This chapter gives an introduction to the different methods adopted for tailoring the microwave dielectric properties of the \( \text{Sr}_{2+n}\text{Ce}_2\text{Ti}_{5+n}\text{O}_{15+3n} \) \((n=0, 7)\) ceramics. The influence of various dopants with valency ranging from 2\(^{+}\) to 6\(^{+}\) on the microwave dielectric properties of \( \text{Sr}_2\text{Ce}_2\text{Ti}_6\text{O}_{15} \) ceramics is discussed. The chapter also discusses the effect of substitution of \( \text{Pb}^{2+} \) ions on the structure and microwave dielectric properties of the ceramics. Neither doping nor substitution could change the temperature coefficient of resonant frequency \((\nu_t)\) of the SCT ceramics. Hence the \( \nu_t \) of these ceramics is tuned by stacking it with a high negative \( \nu_t \) material.
CHAPTER 4

4.1 INTRODUCTION

The microwave dielectric properties $\text{Sr}_{2+n}\text{Ce}_2\text{Ti}_{5+n}\text{O}_{15+3n}$ ceramics were investigated in the previous chapter. These materials have relative permittivity in the range of 113 to 180, quality factor of 6000 to 11000 GHz (at 2.5 GHz) and very high temperature coefficient of resonant frequency. For practical applications the $\tau_r$ of the ceramics must be tuned to a value close to zero. The microwave dielectric properties of the ceramics are usually tuned by chemical methods like doping, slight non stoichiometry, formation of solid solution or mixing dielectrics of opposite $\tau_r$ and substitution\textsuperscript{1}. Doping of ceramics with suitable oxides$^{2,3,4,5,6,7,8,9}$ have been established as an effective tool for tuning the properties of microwave dielectric materials. Templeton et al.\textsuperscript{7} investigated the effect of various dopants on the microwave dielectric response of TiO$_2$ ceramic. Recently Bijumon et al.\textsuperscript{8} and Surendran et al.\textsuperscript{9} investigated the effect of dopants on the microwave dielectric properties of Ca$_3$B$_2$TiO$_{12}$ (B = Nb, Ta) and Ba(3Mg$_{1/3}$Ta$_{2/3}$)O$_3$ ceramics respectively. The addition of dopants in these systems improved the dielectric properties. Hence in order to tailor the dielectric properties, iso-valent and alio-valent dopants were added in the SCT ceramic system. Sr$_2$Ce$_2$Ti$_5$O$_{15}$ ceramics was selected for the dopant addition studies, since the effect of dopants on other compositions in SCT is expected to be similar. The various dopants were selected based on their valency or ionic radius.

Another method, commonly used for tailoring the dielectric properties is the solid solution or substitutions of the iso-valent ions at the respective sites. There are some fundamental criteria to be obeyed for ionic material solid solution to occur; which include (i) the ionic radii of the solute element should be comparable with that of the solvent ion.
CHAPTER 4

which is to be simplified (ii) the valence charge of the substitute ion has to be identical to the charge of the replaced ion and (iii) the solute and solvent ion to be substituted should have similar chemical affinity with other ions in the case of solid solution formation in polycrystalline materials. In most of the practical cases, while forming solid solutions in polycrystalline ceramics, the above mentioned ideal conditions will not be maintained. The slight difference in ionic radius, polarizability etc. of the substituted ion leads to significant changes in the properties of the host material. Hence this method has been extensively used for tailoring the microwave dielectric properties of dielectric resonator materials. In this chapter detailed investigations were done on Pb substituted Sr$_9$Ce$_2$Ti$_{12}$O$_{36}$ ($n=7$) ceramics. The Sr$_9$Ce$_2$Ti$_{12}$O$_{36}$ ceramics were taken because of its high relative permittivity and low dielectric loss. Even though other ions of Ba, Ca, La, Nd, Sn and Zr were tried to substitute for Sr, Ce and Ti respectively, they neither improved the microwave properties nor obtained a single phase material. The chapter also includes tailoring of temperature coefficient of resonant frequency of the Sr$_2$Ce$_2$Ti$_5$O$_{15}$ ceramics using stacking method.

4.2 EXPERIMENTAL PROCEDURE

Sr$_2$Ce$_2$Ti$_5$O$_{15}$ and Sr$_{9-x}$Pb$_x$Ce$_2$Ti$_{12}$O$_{36}$ ($x=0$ to 9) ceramics were prepared by solid-state ceramic route. Stoichiometric amount of powder mixtures were ball milled in distilled water medium using yttria stabilized zirconia balls in a plastic container for 24h. The slurry was dried, then ground well, and calcined at 1100°C/5h for Sr$_2$Ce$_2$Ti$_5$O$_{15}$ ceramic. Sr$_9$.Pb$_x$Ce$_2$Ti$_{12}$O$_{36}$ ceramics were calcined in the temperature range of 950 to 1100 °C depending on the Pb content. The calcined material was ground into fine powder and
divided into different batches for optimizing sintering temperature and dopant addition. In order to dope Sr$_2$Ce$_2$Ti$_5$O$_{15}$, different weight percentages (0 to 0.6) of various dopants like divalent (ZnO, MgO, MnO, BaO, CaO, Co$_3$O$_4$, NiO and PbO), trivalent (Bi$_2$O$_3$, In$_2$O$_3$, Sm$_2$O$_3$, Al$_2$O$_3$, Nd$_2$O$_5$, Cr$_2$O$_3$, Fe$_2$O$_3$, Gd$_2$O$_3$, La$_2$O$_3$, Er$_2$O$_3$, Eu$_2$O$_3$ and Pr$_6$O$_{11}$), tetravalent (ZrO$_2$, CeO$_2$ and SnO$_2$), pentavalent (Sb$_2$O$_5$, Nb$_2$O$_5$ and Ta$_2$O$_5$) and hexavalent (WO$_3$ and MoO$_3$) were added to the selected weight of the calcined parent material. The Sr$_2$Ce$_2$Ti$_5$O$_{15}$ containing dopants were mixed thoroughly in distilled water medium. It was then dried and mixed with 4 wt % PVA (Molecular Weight 22000, BDH Lab Suppliers, England) and again dried and ground well. Cylindrical pucks of about 6-7 mm height and about 14 mm diameter were made by applying a pressure of 100 MPa. These compacts were then fired at 600°C for 30 minutes to expel the binder before sintering at a temperature of 1300°C for the Sr$_2$Ce$_2$Ti$_5$O$_{15}$ ceramics. All the doped material except Bi$_2$O$_3$ was sintered at 1300°C/2h. The sintering temperature was 1260°C/2h for 0.2wt % Bi$_2$O$_3$ doped Sr$_2$Ce$_2$Ti$_5$O$_{15}$ ceramics. Sr$_9$.xPb$_x$Ce$_2$Ti$_{12}$O$_{36}$ ceramics were sintered in the temperature range of 1100 to 1375 °C. The pellets were muffled in the same powder in order to prevent escape of volatile Pb. The bulk densities of the sintered samples were measured by dimensional method.

Sr$_2$Ce$_2$Ti$_5$O$_{15}$ has a high positive $\tau_f$ and hence negative $\tau_f$ material were prepared and added to it. High negative $\tau_f$ materials like BaNb$_2$O$_6$, Bi$_2$Ti$_4$O$_{11}$, Li$_{1/2}$Nd$_{1/2}$TiO$_3$, Mg$_2$P$_2$O$_7$ and PbZrO$_3$-CeO$_2$ were prepared through solid-state ceramic route. High purity BaCO$_3$, Bi$_2$O$_3$, TiO$_2$, (MgCO$_3$)$_4$Mg(OH)$_2$.5H$_2$O, Li$_2$CO$_3$ and ZrO$_2$ (99.9+% Aldrich Chemicals), CeO$_2$ and Nd$_2$O$_3$ (99.99% Indian Rare Earth Ltd.) and PbO (CDH, India) were
used as the raw materials. As the $\tau_f$ of Sr$_2$Ce$_2$Ti$_5$O$_{15}$ is high in the positive side, only higher weight percentage (>1 wt %) of the above negative $\tau_f$ materials were added.

