THE EFFECT OF VARIOUS SUBSTITUTIONS ON THE
MICROSTRUCTURE AND PROPERTIES OF SrTiO₃-Sr₂Nb₂O₇
BASED ELECTROCERAMICS FOR MICROWAVE
APPLICATIONS

By

Abdul Manan

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of Doctor of Philosophy

Supervisor: Prof. Yaseen Iqbal
Co-Supervisor: Dr. Ibrahim Qazi

Institute of Physics and Electronics
University of Peshawar, Pakistan

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SR5Nb4TiO17 is known to exhibit low loss in comparison to other compounds in the SrTiO3–Sr2Nb2O7 system; therefore, the aim of this work was to investigate the effect of various cation substitutions on the phase, microstructure and electrical properties of Sr5Nb4TiO17 for possible microwave (MW) applications. All the compositions were prepared through a mixed oxide solid state sintering route. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used for phase and microstructural analysis, and LCR meter and a vector network analyzer for the measurement of electrical properties. Compositions in the Sr5-xCa4+xTi1+xO17 (x = 0-5) series formed single phase ceramics at ~1400°C; however, at temperatures ≥1500°C, secondary phases with general formula (Sr,Ca)6Nb4Ti2O20 formed along with the parent Sr5-xCa4+xTi1+xO17 phases with x = 0 – 5. Optimum MW dielectric properties (εr ~54, τf ~6.5 ppm/°C, Quf ~1166 GHz) were achieved for the ~97% dense Sr2Ca3Nb4TiO17 ceramics. Compositions in the Sr5-xLa4-xTi5-xO17 (x = 0-4) series also formed single phase ceramics at 1450°C to 1550°C. Optimum values for Quf (~ 9969 GHz), εr (~ 61) and τf (~ 117 ppm/°C) were achieved for the Sr5-xLa4-xNb4+xTi1+xO17 composition with x = 4 (i.e. SrLa4Ti5O17). In an attempt for further improvement in the electrical properties, compositions in the SrLa4-xA4Ti5O17 series (A = Nd or Sm, x = 0 ≤ x ≤ 4) were also investigated. An analysis of the properties vs. composition plots indicated that the optimum MW dielectric properties i.e. εr ~ 54, Quf ~ 6000 GHz and τf ~ 0 ppm/°C corresponded to the SrLa4-xNd4Ti5O17 composition with x ~ 1.6. SrLa4-xSm4Ti5O17 compositions formed single phase ceramics at x ≤ 3 and a mixture of Sm2Ti2O7 and SrTiO3 at x = 4. Here again, an analysis of the results indicated that the optimum properties i.e. εr = 53, τf ~ 0 ppm/°C and Quf ~ 3200 GHz corresponded to the SrLa4-xSm4Ti5O17 composition with x~1.4. Compounds in the Sr1-xCa3La4Ti5O17 (x = 0 - 1) and SrLa4Ti5-xZr4O17 (x = 0 – 0.1) composition series exhibited εr~53.7, Quf ~11532 GHz and τf ~1.4 ppm/°C, and εr~57.3, τf ~ +71.5 ppm/°C and Quf ~9841 GHz for x = 0.6 (Ca2+) and x = 0.1 (Zr4+). Consistent with previous, the substitutions of smaller cations for larger ones led to the development of fine grained microstructures indicating improved density.
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<th>Description</th>
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<td>DR</td>
<td>Dielectric Resonator</td>
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<tr>
<td>MW</td>
<td>Microwave</td>
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<tr>
<td>GHz</td>
<td>Giga hertz</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogavimetry analysis</td>
</tr>
<tr>
<td>DTA</td>
<td>Differential thermal analysis</td>
</tr>
<tr>
<td>PVA</td>
<td>Poly vinyl alcohol</td>
</tr>
<tr>
<td>dB</td>
<td>Decibel</td>
</tr>
<tr>
<td>VNA</td>
<td>Vector network analyzer</td>
</tr>
<tr>
<td>LCR</td>
<td>Inductance capacitance resistance</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>AC</td>
<td>Alternating current</td>
</tr>
<tr>
<td>RADAR</td>
<td>Radio detection and ranging</td>
</tr>
<tr>
<td>UHF</td>
<td>Ultra high frequency</td>
</tr>
<tr>
<td>STL</td>
<td>Studio transmitter link</td>
</tr>
<tr>
<td>TE</td>
<td>Transverse electric field</td>
</tr>
<tr>
<td>TM</td>
<td>Transverse magnetic field</td>
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<tr>
<td>PCS</td>
<td>Personal communication system</td>
</tr>
<tr>
<td>GPS</td>
<td>Global positioning system</td>
</tr>
<tr>
<td>WLAN</td>
<td>Wireless local area network</td>
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<tr>
<td>LTCC</td>
<td>Low temperature co-fired ceramics</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>MIC</td>
<td>Microwave integrated circuit</td>
</tr>
<tr>
<td>MMIC</td>
<td>Monolithic microwave integrated circuit</td>
</tr>
<tr>
<td>BW</td>
<td>Band width</td>
</tr>
<tr>
<td>SEI</td>
<td>Secondary electron imaging</td>
</tr>
<tr>
<td>ST</td>
<td>Sintering temperature</td>
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<tr>
<td>-----</td>
<td>-----------------------</td>
</tr>
<tr>
<td>CT</td>
<td>Calcination temperature</td>
</tr>
</tbody>
</table>
NOTATIONS

\( f \)  
Frequency

\( \lambda_o \)  
Wavelength in free space

\( \lambda_d \)  
Wavelength in a dielectric medium

\( f_o \)  
Resonant frequency

\( Q \)  
Quality factor

\( Q_L \)  
Loaded quality factor

\( Q_u \)  
Unloaded quality factor

\( Q_{ext} \)  
External quality factor

\( O \)  
Odd

\( e \)  
even

\( \varepsilon_r \)  
Dielectric constant (real part of relative permittivity)

\( \varepsilon_{r//} \)  
Dielectric loss (imaginary part of relative permittivity)

\( \varepsilon \)  
Permittivity of the dielectric media

\( \varepsilon_o \)  
Permittivity of free space

\( I_c \)  
Charging current

\( I_l \)  
Loss current

\( \tan\delta \)  
Dielectric Loss tangent

\( \tau \)  
Tolerance factor

\( L \)  
Thickness of the sample

\( D \)  
Diameter of the sample

\( a, b, & c \)  
Lattice parameters

\( V_m \)  
Molar volume

\( ^\circ C \)  
Degree Celsius

\( \tau_f \)  
Temperature coefficient of resonant frequency

\( \tau_{e} \)  
Temperature coefficient of dielectric constant

\( \tau_{c} \)  
Temperature coefficient of capacitance

\( V_{unit} \)  
Unit cell volume

\( Z \)  
No. of formula units
<table>
<thead>
<tr>
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<th>Definition</th>
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<tbody>
<tr>
<td>$\beta$</td>
<td>The angle between a and c axes</td>
</tr>
<tr>
<td>$\rho_{ap}$</td>
<td>Apparent density</td>
</tr>
<tr>
<td>$\rho_{th}$</td>
<td>Theoretical density</td>
</tr>
<tr>
<td>$\rho_{rel}$</td>
<td>Relative density</td>
</tr>
<tr>
<td>$P$</td>
<td>Polarization</td>
</tr>
<tr>
<td>$E$</td>
<td>Applied electric field</td>
</tr>
<tr>
<td>$E_o$</td>
<td>Electric field inside a dielectric material</td>
</tr>
<tr>
<td>$D$</td>
<td>Displacement vector</td>
</tr>
<tr>
<td>$\alpha_D$</td>
<td>Ionic dielectric polarizability</td>
</tr>
<tr>
<td>$\alpha_s$</td>
<td>Space charge polarizability</td>
</tr>
<tr>
<td>$\alpha_o$</td>
<td>Orientational polarizability</td>
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<td>$\alpha_i$</td>
<td>Ionic polarizability</td>
</tr>
<tr>
<td>$\alpha_e$</td>
<td>Electronic polarizability</td>
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<tr>
<td>$P_e$</td>
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<td>Ionic polarization</td>
</tr>
<tr>
<td>$P_s$</td>
<td>Space charge polarization</td>
</tr>
<tr>
<td>$P_o$</td>
<td>Orientational polarization</td>
</tr>
<tr>
<td>$c$</td>
<td>Speed of light in vacuum</td>
</tr>
<tr>
<td>$v_d$</td>
<td>Speed of light in a dielectric medium</td>
</tr>
<tr>
<td>$W_i$</td>
<td>Total stored electric energy</td>
</tr>
<tr>
<td>$P_c$</td>
<td>Power losses in conductor</td>
</tr>
<tr>
<td>$P_d$</td>
<td>Power losses in dielectrics</td>
</tr>
<tr>
<td>$P_r$</td>
<td>Power losses due to radiation</td>
</tr>
<tr>
<td>$T$</td>
<td>Transmission coefficient</td>
</tr>
<tr>
<td>$k$</td>
<td>Coupling coefficient</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Thermal coefficient of expansion</td>
</tr>
<tr>
<td>$\alpha_i$</td>
<td>Thermal coefficient of expansion of $i^{th}$ part</td>
</tr>
<tr>
<td>$N_A$</td>
<td>Avogadro Number $(6.023 \times 10^{23}$ atom / mole $)$</td>
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</table>
CHAPTER 1

1. INTRODUCTION

Advances in microwave (MW) technology and telecommunication industry have led to the speedy development of wireless communication and information systems during the past several decades. The development of cellular mobile phone and enormous increase in the number of its users is a common example of its wide spread applications [1]. Advancement in the wireless communication is the result of continuous research in materials particularly ceramic dielectrics. Ceramic dielectrics with particular combination of physical properties make them suitable for applications at MW frequencies as dielectric resonators (DRs). High dielectric constant of these dielectric materials can lead to the miniaturization of electronic devices. Complex perovskites based on titanates and niobates with very high quality factor \( Q_u \times f_o \geq 250,000 \text{ GHz} \) are currently used as DRs in base stations and mobile phones handsets [2]. For MW applications, a material must exhibit i) high dielectric constant \( \varepsilon_r \), ii) high \( Q_u \times f_o \) (GHz) and iii) near zero temperature coefficient of resonant frequency \( \tau_f \). These properties can be achieved by various routes. The growth of mobile phone market in the early 1990 led to an extensive research in order to develop low cost materials with improved properties.

1.1 Ceramics

The word ceramics is derived from a Greek word “keromos” used for potter’s clay or ware made from clay and fire [3]. Ceramics constitutes a class of materials broadly defined as inorganic, nonmetallic compounds consisting of metallic and nonmetallic elements, which arguably provide the broadest range of functions of all known materials. Depending on the difference in electronegativity of the constituent atoms, the atomic bonding in ceramics ranges from purely ionic to entirely covalent. The nature of the ionic bonding is responsible for greater strength of ceramics than metals. Recent developments in ceramics processing have resulted in the achievement of a great control over the compositions and microstructure that govern the dielectric properties. This makes it possible to engineer ceramics in accordance with the special chemical, thermal, mechanical, and electrical requirements that could not be met by other materials.
Advanced ceramics have played an important role in the development of new technologies such as computers and telecommunication, and are expected to continue to play a leading role in technologies of the future. The incredible growth in wireless communication would have not been possible without the miniaturization permitted by oxide ceramics.

1.1.1 Dielectric ceramics

It is difficult to precisely define a dielectric and is often interchanged with insulator or non-conductor. Fundamentally, a dielectric is an insulating but polarizable material which is used either actively or passively in an electric field. The primary function of a dielectric in an electrical circuit is to provide a physical separation between two conductors in order to prevent them from short-circuiting or to prevent a current flow between them. Ceramics that perform primarily such a function are known as ceramic insulators. One of the most important applications of dielectric ceramics is in capacitors where storage of electrical energy is important [3]. These ceramics have also found applications in telecommunication industry as dielectric resonators from the past several decades where microwaves are a big business.

1.1.1.1 Dielectric ceramics in electric fields

The application of an electric field to an ideal dielectric material causes no long range transport of charges but only a limited rearrangement of charges i.e. it acquires a dipole moment, and the material is said to be polarized. Several polarization mechanisms exist in a dielectric. The basic mechanisms are

1) Electronic or Atomic polarization, is a small displacement of electrons in an atom relative to the nucleus. This electronic displacement is extremely rapid. Even when the frequency of the applied voltage is in the optical range \((10^{15}\) Hz), electronic polarization occurs during every cycle of the applied voltage. Mathematically, electronic polarization is defined as

\[
P_e = N\alpha_e E_{\text{loc}} \tag{1.1}
\]

Where \(N\) is the total number of atoms or molecules, \(\alpha_e\) is the electronic polarizability, and \(E_{\text{loc}}\) is the local electric field experienced by the atom or molecule. The local electric field
is greater than the average electric field, $E_{\text{ava}}$, due to the polarization of the surrounding atoms.

2) Ionic polarization, exhibited by ionic materials, involves the relative displacement of cation and anion sub-lattices relative to each other. The frequency with which ions are displaced is of the same order as the lattice vibrational frequency ($10^{13}$ Hz).

For an ionic solid, the ionic polarization is given by

$$P_i = N\alpha_i E_{\text{loc}} \quad (1.2)$$

Where $N$ is the number of atoms per unit volume, and $\alpha_i$ is the ionic polarizability. In ionic dielectrics, both ionic and electronic polarization contributes to the formation of induced dipoles.

3) Dipolar or orientational polarization occurs in polar dielectrics and involves the orientation of permanent dipoles in the direction of the applied electric field. Increase in temperature tends to oppose the alignment of the dipoles in the direction of the applied electric field. Thus the dipolar polarization depends on temperature.

In electric fields of moderate intensity, the orientation polarization is also proportional to the local electric field and is given by

$$P_o = N\alpha_o E_{\text{loc}} \quad (1.3)$$

But when the strength of the electric field is enough so that all the permanent dipoles are aligned, then this proportionality is not maintained in strong electric field. In some solid materials, the orientation of dipoles is also restricted by the lattice vibration, which intern can reduce the orientation of the dipoles.

4) Space charge polarization involves a limited transport of charge carriers until they are stopped at a potential barrier, possibly a grain or phase boundary. Space charge polarization occurs at relatively lower frequencies (50 – 60 Hz) when one of the phases has much higher resistivity than the other as shown in Figure 1.1.

The space charge polarization $P_s$ is related to the space charge polarizability ($\alpha_s$) by the eqn (1.4).

$$P_s = N\alpha_s E_{\text{loc}} \quad (1.4)$$

where $N$ is the number of atoms or molecules per unit volume.

The total polarization is the sum of all the contributions from the different types of polarization i.e.
\[ P_T = P_e + P_i + P_o + P_s \] (1.5)

By substituting the value of the different types of polarization from eqns (1.1-1.4) into eqn (1.5), we get

\[ \alpha_T = \alpha_e + \alpha_i + \alpha_o + \alpha_s \] (1.6)

where \( \alpha_T \) is the total ionic dielectric polarizability of the compound.

The various polarization processes are schematically shown in Figure 1.2 [5].

![Diagram showing various polarization processes](image)

Figure 1.1. Frequency dependence of (a) dielectric polarizability and (b) power loss [4].
1.2 Measurement of dielectric constant in static electric fields

The simplest method of measuring dielectric constant of a dielectric material is to sandwich it between two parallel conducting plates. Application of a DC voltage across the plates causes the material to become polarized and thus energy is stored in the capacitor which increases the capacitance of the capacitor as shown in Figure 1.3. The capacitances of a parallel plate capacitor with and without a dielectric material can be written mathematically as

\[ C = \frac{\varepsilon_0 \varepsilon_r A}{d} \]  (1.7)

\[ C_o = \frac{\varepsilon_0 A}{d} \]  (1.8)

where A is the area of the plate and d is the separation between the plates.

Division of equation (1.7) by (1.8) gives
Thus $\varepsilon_r$ is the ratio of the capacitance of the parallel plate capacitor with dielectric to the capacitance without the dielectric. The introduction of a dielectric material increases the storage capacity of a capacitor by neutralizing charges at the electrodes.

Figure 1.3. Schematic of a parallel plate capacitor (DC case).

### 1.3 Dielectrics in alternating electric fields

If an alternating voltage $V$ is applied across a parallel plate capacitor, it stores charges on the plates, given by eq\(^n\). (1.10)

$$V = V_o e^{i\omega t} \hspace{1cm} (1.10)$$

where $V_o$ is the amplitude of the voltage, $\omega$ is the frequency, $t$ is the varying time.

The total current “I” can be written as

$$I = \frac{d(CV)}{dt} = i\omega CV_o e^{i\omega t} \hspace{1cm} (1.11)$$

From eq\(^n\). (1.9) we have

$$C = \varepsilon_r C_o \hspace{1cm} (1.12)$$

Putting eq\(^n\). (1.12) into eq\(^n\). (1.11) we get

$$I = i\omega \varepsilon_r C_o V_o e^{i\omega t} \hspace{1cm} (1.13)$$

For dielectrics in an alternating electric field, $\varepsilon_r$ is defined as

$$\varepsilon_r = \varepsilon_r' - i\varepsilon_r'' \hspace{1cm} (1.14)$$

where $\varepsilon_r'$ is the real part of the relative permittivity and $\varepsilon_r''$ is the imaginary part of the relative permittivity.
Putting eqn. (1.14) into eqn. (1.13) we get

\[ I = i\omega \varepsilon_r \varepsilon_0 V_0 e^{i\theta} = i\omega C_0 \varepsilon_r V + \omega C_0 \varepsilon_r \varepsilon_0 V \]

\[ I = I_c + I_l \quad \text{--------------------------- (1.15)} \]

Where \( I_c \) is the charging current and \( I_l \) is the loss current.

