ratio through SMECH
process. The resulted composite has a dielectric constant of 10.8 with loss tangent of 0.009 at X-band. Hence it clear that a SrTiO\textsubscript{3}/CaTiO\textsubscript{3} and TiO\textsubscript{2} in compositional form provide reproducible microwave dielectric properties by optimizing the calcinations temperature whereas the filling of individual component separately gives inferior dielectric properties.

4.4 Conclusions

Sr\textsubscript{2}Ti\textsubscript{9}O\textsubscript{20} and Ca\textsubscript{2}Ti\textsubscript{9}O\textsubscript{20} ceramics have been prepared through conventional solid state ceramic route. The ceramics were characterized using XRD, SEM, PSA and Laser Raman analysis. Powder X-ray diffraction and Laser Raman studies reveal that both Sr\textsubscript{2}Ti\textsubscript{9}O\textsubscript{20} and Ca\textsubscript{2}Ti\textsubscript{9}O\textsubscript{20} have multiphase nature. Sr\textsubscript{2}Ti\textsubscript{9}O\textsubscript{20} consists of SrTiO\textsubscript{3} and rutile TiO\textsubscript{2} as the constituent phases whereas Ca\textsubscript{2}Ti\textsubscript{9}O\textsubscript{20} has CaTiO\textsubscript{3} and rutile TiO\textsubscript{2} as individual phases. Sr\textsubscript{2}Ti\textsubscript{9}O\textsubscript{20} and Ca\textsubscript{2}Ti\textsubscript{9}O\textsubscript{20} ceramics are sintered at 1380 and 1370 °C respectively and the microwave dielectric properties are evaluated. Sr\textsubscript{2}Ti\textsubscript{9}O\textsubscript{20} has a dielectric constant of 158 with unloaded quality factor ~2000 whereas Ca\textsubscript{2}Ti\textsubscript{9}O\textsubscript{20} has dielectric constant of 117 with comparatively high unloaded quality factor ~5000.

PTFE/Sr\textsubscript{2}Ti\textsubscript{9}O\textsubscript{20} and PTFE/Ca\textsubscript{2}Ti\textsubscript{9}O\textsubscript{20} composites have been prepared through SMECH process. Dielectric properties are evaluated at 1 MHz as well as at X-band frequency region. A reduction in dielectric constant is observed for X-band region compared with that at 1 MHz. The difference is more significant at higher filler loading. This further confirms the interface effect at low frequency region. Both Sr\textsubscript{2}Ti\textsubscript{9}O\textsubscript{20} and Ca\textsubscript{2}Ti\textsubscript{9}O\textsubscript{20} fillers exhibit an optimum loading of 67 wt% in the PTFE matrix. Dielectric constant of Sr\textsubscript{2}Ti\textsubscript{9}O\textsubscript{20} filled PTFE substrate was increased up to 14.4 with a loss tangent of 0.0057 at optimum filler loading. Ca\textsubscript{2}Ti\textsubscript{9}O\textsubscript{20} filled composite has a dielectric constant of 12.9 with comparably low loss tangent of 0.0041 at X-band. The temperature coefficient of dielectric constant of PTFE/Sr\textsubscript{2}Ti\textsubscript{9}O\textsubscript{20} composite is higher (~638 ppm/°C) than that of PTFE/Ca\textsubscript{2}Ti\textsubscript{9}O\textsubscript{20} composites (~448 ppm/°C). Among the different modeling approaches employed Lichtenecker model gives better correlation with experimental results for PTFE/Sr\textsubscript{2}Ti\textsubscript{9}O\textsubscript{20} and PTFE/Ca\textsubscript{2}Ti\textsubscript{9}O\textsubscript{20} composites. The effect of calcination temperature on the microwave dielectric properties was studied as a function of calcination temperatures of the filler. It is observed that even though a multiphase
composition is used for the preparation of filled composites reproducible dielectric properties can be arrived at by optimizing the calcination temperature.

SEM studies show uniform distribution of ceramic particulates in the PTFE matrix. Composites with filler loading higher than that of optimum condition show porosity in the SEM pictures. The moisture absorption of both Sr$_2$Ti$_9$O$_{20}$ and Ca$_2$Ti$_9$O$_{20}$ filled composites is less than 0.03 wt% at optimum filler concentration. Tensile strength of composites decreases with filler loading and at optimum loading it is found to be greater than 7 MPa. CTE of the composite reduced to <20 ppm/°C which is comparable with that of copper conducting layer. The experiments conducted with SrTiO$_3$ and TiO$_2$ independently in 2:7 ratio instead of compositional form (Sr$_2$Ti$_9$O$_{20}$) resulted inferior dielectric constant and loss tangent. CaTiO$_3$ and TiO$_2$ also show similar behavior. Compiling all the above results it is clear that dimensionally stable high dielectric and low loss PTFE substrates can be fabricated using Sr$_2$Ti$_9$O$_{20}$ and Ca$_2$Ti$_9$O$_{20}$ ceramic fillers which can considerably reduce the circuit size.