The XRD profile of the samples was taken in Bragg-Brentano geometry by the X'Pert Pro PANalytical diffractometer equipped with X'Celerator detector using Cu-K$\alpha$ radiation. Unit cell parameters, atomic positions, and isotropic displacement parameters were refined by means of Rietveld method using the FullProf program. Transmission electron microscopy of Sr$_5$Ce$_2$Ti$_{12}$O$_{36}$ and Pb$_5$Ce$_2$Ti$_{12}$O$_{36}$ ceramics was carried out on a JEOL JEM 3010 microscope operated at 300 kV (LaB$_6$ cathode, point resolution 1.7Å). Powder samples were dispersed in ethanol and the suspension was treated in ultrasound for 10 minutes. A drop of very dilute suspension was placed on a holey-carbon-coated copper grid and allowed to dry by evaporation at ambient temperature.

The sintered samples were thermally etched for 20 minutes at a temperature of about 25°C below the sintering temperature and the surface morphology was studied by using a scanning electron microscope (JEOL-JSM 5600 LV, Tokyo, Japan).

The microwave dielectric properties were measured by a Vector Network Analyzer (8753 ET, Agilent Technologies). Low-frequency dielectric response was investigated between 100 Hz and 1 MHz from 10 to 700 K using an impedance analyzer HP 4192A. A high-frequency response (1 MHz – 1.8 GHz) was obtained by means of the impedance analyzer Agilent 4291B with Novocontrol BDS 2100 coaxial sample cell and a Sigma System M18 temperature chamber (operating range 100–570 K). At microwaves, cylindrical samples were measured as dielectrics resonators in the shielding cavity between 100 and 370 K using a network analyzer Agilent E8364B. Their resonance frequencies
(0.9-3.2 GHz) are dependent on the values of \( \varepsilon' \) and size of the sample pellets (diameter 9 mm, height 4.0-4.7 mm). Measurements at THz frequencies from 0.2 to 2.5 THz (7 – 80 \( \text{cm}^{-1} \)) were performed at room temperature using a time-domain THz spectrometer, only THz spectra of \( \text{Pb}_9\text{Ce}_2\text{Ti}_{12}\text{O}_{36} \) ceramics were investigated up to 900 K. Room-temperature IR spectra were obtained using a Fourier transform IR spectrometer Bruker IFS 113v in the frequency range of 20 - 3000 \( \text{cm}^{-1} \) (0.6 – 90 THz). Selected \( \text{Sr}_9.x\text{Pb}_x\text{Ce}_2\text{Ti}_{12}\text{O}_{36} \) samples with \( x = 0, 6 \) and 9 were investigated between 10 and 900 K. Details about THz and IR measurements can be found in Ref. 27. Room-temperature Raman spectra were measured in backscattering geometry using a Raman microscope (Renishaw RM 1000) equipped with a grating filter (NExT) to enable measurements of Raman shifts as low as 20 \( \text{cm}^{-1} \). An Ar-laser line (514 nm) was used for excitation.

4.3 RESULTS AND DISCUSSION

4.3.1 Influence of Dopants

Fig. 4.1 (a) shows the powder XRD pattern recorded from the pure sample sintered at 1300°C for 2 hours. The diffraction peaks were indexed based on pseudocubic \( \text{Sr}_2\text{Ce}_2\text{Ti}_5\text{O}_{15} \) [ICDD File No. 49-1554]. However, a detailed structural analysis described in the chapter 3 reveals lowering of symmetry due to octahedral tilting. A combined analysis of electron and neutron diffraction indicates that the most likely space group for \( \text{Sr}_{2n}\text{Ce}_2\text{Ti}_{5+n}\text{O}_{15+3n} \) (\( n \leq 10 \)) series except \( n=0 \) composition is \( \text{R} \text{3c} \). The XRD patterns recorded from most of the doped samples did not show any additional peaks. It may be noted that addition of very small amount of dopants (< 0.6 wt %) usually do not give any detectable changes in the XRD pattern. However, addition of 0.6 wt % of ZnO (Fig. 4.1 d)
and 1 wt % of PbZrO₃-CeO₂ (Fig. 4.1 c) show presence of CeO₂. Hence XRD profiles of only some representative dopants, which improve or deteriorate quality factor are shown in the Fig. 4.1. Fig. 4.2 (a) shows the SEM picture of the pure Sr₂Ce₂Ti₅O₁₅, with well-packed grains having size of 3-8 µm.

![XRD Pattern](image)

**Fig. 4.1** (a) The XRD pattern of the material Sr₂Ce₂Ti₅O₁₅ (b) Doped with 0.4wt % of NiO (c) Doped with 1wt % of PbZrO₃ + CeO₂ and (d) Doped with 0.6wt % of ZnO (The peaks marked C are that of CeO₂).

Effect of 0.2 wt % of various dopants on the microwave dielectric properties of Sr₂Ce₂Ti₅O₁₅ is given in Table 4.1. Addition of small weight percentage (0.2wt %) of
dopants does not change the structure and no additional phases were observed in the XRD profile. However, higher amount of dopants produce additional phases as evident from XRD (Fig. 4.1 (c) and 1 (d)) and SEM (Fig. 4.2 (b) and 2 (c)). Addition of 0.2 wt % of dopants such as MnO, NiO, MoO₃, In₂O₃, Nd₂O₃, Pr₆O₁₁, Gd₂O₃, Fe₂O₃, PbO, La₂O₃ and Eu₂O₃ improved the quality factor. Dopants such as ZnO, MgO, BaO, Bi₂O₃, Co₃O₄, SmO₃, Sb₂O₅, Ta₂O₅, Nb₂O₅, V₂O₅ and WO₃ degraded the quality factors. Hence higher amounts of only those dopants, which improved the quality factor, were investigated further.

![SEM pictures](image)

Fig. 4.2 (a) SEM picture of the pure Sr₂Ce₂Ti₆O₁₅, (b) Doped with 1wt % of PbZrO₃ + CeO₂ and (c) Doped with 0.6wt % of ZnO.

Variation of density with of 0.2wt % of dopants is shown in Table 4.1 and Fig. 4.3 shows the variation of density as a function of dopant concentration. All the dopants (0.2 wt %)
except ZnO, MoO₃ and Fe₂O₃ improved densification of Sr₂Ce₂Ti₅O₁₅. The quality factor of Sr₂Ce₂Ti₅O₁₅ is improved by 0.2 wt % addition of dopants like NiO, PbO and MnO. Surface micrograph of 0.6 wt % ZnO doped Sr₂Ce₂Ti₅O₁₅ is shown in Fig. 4.2 (c).

Table 4.1 Effect of 0.2wt % dopants on the microwave dielectric properties of Sr₂Ce₂Ti₅O₁₅.

<table>
<thead>
<tr>
<th>Sr₂Ce₂Ti₅O₁₅ + 0.2wt% Dopants</th>
<th>Percentage Density</th>
<th>εᵣ</th>
<th>Q₀ x f (GHz)</th>
<th>τᵣ (ppm/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped</td>
<td>95</td>
<td>113</td>
<td>8000</td>
<td>306</td>
</tr>
<tr>
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<td>100</td>
<td>5400</td>
<td>269</td>
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<td>271</td>
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<td>114</td>
<td>7600</td>
<td>299</td>
</tr>
<tr>
<td>CaO</td>
<td>95</td>
<td>113</td>
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</tr>
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<td>344</td>
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<td>113</td>
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<tr>
<td>Eu₂O₃</td>
<td>94</td>
<td>113</td>
<td>9300</td>
<td>304</td>
</tr>
</tbody>
</table>