Eqn. (1.15) shows that for a real dielectric, the current “I” divides into two components i.e. \( I_c \) and \( I_l \). The current “\( I_c \)” is utilized in charging the capacitor. It is frequency dependent and leads the voltage by 90º while the current “\( I_l \)” represents the energy loss or power dissipation in a dielectric and is in-phase with the applied voltage. Losses in a dielectric can be represented as conductance ‘\( G \)’ in a parallel plate capacitor (Figure 1.4).

Figure 1.4. Schematic of a parallel plate capacitor (AC case).

The loss tangent “\( \tan\delta \)” is defined as the ratio of the dissipation current “\( I_l \)” to the charging current “\( I_c \)” and is given as

\[ \tan \delta = \frac{|I_l|}{|I_c|} = \frac{i\omega C_0 \varepsilon_r^\prime V}{\omega C_0 \varepsilon_r \varepsilon_0 V} = \frac{\varepsilon_r^\prime}{\varepsilon_r} \quad \text{----------------- (1.16)} \]

Eqn. (1.16) shows that the dielectric loss factor “\( \varepsilon_r^\prime \)” is the product of the material property “\( \varepsilon_r \)” and the loss tangent “\( \tan \delta \)” [6].

1.4 Microwaves

Electromagnetic waves with wavelengths shorter than those of radio waves but longer than those of infrared waves are called microwaves. Microwaves have occupied a separate position in the electromagnetic spectrum that ranges from gamma rays to long radio waves as shown in Figure 1.5
The frequency range of microwaves is from 300 MHz to 300 GHz with wavelengths ranging from ~1 mm to 1 m. The microwave region is further divided into the following three regions [7]:

1. Ultra high frequency (UHF) region from 300 MHz to 3 GHz,
2. Super high frequency (SHF) region from 3 GHz to 30 GHz
3. Extremely high frequency (EHF) region from 30-300 GHz.

Further division of microwave spectrum into various bands is shown in Figure 1.6.

Figure 1.5. The electromagnetic spectrum, showing the MW region [7]

Figure 1.6. Subdivision of microwave spectrum into various frequency bands [8].

Microwaves with frequencies greater than 30 GHz make the link between the earth and satellite unreliable, because these waves are highly absorbed (attenuated) by the
atmosphere due to clouds, rain, sand, hydro-meteors and dust; however, these are still used for communication among the satellites in space [9].

1.4.1 Advantages of microwaves over radio waves (RF)
Microwaves are used for communication purposes instead of radio waves because they have the following advantages [9-10]:

1. Microwaves provide an increase in bandwidth.
2. Microwaves travel in a straight line and are not absorbed by the ionosphere; therefore, are used in radar (Radio detection and ranging) system where they pass through the clouds but bounce back by a metal target (normally an airplane, missile or a ship) and return to the transmitter.
3. The high frequency of microwaves enables them to be used for high gain directive antennae (satellite dishes). Gain of an antenna is proportional to the ratio of the wavelength of the radiation being collected to the diameter (D) of the antenna i.e. \((\lambda/D)\).
4. The effective reflection area of a radar target is proportional to the target’s size. Various molecular, atomic and nuclear resonances occur at microwave frequencies; therefore, these radiations have found a variety of applications in basic science, remote sensing, medical diagnostics and treatments, and heating methods.

1.4.2 Microwave telecommunication
Long-range military search radar (radio detection and ranging) operates at 450 MHz, ultra-high frequency (UHF) TV broadcasts at 470-870 MHz, and most cellular telephones transmit at ~ 900 MHz. Air traffic control transponders are set at just above 1 GHz, and space telemetry systems which transmit data from deep-space probes to earth operate at just below 2 GHz. Troposcatter communications systems operate at just above 2 GHz, where microwave signals are scattered off the troposphere to achieve long-distance communication. Microwave heating equipment operates at 2.45 GHz. Airport search radar operates at just above 3 GHz. Point-to-point microwave relay, carrying telephone and television channels, transmit at just below 4 GHz. Communication satellite
downlinks are at 4 GHz, and the uplinks are at 6 GHz. Just above 7 GHz is the studio transmitter link (STL), which transmits radio and television broadcasts from the studio to the transmitter. Airborne fire control radar operates at 10 GHz, and just above that is another microwave relay band for telephone transmissions. Just below 20 GHz is another satellite downlink band, and just above 30 GHz is the corresponding uplink band. These bands are allocated for future satellite communication. Police radars are set at 24 GHz and 10.25 GHz. Frequencies from 30 – 300 GHz range are absorbed in the atmosphere and render the long-range communication; however, transmission windows exist between these absorption bands. Missile-seeker radars use such a window at 94 GHz. With continuous advances in microwave devices, more systems are being developed for the millimeter portion of the microwave band [11]. The operation frequency ranges of microwave devices are summarized in Table 1.1.
Table 1.1. Applications of microwave devices and the range of frequencies at which they operate [11].

<table>
<thead>
<tr>
<th>Application</th>
<th>Frequency Range (GHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radio detection and ranging (RADAR)</td>
<td>0.450</td>
</tr>
<tr>
<td>Ultra high frequency UHF (TV)</td>
<td>0.470-0.480</td>
</tr>
<tr>
<td>Cellular phones</td>
<td>~0.900</td>
</tr>
<tr>
<td>Air traffic control</td>
<td>1</td>
</tr>
<tr>
<td>Space telemetry communications (long distance communication)</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Microwave heating</td>
<td>&gt;2</td>
</tr>
<tr>
<td>Air port search (RADAR)</td>
<td>&gt;3</td>
</tr>
<tr>
<td>Point to point microwave relay (telephone and TV channels)</td>
<td>&lt;4</td>
</tr>
<tr>
<td>Communication satellite</td>
<td></td>
</tr>
<tr>
<td>Down link</td>
<td>4</td>
</tr>
<tr>
<td>Uplink</td>
<td>6</td>
</tr>
<tr>
<td>Studio transmitter link (STL)</td>
<td>7</td>
</tr>
<tr>
<td>Future satellite</td>
<td></td>
</tr>
<tr>
<td>Down link</td>
<td>20</td>
</tr>
<tr>
<td>Up link</td>
<td>30</td>
</tr>
<tr>
<td>Police RADAR</td>
<td>24-10.25</td>
</tr>
</tbody>
</table>

1.5 Microwave dielectric resonators

A dielectric resonator (DR) is a non-metallized component made of ceramics and is able to resonate at a particular frequency of the carrier signal to allow that signal to be efficiently separated from other unwanted signals. The frequency at which a DR resonates is called the resonant frequency [12]. The TE_{01δ} mode is widely used in the characterization of a material for its potential to be used as a DR. Figures 1.7 -1.8 shows the distribution of electric and magnetic fields for the TE_{01δ} mode respectively [13]. The electric field distributes along an equatorial plane where the magnetic field is zero and the magnetic field distributes along a meridian.
plane, where the electric field is zero. Since this is an azimuthally symmetric mode; therefore, the plot of magnetic field will be the same in any meridian plane. The direction of magnetic field is perpendicular to the direction of an electric field and its maximum value occurs one-quarter period later in time.

Cylindrical shape is the most common and simplest form of a DR. It sustains electromagnetic waves at microwave frequencies in its body as a result of the internal reflection at the dielectric air interface, thus confining the electromagnetic energy as shown in Figure 1.9 [14].

![Figure 1.7. Schematic representation of an electric field distribution in an equatorial plane for TE_{01\delta} mode of a DR.](image)

Coupling to the TE_{01\delta} mode is often accomplished through the magnetic field via a small horizontal loop placed in the equatorial plane or by placing the resonator end face on a substrate near a microstrip line, so that the magnetic field lines link with those of the loop or microstrip. Coupling to this mode via the electric field can also be achieved by using a small horizontal dipole, or a bent monopole. Knowledge of various modes will be useful in selecting the coupling device, which is best suited for a particular mode. A short electric probe would be the most efficient, if it is oriented along the electric field lines and placed at the location, where the electric field is strong. A small loop should be effective, if it is placed so that it couples with many magnetic field lines.
Figure 1.8. Schematic representation of the distribution of magnetic field lines in meridian plane for TE$_{01\delta}$ mode of a DR.

Figure 1.9. Schematic representation of the interaction of electric and magnetic field lines with the cylindrical ceramic resonator in the TE$_{01\delta}$ mode [14].

In the beginning of mobile technology, people used to utilize an air filled metallic cavity as a microwave resonator which made the microwave circuitry too large for practical applications [14].

The concept of using a solid dielectric material as a microwave resonator in place of the air filled metallic cavity resonator was introduced by Richtmyre in 1939 [15]. His theoretical work could not generate significant interest, and practically no development was made in this area for over 25 years. In 1953, Schlicke [16] published a paper on super high dielectric constant (~ 1000 or more) materials to be used in capacitors at relatively low RF frequencies.

In the early 1960s, Okaya [17] and Baras [18] reported $\varepsilon_r \sim 100$, $Q_u \sim 10,000$ (at 4 GHz) and $\tau_f \sim +400$ ppm/°C for TiO$_2$ (rutile); however, the high positive $\tau_f$ precluded its use as
a DR [17]. In mid 1960s, Cohn and his coworkers [19] performed an extensive theoretical and experimental evaluation of DRs at Rantec Corporation. They performed experiments on TiO$_2$ (rutile) and reported $\varepsilon_r \sim 100$, but again its poor $\tau_f$ rendered it unsuitable for the development of practical components. A real breakthrough in ceramic technology occurred in the early 1970s when Masse et al. [20] developed the first temperature stable, low loss barium tetratitanate ceramics. Temperature stable MW DRs utilizing the composite structure of positive and negative $\tau_f$ were reported by Konishi [21]. Later, a modified form of barium tetratitanate with $\varepsilon_r = 39.8$, $Q_u > 8000$ (4 GHz) and $\tau_f \sim 2$ ppm/$^\circ$C was reported by Bell Laboratories (New Jersey, USA) [12]. These encouraging results led to the actual implementations of DRs as MW components; however, these materials were in scarce supply and were not commercially available at that time.

The next major breakthrough came when the Murata manufacturing company (Japan) produced (Zr, Sn)TiO$_4$ ceramics [22-23]. They developed adjustable compositions with $\tau_f$ varying between +10 and -12 ppm/$^\circ$C. These devices became commercially available at reasonable prices. Afterwards, the theoretical work and use of DRs expanded rapidly.

1.5.1 Properties of a microwave DR

Any ceramic material to be used as a DR for communication applications utilizing microwaves as carrier signals must exhibit the following three basic characteristics with optimum values:

1.5.1.1 Dielectric constant

Dielectric constant is the measure of the ability of a dielectric material to store electrical charge, relative to the dielectric constant of vacuum ($\varepsilon_0 = 8.85 \times 10^{-12}$ F/m). Dielectric constant is not truly constant for a material, but changes with temperature, pressure, frequency, second phase formation and crystal structure of the material [3]. Dielectric constant relates the microscopic quantity (polarizability) ‘$\alpha$’ to the macroscopic quantities, such as polarization and capacitance.

Solid dielectrics with high $\varepsilon_r$ are desirable for circuit miniaturization, because the size of a microwave component is inversely proportional to the square root of its dielectric constant. In reality, the range $20 < \varepsilon_r < 100$ is restricted in order that other conditions for
MW applications can be met [2]. The wavelength of microwaves decreases by a factor $1/\sqrt{\varepsilon_r}$ on entering into a dielectric material. Mathematically, we can write

$$\lambda_d = \frac{\lambda_o}{\sqrt{\varepsilon_r}} \quad \text{(1.17)}$$

where $\lambda_d$ and $\lambda_o$ are the wavelengths of microwaves in a dielectric medium and vacuum respectively. The width of a cylindrical resonator must be an integral multiple of the wavelength to resonate. If that wavelength is decreased, then the physical dimensions of the resonator must be reduced as well. The resonant frequency ($f_o$) of a DR is related to its $\varepsilon_r$ by the eqn (1.18)

$$f_o = \frac{v_d}{\lambda_d} = \frac{c}{\lambda_d \sqrt{\varepsilon_r}} = \frac{c}{\lambda_d \sqrt{\varepsilon_r}} = \frac{c}{D \sqrt{\varepsilon_r}} \quad \text{(1.18)}$$

where $v_d$ is the velocity of the microwaves in a dielectric material, $c$ is the speed of light in vacuum ($3\times10^8$ m/s), and D is the diameter of the cylindrical dielectric resonator [14]. Eqn (1.18) shows that for a constant $f_o$, the greater is the dielectric constant, the smaller will be the diameter (D) of the resonator and hence the size of the component will be reduced.

1.5.1.2 Quality factor

For MW applications, materials are characterized at microwave frequencies by using resonance methods. Energy exchange occurs at the resonance. In the electromagnetic resonance, the electric and magnetic energy periodically change totally from one form to the other.

The quality factor ($Q$) is the ability of a DR to store MW energy with minimum signal loss. A perfect or an ideal dielectric has no losses due to its zero conductivity, but real dielectric materials are partially conducting. An electromagnetic signal looses power when passes through a dielectric material; therefore, for MW applications, it is important that the losses in the dielectric material are minimum (or alternatively $Q$-factor is as high as possible).
The $Q$-factor is a measure of the energy loss per cycle as compared to the energy stored in the fields outside the ceramics. It is a dimensionless number and can be expressed mathematically as

$$Q = \frac{E_{\text{max}}}{E_{\text{av}}} \quad \text{(1.19)}$$

where $E_{\text{max}}$ is the energy stored per cycle and $E_{\text{av}}$ is the average energy dissipated per cycle.

In 1964, Schlömann [24] presented a theory for the dielectric loss tangent in non-conducting ionic crystals, and predicted that the tan\(\delta\) increases when the ions are distributed disorderly in such a way that they break the periodic arrangement of charges in the crystal [24].

The total dielectric loss is the sum of intrinsic and extrinsic losses. The intrinsic losses depend on the composition, crystal structure and temperature of a material. The intrinsic losses occur due to the interaction of an alternating electric field with the phonons. Since the MW frequency is less than the lattice vibration; therefore, the lattice vibration will be anharmonic in nature and consequently, energy of the field will dissipate into heat and the sample will get heated up [25]. The extrinsic losses depend on the microstructure of a material, impurities, vacancies, grain boundaries, porosity, order disorder, orientations of the crystallites, dopants, microcracks and dislocations etc [26].

The four types of losses, known in DRs are dielectric, conduction, radiation and external losses. The dielectric $Q_d$, conduction $Q_c$ and the radiaton $Q_r$ quality factors are mathematically written as

$$Q_d = \frac{2\omega_o W_d}{P_d}, \quad Q_c = \frac{2\omega_o W_c}{P_c}, \quad Q_r = \frac{2\omega_o W_r}{P_r} \quad \text{(1.20)}$$

where $W_l$ is the total stored electric energy, and $P_c$, $P_d$, and $P_r$ are the power dissipation due to conductance, dielectric and radiation respectively and $\omega_o$ is the angular resonant frequency.

The unloaded quality factor $Q_u$ of a DR can be written as

$$Q_u = \left[\frac{1}{Q_d} + \frac{1}{Q_c} + \frac{1}{Q_r}\right]^{-1} \quad \text{-------------------------- (1. 21)}$$

In actual practice, a dielectric resonator is enclosed in a metallic cavity that is completely shielded to isolate it from radiation so that the term $1/Q_r$ can be ignored.
The external losses arise due to external circuit coupling. In order to feed the electromagnetic waves, conducting probes are used which are externally coupled to the resonator. The coupling probes often used for dielectric resonators include electric and magnetic dipoles. Resonators exhibiting high dielectric constants require the probe to be closer to the resonator. At relatively shorter distances, the fields emerging from the probe and the resonator begin to influence each other and other external losses arise due to coupling. The magnetic field around the probe introduces a magnetic field in the part, and so they are magnetically coupled; however, the presence of conducting probes in the electromagnetic field lines of the resonator (and obviously a resonator in the field lines of the probes) introduce losses. The total or loaded quality factor is defined as

\[ Q_L = \left[ \frac{1}{Q_u} + \frac{1}{Q_c} + \frac{1}{Q_{rad}} + \frac{1}{Q_{ext}} \right]^{-1} = \frac{1}{Q_u + 1/Q_{ext}} \]  

(1.22)

High \( Q_L \) means very fine tuning (a fine resonance peak with a narrow bandwidth) and is determined experimentally from the resonance peak as shown in Figure 1.10. Fine tuning means more frequency selections in a frequency range and better signal to noise ratio. When the sample is introduced into the cavity, a peak of finite breadth appears in the transmitted signal amplitude at the resonant frequency. A bandwidth (BW) is defined as the width of the peak at half its maximum amplitude (3 dB down from the top of the peak in Figure 1.10). The resonant frequency \( f_o \) divided by the bandwidth is equal to \( Q_L \) i.e.

\[ Q_L = \frac{f_o}{\Delta f_o} \]  

(1.23)

If conduction, radiation and external losses are negligible, then \( Q_L = 1/tan\delta \) (at the resonant frequency).