It is to be noted that the grain size is reduced and porosity is considerably increased. It can be concluded from the XRD pattern [Fig. 4.1 (d)] and SEM micrograph [Fig. 4.2 (c)] that the secondary phase formation and poor densification of the specimen are the reasons for poor microwave dielectric properties.
Fig. 4.3 Variation of percentage density of $\text{Sr}_2\text{Ce}_2\text{Ti}_6\text{O}_{15}$ ceramic with doping.
Addition of MgO and ZnO decreased $\tau_f$ and quality factors. Among the divalent dopants, the best $Q_xrf$ (>10000 GHz) is obtained for 0.4 wt % of NiO. However, no remarkable change in the XRD pattern of the specimen doped with 0.4 wt % of NiO is observed [see Fig. 4.1 (b)]. More than 0.4 wt % doping of the NiO and MnO deteriorate microwave properties even though a slight improvement in $\tau_f$ is observed as shown in Fig. 4.4. Out of the eight divalent dopants investigated only MnO, NiO, and PbO improved the quality factor (27 %, 19 % and 15 % respectively). The ionic radius and charge of Pb (1.49 Å) is comparable to that of Sr (1.44 Å)\(^{10}\). Hence the improvement in quality factor of the Sr\(_2\)Ce\(_2\)Ti\(_5\)O\(_{15}\) with 0.2 wt % doping of PbO may be due to the partial substitution of Pb at Sr ion. However, other divalent dopant ions like Zn\(^{2+}\), Mg\(^{2+}\), Co\(^{2+}\), and Ba\(^{2+}\) does not improve quality factor, as their ionic radii is very much different from that of the Sr ion. But Ca\(^{2+}\) has ionic radius of 1.34 Å\(^{10}\) almost close to that of Sr (1.44 Å) and so the quality factor of Sr\(_2\)Ce\(_2\)Ti\(_5\)O\(_{15}\) is not degraded. The reduction of Ti\(^{4+}\) to Ti\(^{3+}\) during sintering and the associated degrading of quality factor are well known (Nomura et al.\(^{11}\)). The enhancement in quality factor with Mn\(^{2+}\) doping is due to such charge compensation mechanism that takes place in dielectric resonator materials involving Ti (Mn\(^{2+}\) + Ti\(^{4+}\) $\leftrightarrow$ Mn\(^{3+}\) + Ti\(^{3+}\))\(^{7}\). However, addition of more than 0.6 wt % of MnCO\(_3\) degrades the quality factor.

The variation in microwave dielectric properties of the dopants having oxidation state 3\(^+\) is shown in Fig. 4.5. The use of trivalent ions having ionic radii in the range 0.5 to 0.95 Å (Al\(^{3+}\), Cr\(^{3+}\), Fe\(^{3+}\), In\(^{3+}\), Gd\(^{3+}\), Eu\(^{3+}\) and Er\(^{3+}\)) improved the quality factor. This is due
to a favourable compensation mechanism that prevents TiO$_2$ reduction. This result is in agreement with the report of Templeton et al.\textsuperscript{7}.

Fig. 4.4 Variation in microwave dielectric properties of Sr$_2$Ce$_2$Ti$_2$O$_{15}$ material with the addition of divalent dopants.

Fig. 4.5 Variation in microwave dielectric properties of Sr$_2$Ce$_2$Ti$_2$O$_{15}$ material with the addition of trivalent dopants.
Recently Sreemoolanadhan et al.\textsuperscript{12} reported that in BaO-2CeO\textsubscript{2}-nTiO\textsubscript{2} system about 35\% of the Ce exists in the trivalent state and remaining in the tetravalent state. The XPS analysis of Sr\textsubscript{2}Ce\textsubscript{2}Ti\textsubscript{5}O\textsubscript{15} described in chapter 3 reveals about 90 \% of Ce is in 3\textsuperscript{+} state. Hence the improvement in quality factor of Sr\textsubscript{2}Ce\textsubscript{2}Ti\textsubscript{5}O\textsubscript{15} with the addition of trivalent dopants like La\textsubscript{2}O\textsubscript{3}, Nd\textsubscript{2}O\textsubscript{3} and Pr\textsubscript{6}O\textsubscript{11} may be due to the partial substitution of these ions in the trivalent Ce site. This is further supported by the fact that their ionic radii are appropriate for substitution in the trivalent Ce site.

Effect of tetravalent dopants, ZrO\textsubscript{2}, SnO\textsubscript{2} and CeO\textsubscript{2} on the microwave dielectric properties of Sr\textsubscript{2}Ce\textsubscript{2}Ti\textsubscript{5}O\textsubscript{15} is depicted in Fig. 4.6. Addition of the tetravalent dopants upto 0.4 wt \% improves Q\textsubscript{uf}. Ionic radii of Zr (0.72 Å) and Sn (0.69 Å) are comparable to that of Ti (0.605 Å). The enhancement in quality factor of the Sr\textsubscript{2}Ce\textsubscript{2}Ti\textsubscript{5}O\textsubscript{15} material with 0.2 wt \% doping of ZrO\textsubscript{2} and SnO\textsubscript{2} may be due the partial substitution of these ions in the Ti\textsuperscript{4+} site. However, the quality factor is reduced if more than 0.4 wt \% of the tetravalent dopant is added. CeO\textsubscript{2} is doped to improve the \( \tau_f \) of Sr\textsubscript{2}Ce\textsubscript{2}Ti\textsubscript{5}O\textsubscript{15} since it has a negative \( \tau_f \) (-53 ppm/°C)\textsuperscript{13}. Addition of 0.2 wt \% of CeO\textsubscript{2} increased the \( \tau_f \) to 333 ppm/°C. However, addition of higher weight percentage improves the \( \tau_f \) (see Fig.4.6). As the \( \tau_f \) of the parent material is high, 20 wt \% of CeO\textsubscript{2} is added to the Sr\textsubscript{2}Ce\textsubscript{2}Ti\textsubscript{5}O\textsubscript{15}. But it is worth to note that the \( \tau_f \) of the material is 298 ppm/°C and also significantly decreased the permittivity. The decrease in permittivity is expected, as CeO\textsubscript{2} has \( \varepsilon_r \) of 23 only. Among the tetravalent dopants maximum Q\textsubscript{uf} (9400 GHz, 17.5\% increase) is obtained for 0.4 wt \% doping of CeO\textsubscript{2}. The higher weight percentage addition of tetravalent dopants is found to deteriorate
microwave dielectric properties. This may be due to the formation of lossy secondary phases.

Fig. 4.6 Variation in microwave dielectric properties of Sr\(_2\)Ce\(_2\)Ti\(_5\)O\(_{15}\) material with the addition of tetravalent dopants.

Fig. 4.7 Variation in microwave dielectric properties of Sr\(_2\)Ce\(_2\)Ti\(_5\)O\(_{15}\) material with the addition of hexavalent dopant.
Although pentavalent dopant ions like $V^{5+} (0.54 \text{ Å})$, $Ta^{5+} (0.64 \text{ Å})$, $Sb^{5+} (0.69 \text{ Å})$ and $Nb^{5+} (0.64 \text{ Å})$ have comparable ionic radii to that of $Ti^{4+} (0.605 \text{ Å})$, the quality factor is considerably low. This is due to the fact that these ions have a +5 charge which in turn increases the dielectric loss. However, 0.2 wt % doping of pentavalent oxides such as $V_2O_5$, $Ta_2O_5$, $Nb_2O_5$ and $Sb_2O_5$ improved density. It is interesting to note that doping of $MoO_3$ decreased the density but increased the $Q_{xf}$ considerably. Further studies are required to know the mechanism for this. The permittivity is decreased by $MoO_3$ addition with a slight decrease in the $\tau_f$ (see Fig. 4.7). The lowering of $\varepsilon_r$ is due to poor densification of the specimen. Higher weight percentage (>0.4) doping degrades the quality factor.

The temperature coefficient of resonant frequency of the microwave ceramics depends on the temperature coefficient of permittivity ($\tau_e$) and linear coefficient of thermal expansion ($\tau_\ell = -\alpha - \tau_f/2$). The variation in $\tau_f$ with the addition of NiO, MnO and $MoO_3$ may be due to the change occurred in the permittivity (113-100) and hence on the $\tau_e$ of the specimen. Addition of 0.6 wt % of $Al_2O_3$, $Pr_6O_{11}$, $Cr_2O_3$ and $CeO_2$ reduce the $\tau_f$ to 266, 261, 275 and 290 ppm/°C respectively. The reduction in $\tau_f$ with the addition of $Al_2O_3$ and $CeO_2$ is expected, as they are well-known negative $\tau_f$ materials. The formation of negative $\tau_f$ materials may be the reason for the low $\tau_f$ in $Sr_2Ce_2Ti_5O_{15}$ ceramics with the addition of higher weight percentage of $Pr_6O_{11}$ and $Cr_2O_3$. It is to be noted that 0.6 wt % $SnO_2$ improved the $\tau_f$ to 276 ppm/°C. A similar observation has also been made by Matasumoto et al. on $Ba(Mg_{1/3}Ta_{2/3})O_3$ with $SnO_2$ doping.

In order to tune the $\tau_f$ of $Sr_2Ce_2Ti_5O_{15}$ a few materials having high negative $\tau_f$ were prepared and added to it. Addition of 1wt % negative $\tau_f$ materials like $BaNb_2O_6$ (-800
(540 ppm/°C), Bi$_2$Ti$_4$O$_{11}$ (-310 ppm/°C), Li$_{1/2}$Nd$_{1/2}$TiO$_3$ (-310 ppm/°C), and Mg$_2$P$_2$O$_7$ (-746 ppm/°C) not only increased the $\tau_f$ but also degraded the quality factor and permittivity. This may be due to the formation of secondary phases. However, addition of 1 wt % PbZrO$_3$ + CeO$_2$ (-1080 ppm/°C) improved the $Q_{uf}$ (> 11000 GHz) with a $\tau_f$ of 360 ppm/°C and $\varepsilon_r$ of 113. The increase in quality factor is attributed to the presence of CeO$_2$ [see Fig. 4.1 c] which has a $Q_{uf}$ > 60000 GHz.

4.3.2 Effect of Pb Substitution

4.3.2.1 Introduction

Nowadays, tunable dielectric materials are widely used in microwave (MW) devices like filters, phase shifters and antennas. Ferroelectric materials are used for this application as they have high dielectric permittivity $\varepsilon_r$ close to the structural phase transition and this $\varepsilon_r$ can be tuned with electric field. However, in general, materials in ferroelectric phase exhibit higher dielectric loss due to absorption on ferroelectric domain walls. Therefore, it is more appropriate to use materials in paraelectric phase close to above ferroelectric phase transition temperature $T_c$. Moreover, it is necessary to use materials with displacive ferroelectric phase transition driven by unstable lattice vibration (called ferroelectric soft optic phonon or shortly soft mode) lying in THz range. Permittivity of such systems is completely described by contribution of polar optic phonons, therefore there is no dielectric relaxation below phonon frequencies and dielectric loss in MW range is low, because it is caused only by intrinsic multiphonon absorption and possibly extrinsic contributions coming from the defects. However, most of the ferroelectrics exhibit an order-disorder type of phase transition. In this case, the soft ferroelectric mode is not the optic phonon but a soft dielectric relaxation expressing...
hopping of some disordered atoms (or molecules) among more equivalent positions. The relaxation lies typically in MW region, therefore dielectric loss $\varepsilon''$ is high in materials with order-disorder ferroelectric phase transitions. Such materials are not suitable for MW applications.

SrTiO$_3$, CaTiO$_3$ and KTaO$_3$ exhibit high permittivity and no MW dielectric dispersion (i.e. low MW loss). These materials belong to so called incipient ferroelectrics or quantum paraelectrics, which are characterized by increasing permittivity on cooling due to softening of the lowest frequency polar optic phonon. The soft mode frequency $\omega_{SM}$ follows at high temperatures, the Cochran law $\omega_{SM} = \sqrt{A(T-T_{cr})}$ like in other ferroelectrics, but the only difference is, that such materials never reach ferroelectric phase, because their critical temperature $T_{cr}$ lies hypothetically below 0 K (in CaTiO$_3$ and KTaO$_3$) or $T_{cr} > 0$ K ($T_{cr} \approx +37$ K in SrTiO$_3$), but quantum fluctuations prevent the creation of ferroelectric order and permittivity only saturates at low temperatures. In the latter case the quantum fluctuations prevent excessive phonon softening, and therefore the soft mode frequency does not follow any more Cochran Law at low temperature and it saturates at final low value according to Barrett formula.

$$\omega_{SM} = \sqrt{A\left[\frac{T_1}{2}\coth\left(\frac{T_1}{2T}\right)\right]}.$$  

(4.1)

$T_1$ marks temperature below which the quantum fluctuations start to play a role and above this temperature the soft mode follows Cochran law. $T_{cr}$ is extrapolated (hypothetical) critical temperature from Cochran law.
All the above mentioned incipient ferroelectrics exhibit huge permittivities ($\varepsilon_r = 10^3 - 10^4$) at low temperatures, but their room temperature values are only 150–300. Their dielectric loss is rather low, but temperature coefficient of resonance frequency $\tau_f$ is very high. There were many attempts to dope them or to make solid solutions of incipient ferroelectrics with other polar compounds. It was possible to reduce $\tau_f$, but $\varepsilon_r$ was simultaneously drastically reduced. Only in the case of solid solutions with ferroelectrics (like BaTiO$_3$ or PbTiO$_3$) it is possible to enhance permittivity at room temperature, but simultaneously $\tau_f$ and dielectric loss dramatically rose up. In spite of it, Ba$_{1-x}$Sr$_x$TiO$_3$ is the most used material today in microwave tunable devices thanks to its high $\varepsilon_r$, which can be tuned with electric field. Nevertheless, there is still a search for a new microwave materials with low loss tangent and $\tau_f$ but high $\varepsilon_r$, which can be tuned with external electric field.

Sr$_{2+n}$Ce$_2$Ti$_{5+n}$O$_{15+3n}$ ceramics has reasonably high permittivity greater than 100. The matching ionic radius of Pb (for 12 coordination 1.49 Å) to that of Sr (1.44 Å) and relatively high polarizability of Pb makes it an interesting ion for substitution. Sr$_6$Ce$_2$Ti$_{12}$O$_{36}$ is selected for Pb substitution as it has relatively high $\varepsilon_r$ and low loss tangent among Sr$_{2+n}$Ce$_2$Ti$_{5+n}$O$_{15+3n}$ ceramics. The materials will be investigated by means of THz and IR spectroscopy. THz spectra are mainly sensitive to intrinsic contributions of dielectric loss and because THz loss can be linearly extrapolated in to the microwave frequency range, the contribution of intrinsic loss to total measured MW loss will also be estimated.
4.3.2.2 Phase Diagram of Sr$_{9-x}$Pb$_x$Ce$_2$Ti$_{12}$O$_{36}$ (x=0-9) Ceramics

Figure 4.8 shows the X-ray powder diffraction pattern of Sr$_{9-x}$Pb$_x$Ce$_2$Ti$_{12}$O$_{36}$ (x=0-9) ceramics. XRD pattern and vibrational analysis of the parent Sr$_9$Ce$_2$Ti$_{12}$O$_{36}$ ceramics showed cubic perovskite like structure. However, a detailed structural analysis using electron and neutron diffraction of Sr$_{2+n}$Ce$_2$Ti$_{5+n}$O$_{15+3n}$ or Sr$_{1.3x/2}$Ce$_x$TiO$_3$ (x≤0.40) ceramics, revealed superlattice reflections (not seen in X-ray diffraction) and therefore, Sr$_9$Ce$_2$Ti$_{12}$O$_{36}$ has non-cubic supercell caused by antiphase tilting of oxygen octahedra. Its space group is R$ar{3}$c, corresponding to a' a' a' tilt system as described in chapter 3.