The unloaded quality factor \( (Q_u) \) is calculated from the value of \( Q_L \) and the loss due to external coupling \( (1/Q_L) \) using the following equation:

\[ 1/Q_L = [1/Q_u + 1/Q_{ext}] \]

\[ 1/Q_u = [1/Q_L - 1/Q_{ext}] \]

\[ \frac{1}{Q_u} = \frac{Q_{ext} - Q_L}{Q_{ext} - Q_L} \]

\[ Q_u = \frac{Q_L Q_{ext}}{Q_{ext} - Q_L} \]
where $T$ is the transmission coefficient and $IL$ is the insertion loss and is positive, according to the convention. The coupling coefficient $k$ is defined as the ratio of external to internal power dissipation, i.e.

$$k = \frac{P_{\text{ext}}}{P_{\text{int}}} = \frac{Q_u}{Q_{\text{ext}}} = \frac{Q_u}{Q_L - 1}$$

(1.25)

The coupling coefficient “$k$” can be used to derive the relationship between $Q_u$ and $Q_L$ as given in eq. (1.24). For the measurement of $Q_u$ in the transmission mode, each port (signal entering and exiting the chamber) has its own $k$. In this case, $Q_u$ is related to $Q_L$ through $k$ by eq. (1.26)

$$Q_u = \frac{Q_L}{1 - 10^{-d/20}}$$

(1.24)

$$Q_u = \frac{Q_L}{1 - \frac{Q_L}{Q_{\text{ext}}}}$$

$$Q_u = \frac{Q_L}{1 - \frac{Q_L}{Q_{\text{ext}}}}$$

(1.25)

$$Q_u = \frac{Q_L}{1 - 10^{-d/20}}$$

(1.24)

where $k_1$ and $k_2$ are the coupling coefficients on the entrance and exit of the chamber respectively. When $k = 1$, the external and internal losses are equal and the cavity is said to be critically coupled, indicating the best match. For $k < 1$, the resonator is under-coupled and for $k > 1$, the resonator is over-coupled.
Theoretically, $Q_u$-factor decreases linearly with increasing frequency; comparing just the $Q_u$-factors of different resonators would not be a fair comparison. It is therefore customary to report $Q_u$-factor as the $Q_u$-factor multiplied by the resonant frequency ($f_o$) i.e. $Q_u \times f_o$. As $Q_u$-factor is dimensionless, $Q_u \times f_o$ value will have the unit of the resonant frequency, usually GHz [27].

1.5.1.3 Temperature coefficient of resonant frequency

The other important characteristic of a MW dielectric resonator is that the resonant frequency should not change with change in temperature. This characteristic is known as the temperature coefficient of resonant frequency ($\tau_f$) which is a measure of the thermal stability of a resonator with change in temperature. Two mechanisms are known to cause variation in the resonant frequency with change in temperature. The first is the dimension ‘$L_i$’ of the $i^{th}$ part the resonator which expands with increase in temperature and is described by linear thermal expansion coefficient ‘$\alpha_i$’ of the $i^{th}$ part of the resonator and is given by eqn. (1.27)

$$\alpha_i = \frac{1}{L_i} \frac{\Delta L}{\Delta T} \, \text{-------------------------} \, (1.27)$$
Since the dimensions of a resonator are proportional to the wavelength of the microwave radiation; therefore, the resonant frequency decreases with increase in the dimensions of the resonator.

The second mechanism through which the resonant frequency can change with temperature is related with the dependence of \( \varepsilon_r \) with change in temperature. The linear variation in \( \varepsilon_r \) with temperature is called temperature coefficient of dielectric constant (\( \tau_\varepsilon \)) and is given mathematically by eq\(^n\). (1.28)

\[
\tau_\varepsilon = \frac{1}{\varepsilon_r} \frac{\Delta \varepsilon_r}{\Delta T} \tag{1.28}
\]

The temperature coefficient of resonant frequency (\( \tau_f \)) is given mathematically by eq\(^n\). (1.29)

\[
\tau_f = \frac{1}{f_0} \frac{\Delta f_0}{\Delta T} \tag{1.29}
\]

The resonant frequency \( (f_0) \) is related to \( \varepsilon_r \) of a dielectric material by the eq\(^n\). (1.30)

\[
f_0 = \frac{c}{\lambda_d} = \frac{c}{D \sqrt{\varepsilon_r}} \tag{1.30}
\]

where \( D \) is the diameter of the DR, \( c \) is the speed of light in vacuum, \( \lambda_d \) is the wavelength of the standing electromagnetic wave; therefore, appropriate tailoring of \( \varepsilon_r \) and \( D \) can lead to a reduction in size of the DR without changing the resonant frequency, which is a requirement of the microwave integrated circuits [28].

Differentiating both sides of eq\(^n\). (1.30) with respect to temperature “\( T \)” and rearranging we get

\[
\frac{1}{f_0} \frac{\partial f_0}{\partial T} = - \frac{1}{D} \frac{\partial D}{\partial T} - \frac{1}{2} \frac{1}{\varepsilon_r} \frac{\partial \varepsilon_r}{\partial T} \tag{1.31}
\]

Putting eq\(^n\). (1.27-1.29) in eq\(^n\). (1.31), yield

\[
\tau_f = -\alpha_L - (1/2) \tau_\varepsilon \tag{1.32}
\]

For an ideal DR, \( \tau_f \) should be near to zero. It is evident from eq\(^n\). (1.32) that for a zero \( \tau_f \), \( \tau_\varepsilon \) should have twice the value of \( \alpha_L \) and should be negative [28]. Since resonators are used in communication systems, therefore, temperature stability is an important factor and \( \tau_f \) should be close to zero. For most of the electronic ceramic materials, \( \alpha_L \) is about 10 ppm/°C indicating the significance of the influence of \( \tau_f \) on \( \tau_\varepsilon \). In order to measure \( \tau_f \),
a DR is kept end-shorted between two copper plates or on a low loss quartz spacer at the centre of a metallic cavity. This is then kept inside a temperature-controlled oven. The E-field probe is kept near the DR in such a manner to get the resonance peak. The TE$_{011}$ or TE$_{01\delta}$ mode is identified and the cavity containing the DR is slowly heated (e.g. at 1°C/min) in the range say 20–70°C. The probe of the thermocouple is kept just inside the cavity so that it does not disturb the resonant frequency. Shift of the resonant frequency as a result of heating in the reflection mode is noted using a network analyzer after stabilizing the temperature at equal intervals. The variation of resonant frequency is plotted as a function of temperature and $\tau_f$ is calculated from the slope of the curve using the eq\textsuperscript{a}(1.29)

$$\tau_f = \frac{f_{70} - f_{20}}{f_{25}(70 - 20)} = \frac{\Delta f_o}{f_o \Delta T} \quad \text{(1.29)}$$

$\tau_f$ is expressed as parts per million per degree Celsius (ppm/$^\circ$C) or M/K [29-30].

1.5.2 Measurement of microwave dielectric properties

The post resonator technique proposed by Hakki and Coleman was the first method developed for the measurement of microwave dielectric properties of a DR [4, 31]. In this technique, a specimen in the form of a cylinder with diameter D and length L is sandwiched between two parallel conducting plates of diameter d (\texttt{\vline}10 D) as shown in Figure 1.11. The TE$_{01\delta}$ mode is normally used to make the measurement. The diameter to height ratio of a dielectric puck should be about two to get wide mode separation so that the TE$_{01\delta}$ mode is not disturbed by the other adjacent modes. Two small antennas are positioned in the vicinity of the dielectric puck in order to couple power in and out of the resonator. The other ends of the antennas are connected to the two ports of a network analyzer. This method was modified by Courtney by introducing the effect of temperature and is now known as Courtney method. The Courtney method is a transmission type measurement for which a small brass cavity is used. The sample is placed at the center of the cavity away from the side’s walls. The method has been further improved and the dielectric resonator is placed on a low loss single crystal quartz or Teflon spacer at the center of the cavity as shown in Figures 1.13-1.14. $\varepsilon_r$, $Q_u$ and $\tau_f$ can be measured using the transmission mode cavity proposed by Krupka \textit{et al.} [32-33]. This
technique uses the $S_{21}$ parameter and the $TE_{01\delta}$ mode. $S_{21}$ parameter is the ratio of the electric field of the signal entering the component input to the electric field of the signal leaving the component output. The resonant frequency at the $TE_{01\delta}$ mode, 3dB half power bandwidth, and the insertion loss ($S_{21}$ parameter) are obtained from the network analyzer. This data along with the dimensions of the DR are entered into the software whose schematic is shown in Figure 1.15, and thus the dielectric constant and unloaded quality factor are calculated.

Figure 1.11. Schematic of a vector network analyzer (VNA) and a dielectric under test in Hakki-Coleman plates [4].

Figure 1.12. Schematic representation of a DR under test [8].
Figure 1.13. The cavity manufactured by QWED for quality factor measurement (Courtesy, J Krupka QWED, Warsaw, Poland) [27].

Figure 1.14. Schematic of the cavity set up for the measurement of $Q_u$ of a DR.
1.5.3 Applications of DRs

Applications of dielectric materials are very cost effective in various MW components and lead to significant miniaturization, particularly when microwave integrated circuits (MIC) or monolithic microwave integrated circuits (MMIC) are used. Small size, light weight, low cost along with the features like high $Q_u$ value, temperature compensated performance, good coupling characteristics, frequency tunability and a choice of modes with different characteristics make a DR an important device in MICs. DRs are used as resonating elements, feedback elements or as radiating elements in various applications. The microwave circuits, which employ DRs, are primarily oscillators, filters, duplexers and miniature radiating elements. These circuits are key elements in systems used for microwave communications, radars, navigation, electronic warfare systems, cellular telephones, base stations, hand held radio transmitters, speed guns and automatic door openers. DRs are nowadays widely used in the frequency range of ~1 to 30 GHz [34]. Additional applications of DRs include dielectric or superconductor testing and antenna applications. Miniature dielectric-filled coaxial resonators are commonly used in wireless handsets such as cellular phones and personal communication systems (PCS) [35]. DRs with $\varepsilon_r \sim 80$-100 have a significant impact on microwave devices operating in the 1 GHz region and are used particularly in all cellular and PCS base stations [35]. Emerging
working frequencies from 900 MHz to 2.4 GHz, 2.8 GHz and even to 5.8 GHz require
dielectric materials with $\varepsilon_r \sim 20$ and high quality factors. Low loss dielectric materials
with $\varepsilon_r \sim 20$ are being used in today’s global positioning system (GPS) patch antennas,
wireless local area network (WLAN) band pass filters and even for 5.8 GHz industrial,
scientific and medical applications (ISM) band pass filters [36].
New applications for DRs are constantly emerging such as global positioning systems
low temperature co-fired ceramics (LTCC) for embedded microwave circuitry, tunable
filters and higher frequency applications for advanced radar technology.

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CHAPTER 2

2. LITERATURE REVIEW

2.1 Historical development
Maxwell was the first to discuss light waves as a form of electromagnetic energy and mathematically defined their propagation. Lord Rayleigh showed that an infinitely long cylinder of a dielectric material could act as a wave-guide for electromagnetic waves [1]. In 1939, Richtmeyer [2] introduced the concept that a solid dielectric material in the form of a cylinder could act as a resonator, with resonant frequency dependent upon the geometry and dielectric constant of the resonator.

Ceramic materials with interesting electro-magnetic properties are in use since the medieval times. Magnetite (Fe$_3$O$_4$) with ferromagnetic properties was investigated by the early navigators and was called lodestone. The emergence of radio and telephone communications in the early part of the 20th century led to research on ferrites, which were used at frequencies up to $\sim$1 MHz [3].

2.2 Perovskites and perovskite related structures
A German mineralogist Gustav Rose discovered the mineral CaTiO$_3$ and named it perovskite after the eminent Russian mineralogist, Count Lev Alexevich Von Perovsky [4]. Later, the name perovskite was used to designate a whole group of ABO$_3$–type compounds, in which BO$_6$ octahedra share their corners, creating a space to accommodate the A cation. CaTiO$_3$ itself exhibits an orthorhombic structure at temperatures up to 900°C with lattice constants $a = 5.367$ Å, $b = 7.644$ Å and $c = 5.444$ Å while SrTiO$_3$ possesses the ideal cubic perovskite structure [4].

The perovskite structure has shown great flexibility for incorporating nearly every member of the periodic table. The basic perovskite framework (shown in Figure 2.1) is a 3-dimensional array of corner sharing octahedra, and can behave as a basis for the related structures, collectively known as layered perovskites.
Figure 2.1. Structure model of the ABO$_3$ perovskite with B cation at the center of BO$_6$ octahedra and A cation in the space created by the corner sharing BO$_6$ octahedra [5].

Much of the early work on synthetic perovskites was done by V.M. Goldschmidt [6], who developed the principle for the tolerance factor given by eq. 2.1

$$\tau = \frac{R_A + R_O}{\sqrt{2(R_B + R_O)}} \quad \text{(2.1)}$$

where $R_A$ and $R_B$ denote the radii of cations at the A and B sites, and $R_O$ is the radius of the oxygen ion. Generally a perovskite structure will form when $\tau$ is close to 1. This is demonstrated by SrTiO$_3$ with $\tau = 1.00$. If $\tau$ is very far away from 1, the perovskite structure will not form, e.g. $\tau = 0.81$ for MgTiO$_3$ which adopts the ilmenite structure [7]. The perovskite structures having low tolerance factor exhibit low symmetry and vice versa [8].

The perovskite family encompasses a variety of compounds ranging from MW dielectrics or DRs (e.g. BaMg$_{1/3}$Ta$_{2/3}$O$_3$ and BaZn$_{1/3}$Ta$_{2/3}$O$_3$) [9-10], ferroelectrics (e.g. PbTiO$_3$ and BaTiO$_3$) [11-12], piezoelectrics (e.g. PbZr$_{1-x}$Ti$_x$O$_3$) [13], relaxor ferroelectrics (e.g. PbMg$_{1/3}$Nb$_{2/3}$O$_3$) [14], multiferroics (e.g. BiFeO$_3$) [15] to colossal magneto resistance materials (e.g. La$_{1-x}$Ca$_x$MnO$_3$) [16], superconductors (e.g. Ba$_{1-x}$K$_x$BiO$_3$) [17] and materials exhibiting non-linear optical behavior (e.g. KNbO$_3$) [18].
The unit cell of an ideal perovskite structure is referred to as pseudo-cubic and its elements are denoted with the subscript ‘p’ for perovskite. The non-ideal perovskite structure is referred to as a distorted perovskite structure. Planes, directions and lattice parameters of the distorted perovskite unit cell are usually expressed in terms of the prototype cubic unit cell. This facilitates useful comparison between completely different symmetries [19].

Knight [20] proposed ionic displacement, chemical ordering, tilting of octahedra and combination of these as the four mechanisms resulting in the deviation from the ideal perovskite structure. The first two distortion mechanisms are driven by electronic instabilities of the octahedral metal ion. The common examples of electronic instabilities are a) the Jahn-Teller distortion in KCuF$_3$ [21] that lead to octahedral distortion and b) ferroelectric displacement of titanium in BaTiO$_3$ [22] that lead to a cation displacement. The third and most common distortion, the octahedral tilting, can be realized by tilting of the rigid BO$_6$ octahedra while maintaining their corner shared connectivity [23, 24-25]. This type of distortion is generally observed when the A-site cation is too small for the cubic BO$_6$ corner sharing octahedral network [26].

Nomenclature describing distortions due to octahedral tilting in perovskites was developed by Glazer in 1972 [9]. This nomenclature describes octahedral tilting occurring about the x, y and z-axes. The magnitude of the tilting of octahedra along the three axes is denoted by a set of three letters, $abc$. If tilting along two or more axes is equal in magnitude, the same letter is repeated. For example, equal tilting about the x and y-axes is denoted by $aab$. When tilting occurs along a particular axis, the octahedra perpendicular to that axis are forced to tilt in the opposite direction to maintain corner sharing connectivity. The absence of tilting is denoted by a superscript “0” (Figure 2.2a). Successive identical tilting of adjacent layers along a particular axis is known as in-phase tilting as shown in Figure 2.2b and is denoted by the superscript “+”. If tilting of successive octahedral layers along an axis is opposite to one another, it is called out-of-phase tilting as shown in Figure 2.2c and is denoted by the superscript “-”.

Glazer initially defined 23 tilt systems and assigned them to 15 different space groups [9]. Since then, the number of tilt systems and their corresponding space group’s
assignments has been revised [27-28]. Glazer tilts system and the corresponding space groups for simple (or disordered 1:1 B site) perovskites are given in Table 2.1.

![Diagram of octahedral frameworks](image)

Figure 2.2. Schematic of the tilting of octahedral frameworks, a) untitled, b) an in-phase tilted and c) an anti-phase tilted [29].

Perovskite microwave dielectrics constitute the class of materials with octahedral tilting and cation ordering. Octahedral tilting in perovskite affects the MW dielectric properties particularly $\varepsilon_r$ and $\tau_f$ i.e. the greater is the tilting angle of the octahedra (Figure 2.3), the smaller will be the $\varepsilon_r$ and $\tau_f$ [30].

Table 2.1. Space groups for all possible tilt systems both random B site cations and with 1:1 B-site cation ordering.

<table>
<thead>
<tr>
<th>Tilt system #</th>
<th>Tilt system symbol</th>
<th>Space group (random)</th>
<th>Space group ordered</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$a^+b^+c^-$</td>
<td>Immm</td>
<td>$P_{nnn}$</td>
</tr>
<tr>
<td>2</td>
<td>$a^+b^+b^+$</td>
<td>Immm</td>
<td>$P_{nnn}$</td>
</tr>
<tr>
<td>3</td>
<td>$a^+a^+a^+$</td>
<td>$I\bar{m}3$</td>
<td>$P_{n\bar{3}}$</td>
</tr>
<tr>
<td>4</td>
<td>$a^+b^+c^-$</td>
<td>$P_{mmm}$</td>
<td>$P_{2/c}$</td>
</tr>
<tr>
<td>5</td>
<td>$a^+a^+c^-$</td>
<td>$P_{42/nmc}$</td>
<td>$P_{4_{2}/n}$</td>
</tr>
<tr>
<td>6</td>
<td>$a^+b^+b^-$</td>
<td>$P_{mmm}$</td>
<td>$P_{2/c}$</td>
</tr>
<tr>
<td>7</td>
<td>$a^+a^+a^-$</td>
<td>$P_{42/nmc}$</td>
<td>$P_{4_{2}/n}$</td>
</tr>
<tr>
<td>8</td>
<td>$a^+b^+c^-$</td>
<td>$P_{2_{1}/m}$</td>
<td>$P_{1}$</td>
</tr>
<tr>
<td>9</td>
<td>$a^+a^+c^-$</td>
<td>$P_{2_{1}/m}$</td>
<td>$P_{1}$</td>
</tr>
<tr>
<td>10</td>
<td>$a^+a^+c^+$</td>
<td>$P_{nma}$</td>
<td>$P_{2_{1}/n}$</td>
</tr>
</tbody>
</table>
Octahedral tilting in perovskite results into the super-structural reflections [31]. Ohsato [32] found splitting in the oxygen ion position of TiO$_6$ octahedra on the Fourier map in Ba$_{6-3x}$Ln$_{8+2x}$Ti$_{18}$O$_{54}$ [Ln = La, Pr, Nd, Sm] ceramics. The observed splitting was attributed to the tilting of octahedra as shown in Figure 2.4. The superstructure is caused by the tilting of octahedral strings along the c-axis which was deduced from the splitting of oxygen ion position on the fundamental lattice.
Figure 2.3. Octahedral tilting in $\text{Ba}_{6-3x}\text{Ln}_{8+2x}\text{Ti}_{18}\text{O}_{54}$ (Ln = La, Pr, Nd, Sm) [32]

Figure 2.4. Tilting of TiO$_6$ octahedra deduced from the splitting of oxygen ion on the fundamental structure [32].

2.3 Perovskites as DRs

The discovery of ferroelectricity in BaTiO$_3$ in the 1940s [33] prompted research into the development of new ferroelectric and piezoelectric materials in the perovskite family. BaTiO$_3$ has cubic structure above 130°C and tetragonal structure below 130°C [34]. For $y > 0.15$, BaTi$_{1-2y}$Ga$_y$Nb$_y$O$_3$ is paraelectric at $\sim 200$ K with $\varepsilon_r \sim 50$–100 and resonate in the microwave frequency region with a $Q_u \times f_o \sim 2500$–3700 GHz. CaTiO$_3$ has a high $\varepsilon_r$ (160).
with good $Q_u \times f_o$ value (~7000 GHz) but its high positive $\tau_f$ value (+850 ppm/°C) disqualifies it to be used as a dielectric resonator [25-36].

In the late 1970s and early 1980s, a range of materials including MgTiO$_3$–CaTiO$_3$ [37], (Zr,Sn)TiO$_4$ [38] and BaTi$_4$O$_9$ [39] attracted increased interest due to their excellent microwave dielectric properties. The rapid growth of mobile communications market in the 1990s stimulated research in microwave dielectrics, particularly for high relative permittivity materials ($\varepsilon_r$~75–90) for mobile telephone handset applications, and very high $Q_u$ materials ($Q_u$~30,000 at 3 GHz) for base station applications. For the former group, the high $\varepsilon_r$ tungsten bronze-structured materials (e.g. BaO–Nd$_2$O$_3$–TiO$_2$) remained the primary choice, whilst complex perovskites (e.g. BaMg$_{1/3}$Ta$_{2/3}$O$_3$, BaZn$_{1/3}$Ta$_{2/3}$O$_3$ with $\varepsilon_r$~24–29) provided the highest $Q_u$ (~250000-150000) values for the base station applications. There was still a significant gap in terms of the relative permittivity between the two families of compounds; the simple perovskites (e.g. CaTiO$_3$–LaAlO$_3$, with $\varepsilon_r$~45) and the two-phase - PbO$_2$-structured ZrTiO$_4$–ZnNb$_2$O$_6$ (with $\varepsilon_r$~44) with $Q_u \times f_o$~48,000 GHz which went some way for providing ‘midrange’ materials [40]. A summary of typical materials which were available as dielectric resonator antennas for base station applications in 2007 is given in Table 2.2. A striking feature is still the gap in the available materials with $\varepsilon_r$~45–75, high $Q_u \times f_o$ value and zero $\tau_f$ [41].

Table 2.2. Dielectric materials applied as dielectric resonators for base station applications in 2007 with zero temperature coefficient of resonant frequency

<table>
<thead>
<tr>
<th>Material</th>
<th>$\varepsilon_r$</th>
<th>$Q_u \times f_o$ (GHz)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaTiO$_3$–NdAlO$_3$</td>
<td>45</td>
<td>48 000</td>
<td>42</td>
</tr>
<tr>
<td>ZrTiO$_4$–ZnNb$_2$O$_6$</td>
<td>47</td>
<td>34 000</td>
<td>43</td>
</tr>
<tr>
<td>BaMg$<em>{1/3}$Ta$</em>{2/3}$O$_3$</td>
<td>24</td>
<td>250 000</td>
<td>40</td>
</tr>
<tr>
<td>SrTiO$_3$–LaAlO$_3$</td>
<td>39</td>
<td>60 000</td>
<td>40</td>
</tr>
<tr>
<td>BaZn$<em>{1/3}$Ta$</em>{2/3}$O$_3$</td>
<td>29</td>
<td>150 000</td>
<td>41</td>
</tr>
<tr>
<td>Ba(Co,Zn)$<em>{1/3}$Nb$</em>{2/3}$O$_3$</td>
<td>34</td>
<td>90 000</td>
<td>41</td>
</tr>
</tbody>
</table>
2.4 \( A_nB_nO_{3n+2} \) type layered pervoskites

Perovskites with layered structures display a wide range of structural, chemical and physical properties. Compounds belonging to \( A_nB_nO_{3n+2} \) \((A = \text{Sr, Ca, Mg, La, Nd, Sm, Cr, Na and } B = \text{Nb, Ta or Ti, Zn, Zr})\) homologous series are a special group of perovskite-related layered materials due to their flexibility in accommodating various elements. Materials with \( n = 4, 4.33, 4.5, 5, 6 \) and \( 7 \) have been the subject of much interest because of their interesting physical and electrical properties [19,44-47].

The structure of compounds belonging to \( A_nB_nO_{3n+2} \) series consists of slabs or blocks, which are \( n \) octahedra thick and the number ‘\( n \)’ is determined from the composition. The slabs are stacked along the \([110]_P\) direction of the ideal perovskite structure [48]. In \( A_nB_nO_{3n+2} \)-type structures, the consecutive blocks or slabs of octahedra shift with respect to each other by half the body diagonal of the octahedron i.e. \( \frac{1}{2}[011]_P \) perovskite translation vector [49-50]. The interlayer region is left in such a manner that the octahedra do not share two oxygen atoms as shown in Figures 2.5-2.6. The lattice constants of the idealized (i.e. non-distorted) \( A_nB_nO_{3n+2} \) type compounds are derived from a cubic perovskite with unit cell length \( a_o \):

\[
\begin{align*}
a &= a_o \\
b &= a_o\sqrt{2} \\
c &= 2s + n a_o\sqrt{2} \quad (2.2)
\end{align*}
\]

where \( s \sim 2.3 \) Å is the distance between the neighboring layers. Compared to these cell parameters, the real materials often display a double \( a \)-axis and / or a half or doubled \( c \)-axis. The composition of the \( A_nB_nO_{3n+2} \) type oxides are expressed as \( ABOx \), thus normalized to one B cation, whereby the corresponding ideal oxygen content \((x)\) of a structure with \( n \) blocks of octahedra is given by \( x = 3+2/n \) [19]. The ideal structure corresponds to the limiting value \( n = \infty \) i.e. with a single infinitely thick slab of octahedra. On the other hand, \( n = 4 \) is the lower limit due to valance considerations. Integral values of \( n \) correspond to equally thick sequences of blocks, but non-integer values are also possible and correspond to sequences of octahedra-based blocks with alternating blocks of layers. For example, for \( n = 4.5 \), the structure of the material consists of alternating blocks of four and five layers [48]. A general description and symmetry classification of the \( A_nB_nO_{3n+2} \) layered structures has been reported by Levin.
and Bendersky [51]. They have discussed a classification scheme that relates the stacking sequences and octahedral tilt to the symmetry of these structures. The displacive transition from a high temperature untilted structure to a low–temperature tilted structure occurs in two stages; untilted $\rightarrow a^+ \rightarrow a^+b$ or $a^+c$ with doubling of the lattice parameter “$a$” at the final transition. The first layered perovskite-like ferroelectric of the $A_nB_nO_{3n+2}$ type compounds was Sr$_2$Ta$_2$O$_7$ [52].

![Diagram of crystal structure](image)

Figure 2.5. Sketch of the idealized (i.e. non-distorted) crystal structure of the $n = 2, 3, 4$ and 4.33 members of the perovskite-related layered $A_nB_nO_{3n+2}$ homologous series projected along the a-axis [19].
Figure 2.6. Schematic of the idealized (i.e. non-distorted) crystal structure of $n = 4.5$, $5$, $6$ and $\infty$ members of the perovskite-related layered homologous $A_nB_nO_{3n+2}$ series projected along the a-axis [19].

The real crystal structure of the $A_nB_nO_{3n+2}$ type compounds are highly distorted and the structure models for $La_2Ti_2O_7$, $SrLa_4Ti_5O_{17}$ and $Sr_2La_4Ti_6O_{20}$ [50] are shown in Figure 2.7.
A number of families of compounds belonging to the $A_nB_nO_{3n+2}$ homologues series have been investigated along the $A_2B_2O_7$-$ABO_3$ tie line due to their electrical properties [50, 53-54]. One such family of compounds belonging to the $A_nB_nO_{3n+2}$ homologues series is $Sr_nNb_nTi_{n-4}O_{17}$ with $n = 4, 4.33, 4.5, 4.78, 5, 6, 7$ which has been studied along the $Sr_2Nb_2O_7$-$SrTiO_3$ tie line [55]. $SrTiO_3$ is considered as a member of the $A_nB_nO_{3n+2}$ series with $n = \infty$. Chemically and compositionally $SrTiO_3$ is very stable with a melting temperature of $\sim 2080^{\circ}C$ [56]. $SrTiO_3$ is cubic at 105 K [57]. Although, it has a high dielectric constant ($\varepsilon_r \sim 205$), but its low $Q_o\times f_o$ value ($\sim 4200$ GHz at 10.6 GHz) and a high positive $\tau_f$ ($\sim 1700$ ppm$/^{\circ}C$) are not suitable for its use as DR [58-59].

Pyroniobate $Sr_2Nb_2O_7$ ($Sr_4Nb_4O_{14}$) belongs to the $A_nB_nO_{3n+2}$ series of compounds with $n = 4$. It exists along the $SrO-Nb_2O_5$ tie-line as shown in Figure 2.8.
Figure 2.8. Phase relations in the SrO-Nb$_2$O$_5$ binary system [60].

Sr$_2$Nb$_2$O$_7$ crystallizes into layers of perovskite-like slabs in which 4NbO$_6$ octahedra share their corners that distort and tilt with changes in temperature, undergoing successive phase transitions [61]. Sr$_2$Nb$_2$O$_7$ is ferroelectric below 1615K (A phase transition occurs from cubic to orthorhombic accompanied by distortion and rotation of the NbO$_6$ octahedra). At this phase transition temperature, the spontaneous polarization vector points along the c-axis of its orthorhombic unit cell [62] with space group $Cmc2_1$ [63]. It is paraelectric above the Curie temperature (1615K) [62], with space group $Cmcm$ which corresponds to the high temperature paraelectric form of Sr$_2$Ta$_2$O$_7$ [64]. At room temperature, the structure of Sr$_2$Nb$_2$O$_7$ is orthorhombic with lattice constants $a = 3.97$ Å, $b = 26.86$ Å and $c = 5.72$ Å [65] and its structure model is shown in Figure 2.9.
Other ferroelectric phase transitions in Sr$_2$Nb$_2$O$_7$ were also observed at ~ 488 K, 117 K and 100 K respectively [67-69].

The existence of members of Sr$_n$Nb$_n$Ti$_{n-4}$O$_{3n+2}$ with n = 5 and 6 were first reported by Isupov [52]. Based on the reflection conditions in the X-ray diffraction patterns, the *Pnnm* and *Cmc2$_1$* space groups were assigned to the structures with n = 5 and n = 6 respectively. It was also reported that Sr$_5$Nb$_4$TiO$_{17}$ was anti-ferroelectric with $T_c \geq 860$ K. Drew *et al.* [60] reported an orthorhombic crystal structure for Sr$_5$Nb$_4$TiO$_{17}$ with space group *Pnnm* and lattice constants $a = 5.6614$ Å, $b = 32.515$ Å and $c = 3.9525$ Å and $Z = 2$. The structure model of Sr$_5$Nb$_4$TiO$_{17}$ is shown in Figure 2.10.
Levin et al. [70] reported the dielectric properties of compounds belonging to the Sr$_n$Nb$_n$Ti$_{n-4}$O$_{3n+2}$ homologous series with $n = 4, 4.33, 4.5, 5, 6$ and $7$ in the SrTiO$_3$-Sr$_2$Nb$_2$O$_7$ binary phase diagram using solid state mixed oxide route and are summarized in Table 2.3. The structure of all the compounds in the Sr$_n$Nb$_n$Ti$_{n-4}$O$_{3n+2}$ series was found to be orthorhombic with different values of the lattice parameters using X-ray diffraction as well as electron diffraction techniques. From the selected area electron diffraction investigations, it was found that the structure of all the members of the Sr$_n$Nb$_n$Ti$_{n-4}$O$_{3n+2}$ homologous series was incommensurately modulated. The modulation was due to the tilting of the BO$_6$ octahedra.

Table 2.3. Permittivity and temperature coefficient of permittivity of SrTiO$_3$ and other compounds in the Sr$_n$(Ti, Nb)$_n$O$_{3n+2}$ composition series [70].

<table>
<thead>
<tr>
<th>Composition</th>
<th>N</th>
<th>$\varepsilon_r$ (100 KHz)</th>
<th>$\tau_\varepsilon$ (100 KHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr$_4$Nb$<em>4$O$</em>{14}$</td>
<td>4</td>
<td>42</td>
<td>$-1.1\times10^{-3}$</td>
</tr>
<tr>
<td>Sr$<em>{4.33}$Ti$</em>{0.33}$Nb$<em>4$O$</em>{15}$</td>
<td>4.33</td>
<td>56</td>
<td>$-1.9\times10^{-4}$</td>
</tr>
<tr>
<td>Sr$_5$TiNb$<em>4$O$</em>{17}$</td>
<td>5</td>
<td>80</td>
<td>$-7.6\times10^{-4}$</td>
</tr>
<tr>
<td>Sr$_5$Ti$_2$Nb$<em>4$O$</em>{20}$</td>
<td>6</td>
<td>77</td>
<td>$+1.3\times10^{-3}$</td>
</tr>
<tr>
<td>Sr$_7$Ti$_3$Nb$<em>4$O$</em>{23}$</td>
<td>7</td>
<td>61</td>
<td>$-4.0\times10^{-4}$</td>
</tr>
<tr>
<td>SrTiO$_3$</td>
<td>$\infty$</td>
<td>67</td>
<td>$-1.1\times10^{-3}$</td>
</tr>
<tr>
<td>SrTi$<em>{0.80}$Nb$</em>{0.16}$O$_3$</td>
<td>$\infty$</td>
<td>283</td>
<td>$-2.8\times10^{-3}$</td>
</tr>
</tbody>
</table>
Pasero et al. [71] studied perovskite related phases in the SrO-Nb$_2$O$_5$-TiO$_2$ ternary system using transmission electron microscopy (TEM) and reported the formation of Sr$_n$Nb$_n$Ti$_{n-4}$O$_{3n+2}$ homologous series of compounds in the SrO-Nb$_2$O$_5$-TiO$_2$ ternary system with $n = 4, 5, 6, 7$. Various phases forming in the SrO-Nb$_2$O$_5$-TiO$_2$ ternary phase diagram are shown in Figure 2.11.