![X-Ray diffraction pattern of Sr$_{9-x}$Pb$_x$Ce$_2$Ti$_{12}$O$_{36}$ ceramics sintered at temperatures ranging from 1100 to 1400 °C.](image)

It is worth to note that the XRD patterns of Sr$_{9-x}$Pb$_x$Ce$_2$Ti$_{12}$O$_{36}$, where x> 7, split due to the change of crystal symmetry. Refinement of XRD patterns of samples with x ≤ 6 was
successful in all cubic, tetragonal and trigonal structures. However, the most likely space group as observed in chapter 3 is $R \overline{3} c$. Rietveld refinement of Pb$_9$Ce$_2$Ti$_{12}$O$_{36}$ phase in trigonal $R \overline{3} c$ structure was not successful (see inset of Fig. 4.10), however the monoclinic $Cc(C_1^1)$ structure with lattice parameters $a = 9.7342(5)$ Å, $b = 5.5330(6)$ Å, $c = 5.5343(6)$ Å and $\beta = 124.78(3)^\circ$ corresponds well to the powder diffraction (Fig. 4.10) and SAED data (Fig. 4.9). This monoclinic structure model was derived from the Sr$_9$Ce$_2$Ti$_{12}$O$_{36}$ structure by means of appropriate crystallographic transformation (i.e. Wyckoff splitting) from $R \overline{3} c$ space group to its subgroup $Cc$ using PowderCell program.$^{31}$ The final cycles of Rietveld refinement of Pb$_9$Ce$_2$Ti$_{12}$O$_{36}$ converged to residual factors $R_p = 6.54$, $R_{wp} = 8.76$ and $R_{Bragg} = 5.61\%$; crystallographic data of Pb$_9$Ce$_2$Ti$_{12}$O$_{36}$ are summarized in Table 4.2.

![Fig. 4.9](image.png)  
**Fig. 4.9** Selected-area electron diffraction patterns of Pb$_9$Ce$_2$Ti$_{12}$O$_{36}$ corresponding to corresponding (a) [011], (b) [010] and (c) [103] directions showing the pseudotetragonal relationship.
It should be noted, that the positions of oxygen atoms in this structure cannot be accurately refined from the XRD data, because of high scattering contrast among Pb and O atoms. Nonetheless, this structure is quite informative, especially with respect to lowering symmetry in the Sr$_9$Pb$_4$Ce$_2$Ti$_2$O$_{36}$ ceramic system. It can be noted that the slight increase of the lattice parameter with Pb content was observed due to a larger ionic radius of Pb (1.49 Å) compared to 1.44 Å of Sr$^{10}$. It is worth noting that the elementary perovskite subcell parameters $a_p = \frac{a_m}{\sqrt{3}} \approx 3.913$ Å, $b_p = \frac{b_m}{\sqrt{2}} \approx 3.912$ Å, $c_p = 0.5(a_m^2 + c_m^2 - 2a_mc_m \cos(\pi/3))^{1/2} \approx 3.998$ Å of Pb$_9$Ce$_2$Ti$_2$O$_{36}$ phase indicate pseudotetragonal relationship ($a_p = b_p \neq c_p$), which can be also observed in SAED patterns (Fig. 4.9).

\[ \text{Fig. 4.10 Rietveld refinement of Pb}_9\text{Ce}_2\text{Ti}_2\text{O}_{36} \text{ ceramics in the space group Cc. The inset shows unsuccessful refinement in space group R3c. Observed data are shown by circles, calculated and differences profiles are represented by solid lines. The upper reflections bars correspond to Pb}_9\text{Ce}_2\text{Ti}_2\text{O}_{36} \text{, the middle and lower bars to 3 and 2 mass percent of CeO}_2 \text{ and TiO}_2 \text{ impurity, respectively.} \]
Unfortunately, presence of small amount of unreacted TiO$_2$ and CeO$_2$ are detected in Pb$_9$Ce$_2$Ti$_{12}$O$_{36}$ ceramics.

Table 4.2 The Rietveld refinement result for ferroelectric Pb$_9$Ce$_2$Ti$_{12}$O$_{36}$ (space group Cc). The oxygen atoms were not refined, coordinates of Pb/Ce positions did not deviate significantly from their ideal position. The isotropic displacement factors for oxygen atoms were constrained to be equal.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>$x$</th>
<th>$y$</th>
<th>$Z$</th>
<th>$B_{iso}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb,Ce</td>
<td>4f</td>
<td>0.25</td>
<td>0.25</td>
<td>0.75</td>
<td>1.34(3)</td>
</tr>
<tr>
<td>Ti</td>
<td>4f</td>
<td>0.520(1)</td>
<td>0.243(2)</td>
<td>0.515(2)</td>
<td>1.2(1)</td>
</tr>
<tr>
<td>O1</td>
<td>4f</td>
<td>0.006</td>
<td>0.993</td>
<td>0.763</td>
<td>1.6(1)</td>
</tr>
<tr>
<td>O2</td>
<td>4f</td>
<td>0.75</td>
<td>0.76</td>
<td>0.25</td>
<td>1.6(1)</td>
</tr>
<tr>
<td>O3</td>
<td>4f</td>
<td>0.99</td>
<td>0.49</td>
<td>0.736</td>
<td>1.6(1)</td>
</tr>
</tbody>
</table>

The temperature dependence of dielectric response in Sr$_{9-x}$Pb$_x$Ce$_2$Ti$_{12}$O$_{36}$ ceramics between 100 Hz and 3.2 GHz is investigated. Representative curves for all ten samples ($x = 0$ - 9) are shown in Fig. 4.11. No dielectric dispersion, i.e. change of permittivity with frequency, was observed in high-frequency and MW data, therefore the curves were plotted only at 100 MHz. Samples with $x \leq 3$ and $x = 9$ have anomalies out of temperature region of high-frequency setup, therefore curves for such compositions are plotted at 100 kHz. Low-frequency data taken below 1 MHz show small (less than 3%) dielectric dispersion, which is the best pronounced at temperatures of permittivity maxima.

The peak of $\varepsilon_r(T)$ is not shifted with frequency and no dispersion was observed in high-frequency data above 1 MHz, so the samples are not relaxor ferroelectrics. The low-frequency dispersion comes probably from defects in ceramics like point defects (vacancies etc.) or grain boundaries. Maxima of $\varepsilon'(T)$ correspond to temperatures of ferroelectric phase transitions. Ferroelectric hysteresis loop taken at room temperature in
Chapter 4

$\text{Pb}_x\text{Ce}_2\text{Ti}_12\text{O}_{36}$ shows spontaneous polarization of 16 $\mu\text{C/cm}^2$ (see inset of Fig. 4.12).

Ferroelectric phase transition temperature $T_c$ linearly increases with Pb concentration (see the phase diagram in Fig. 4.12).

![Graph](image)

Fig. 4.11 Temperature dependences of real and imaginary parts of complex permittivity in $\text{Sr}_{9-x}\text{Pb}_x\text{Ce}_2\text{Ti}_{12}\text{O}_{36}$ ($x=0-9$) ceramics. Data were taken at 100 kHz ($x=0-3, 9$) and at 100 MHz ($x=4-8$).

Room-temperature Microwave dielectric properties are summarized in Fig. 4.13. MW dielectric resonances were obtained in all $\text{Sr}_{9-x}\text{Pb}_x\text{Ce}_2\text{Ti}_{12}\text{O}_{36}$ ceramics with exception of $x=6$ sample, which exhibits maximum $\varepsilon'$ (only its value in Fig. 4.12 is from coaxial high-frequency experiment) and high dielectric loss $\varepsilon''$, because this sample has $T_c$ close to room temperature. One can see that the best $Q_{xf}$ was obtained for $x=1$ sample, where $Q_{xf}$

- 157 -
= 5800 GHz and $\varepsilon' = 240$. However, its $\tau_f = 920$ ppm/°C is too high for MW applications, although it is almost twice smaller than in SrTiO$_3$.

Fig. 4.12 Phase diagram of Sr$_9$-xPb$_x$Ce$_2$Ti$_{12}$O$_{36}$ (x = 0-9) ceramics. Inset shows ferroelectric hysteresis loop taken at 0.1 Hz and 300 K in Pb$_9$Ce$_2$Ti$_{12}$O$_{36}$ ceramics.

Fig. 4.13 Concentration dependence of microwave permittivity and Q$_x$f factor in Sr$_9$-xPb$_x$Ce$_2$Ti$_{12}$O$_{36}$ (x = 0-9) ceramics. Data were collected at room temperature between 0.9 and 3.2 GHz.
4.3.2.3 Room-Temperature IR and Raman Spectra and Crystal Structure

IR and Raman spectra can help in refinement of the crystal structure and in the case of displacive phase transition the FE soft mode should be observable. Moreover, dielectric loss calculated from the fits of IR and THz spectra can be extrapolated to the MW range and one can estimate the contribution of intrinsic and extrinsic loss to the experimentally observed MW loss\textsuperscript{23}. Room-temperature IR reflectivity, THz transmission and Raman scattering spectra of all Sr\textsubscript{9-x}Pb\textsubscript{x}Ce\textsubscript{2}Ti\textsubscript{12}O\textsubscript{36} (x=0-9) samples were measured. IR spectra of some selected compounds are shown in Fig. 4.14, Raman spectra of all the samples (x=0-9) are presented in Fig. 4.15.