![Figure 2.11. Phase relations in the SrO-Nb$_2$O$_5$-TiO$_2$ ternary system [71].](image)

Iqbal and Reaney [72] also reported the dielectric properties of the Sr$_n$Nb$_n$Ti$_{n-4}$O$_{3n+2}$ homologous series of compounds with $n = 4, 4.33, 5, 6,$ and $7$. The dielectric properties of all the compounds (except for $n = 7$ which was reported as multi-phasic) are given in Table 2.4. They reported a high quality factor for Sr$_5$Nb$_4$TiO$_{17}$ than the other studied compositions in the Sr$_n$Nb$_n$Ti$_{n-4}$O$_{3n+2}$ series, but not high enough for practical applications.
Table 2.4. Dielectric properties of compounds in the (1-x) Sr$_4$Nb$_4$O$_{14}$-xSrTiO$_3$ binary system [72].

<table>
<thead>
<tr>
<th>X</th>
<th>$\varepsilon_r$</th>
<th>Loss (10 KHz)</th>
<th>$\tau_c$</th>
<th>$Q_u \times f_o$ (GHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>47</td>
<td>0.0300</td>
<td>+0.0040</td>
<td>281</td>
</tr>
<tr>
<td>0.33</td>
<td>55</td>
<td>0.0060</td>
<td>-0.0005</td>
<td>397</td>
</tr>
<tr>
<td>0.5</td>
<td>57</td>
<td>0.0045</td>
<td>-0.0007</td>
<td>1070</td>
</tr>
<tr>
<td>0.67</td>
<td>63</td>
<td>0.0090</td>
<td>+0.0004</td>
<td>198</td>
</tr>
</tbody>
</table>

Slobodyanik et al. [54] synthesized Ca$_{5-x}$Sr$_x$TiNb$_4$O$_{17}$ (x = 0-5) compositions i.e. Ca$_5$Nb$_4$TiO$_{17}$, Ca$_4$SrNb$_4$TiO$_{17}$, Ca$_3$Sr$_2$Nb$_4$TiO$_{17}$, Ca$_2$Sr$_3$Nb$_4$TiO$_{17}$, CaSr$_4$Nb$_4$TiO$_{17}$ and Sr$_5$Nb$_4$TiO$_{17}$ from systems of co-precipitated hydroxo-carbonates using aqueous solutions of Ca(NO$_3$)$_2$, Sr(NO$_3$)$_2$, TiCl$_4$ and NbCl$_5$. They reported that at T>1570 K, the formation of Sr$_5$TiNb$_4$O$_{17}$ starts and a temperature well above 1670 K was needed for the formation of single phase Sr$_5$TiNb$_4$O$_{17}$ ceramics. The temperatures required for the formation of the five compounds with layered perovskite related structures in the Ca$_{5-x}$Sr$_x$Nb$_4$TiO$_{17}$ (x = 0-5) composition series were found to be different for different compounds.

The crystal structure along with the lattice parameters of some of the compounds belonging to the $A_xB_nO_{3n+2}$ homologous series are given in Table 2.5.
Table 2.6. Crystal structures and the lattice parameters of the compounds belonging to the homologous \( A_nB_nO_{3n+2} \) series

<table>
<thead>
<tr>
<th>Compound</th>
<th>( a(\text{Å}) )</th>
<th>( b(\text{Å}) )</th>
<th>( c(\text{Å}) )</th>
<th>( \beta(°) )</th>
<th>Crystal structure</th>
<th>S.G</th>
<th>Ref.</th>
<th>Special remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n=4 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Sr}_4\text{Nb}<em>4\text{O}</em>{14} )</td>
<td>3.956</td>
<td>26.80</td>
<td>5.696</td>
<td>Orthorhombic</td>
<td>( Pnnm )</td>
<td>70</td>
<td></td>
<td>Ferroelectric at 1615K[25]</td>
</tr>
<tr>
<td>( \text{Sr}_5\text{Ta}_3\text{O}_7 )</td>
<td>3.943</td>
<td>27.16</td>
<td>5.682</td>
<td>Orthorhombic</td>
<td></td>
<td>64</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{La}_2\text{Ti}_2\text{O}_7 )</td>
<td>7.812</td>
<td>5.544</td>
<td>13.01</td>
<td>98.66</td>
<td>Monoclinic</td>
<td>73</td>
<td></td>
<td>Ferroelectric 1770K</td>
</tr>
<tr>
<td>&quot;</td>
<td>7.819</td>
<td>5.239</td>
<td>12.55</td>
<td>99.33</td>
<td>Monoclinic</td>
<td>74</td>
<td></td>
<td>Ferroelectric at 30.2GPa</td>
</tr>
<tr>
<td>&quot;</td>
<td>7.7775</td>
<td>5.5248</td>
<td>13.004</td>
<td>98.58</td>
<td>Monoclinic</td>
<td>74</td>
<td></td>
<td>Ferroelectric at 16.7 GPa</td>
</tr>
<tr>
<td>( \text{Ca}_2\text{Nb}_5\text{O}_7 )</td>
<td>7.967</td>
<td>13.385</td>
<td>5.502</td>
<td>98.34</td>
<td>Monoclinic</td>
<td>75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( n=5 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Ca}_3\text{Nb}<em>5\text{TiO}</em>{17} )</td>
<td>3.8447</td>
<td>32.051</td>
<td>5.4875</td>
<td>Monoclinic</td>
<td>( P2_1 )</td>
<td>76</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Ca}_3\text{Nb}<em>5\text{O}</em>{17} )</td>
<td>7.7494</td>
<td>5.4928</td>
<td>32.241</td>
<td>96.809</td>
<td>Monoclinic</td>
<td>49</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{La}_5\text{SrTi}<em>3\text{O}</em>{17} )</td>
<td>7.824</td>
<td>5.536</td>
<td>31.337</td>
<td>90</td>
<td>Monoclinic</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Nd}_3\text{Ti}<em>3\text{O}</em>{17} )</td>
<td>7.8</td>
<td>5.7</td>
<td>31.6</td>
<td>97.71</td>
<td>Monoclinic</td>
<td>77</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{La}_5\text{Ti}<em>3\text{O}</em>{17} )</td>
<td>7.858</td>
<td>5.5281</td>
<td>31.449</td>
<td>97.166</td>
<td>Monoclinic</td>
<td>78</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{NaCa}_4\text{Nb}<em>5\text{O}</em>{17} )</td>
<td>7.710</td>
<td>32.350</td>
<td>5.4838</td>
<td>96.820</td>
<td>Monoclinic</td>
<td>48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Sr}_5\text{TiNb}<em>5\text{O}</em>{17} )</td>
<td>5.6614</td>
<td>32.515</td>
<td>3.9525</td>
<td>Orthorhombic</td>
<td>( Pnnm )</td>
<td>60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{SrNbO}_{3.41} )</td>
<td>3.99</td>
<td>5.67</td>
<td>32.45</td>
<td>90</td>
<td></td>
<td>19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Sr}<em>{0.963}\text{La}</em>{0.037}\text{NbO}_{3.41} )</td>
<td>3.99</td>
<td>5.67</td>
<td>32.37</td>
<td>90</td>
<td></td>
<td>19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Sr}<em>{0.95}\text{NbO}</em>{3.37} )</td>
<td>3.98</td>
<td>5.67</td>
<td>32.44</td>
<td>90</td>
<td></td>
<td>19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Sr}<em>{0.93}\text{NbO}</em>{3.36} )</td>
<td>3.98</td>
<td>5.67</td>
<td>32.47</td>
<td>90</td>
<td></td>
<td>19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Sr}<em>{0.9}\text{La}</em>{0.1}\text{NbO}_{3.41} )</td>
<td>4.00</td>
<td>2.66</td>
<td>32.27</td>
<td>90</td>
<td></td>
<td>19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Sr}<em>{0.5}\text{Ca}</em>{0.5}\text{NbO}_{3.41} )</td>
<td>3.94</td>
<td>5.60</td>
<td>32.23</td>
<td>90</td>
<td></td>
<td>36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{SrNb}<em>{0.9}\text{Ti}</em>{0.1}^\circ\text{O}_{3.39} )</td>
<td>3.95</td>
<td>5.59</td>
<td>32.6</td>
<td>90</td>
<td></td>
<td>36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{SrNb}<em>{0.8}\text{Ti}</em>{0.2}^\circ\text{O}_{3.40} )</td>
<td>3.95</td>
<td>5.59</td>
<td>32.6</td>
<td>90</td>
<td></td>
<td>24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( n=6 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Sr}_5\text{Ti}_2\text{Nb}<em>2\text{O}</em>{20} )</td>
<td>5.6325</td>
<td>38.049</td>
<td>3.9369</td>
<td>Orthorhombic</td>
<td></td>
<td>70</td>
<td></td>
<td>Ferroelectric at 630°C</td>
</tr>
<tr>
<td>( \text{La}_5\text{Sr}_2\text{Ti}<em>4\text{O}</em>{20} )</td>
<td>7.821</td>
<td>5.541</td>
<td>18.549</td>
<td>96.1</td>
<td>Monoclinic</td>
<td>50</td>
<td></td>
<td>( P11_2 )</td>
</tr>
<tr>
<td>( \text{CaNb}<em>{0.5}\text{Ti}</em>{0.5}\text{O}_{3.33} )</td>
<td>7.72</td>
<td>5.47</td>
<td>37.48</td>
<td></td>
<td></td>
<td>36</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.5 Effect of tolerance factor on the temperature coefficient of resonant frequency/dielectric constant (\(\tau_f/\tau_c\))

In 1960s, Harrop [79] compared the temperature coefficient of capacitance \(\tau_c\) of many paraelectric materials with their permitivities as shown in Figure 2.12.

![Figure 2.12](Image)

Figure 2.12. Plot of \(\tau_c\) versus \(\varepsilon_r\) for a wide range of paraelectric materials [79].

In general, compounds with low permittivity were reported to exhibit low \(\tau_c\) and vice versa. Harrop used Classius-Mosotti (CM) equation to relate the dielectric constant \((\varepsilon_r)\) to the polarizability \((\alpha_j)\), and is given by eq\(^n\). (2.3)

\[
\frac{\varepsilon_r - 1}{\varepsilon_r^2 - 2} = \frac{4\pi}{3} \sum N_j \alpha_j \quad (2.3)
\]

Where \(N_j\) is the concentration of atoms. Harrop differentiated the CM equation to justify the empirical relationship given by eq\(^n\). (2.4) physically; however, the mechanism of structural changes and the consequent effect on \(\tau_c\) was not explained.

\[
\tau_c = -\alpha_j \varepsilon_r \quad (2.4)
\]
Investigating the influence of phase transitions on the microwave dielectric properties of Ba and Sr based complex perovskites, Reaney et al. [80] reported that the onset of the tilt transition was the major factor that influenced $\tau_f$. Tilt transition occurs when corner-shared oxygen octahedra rotate either in-phase or anti-phase around the major axes of the perovskite structure. Colla et al. [81] postulated that in perovskites, the tolerance factor ($\tau$) controls the temperature of the onset of octahedral tilt transitions and hence $\tau_f$. They pooled the previously published data and plotted $\tau_e$ as a function of $\tau$ for a large number of Sr and Ba based complex perovskites as shown in Figure 2.13.

![Figure 2.13](image_url)

Figure 2.13. Plot of $\tau_e$ versus $\tau$ at room temperature for $A(B'B'')O_3$ (A= Sr and Ba, $B'=\text{In, Ca, Mn, Co, Ni, Zn, Mg, Nd, Gd, and } B''=\text{Ta and Nb}$) 1:1 and 1:2 complex perovskites [81].

Three distinct regions were identified in the plot of $\tau_e$ versus $\tau$. First, for $1.06 > \tau > 0.985$, $\tau_e$ is initially close to zero but then decreases to a minimum of -300 MK$^{-1}$ as the tilt transition approaches but does not exceed room temperature. At $\tau = 0.985$, a sharp increase in $\tau_e$, associated with the onset of a tilt transition above room temperature occurs in which the octahedra rotate in anti-phase only. This anti-phase tilting persists for $0.985 > \tau > 0.965$, above which a second phase transition occurs that involve both the anti-
phase and in-phase tilting of the octahedra above the room temperature. In this later phase, the $\tau_e$ increases as $\tau$ decreases accompanied by an increase in the amplitude of tilting. Eventually, as the value of $\tau$ decreases further, the perovskite phase will not be form and the ilmenite structure will preferably form; therefore, it is important to choose suitable cation substitutions in the perovskite-based materials in order to get both $\tau_e$ and $\tau_f$ values near to zero.

A number of dielectric materials belonging to the $A_nB_nO_{3n+2}$ series have been investigated for possible microwave applications and their microwave dielectric properties are summarized in Table 2.6.

Table 2.6. Microwave dielectric Properties of $A_nB_nO_{3n+2}$ type ceramics

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$\varepsilon_r$ (obs)</th>
<th>$\tau_f$ (ppm/°C)</th>
<th>$Q_u\times f_o$ (GHz)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$_2$Ti$_2$O$_7$</td>
<td>43</td>
<td>-6</td>
<td>2200</td>
<td>[82]</td>
</tr>
<tr>
<td>La$<em>9$Mg$</em>{0.5}$Ti$<em>{8.5}$O$</em>{31}$</td>
<td>42</td>
<td>-11</td>
<td>15000</td>
<td>[82]</td>
</tr>
<tr>
<td>La$_{10}$MgTi$<em>9$O$</em>{34}$</td>
<td>29</td>
<td>-22</td>
<td>13000</td>
<td>[82]</td>
</tr>
<tr>
<td>La$_4$NdCrTi$<em>4$O$</em>{17}$</td>
<td>53</td>
<td>-27.6</td>
<td>8800</td>
<td>[83]</td>
</tr>
<tr>
<td>La$_4$SmCrTi$<em>4$O$</em>{17}$</td>
<td>50</td>
<td>-39</td>
<td>6900</td>
<td>[83]</td>
</tr>
<tr>
<td>Ca$_3$Mg$_2$Nb$<em>4$TiO$</em>{17}$</td>
<td>37.5</td>
<td>-4.3</td>
<td>22500</td>
<td>[84]</td>
</tr>
<tr>
<td>Ca$_5$Ta$<em>4$TiO$</em>{17}$</td>
<td>40.1</td>
<td>-53.6</td>
<td>16450</td>
<td>[85]</td>
</tr>
<tr>
<td>Ca$_3$Nb$<em>4$TiO$</em>{17}$</td>
<td>44.9</td>
<td>-112.9</td>
<td>17600</td>
<td>[85]</td>
</tr>
<tr>
<td>CaLa$_4$Ti$<em>5$O$</em>{17}$</td>
<td>53.7</td>
<td>-20</td>
<td>17300</td>
<td>[86]</td>
</tr>
<tr>
<td>CaLa$_8$Ti$<em>6$O$</em>{31}$</td>
<td>48.6</td>
<td>-6</td>
<td>19345</td>
<td>[86]</td>
</tr>
<tr>
<td>SrLa$_4$Ti$<em>5$O$</em>{17}$</td>
<td>39.1</td>
<td>58</td>
<td>14200</td>
<td>[87]</td>
</tr>
<tr>
<td>CaLa$_4$Ti$<em>5$O$</em>{17}$</td>
<td>51.1</td>
<td>-29</td>
<td>13140</td>
<td>[87]</td>
</tr>
<tr>
<td>CaLa$_4$Ti$<em>5$O$</em>{17}$</td>
<td>56.5</td>
<td>3.7</td>
<td>12500</td>
<td>[88]</td>
</tr>
<tr>
<td>Ca$<em>{0.99}$Zn$</em>{0.01}$La$_4$Ti$<em>5$O$</em>{17}$</td>
<td>57.6</td>
<td>4.9</td>
<td>17100</td>
<td>[88]</td>
</tr>
<tr>
<td>CaLa$<em>4$Ti$</em>{4.95}$Zr$<em>{0.05}$O$</em>{17}$</td>
<td>55.9</td>
<td>4.6</td>
<td>15600</td>
<td>[89]</td>
</tr>
<tr>
<td>Ca$<em>{0.99}$Mg$</em>{0.01}$La$_4$Ti$<em>5$O$</em>{17}$</td>
<td>56.3</td>
<td>-9.6</td>
<td>12300</td>
<td>90</td>
</tr>
<tr>
<td>CaLa$<em>{3.995}$Nd$</em>{0.005}$Ti$<em>5$O$</em>{17}$</td>
<td>57.2</td>
<td>-14</td>
<td>15700</td>
<td>91</td>
</tr>
</tbody>
</table>
2.6 Present work

Keeping in view the high loss of Sr$_5$Nb$_4$TiO$_{17}$ ceramics, the present study was aimed at studying the effect of various cation substitutions such as Ca$^{+2}$ and La$^{+3}$ on its microwave dielectric properties. As recently Joseph et al. [45] reported Ca$_5$Nb$_4$TiO$_{17}$ to have good microwave properties i.e. $\varepsilon_r$ ~44.9, $Q_u\times f_0$ ~ 17600 GHz (at 4.13 GHz) and $\tau_f$ ~ 112 ppm/°C. The $\varepsilon_r$ of Ca$_5$Nb$_4$TiO$_{17}$ is lower than that of Sr$_5$Nb$_4$TiO$_{17}$ ($\varepsilon_r$ ~ 80) [51] due to the smaller ionic dielectric polarizability of Ca$^{+2}$ (3.24 Å$^3$) than Sr$^{+2}$ (4.24 Å$^3$) [92].

The substitutions of Ca$^{+2}$ ions for Sr$^{+2}$ ions will decrease the tolerance factor of Sr$_5$Nb$_4$TiO$_{17}$ tuning $\tau_f$ to zero in accordance with the work by Reaney et al.[80] by introducing tilting in the system. Also the substitution of lighter Ca$^{+2}$ ions for the heavier Sr$^{+2}$ ions will results in a decrease in the anharmonicity of the Lattice vibration that will result an increase in $Q$-factor [93]. Similarly the substitutions of La$^{3+}$ ions with smaller ionic radius (1.36 Å) for larger ionic radius (1.44 Å) of Sr$^{2+}$ ions and Ti$^{4+}$ ions with smaller ionic radius (0.64 Å) of Nb$^{5+}$ in Sr$_5$Nb$_4$TiO$_{17}$ will also results in the decrease in the anharmonicity of the lattice vibration that will result an increase in the $Q$-factor [93] as reported for Sr$_{4-x}$La$_x$Nb$_{3-x}$Ti$_x$O$_{12}$ [94] and Ba$_{5-x}$La$_x$Ti$_x$Nb$_{4-x}$O$_{15}$ [95]. The smaller ionic radii of La$^{+3}$ and Ti$^{+4}$ ions will cause a decrease in the tolerance factor of Sr$_5$Nb$_4$TiO$_{17}$ tuning $\tau_f$ to zero in accordance with the work by Reaney et al.[80] by introducing tilting in the system. A previous study [87] has reported $\varepsilon_r$ ~39.1, $Q_u\times f_0$ ~14200 GHz and $\tau_f$ ~ 58 ppm/°C for SrLa$_4$Ti$_5$O$_{17}$ belonging to Sr$_5$La$_{x}$Nb$_{4-x}$Ti$_{1+x}$O$_{17}$ series with $x = 4$. The high positive $\tau_f$ of SrLa$_4$Ti$_5$O$_{17}$ precludes its use as a DR in telecommunication device.

SrLa$_4$TiO$_{17}$ composition will be prepared in the present study to compare its properties with the previously reported properties. The Ca analogy of SrLa$_4$Ti$_5$O$_{17}$ i.e. CaLa$_4$Ti$_5$O$_{17}$ has been reported to have $\varepsilon_r$ ~53.7, $Q_u\times f_0$ ~17300 GHz and $\tau_f$ ~20 ppm/°C [86]. In another study $\varepsilon_r$ ~51.1, $Q_u\times f_0$ ~13140 GHz and $\tau_f$ ~29 ppm/°C have been reported for CaLa$_4$Ti$_5$O$_{17}$ [87]. Therefore, it is possible to get a temperature stable microwave dielectric material by substituting Ca$^{2+}$ ions for Sr$^{2+}$ ions in SrLa$_4$Ti$_5$O$_{17}$ i.e. by making a solid solution of the end members i.e. SrLa$_4$Ti$_5$O$_{17}$ and CaLa$_4$Ti$_5$O$_{17}$.

Nd$^{3+}$ and Sm$^{3+}$ ions are selected to replace La$^{3+}$ partially or completely in SrLa$_4$Ti$_5$O$_{17}$ in order to tune its $\tau_f$ to zero due to their smaller ionic radii i.e. (1.27 Å for Nd$^{3+}$ and 1.24 Å for Sm$^{3+}$).
for Sm$^{3+}$) than that La$^{3+}$ (1.36 Å) [92]. These substitutions will results in a decrease in the tolerance factor which in turn will induce a tilting of the TiO$_6$ octahedra and thus tune $\tau_f$ to zero.

Since the ionic radius of Zr$^{4+}$ (0.83 Å) for coordination no.6 and its polarizability (3.25 Å$^3$) is greater than the ionic radius (0.604 Å) and ionic dielectric polarizability (2.93 Å$^3$) of Ti$^{4+}$, however, it has been reported that “$\alpha/r^3$” ratio for Zr$^{4+}$ is less than Ti$^{4+}$ which led to a decrease in $\varepsilon_f$ and hence in $\tau_f$ of Ca$_5$Nb$_2$Ti$_{1-x}$Zr$_x$O$_{12}$ [96] Therefore, in the present study Zr$^{4+}$ was selected to partially replace Ti$^{4+}$ ions which is expected to lead the tuning of $\tau_f$ to zero of SrLa$_4$Ti$_5$O$_{17}$.

The detailed reason about using the above mentioned cations is also given in the result and discussion chapter.

### 2.7 References

44. Kuntscher, C A.; Gerhold, S.; Nucker, N.; Cummins, R T.; Lu, H D.; Schuppler,
    S.; Gopinath, S C.; Lichtenberg, F.; Mannhart, J.; Bohnen, P K. Phys. Rev. B.,
    2000, 61, 1876-1883.
    89(23), 236403.


CHAPTER 3

3. EXPERIMENTAL PROCEDURE

3.1 Ceramic processing

Solid-state reaction route is a low cost and widely used method in the industry for the production of MW dielectric ceramic materials. This route includes the following steps:

3.1.1 Specification of raw materials

Powdered materials in unprocessed or semi-processed state to various grades of purity used in ceramics production are termed as raw materials. For the preparation of a specific material, it is required to specify the raw materials and their purity level depending on the desired properties of the final product. For example, the preparation of $\text{Sr}_5\text{Nb}_4\text{TiO}_{17}$ requires $\text{SrCO}_3$, $\text{TiO}_2$, and $\text{Nb}_2\text{O}_5$ as raw materials. The quality and nature of the raw materials have a significant effect on the final properties of ceramic components. The purity, particle size, reactivity, polymorphic form and cost of the raw materials are equally important to be considered and controlled in order to make economically feasible products [1]. In the present study, the raw materials used are given in Table 3.1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Manufacturer</th>
<th>Purity%</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{SrCO}_3$</td>
<td>Aldrich-chemicals, Milwaukee, USA</td>
<td>99+</td>
</tr>
<tr>
<td>$\text{CaCO}_3$</td>
<td>Aldrich-chemicals, Milwaukee, USA</td>
<td>99+</td>
</tr>
<tr>
<td>$\text{Nb}_2\text{O}_5$</td>
<td>Aldrich-chemicals, Milwaukee, USA</td>
<td>99.95</td>
</tr>
<tr>
<td>$\text{TiO}_2$</td>
<td>Aldrich-chemicals, Milwaukee, USA</td>
<td>99+</td>
</tr>
<tr>
<td>$\text{La}_2\text{O}_3$</td>
<td>Aldrich-chemicals, Milwaukee, USA</td>
<td>99.95</td>
</tr>
<tr>
<td>$\text{Sm}_2\text{O}_3$</td>
<td>Aldrich-chemical, Milwaukee, USA</td>
<td>99.95</td>
</tr>
<tr>
<td>$\text{Nd}_2\text{O}_3$</td>
<td>Aldrich-chemicals, Milwaukee, USA</td>
<td>99.95</td>
</tr>
<tr>
<td>$\text{ZrO}_2$</td>
<td>Aldrich-chemicals, Milwaukee, USA</td>
<td>99.99</td>
</tr>
</tbody>
</table>
3.1.2 Mixing and milling of raw materials

After selecting the required raw materials, the next step is to weigh out the raw materials in stoichiometric ratios and mix them in order to prepare the batch composition. The batch is then mix-milled using a conventional ball mill or other milling machines such as attritor mill or vibro energy mill depending on the availability and requirement of the product. Although ball mills are slow but mechanically simple and robust. A liquid such as de-ionized water, acetone or propanol is used as a lubricant and Y-toughened zirconia or another suitable media as the grinding media. The volume of the liquid generally used is between 100 to 200% of the powder in order to make freely moving slurry. The slurry is then dried to get a homogenous mixture of the raw materials [1]. Milling has been found to significantly affect the microwave dielectric properties of a material [2].

SrCO₃ (99+%, Sigma Aldrich USA), Nb₂O₅ (99.95%, Sigma Aldrich USA), CaCO₃ (99% +, Sigma Aldrich USA) and TiO₂ (Anatase, 99+% , Sigma Aldrich USA) were weighed in stoichiometric ratios for the synthesis of Sr₅₋ₓCaₓNb₄Ti₅O₁₇ (0 ≤ x ≤ 5) compositions using electronic analytical balance (KERN, Als 220-4) at the Materials Research Laboratory, Institute of Physics & Electronics, University of Peshawar. The mixtures were wet ball milled for 60 h in disposable polyethylene mill jars using ¼” diameter Y-toughened ZrO₂ balls as grinding media and iso-propanol as lubricant to make the slurry. The slurry was dried overnight in a drying oven at ~95°C; however, for the other compositions in the present study i.e. Sr₅₋ₓLaₓNb₄₋ₓTi₁₊ₓO₁₇ (0 ≤ x ≤ 4), SrLa₄₋ₓNdₓTi₅O₁₇ (0 ≤ x ≤ 4), SrLa₄₋ₓSmₓTi₅O₁₇ (0 ≤ x ≤ 4), Sr₁₋ₓCaₓLa₄₋ₓTi₅O₁₇ (0 ≤ x ≤ 1), SrLa₄₋ₓSmₓZrₓO₁₇ (0 ≤ x ≤ 0.1), SrCO₃ (99+%, Sigma Aldrich USA), CaCO₃ (99+%, Sigma Aldrich USA) were dried at ~185 °C and Nb₂O₅ (99.95%, Sigma Aldrich USA), La₂O₃ (99.95%, Sigma Aldrich USA), Nd₂O₃ (99.95%, Sigma Aldrich USA), Sm₂O₃ (99.95%, Sigma Aldrich USA) were dried at ~900°C overnight to remove the moisture before weighing. The dried carbonates and oxides were weighed in stiochiometric ratios and wet ball milled for 24 h in disposable polyethylene mill jars using ½” diameter Y-toughened ZrO₂ balls as grinding media and iso-propanol as lubricant to make the slurry, using horizontal ball mill (Cole-Parmer Lab mill-8000) at the Department of Material Science and Engineering Materials University of Sheffield Uk.
3.1.3 Calcination
Calcination is the process of heating the milled mixture of raw materials at a temperature well below the melting temperature of the reactants in order to make the initial ingredients react and form the desired phase. During calcination, the reactants interact by inter-diffusion of their ions, and reduce the extent of diffusion which will otherwise occur during sintering leading to undesired shrinkage of the final body. The final required product may not be obtained during this process but the remaining chemical gradients may assist sintering. Calcination is carried out by placing the homogenously mixed milled sample of powder in a crucible, which is then placed in a furnace. The crucible must be made of such a material that must not react with the material to be calcined. The calcined powder sample is grinded to dissociate agglomerates (if any). Sometimes, the powder sample is again heated so that the un-reacted reactants left over in the first step of calcination react to form the phase. After regrinding, the calcined powder is sieved to get fine powder samples. Calcination temperature and its duration greatly affect the microstructure, density and hence the dielectric properties of a material [3-4].

In the present study, the mix-milled powder of Sr$_5$Nb$_4$TiO$_{17}$ composition was calcined at 990°C for 2h, and that of Ca substituted Sr$_5$Nb$_4$TiO$_{17}$ compositions at 1350°C for 2h.

For the La substituted Sr$_5$Nb$_4$TiO$_{17}$ compositions the mix milled powder samples were calcined at 1250°C/6h; however, the mix-milled powder of Sr$_5$Nb$_4$TiO$_{17}$ was calcined at 1400°C/6h. The mix-milled powder batches of SrLa$_{4-x}$Nd$_x$Ti$_5$O$_{17}$ and SrLa$_{4-x}$Sm$_x$Ti$_5$O$_{17}$ compositions were calcined at 1350°C/6h with a heating / cooling rate of 5°C/min. For Sr$_{1-x}$Ca$_x$La$_4$Ti$_5$O$_{17}$ and SrLa$_4$Ti$_{5-x}$Zr$_x$O$_{17}$ compositions the mix-milled powder were calcined at 1300°C/6h with a heating / cooling rate of 5°C/min using a furnace (Allied).

3.1.4 Pellet pressing
After calcination, an organic binder such as polyvinyl alcohol is added to the powder and milled for 30 to 40 minutes before pressing into the desired shape in a tool steel die. In the present study, cylindrical steel dies of 10 mm and 13 mm diameter (Specac, England) were used to press the pellets. The powder samples were put into the die and the piston was slowly inserted into the cylindrical die. The calcined powder of Sr$_{5-x}$Ca$_x$Nb$_4$TiO$_{17}$...
compositions were pressed into 4-5 mm high, and 13 mm diameter pellets at \(~140\) MPa. The calcined powder of \(\text{Sr}_5\text{La}_x\text{Nb}_{4-x}\text{Ti}_{1+x}\text{O}_{17}\), \(\text{SrLa}_{4-x}\text{Nd}_x\text{Ti}_5\text{O}_{17}\), \(\text{SrLa}_{4-x}\text{Sm}_x\text{Ti}_5\text{O}_{17}\), \(\text{Sr}_1-x\text{Ca}_x\text{Ti}_5\text{O}_{17}\), \(\text{SrLa}_4\text{Ti}_{15-x}\text{Zr}_x\text{O}_{17}\) samples were pressed into 2-4 mm high pellets of 10 mm diameter at 80 MPa using a manual pellet press (CARVER, USA) at the Department of Materials Science and Engineering Materials University of Sheffield Uk.

3.1.5 Solid state sintering

Density of electronic ceramics is a sensitive parameter and directly affects the final properties; therefore, optimum sintering of the green pellets is required for electrical property measurements.

Solid state sintering refers to the heating of a compact green body to a high temperature lower than the melting temperature of the material to be sintered. When the fine-grained powder particles are compacted, they are in contact with one another at many sites having large number of pores and voids (unfilled space) among them. Solid state sintering causes sufficient atomic diffusion of atoms and sintering is commonly accomplished in three stages. In the initial stage, the surfaces of the particles become smooth, their necks grow and the pores among the interconnected particles become rounded in shape. In the intermediate state, continuous pores channels form along many three-grain junctions, called triple junction. As densification proceeds, the pore channels form closed pores at densities greater than 92%. In the final stage of sintering, isolated pores are eliminated by mass transport from the grain boundaries to the pore. Pores on a grain boundary can be eliminated by motion of grain boundaries or lattice diffusion but pores within the grains can only be eliminated by lattice diffusion, which can be a problem since volume diffusion often has higher activation energy. In the present study, green pellets of \(\text{Sr}_5-x\text{Ca}_x\text{Nb}_4\text{TiO}_{17}\) batch compositions were placed on a \(\text{ZrO}_2\) plate and sintered at a heating/cooling rate of \(10^\circ\text{C/min}\) for 2h in a chamber furnace (Nabertherm GmbH, Germany) at the Materials Research Laboratory Institute of Physics and Electronics University of Peshawar Pakistan. The green or as-pressed pellets of \(\text{Sr}_5-x\text{La}_x\text{Nb}_{4-x}\text{Ti}_{1+x}\text{O}_{17}\) batch compositions were placed on a platinum foil in an alumina boat before insertion into the furnace. These samples were sintered at \(1450^\circ\text{C}\) to \(1550^\circ\text{C}\) for 4h at a heating / cooling rate of \(5^\circ\text{C/min}\). Similarly the green pellets of \(\text{SrLa}_{4-x}\text{Nd}_x\text{Ti}_5\text{O}_{17}\), \(\text{SrLa}_{4-x}\text{Sm}_x\text{Ti}_5\text{O}_{17}\), \(\text{Sr}_1-x\text{Ca}_x\text{Ti}_5\text{O}_{17}\), \(\text{SrLa}_4\text{Ti}_{15-x}\text{Zr}_x\text{O}_{17}\), \(\text{SrLa}_4\text{Ti}_{15-x}\text{Zr}_x\text{O}_{17}\) were sintered at 80 MPa using a manual pellet press (CARVER, USA) at the Department of Materials Science and Engineering Materials University of Sheffield Uk.
and SrLa$_{4-x}$Ti$_5$Zr$_x$O$_{17}$ batch compositions were placed on a platinum foil and sintered at 1450°C to 1580°C for 4h at a heating/cooling rate of 5°C/min. The following experimental techniques were employed for the characterization of the samples prepared in the present study.

### 3.2 Thermal analysis

Thermal Analysis is defined as the measure of the change in physical and chemical properties of a material as a function of temperature. Thermal analysis has many applications in solid state science which include the study of solid-state reactions, thermal decompositions, phase transitions and determination of phase diagrams. The two main thermal analysis techniques used in the present study were thermo-gravimetric analysis (TGA) and differential thermal analysis (DTA) [5].