![Figure 4.14 Room-temperature infrared reflectivity of selected Sr\textsubscript{9-x}Pb\textsubscript{x}Ce\textsubscript{2}Ti\textsubscript{12}O\textsubscript{36} ceramics.](image)

Fig. 4.14 Room-temperature infrared reflectivity of selected Sr\textsubscript{9-x}Pb\textsubscript{x}Ce\textsubscript{2}Ti\textsubscript{12}O\textsubscript{36} ceramics.
Table 4.3. Brillouine zone centre (Γ) factor group analysis of optical lattice vibrations in possible 
paraelectric and FE phases. IR and R means activity of the phonons in the IR and Raman spectra, 
respectively. (-) marks silent phonons inactive in any spectra. The 3 acoustic modes are subtracted.

In various possible paraelectric phases:

\[ \Gamma_{\text{Pnma}} = 3A_{1u} (IR) + 1F_{2u} (-) \]
\[ \Gamma_{\text{I4/mcm}} = 3A_{1u} (-) + 4A_{2u} (IR) + 8E_u (IR) + E_g (R) + B_{2g} (R) + B_{1u} (-) \]
\[ \Gamma_{\text{R3c}} = 3A_{2g} (-) + 3A_{2u} (IR) + 2A_{1u} (-) + A_{1g} (R) + 4E_g (R) + 5E_u (IR) \]

In various possible FE phases:

\[ \Gamma_{\text{R3c}} = 4A_{1} (IR, R) + 5A_{2} (-) + 9E (IR, R) \]
\[ \Gamma_{\text{Ct}} = 15 A'(IR,R) + 15A''(IR,R) \]

Fig. 4.15 Room-temperature micro-Raman spectra of Sr_{9-x}Pb_x Ce_2 Ti_{12} O_{36} ceramics (x=0-9). The peak at 465 cm\(^{-1}\) comes from CeO\(_2\) second phase.
In order to obtain polar phonon parameters of all investigated compounds, the IR and THz spectra were fitted simultaneously using the generalized-oscillator model with the factorize form of the complex permittivity\textsuperscript{24}.

\[
\varepsilon^*(\omega) = \varepsilon_\infty \prod_j \frac{\omega_{LOj}^2 - \omega^2 + i \omega \gamma_{LOj}}{\omega_{TOj}^2 - \omega^2 + i \omega \gamma_{TOj}}
\]

(4.2)

where \(\omega_{TOj}\) and \(\omega_{LOj}\) denote the transverse and longitudinal frequency of the \(j\)-th polar phonon, respectively, and \(\gamma_{TOj}\) and \(\gamma_{LOj}\) denote their corresponding damping constants. The high-frequency permittivity \(\varepsilon_\infty\) resulting from electronic absorption processes was obtained from the frequency-independent reflectivity above phonon frequencies. \(\varepsilon^*(\omega)\) is related to the IR reflectivity \(R(\omega)\) by

\[
R(\omega) = \left| \frac{\sqrt{\varepsilon^*(\omega) - 1}^2}{\sqrt{\varepsilon^*(\omega) + 1}} \right|
\]

(4.3)

The real and imaginary parts of complex dielectric spectra \(\varepsilon^*(\omega) = \varepsilon'(\omega) - i \varepsilon''(\omega)\) obtained from the fits to the room-temperature IR and THz spectra of all investigated ceramics are shown together with THz experimental points in Fig. 4.16. Polar phonon frequencies are plotted versus Pb concentration in Fig. 4.17. One can see that many new modes are activated in both IR and Raman spectra in samples with \(x \geq 7\). This is due to change of crystal symmetry. It can be confirmed from Figs. 4.11 and 4.12 that with \(x \geq 7\) the ceramics are already in ferroelectric phase at room temperature, while the samples with \(x \leq 6\) are paraelectrics. Inset in Fig. 4.17 clearly shows ferroelectric soft mode, whose
frequency is remarkably dependent on Pb concentration and which exhibits minimum frequency for \( x=6 \), because \( \text{Sr}_3\text{Pb}_6\text{Ce}_2\text{Ti}_{12}\text{O}_{36} \) sample has \( T_c = 260 \text{ K} \) which is close to room temperature. Softening of the mode is manifested in Fig. 4.16 by shift of peak in \( \varepsilon''(\omega) \) to lower frequencies as well as by increase of static permittivity with maximum value at \( x=6 \). The oscillator strength \( f_{SM}=\Delta\varepsilon_{SM} \cdot \omega_{TO}^2 \) of the SM is the strongest out of all phonons in all the samples, therefore this mode could be probably assigned to vibrations of the Ti cation in oxygen octahedron, so called Slater mode\textsuperscript{32}. This is not surprising in Sr rich samples, because Slater vibration is the SM also in the related \( \text{SrTiO}_3 \). However, it is not so expected in Pb rich samples, because the eigenvector of the SM in the related \( \text{PbTiO}_3 \) describes predominantly the Pb displacement against the oxygen octahedron (so called Last mode\textsuperscript{33}). The statement that SM is the Slater mode in all \( x=1-9 \) samples is also supported by our XRD data of \( \text{Pb}_9\text{Ce}_2\text{Ti}_{12}\text{O}_{36} \), which show, that the Pb cations remain in the same position in the FE phase as in the paraelectric phase and only oxygen and predominantly Ti cations shift from their paraelectric positions. For more details how to recognize the Last and Slater mode from the IR spectra see the review by Hlinka et al.\textsuperscript{34}

Let us compare the number of observed phonons with the prediction of the factor group analysis (using the tables by Rousseau et al.\textsuperscript{35}) for different suggested crystal symmetries for the \( \text{Sr}_{9-x}\text{Pb}_x\text{Ce}_2\text{Ti}_{12}\text{O}_{36} \) ceramics. In Table 4.3 we listed the symmetries of phonons and their IR and Raman (R) activities in different acceptable crystal phases. Let us discuss first the spectra in the paraelectric phase. Their typical representative is the lead free \( \text{Sr}_9\text{Ce}_2\text{Ti}_{12}\text{O}_{36} \), whose IR and Raman spectra were presented in chapter 3. Both spectra have similarities.
Fig. 4.16 Complex dielectric spectra of Sr$_{9-x}$Pb$_x$Ce$_2$Ti$_{12}$O$_{36}$ ceramics (x=0-9) obtained from the fit of room-temperature IR reflectivity shown in Fig. 7. Points are experimental THz data. The lowest frequency peak in $\varepsilon''$ spectra corresponds to the ferroelectric soft mode.

They exhibit three distinct reflection bands, which could correspond to previously suggested cubic $Pm\overline{3}m$ space group with 3 triply degenerate polar phonons of $F_{1u}$ symmetry. However, detailed fits of the IR spectra revealed 6 modes in all the paraelectric samples with x ≤ 6 (see Fig. 4.17).

According to Table 4.3, 8 IR active modes are expected in the trigonal $R\overline{3}c$ structure and 12 polar modes should be seen in the tetragonal $I4/mcm$ structure. The six
observed polar modes corresponds better to the trigonal structure (the two missing modes can be overlapped with other stronger modes). Trigonal structure of paraelectric phase is also supported by Raman spectra. In Fig. 4.15 only a few very weak Raman bands in Sr$_9$Ce$_2$Ti$_{12}$O$_{36}$ can be seen and from the Table 4.3 five Raman active phonons should be expected in the trigonal $R\overline{3}c$ crystal structure, while only two modes are expected in the $Rmm\overline{c}$ structure.