#### 3.2.1 Thermo-gravimetric analysis (TGA)

Thermo-gravimetric is a technique used to measure the change in mass of a substance as a function of increasing temperature. A sample (heated at a constant rate typically at 1-20 °C/min) has an initial mass $m_i$ at a temperature $T_i$. Under dynamic heating conditions, when decomposition of sample occurs over a range of temperature from $T_i$ to $T_f$, a downward slope is observed. Above $T_f$, a continuous line on chart appears which corresponds to the residue mass ($m_f$). The decomposition temperature of a substance depends on a number of variables such as heating rate, the nature of the material, particle size and immediate atmosphere of the sample [5].

#### 3.2.2 Differential thermal analysis (DTA)

Differential thermal analysis (DTA) is the simplest and the most widely used thermal analysis technique. In DTA, the test sample and an inert reference material are subjected to the same heating conditions. The change in temperature of the unknown is measured relative to the inert reference. The difference in temperatures of the test material and inert reference material indicates when an endothermic or an exothermic reaction occurs at particular temperatures. The temperature change should be approximately the same for both the test sample and the inert reference material until a reaction occurs in the test.
sample that will either require an excess of heat energy (endothermic reaction) or evolve energy (exothermic reaction) [6].

In the present study, TGA and DTA were performed for the Sr_{5-x}Ca_xNb_4TiO_{17} compositions from 30°C to 1200°C at a heating/cooling rate of 5°C/min in the nitrogen atmosphere for the compositions with x = 0 and 1 and at 10°C/min for the compositions with x = 2, 3, 4 and 5, using TG/DTA unit (Perkin Elmer Diamond TG-DTA) at the Centralized Resource Laboratory Institute of Physics and Electronics University of Peshawar Pakistan

3.3 X-ray diffraction (XRD)

X-rays were discovered in 1895 by a German physicist Roentgen. These rays were called X-rays because of their unknown nature at that time. X-rays are electromagnetic radiations with wavelengths ranges from 0.5 Å to 2.5 Å, and lie in the region between gamma and ultraviolet rays in the electromagnetic spectrum. X-rays are of particular importance in solid state science due to their capability and use in identification of the constituent phase(s) in a material and determination of crystal structures with high precession.

X-rays are produced when high energy electrons accelerated thorough a potential difference >30 kV strike a metal target (e.g. copper). The incident electrons have sufficient energy to knockout some of the 1s electrons from the K shell of the target atom. In order to fill the vacancy created in the 1s orbital, an electron from an outer orbital (2p or 3p) immediately drops down to occupy the vacancy in the 1s shell. The energy released during transition appears as X-rays as shown in Figure 3.1.
Figure 3.1. Schematic of the generation of CuK\textsubscript{\alpha} X-rays by ionization of the 1s electron followed by the transition of the 2p electron into the 1s orbital [7].

The transition from 2p to 1s shell gives K\textsubscript{\alpha}-radiation while the transition from 3p to 1s shell gives K\textsubscript{\beta}-radiations. The intensity of K\textsubscript{\alpha} radiations is more than that of K\textsubscript{\beta}-radiations; therefore, K\textsubscript{\alpha} radiations are used in the diffraction experiments. In the case of Cu target, the K\textsubscript{\alpha} transition is a doublet with \( \lambda = 1.54051 \) Å for K\textsubscript{\alpha1} and \( \lambda = 1.54433 \) Å for K\textsubscript{\alpha2} because these transitions have slightly different energies for the two possible spin states of the 2p electrons which make the transition relative to the spin of the vacant 1s orbital. In some experiments, the peaks due to K\textsubscript{\alpha1} and K\textsubscript{\alpha2} overlap each other appearing as a single line instead of a doublet while in other experiments, the diffraction peaks due to K\textsubscript{\alpha1} and K\textsubscript{\alpha2} can be resolved and observed separately.

Powder X-ray diffraction (XRD) method is commonly used in material science because of the random distribution of particles with nearly all possible orientations. This enables X-rays scattering from almost all the lattice plans in all possible directions with considerable intensity. A monochromatic beam of X-rays is made incident upon a powder sample and the plans oriented at the Bragg’s angle \( \theta \) to the incident beam satisfy the Bragg’s law \( 2dsin\theta = n\lambda \), where \( \theta \) is the diffraction angle, \( d \) is the inter-planner spacing, \( \lambda \) is the wavelength of the incident monochromatic X-ray beam and \( n = 1, 2, 3, \ldots \) is the order of diffraction. A modern X-ray diffractometer has a proportional, Scintillation or
Geiger counter as detector. The detector (counter) is set to scan over a range of 2θ values at a constant angular velocity and receives the diffracted rays. The counts (intensity) of the diffracted rays (Bragg’s peaks) received by detector are plotted against the 2θ values, and the resulting pattern is called as the X-ray diffraction pattern. Each peak on the pattern corresponds to a particular d-spacing. Each crystalline material has its one characteristics X-ray diffraction pattern. From the diffraction pattern one can get useful information such as the phase(s) present in the material, grain size, stresses developed in a material, crystal structure of a crystalline material and its precise lattice parameters. Compounds having the same crystal structure do not give rise to the same diffraction pattern due to different lattice parameters of the unit cells which make the d-spacings and the peak positions vary. The intensities of the peaks also vary due to the different types of atoms or ions having different atomic numbers with different X-ray scattering power (structure factor) [7].

Hanawalt (USA) used X-ray diffraction method for the first time in 1938 for the identification of a phase. In characterizing an unknown specimen in terms of the phase(s) present with this technique, almost all the d-values, positions of the peaks, and their intensities must be accounted for. Furthermore, all the peaks expected from the substance must be present in the observed diffraction pattern.

The observed d values and the corresponding intensities are compared with standard powder diffraction files (PDF). Four routine steps are generally required to identify a single phase, or a component of a mixture. Identification involves designating the strongest, second strongest, third strongest lines and so on, i.e. d-values of the pattern as d₁, d₂, d₃ and so on. The steps are:

1) The proper Hanawalt group for d₁ is located in the numerical index
2) The values of d₂ and d₃ are next sought within the group
3) When the d values are matched, the relative intensities of the peaks corresponding to the d₁, d₂, and d₃ values are compared with the standard or reference
4) Agreement between the observed and reference peak intensities will suggest the identity of the phase and confirmation is obtained by reference to the compound’s data file [12].
Rapid identification is possible by computer using software packages for the purpose with the aids of the PDF data base. Computer systems attached with most of the latest versions of the X-ray powder diffractometers are equipped with these software packages. The identification of a phase(s) using the diffraction data is accomplished in two stages. The search step and the match step. The detection limit of a phase by X-ray diffraction technique in a mixture is about 3-5-wt% [8].

In the present study, XRD of samples was performed at various stages of processing. The starting powder samples were examined by XRD to analyze the phase(s) present to confirm the identity of the raw materials. After calcination, XRD of each batch composition was performed to investigate the phase(s) developed in the calcined samples. Finally, XRD was employed on finely grounded sintered pellets to determine the phase(s) present in the samples. XRD was performed at 2θ = 10 to 70° at 1°/min with a step size of 0.02° using a Philips 1700 series X-ray diffractometer operating at 30 kV and 40 mA for phase analysis and a STOE PSD transmission powder X-ray diffractometer system with CuKα radiation (λ = 1.540598 Å) operating at 35 kV and 40 mA for measurement of the lattice parameters at the X-ray diffraction laboratory, Department of Material Science & Engineering Materials, University of Sheffield (UK). XRD traces analysis was conducted using STOE WinXPOW software (version 1.06, © STOE & Cie GmbH, Darmstadt, Germany).

3.4 Scanning electron microscopy

Scanning electron microscope (SEM) is able to produce 3-D images of a specimen. SEM uses a narrow beam of accelerated electrons that scan the surface of the sample under examination. SEM analysis reveals detailed information about the surface texture, grain size, morphology, orientation and grain boundaries.

For microstructural characterization of a sample with SEM, the surface of the sample must be highly polished and conductive by sputtering a very thin layer of gold on the surface. The coating allows the electrons to conduct away from the specimen. The sample is mounted on a stub (usually made of aluminum), which is screwed into the sample holder for insertion into the sample chamber of SEM. Sucking the air present in the column of the microscope creates a high vacuum within the column. Once the vacuum is
achieved, an electron gun placed right on top of the sample emits a high-energy beam of electrons, which is focused onto a very fine spot on the specimen. The focused beam is then made to scan the surface by moving the beam back and forth, which is controlled through magnetic lenses. As the high energy electrons hit the surface, some of the electrons from the beam are bounced back or backscattered while some are absorbed in the material. The absorbed electrons may knockout electrons from the orbital that are called secondary electrons. These secondary electrons then enter into the detector called secondary electron detector and give information on the topography of the sample from which a high resolution image is made.

SEM can be coupled with an X-ray electron energy dispersive spectrometer (EDS), to detect the energy of X-rays emitted from the atoms. X-ray photons enter the EDS detector and produce a spectrum comprising peaks of various intensities, characteristic of the elements present in the material. The height of the peak is related to the concentration of the element in the specimen.

In the present study, sintered samples were cut, polished and thermally etched at temperature 10% less than the corresponding sintering temperatures to resolve the grains. The samples were gold-coated to avoid charging in the SEM. Microstructural characterization was performed using a JEOL 6400 SEM operating at 20 kV, at the centralized resource laboratory University of Peshawar, Pakistan.

### 3.5 Density measurements

Density of a sintered material is found to be one of the important parameters that influence the dielectric properties [9]. In the present study, experimental densities of the sintered samples were measured using Archimedes method. This method is based on the principle which states that, “a solid sample heavier than fluid, when weighted in the fluid, be lighter than its true weight by an amount equal to the weight of the fluid displayed”.

Distilled water was used as the fluid in the present study. In this method, the sample was initially weighted \( m_1 \), then tied with a very thin thread, then suspended and the weight of the sample was weighted \( m_2 \) along with the thread. The suspended sample was then immersed in a beaker containing the distilled water and was weighted \( m_3 \) when immersed in the water. In this case the decrease in the mass was buoyancy due to the
water displaced. The pellet was then removed from the thread and the pellet density was calculated using eq\(^n\). (3.1)

\[
\rho_{\text{obs}} = \frac{m_1}{m_2 - m_3} \times \rho_{\text{H}_2\text{O}} \quad \text{------------------ (3.1)}
\]

where

\( m_1 \) = mass of the sample in air (g)
\( m_2 \) = mass of the sample with thread (g)
\( m_3 \) = mass of the sample with thread when immersed in water (g)

\( \rho_{\text{H}_2\text{O}} \) = density of water at the experimental temperature (kg/m\(^3\))

\( \rho_{\text{obs}} \) = bulk density of the sintered sample (kg/m\(^3\))

The theoretical density or X-ray density of each composition was calculated using eq\(^n\). (3.2)

\[
\rho_{\text{th}} = \frac{Z \times M\text{.}W}{V_{\text{cell}} \times N_A} \times 10^{27} \quad \text{------------------ (3.2)}
\]

where

\( Z \) = formula unit or no. of atoms per unit cell
\( M\text{.}W \) = molecular weight of the composition (g)
\( V_{\text{cell}} \) = volume of the unit cell (Å\(^3\))

\( \rho_{\text{th}} \) = theoretical density (kg/m\(^3\))

\( N_A \) = Avogadro no = 6.022x10\(^{23}\) /mol

The volume of the unit cell was calculated from the Lattice parameters of the unit cell which were refined by the least squares method.

The relative density or percentage theoretical density for each sintered sample was calculated using eq\(^n\).(3.3)

\[
\rho_{\text{rel}} = \frac{\rho_{\text{obs}}}{\rho_{\text{th}}} \times 100 \quad \text{------------------ (3.3)}
\]

where

\( \rho_{\text{obs}} \) = observed or experimental density
\( \rho_{\text{rel}} \) = relative density
3.6 Measurement of dielectric properties at low frequencies

An inductance/capacitance/resistance (LCR) meter (Model 4284A, Hewlett Packard) linked to a computer via a CP-IB interface was used for capacitance and tan δ measurements at the University of Sheffield (UK). The measurements were carried out from room temperature to ~800°C. Samples were heated at a rate of 1°C/min in a non-conductively wound tube furnace and the capacitance and tan δ were measured every 60s. The capacitance values were then converted to dielectric constant using eq. (3.4)

\[ \varepsilon_r = \frac{C \cdot t}{\varepsilon_o \cdot A} \]  

(3.4)

where

- \( C \) = capacitance (F)
- \( t \) = thickness of a disc sample (m)
- \( A \) = area of the face of disc sample (m²)
- \( \varepsilon_o \) = permittivity of free space (8.85419.10⁻¹² F.m⁻¹)
- \( \varepsilon_r \) = dielectric constant

3.7 Network analyzer

A network analyzer is an instrument used for doing a variety of measurements on active as well as on passive microwave components. Network analyzer can measure both the impedance (Reflection) and gain (Transmission) characteristics of a device by applying a known swept signal. A vector network analyzer consists of a source, receiver and a display. Schematic of a vector network is shown in Figure 3.2. In this measurement technique, a sample is placed in a fixture and the source launches a signal frequency to the material under test in the fixture. The receiver is tuned to that frequency to detect the reflected and transmitted signals from the material and compares them with the incident signal and finally the response of the material is measured by producing the phase at that frequency. The source is then stepped to the next frequency and the measurement is
repeated to display the reflection and transmission measurement response as a function of frequency. The vector network analyzer measures the response of the material under test in terms of scattering parameters which determines signal flow conditions when a device is inserted into a microwave circuit as shown in Figure 3.3 [10]. For example, for transmission method measurement ($S_{21}$), the electric field of the microwave signal entering the component input is compared to the electric field of the microwave signal leaving the component output or more simply, the signal entering one side of a cavity is compared to the signal collected on the other side of the cavity [10].

![Diagram of a generalized vector network analyzer (VNA)](image)

Figure 3.2. Block diagram of a generalized vector network analyzer (VNA) [11].
Figure 3.3. Parameters describing the signals that are measured with a network analyzer. The dielectric constant is measured by the $S_{21}$ parameter and $Q_u$ is measured using the $S_{11}$ parameter [10].

### 3.7.1 Measurement of microwave dielectric properties

Cavity method was employed for the measurement of MW dielectric properties. A cylindrical DR was placed at the center of a cavity made of bras (20 mm height and 20 mm diameter) on a low loss quartz spacer to avoid conduction loss from the walls of the cavity (Figure 3.4). The microwave energy was coupled to the test piece using two ports. Measurements were taken in the transmission mode using a network analyzer (R3767CH) at the Department of Materials Science and Engineering Materials University of Sheffield (UK). The temperature coefficient of resonant frequency ($\tau_f$) was calculated in the temperature range of 20 to 70°C using the eq. (3.5)

$$\tau_f = \frac{f_1 - f_2}{f_1(T_{70} - T_{20})} \quad (3.5)$$

Where $f_1$ and $f_2$ are the initial and final resonant frequencies at 20°C and 70°C respectively.
Figure 3.4. Schematic of the cavity setup used for the measurement of MW dielectric properties.

3.8 References

CHAPTER 4
CHARACTERIZATION OF Sr\textsubscript{5-x}Ca\textsubscript{x}Nb\textsubscript{4}Ti\textsubscript{5}O\textsubscript{17}

4.1 Introduction

Sr\textsubscript{5}Nb\textsubscript{4}Ti\textsubscript{5}O\textsubscript{17} has a high dielectric constant but a low quality factor [1] which precludes its use as a DR in microwave communication systems. Some Ca-containing ceramic compounds are known to exhibit good microwave dielectric properties in comparison to Sr containing compounds. Bijumon et al. [2] investigated Ca\textsubscript{5-x}Sr\textsubscript{x}Nb\textsubscript{2}TiO\textsubscript{12} (0 ≤ x ≤ 5) compounds for possible microwave applications. Substantial Sr\textsuperscript{2+} ions substituted for Ca\textsuperscript{2+} ions decreased \( Q_u \times f_o \) from 26000 to 6000 GHz accompanied by an increase in the \( \tau_f \) from 40 to 51 ppm/°C. Suvorov et al. [3] investigated the microwave dielectric properties of CaTiO\textsubscript{3}-NdAlO\textsubscript{3} solid solution and showed that these materials had a high dielectric constant (\( \varepsilon_r > 45 \)), high quality factor (\( Q_u \times f_o > 40,000 \) GHz) and \( \tau_f \sim 0 \). Recently Ca\textsubscript{5}Nb\textsubscript{4}TiO\textsubscript{17} and Ca\textsubscript{5}Ta\textsubscript{5}TiO\textsubscript{17} were reported to have \( \varepsilon_r = 44.9, Q_u \times f_o = 17600 \) GHz and \( \tau_f \sim -112.9 \) ppm/°C and \( \varepsilon_r = 40.1, Q_u \times f_o = 16450 \) GHz and \( \tau_f \sim -53.6 \) ppm/°C respectively [4].

In this chapter, results regarding the characterization and dielectric properties of Ca-substituted Sr\textsubscript{5}Nb\textsubscript{4}TiO\textsubscript{17} are presented and discussed as an attempt to improve its MW dielectric properties.