![Graph showing room-temperature transverse-phonon frequencies as function of Pb concentration in Sr$_9$Pb$_x$Ce$_2$Ti$_{12}$O$_{36}$ ceramics. Inset shows the same dependence of the ferroelectric soft mode frequency. Note the appearance of new modes in compounds with $x \geq 7$ due to loss of centrum of symmetry in ferroelectric phase.](image)

It follows that IR and Raman spectra are in agreement with the result of XRD and SAED measurements and the structure of paraelectric Sr$_9$Ce$_2$Ti$_{12}$O$_{36}$ ceramics is trigonal $R\overline{3}c$. The
Sr$_9$xPb$_x$Ce$_2$Ti$_{12}$O$_{36}$ ceramics with $x \leq 6$ show the same number of active phonons which suggests that their structure is the same. It is worth to note that the sharp Raman peak seen at 465 cm$^{-1}$ in the $x \geq 4$ samples originates from the CeO$_2$ second phase$^{37}$ detected also in the XRD analysis.

The $x \geq 3$ samples undergo a FE phase transition (see Figs. 4.11 and 4.12). According to the structural data the FE phase is monoclinic with the $Cc$ space group. Let us compare the factor group analysis performed in the $Cc$ phase with the IR and Raman spectra of Pb$_9$Ce$_2$Ti$_{12}$O$_{36}$ having the highest $T_C$ where the modes activated in the FE phase are expected to be the strongest in the room temperature spectra. (From Fig. 4.17 one can see that Pb$_9$Ce$_2$Ti$_{12}$O$_{36}$ exhibits the highest number of polar modes. Similar situation holds in the Raman spectra – see Fig. 4.15). 14 polar phonons in the IR reflectivity spectra of Pb$_9$Ce$_2$Ti$_{12}$O$_{36}$ are observed out of which the one near 380 cm$^{-1}$ probably corresponds to a polar phonon of TiO$_2$,$^{38}$ identified as the second phase in our XRD analysis. So it can be affirmed 13 IR and 9 Raman active (see Fig. 4.15) modes, whereas the factor group analysis in Table 4.3 predicts 27 modes both IR and Raman active. The disagreement is rather large, but it can be understood by low strengths and overlapping of many newly activated modes which might not be resolved in the spectra.

It can be concluded that IR and Raman spectra of Sr$_9$xPb$_x$Ce$_2$Ti$_{12}$O$_{36}$ ceramics helped in refinement of the crystal structures of this complex ceramic system. Although XRD and SAED analysis give no unambiguous results for the paraelectric phase and both tetragonal $I4/mcm$ and trigonal $R3c$ symmetry was possible, IR and Raman spectra
supported trigonal $R\bar{3}c$ phase. In the same way supported the monoclinic FE phase with the space group $Cc$.

4.3.2.4 Dynamics of Phase Transitions

Figure 4.17 shows temperature dependence of IR reflectivity of $\text{Sr}_9\text{Ce}_2\text{Tit}_20_3$ ceramics. One can see a small increase of reflectivity and appearance of a new mode near 430 cm$^{-1}$ on cooling. Both effects come from reduced phonon damping at low temperatures. Only the rising of low-frequency reflection below ~100 cm$^{-1}$ is caused by a small phonon softening, which fully explains the increase of low-frequency permittivity (see the inset of Fig. 4.17) on cooling and its saturation below ~30 K. The $\text{Sr}_9.\text{Pb}_x\text{Ce}_2\text{Tit}_20_3$ samples with $1 \leq x \leq 2$ exhibit qualitatively the same temperature dependence of reflectivity as previously mentioned sample with $x=0$, because of absence of structural phase transitions at low temperatures. Only the value of reflectivity is increasing with rising of $x$ because of higher value of permittivity (shown in Fig. 4.10).

Qualitatively different temperature dependence of IR reflectivity spectra and higher number of polar phonons were observed in $\text{Sr}_{9-x}\text{Pb}_x\text{Ce}_2\text{Tit}_20_3$ samples with $x \geq 3$ due to phase transition to ferroelectric phase. The lowest frequency phonon softens on cooling to $T_c$ and again hardens on subsequent cooling. Moreover higher number of polar phonons is seen in ferroelectric phase in comparison to paraelectric one due to change of symmetry. As the example in Fig. 4.18 are plotted the IR reflectivity spectra of $\text{Pb}_9\text{Ce}_2\text{Tit}_20_3$ (i.e. $x=9$) ceramics taken at temperatures between 10 and 900 K. One can see dramatic change of spectra shape with temperature due to change of symmetry.
Fig. 4.17 Temperature dependence of IR reflectivity spectra of Sr$_9$Ce$_2$Ti$_{12}$O$_{36}$ ceramics. The spectra are plotted each 50 K below 300 K. Inset shows temperature dependence of permittivity measured at 1 MHz. Note the saturation of $\varepsilon'(T)$ at low temperatures due to quantum fluctuations.

Fig. 4.18 Temperature dependence of IR reflectivity of Pb$_9$Ce$_2$Ti$_{12}$O$_{36}$ ceramics.
Three broad reflection bands (actually fitted with x modes) are seen in paraelectric phase at 900 K, while 15 modes were necessary for the fits at 10 K. Resulting complex permittivity obtained from IR spectra fit is shown in Fig. 4.19 (note that maxima in $\varepsilon''(\omega)$ spectra correspond roughly to phonon frequencies). The most dramatic change with temperature exhibits the lowest frequency phonon (see Fig. 4.20).

![Figure 4.19](image_url)

**Fig. 4.19 Temperature dependence of complex dielectric response in Pb$_3$Ce$_2$Ti$_{12}$O$_{36}$ ceramics obtained from the fit of IR reflectivity and THz data (points). The sample was almost opaque near $T_c=550\,K$, therefore the THz data have at 575 K larger error bars than the rest of spectra.**

Its softening in paraelectric phase completely explains a low frequency dielectric anomaly observed in Fig. 4.10. It means that the phase transition is of displacive type. In ferroelectric phase the ferroelectric soft mode remarkably hardens from 13 (at 575 K) to 80 cm$^{-1}$ (at 10 K). Nevertheless, the experimental low-frequency $\varepsilon'$ is larger in ferroelectric
phase than the contributions of phonons probably due to microwave relaxation arising from ferroelectric domain wall motion.

Fig. 4.20 Temperature dependence of two lowest-frequency polar modes in Pb$_9$Ce$_2$Ti$_{12}$O$_{36}$ ceramics. Ferroelectric soft mode shows clear anomaly near $T_c = 550$ K.

4.3.2.5 Estimation of Intrinsic and Extrinsic Dielectric Loss

Already more than twenty years ago, Wakino et al.\textsuperscript{39,40} proposed IR reflectivity spectroscopy as a tool for investigating the intrinsic MW dielectric properties of dielectric resonators. They used model of sum of quasi-harmonic oscillators for description of dielectric dispersion in IR frequency range:

$$
\varepsilon^*(\omega) = \sum_{j=1}^{n} \frac{\Delta \varepsilon_j \omega_{T_0j}^2}{\omega_{T_0j}^2 - \omega^2 + i \omega \gamma_{T_0j}} + \varepsilon_{\infty}
$$

(4.6)
The parameters $\omega_{ij}$ and $\gamma_{ij}$ in Eq. (4.6) have the same meaning as in Eq. (4.3), $\Delta \epsilon_j$ marks contribution of $j$-th phonon to static permittivity. Actually, the Eq. (4.6) is a special case of general formula in Eq. (4.2), which can be used in the case of small splitting of longitudinal and transverse phonons. Wakino et al. suggested that extrapolation of Eq.(4.6) from IR down to MW range, i.e. 2-3 orders of magnitude below phonon frequencies gives constant real part of permittivity

$$\epsilon' = \epsilon_\infty + \sum_{j=1}^{n} \Delta \epsilon_j,$$  \hspace{1cm} (4.7)$$

while the dielectric losses $\epsilon''$ are proportional to frequency $\omega$

$$\epsilon''(\omega) \propto \omega \sum_{j=1}^{n} \frac{\Delta \epsilon_j \gamma_j}{\omega_j^2}.$$ \hspace{1cm} (4.8)$$

It implies that the dielectric loss could be linearly extrapolated from the THz range (0.1-3 THz) down to the MW region. Later on it was shown that for an accurate determination of the complex permittivity in the THz range it is more suitable to combine the THz transmission spectroscopy with IR reflectivity, because the former one is much more sensitive to weak absorption processes below frequencies of strong one phonon absorption. Simultaneously, it was shown that the extrinsic absorption mechanisms contribute only slightly to the THz and IR absorption, therefore the linear extrapolation
from THz to the MW range allows us to estimate predominantly the intrinsic dielectric
losses stemming from the multiphonon absorption\textsuperscript{41,42,43,23}.

The method described above was used in the study of many MW ceramics\textsuperscript{23,43} and it was shown that it gives rather good estimate of intrinsic MW losses, although the Eq. (4.6) is valid only in the range near phonon frequencies and the use of this formula is not theoretically justified\textsuperscript{20} for frequencies much lower than $\omega_{\text{R}}$, i.e. in MW range. Nevertheless, Gurevich and Tagantsev developed a comprehensive microscopic phonon transport theory\textsuperscript{44} and have shown, that in the MW range two-phonon difference decay processes dominate at room and medium-high temperatures and the theory predicts

$$\varepsilon''(\omega, T) = \alpha T^2$$

(4.9)

It means that both approaches, damped oscillator model as well as microscopic phonon transport theory give the same linear frequency dependence of $\varepsilon''(\omega)$. Moreover the microscopic theory predicts quadratic temperature dependence of the dielectric loss.

Figs. 4.21 and 4.22 show real and imaginary parts of complex permittivity calculated from the IR and THz spectra fits extrapolated down to MW region. Experimental MW and THz data are also plotted with exception of x=6 sample, where high opacity of the sample ruled out the successful THz experiment. One can see that MW values of $\varepsilon'$ in Sr$_9$xPb$_x$Ce$_7$Ti$_{12}$O$_{36}$ samples with $x \leq 4$ are well described by phonon contributions, but in the samples with $x \geq 5$ the extrapolated MW values of $\varepsilon_\text{r}$ are much lower than the experimental ones. This is due to additional MW relaxation arising from
ferroelectric domain wall absorption in ferroelectric samples with \( x \geq 7 \) and from possible Pb disorder in paraelectric phase of \( x = 5 \) sample (note that this sample is highly absorbing in THz range, therefore we obtained only three THz experimental points).

Extrapolation of dielectric losses \( \varepsilon'' \) down to MW region shows that the experimental MW values of \( \varepsilon'' \) in samples \( 2 \leq x \leq 4 \) correspond rather well with extrapolated ones.

![Graph](image)

**Fig. 4.21** Real part of complex permittivity calculated from room-temperature IR spectra fits and extrapolated down to MW range. Black solid squares mark experimental THz data, black solid points below 0.1 cm\(^{-1}\) (i.e. 3 GHz) mark experimental MW \( \varepsilon' \) data.

It means that these samples are optimally prepared, because they show almost no extrinsic dielectric loss. The loss spectra of \( x = 0 \) and \( x = 1 \) samples show deviation of theoretical \( \varepsilon''(\omega) \) curves from experimental points not only in MW but also in THz range. It gives evidence about an extrinsic contribution to losses. It means that the procedure of sample
preparation can be in these cases improved. The samples with \( x \geq 5 \) show much higher experimental MW loss than the theoretical one, but one cannot say, that it is only due to extrinsic contribution, because these samples exhibit a strong MW relaxation (seen also in \( \varepsilon'(\omega) \) spectra) from ferroelectric domain walls and this relaxation is in principle of intrinsic origin.

![Graphs showing imaginary part of complex permittivity](image)

Fig. 4.22 Imaginary part of complex permittivity of \( \text{Sr}_{9-x}\text{Pb}_{x}\text{Ce}_{2}\text{Ti}_{12}\text{O}_{36} \) \((x=0-9)\) ceramics calculated from room-temperature IR spectra fits and extrapolated down to MW range. Black solid squares mark experimental THz data, black solid points below 0.1 \( \text{cm}^{-1} \) (i.e. 3 GHz) mark experimental MW \( \varepsilon'' \) data.

### 4.3.3 Stacking

The addition of dopants, with high negative \( \tau_f \) material and substitution could not lower the high temperature coefficient of resonant frequency of the SCT ceramics. Hence we made an attempt to stack negative \( \tau_f \) samples over the SCT to tune the \( \tau_f \). The
Recently Sebastian et al.\textsuperscript{46} tailored the dielectric properties of microwave ceramics by stacking two different resonators materials with positive and negative $\tau_f$. The ceramics resonators of same diameters were stacked over the other with axial symmetry as shown in Fig. 4.23. Later on Li et al.\textsuperscript{47} and Chen et al.\textsuperscript{48} used the stacking technique effectively for tailoring the $\tau_f$ of MgTiO$_3$/CaTiO$_3$, SrTiO$_3$/MgTiO$_3$ systems. They also employed finite element method for predicting the dielectric properties of the stacked resonators. In the present investigation the high temperature coefficient of resonant frequency (306 ppm/°C) of the Sr$_2$Ce$_2$Ti$_5$O$_{15}$ ceramics is tuned using Bi$_2$Ti$_4$O$_{11}$ ceramics which has permittivity, $Q_{xf}$ and $\tau_f$ of 47, 4800 and -540 ppm/°C. Finely polished ceramic pucks (Bi$_2$Ti$_4$O$_{11}$ and Sr$_2$Ce$_2$Ti$_5$O$_{15}$) of different volume percentages were stacked as shown schematically in Fig. 4.23. The temperature coefficient of resonant frequency of Sr$_2$Ce$_2$Ti$_5$O$_{15}$ is tuned to -9 ppm/°C for 60 volume percentage of Bi$_2$Ti$_4$O$_{11}$ with relative permittivity of 75 and $Q_{xf}$ of 1500 GHz.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{schematic.png}
\caption{Schematic sketch stacking of resonators for temperature stability.}
\end{figure}
4.4 CONCLUSIONS

The dielectric properties of the Sr$_2$Ce$_2$Ti$_6$O$_{15}$ ceramics were tailored by adding various dopants. Addition of small amounts of dopants such as MnO, MoO$_3$, NiO, Nd$_2$O$_3$, Cr$_2$O$_3$, Pr$_6$O$_{11}$, Fe$_2$O$_3$, PbO, La$_2$O$_3$, Eu$_2$O$_3$, CeO$_2$, ZrO$_2$ and Al$_2$O$_3$ improved the quality factor. However, higher weight percentage of the dopants degrades the dielectric properties. The maximum $Q_{u\times f}$ ($>11,000$ GHz) was obtained for $1$ wt % doping of PbZrO$_3$-CeO$_2$. Sr$_{9_x}$Pb$_x$Ce$_2$Ti$_{12}$O$_{36}$ ($x=0-9$) ceramic system was sintered and characterized in the broad frequency (100 Hz – 100 THz) and temperature (10 - 900 K) regions. The samples with low content of Pb ($x \leq 2$) exhibit incipient FE behavior like related SrTiO$_3$. Higher content of Pb induces displacive FE phase transition with linearly increasing with Pb concentration Curie-Weiss temperature $T_C$. The refinement of the crystal structures by X-ray, SAED, IR and Raman data yield trigonal $R\bar{3}c$ space group for the paraelectric phase and monoclinic space group $Cc$ for the FE phase. Optical soft phonon was observed in the IR and THz spectra of Pb$_9$Ce$_2$Ti$_{12}$O$_{36}$ so that the FE phase transition is of displacive type.

Room-temperature MW dielectric properties of Sr$_{9-x}$Pb$_x$Ce$_2$Ti$_{12}$O$_{36}$ ($x=0-4$) ceramic are completely described by polar phonon contributions. The $x \geq 5$ samples exhibit strong MW relaxation due to the contribution of the FE domain walls (for $x \geq 7$) and due to Pb anharmonic vibrations probably leading to crossover from displacive to order-disorder behavior (in the $x=5$ sample). The best MW properties were observed for Sr$_9$PbCe$_2$Ti$_{12}$O$_{36}$, although this ceramics was apparently not optimally processed and exhibited a large extrinsic dielectric loss. The high temperature coefficient of resonant frequency of the ceramic system can be tuned by stacking using materials having negative $\tau_f$. 
REFERENCES