4.2 Results and discussion

4.2.1 TG/DTA analysis

Figure 4.1(a-b) shows the mass loss\% for the as-milled mixture of 5SrCO\textsubscript{3}: 4Nb\textsubscript{2}O\textsubscript{5}: 1TiO\textsubscript{2} and 4SrCO\textsubscript{3}: 1CaCO\textsubscript{3}: 4Nb\textsubscript{2}O\textsubscript{5}: 1TiO\textsubscript{2} compositions. The downward slope on the TGA curve recorded at 5°C per min for the 5SrCO\textsubscript{3}: 4Nb\textsubscript{2}O\textsubscript{5}: 1TiO\textsubscript{2} batch composition was associated with mass loss in the temperature range 650°C to 880°C while the downward slope for the 4SrCO\textsubscript{3}: 1CaCO\textsubscript{3}: 4Nb\textsubscript{2}O\textsubscript{5}: 1TiO\textsubscript{2} batch composition at 650°C to 889°C was due to the decomposition of SrCO\textsubscript{3} and CaCO\textsubscript{3} [5, 7].

Two downward slopes were observed on the TGA curve (Figure 4.2a) in the temperature range 650°C to 750°C and 750°C to 902°C for 3SrCO\textsubscript{3}: 2CaCO\textsubscript{3}: 4Nb\textsubscript{2}O\textsubscript{5}: 1TiO\textsubscript{2} batch composition. This indicated an increase in the decomposition temperature of SrCO\textsubscript{3} from
880°C to 902°C, probably due to the increase in the heating rate from 5°C/min to 10 °C/min [5-6]. Consistent with the TGA results, two endotherms were observed at 750°C and 902°C on the DTA curve as well (Figure 4.2a). By flipping the DTA curve, the endotherms associated with the decomposition of carbonates followed by their reactions with Nb2O5 and TiO2 point downward rather than upward. The mass loss occur due to the evolution of CO2 during the decomposition of CaCO3 in the temperature range 650°C to 750°C [5] and 650°C to 902°C from SrCO3 [7]. TGA and DTA results for 2SrCO3: 3CaCO3: 4Nb2O5: 1TiO2 and 1SrCO3: 4CaCO3: 4Nb2O5: 1TiO2 batch compositions shown in Figures 4.2(b-c) were almost similar to those of 3SrCO3: 2CaCO3: 4Nb2O5: 1TiO2 (Figure 4.2a) with the only difference that the final decomposition temperature of SrCO3 decreased with increase in the CaCO3 content [8]. The TGA curve in Figure 4.2 (d) is from 5CaCO3: 4Nb2O5: 1TiO2 showing a single downward slope at 650°C to 750°C indicating the mass loss due to the decomposition of CaCO3 into CaO and CO2. The corresponding DTA curve also showed only one endothermic dip at 750°C.

For the as mix-milled powder of 3SrCO3: 2CaCO3: 2Nb2O5: 1TiO2 ratio, a total ~18.60% mass loss was recorded in the entire heating cycle from 30 to 1200°C which was consistent (within ±1%) with the total CO2 forming during the reaction given in eqn. (4.1).

\[ 3\text{SrCO}_3:2\text{CaCO}_3:2\text{Nb}_2\text{O}_5:1\text{TiO}_2 \rightarrow \text{Sr}_3\text{Ca}_2\text{Nb}_4\text{TiO}_{17} + 5\text{CO}_2 \]  

-----(4.1)
Figure 4.1. TGA curves from the as-milled mixture of, a) 5SrCO$_3$: 4Nb$_2$O$_5$: 1TiO$_2$ and b) 4SrCO$_3$: 1CaCO$_3$: 4Nb$_2$O$_5$: 1TiO$_2$, showing downward slopes associated with mass loss% for these compositions.
4.2. DTA / TGA curves for the as-milled mixtures of the batch compositions a) 3SrCO$_3$: 2CaCO$_3$: 4Nb$_2$O$_5$: 1TiO$_2$, b) 2SrCO$_3$: 3CaCO$_3$: 4Nb$_2$O$_5$: 1TiO$_2$, c) 1SrCO$_3$: 4CaCO$_3$: 4Nb$_2$O$_5$: 1TiO$_2$, and d) 1CaCO$_3$: 4Nb$_2$O$_5$: 1TiO$_2$, showing two downward slopes and two endotherms for 3SrCO$_3$: 2CaCO$_3$: 4Nb$_2$O$_5$: 1TiO$_2$, 2SrCO$_3$: 3CaCO$_3$: 4Nb$_2$O$_5$: 1TiO$_2$, and 1SrCO$_3$: 4CaCO$_3$: 4Nb$_2$O$_5$: 1TiO$_2$ compositions associated with the decomposition of SrCO$_3$ and CaCO$_3$ while only one downward slope and one endotherm for 5CaCO$_3$: 4Nb$_2$O$_5$: 1TiO$_2$ composition associated with the decomposition of CaCO$_3$.

4.2.2 X-ray diffraction

The room temperature XRD patterns recorded from the calcined (990°C for x = 0 and 1350°C for x = 1-5 for 2h) Sr$_{5-x}$Ca$_x$Nb$_4$TiO$_{17}$ (0 ≤ x ≤ 4) samples are shown in Figure 4.3. The major phase observed in the sample with x = 0, calcined at 990°C/2h was Sr$_5$Nb$_4$TiO$_{17}$; however, a few XRD peaks labeled as “*” matched PDF# 28-1247 for Sr$_2$Nb$_2$O$_7$ indicating incomplete reaction. XRD patterns from compositions with x =1 to 4 calcined at 1350°C/2h were similar and matched PDF# 87-1170 for Sr$_5$Nb$_4$TiO$_{17}$ indicating the formation of single phase ceramics. For the composition with x = 5, the observed major XRD peaks matched PDF# 51-412 for Ca$_3$Nb$_5$O$_{17}$ and were indexed accordingly; however, a few peaks labeled as “■” and “●” in Figure 4.3, matched PDF# 47-1668 for orthorhombic CaNbO$_3$ and PDF# 39-1392 for CaNb$_2$O$_6$. It is noticeable that no reference PDFs could be found for Ca$_5$Nb$_4$TiO$_{17}$; however, the observed XRD peaks for Sr$_{5-x}$Ca$_x$Nb$_4$TiO$_{17}$ composition with x = 5 were indexed using a model analogous to
monoclinic Ca$_5$Nb$_5$O$_{17}$ reported in the PDF# 51-412. This indicated the formation of secondary phases in the sample with $x = 5$ along with the parent Ca$_5$Nb$_4$TiO$_{17}$ phase.

XRD of Sr$_{5-x}$Ca$_x$Nb$_4$TiO$_{17}$ ($x = 0-5$) samples sintered at 1450°C for 2h (Figure 4.4) revealed the formation of single phases for the compositions with $x = 0, 1, 2, 3$ and 5, and were indexed accordingly. For the composition with $x = 4$, the observed XRD peaks matched PDF# 87-1170 and 52-1486 for Sr$_5$Nb$_4$TiO$_{17}$ (indexed) and Sr$_6$Nb$_4$Ti$_2$O$_{20}$ respectively, indicating a mixture of $n = 5$ and 6 layered perovskites. The peaks due to Sr$_6$Nb$_4$Ti$_2$O$_{20}$ were labeled as ▲ in Figure 4.4; however, the nature of the layered perovskite with $n = 6$ could not be found in the present study. Above 1450°C, even the compositions with $x = 1, 2, 3$ and 5 were not single phase and XRD of samples sintered at 1500°C revealed the presence of a mixture of Sr$_n$(Nb,Ti)$_n$O$_{3n+2}$ compounds with $n = 5$ and 6 layered perovskites i.e. Sr$_5$Nb$_4$TiO$_{17}$ (PDF# 87-1170) and Sr$_6$Nb$_4$Ti$_2$O$_{20}$ or Ca$_6$Nb$_4$Ti$_2$O$_{20}$ (PDF# 52-1486) for $x = 0$ or 5 respectively. It is noticeable that at 1500°C, the major phases observed in the compositions with $x = 1, 2, 3$ and 4 were Sr$_4$CaNb$_4$TiO$_{17}$, Sr$_3$Ca$_2$Nb$_4$TiO$_{17}$, Sr$_2$Ca$_3$Nb$_4$TiO$_{17}$ and SrCa$_4$Nb$_4$TiO$_{17}$, respectively; however, the nature of the secondary phases i.e. the layered perovskites with $n = 6$ in the compositions with $x = 1-4$ could not be identified due to the same number of elements as that of the $n = 5$ in each composition. The crystal structure of the compounds with $x = 0-4$ was orthorhombic with space group $Pnma$ and the compound with $x = 5$ crystallized into a monoclinic structure with space group $P2_1/b$ or $P2_1/c$ [9]. Levin et al. [10] and Manan et al. [11] also reported the formation of a mixture of Sr$_n$(Nb,Ti)$_n$O$_{3n+2}$ compounds with $n = 5$ and 6 in the Sr$_5$Nb$_4$TiO$_{17}$ along the ySrTiO$_{3-y}$(1-y) Sr$_2$Nb$_2$O$_7$ (y = 0.5) tie line with no Ca$^{2+}$ substitution. The split into secondary phases is more visible in the compositions with $x = 4$ and 5 as compared to the compositions with $x = 0-3$ sintered at 1500°C/2h (Figure 4.5).

All the Sr$_{5-x}$Ca$_x$Nb$_4$TiO$_{17}$ compositions crystallized into A$_5$B$_5$O$_{17}$-type compounds where the large Sr/Ca cations occupy the A site with coordination of 12 O’s and the Ti/Nb cations occupy the B site with coordination of 6 O’s. The resulting structure consists of perovskite-like blocks each of which is five octahedra thick and separated by an extra layer of oxygen. With increasing Ca$^{2+}$ content from $x = 1$ to 5, the XRD peaks shifted towards higher diffraction angle i.e. smaller inter-planar spacings (d values) due to the
smaller ionic radius (1.34 Å) of Ca²⁺ ions substituted for the larger Sr²⁺ (1.44 Å) ions [2, 12] resulting in a decrease in the lattice constants of the corresponding unit cells.

Figure 4.3. XRD patterns from Sr₅₋ₓCaₓNb₄TiO₁₇ samples calcined at 990 °C (for x=0) and 1350 °C (for x=1-5) for 2h, showing the presence of single phase ceramics for x=1-4, a secondary phase Sr₂Nb₂O₇ (for x=0) and CaNbO₃ and CaNb₂O₆ for x=5.

The variation in the unit cell parameters “a”, “b”, and “c” of the Sr₅₋ₓCaₓNb₄TiO₁₇ ceramics refined by the least squares method with the increase in Ca²⁺ content is shown in Figure 4.6 and compared in Table 4.1. The lattice parameters “a”, “b” and “c” were observed to decrease from 5.6614 Å to 5.5360 Å, 32.515 Å to 32.151 Å, and 3.9525 Å to 3.8727 Å respectively as the value of x was increased from 0 to 4. For x = 5, “a” and “c” increased to 7.6889 Å and 32.253 Å respectively but “b” decreased to 5.4763 Å [13] (Figure 4.6). This is consistent with the observed change in structure from an orthorhombic (Pnmm) and z = 2 [9] to a monoclinic (P2₁/c) and z = 4 [13]; consequently, the molar volume (V_m = V_unit cell/Z) of the Sr₅₋ₓCaₓNb₄TiO₁₇ unit cell decreased from 363.788 Å³ to 339.515 Å³ due to the substitution of small Ca²⁺ ion in the unit cell for the larger Sr²⁺ ion as shown Figure 4.7. Other alternative arrangements for the unit cell
parameters of Ca$_5$Nb$_4$TiO$_{17}$ could be i) $a = 3.8447(5)$ Å, $b = 32.051(5)$ Å and 5.4875(7) Å [8].

The theoretical density of Sr$_{5-x}$Ca$_x$Nb$_4$TiO$_{17}$ ($0 \leq x \leq 5$) ceramics decreased from 5.15 g/cm$^3$ to 4.41 g/cm$^3$ with an increase in the Ca$^{+2}$ content from 0 to 5 due to the decrease in “Mw/V” ratio as shown in Figure 4.8.

![Figure 4.4. XRD patterns from Sr$_{5-x}$Ca$_x$Nb$_4$TiO$_{17}$ samples with x = 0-5 sintered at 1450 °C for 2h, showing the presence of single phase compounds for x = 0, 1, 2, 3 and 5 and a mixture of layered perovskite (Sr, Ca)$_n$(Nb,Ti)$_n$O$_{3n+2}$ phases with n = 5 and 6 for the composition with x = 4.](image-url)
Figure 4.5. XRD patterns from Sr$_{5-x}$Ca$_x$Nb$_4$TiO$_{17}$ samples with $x = 0$-$5$ sintered at 1500°C for 2h, showing the presence of a mixture of $(\text{Sr},\text{Ca})_n(\text{Nb},\text{Ti})_n\text{O}_{3n+2}$ compounds with $n = 5$ and 6 for each composition.

Figure 4.6. Plot of the unit cell parameters ‘$a$’, ‘$b$’, ‘$c$’ versus Ca$^{+2}$ content ($x$) for Sr$_{5-x}$Ca$_x$Nb$_4$TiO$_{17}$ ($0 \leq x \leq 5$) compositions, showing a small decrease in ‘$a$’, ‘$b$’, ‘$c$’ for $x \leq 4$ and then an abrupt decrease in $b$ accompanied by and an increase in $a$ and $c$ parameters along with a change in the space group from $Pnmm$ with $z = 2$ to $P2_1/c$ with $z = 4$. 
Figure 4.7. Plot of $V_m$ versus $Ca^{2+}$ content (x) for the $Sr_{5-x}Ca_xNb_4TiO_{17}$ ($0 \leq x \leq 5$) composition series, showing an almost linear decrease in $V_m$ with increasing in $Ca^{2+}$ content.

Figure 4.8. Plot of $\rho_{th}$ versus $Ca^{2+}$ content (x) for $Sr_{5-x}Ca_xNb_4TiO_{17}$ ($0 \leq x \leq 5$) compositions, showing an almost linear decrease in $\rho_{th}$ with increasing $Ca^{2+}$ content.

4.2.3 Density measurement

The variation in the apparent density ($\rho_{ap}$) of $Sr_{5-x}Ca_xNb_4TiO_{17}$ ($x = 0-5$) compounds with the increase in the sintering temperature is shown in Figure 4.9. The density of each composition first increased with increase in the sintering temperature from 1400°C to 1500°C and then decreased upon further increase in the sintering temperature to 1550°C. This indicated that the density of each composition reached to a maximum at ~1500°C. A previous study [11] reported a maximum apparent density of ~ 4.46 g/cm$^3$ for
Sr₅Nb₄TiO₁₇ at ~1450°C. In the present study, a maximum density of ~ 4.74 g/cm³ was achieved for the composition with x = 2, indicating an increase in the density due to the substitution of Ca for Sr and 50°C increase in sintering temperature.

Figure 4.9. Plot of $\rho_{ap}$ versus sintering temperature for Sr₅₋ₓCaₓNb₄TiO₁₇ (0 ≤ x ≤ 5) compounds, showing maximum $\rho_{ap}$ (i.e. 4.74 g/cm³) for the composition with x = 2 sintered at 1500°C for 2h.

4.2.4 Microstructural analysis

The secondary electron SEM images (SEIs) from thermally etched surfaces of Sr₅₋ₓCaₓNb₄TiO₁₇ (0 ≤ x ≤ 5) samples sintered at ~1500°C for 2h are shown in Figure 4.10. The edges of the grains observed in the sintered Sr₅₋ₓCaₓNb₄TiO₁₇ ceramics with x = 0 and 1 appeared less sharp or diffused in comparison to those with x ≥ 2. It is evident from Figure 4.9 that the sintered densities of ceramics with x ≤ 1 were observed to be lower than those with x > 1 sintered at the same temperature, indicating the effect of Ca²⁺ substitution for Sr²⁺ on the density of the final ceramics. In general, the grains were irregular in shape with varying size. The average grain size observed in the microstructure of the compositions with x = 2 and 3 was ~ 2×1 μm² to 5×1.5 μm²; however, a small number of elongated (~23×2.5 μm²) grains were also observed. The number of elongated grains increased with increase in Ca²⁺ content (e.g. for x = 4 and 5) consistent with the XRD results, showing the splitting of the Sr₅₋ₓCaₓNb₄TiO₁₇ compounds into a mixture of layered perovskite (Sr, Ca)ₙ(Nb, Ti)ₙO₃ₙ₊₂ phases with n = 5
and 6. The grains in the microstructure of the compositions with \( x = 2 \) and \( x = 3 \) appeared more compact than those observed in the microstructure of compositions with \( x \leq 1 \) and \( x \geq 4 \) consistent with the observed higher density of these compounds in comparison to the others.

Figure 4.10. SEIs from the thermally etched surfaces of \( \text{Sr}_{5.5}\text{Ca}_x\text{Nb}_4\text{TiO}_{17} \) (\( 0 \leq x \leq 5 \)) samples sintered at 1500 °C for 2h, showing grains of irregular morphology with deformed edges for the compositions with \( x = 0 \) and 1. The average grain size of the compositions with \( x = 2 \) and 3 ranges from \( \sim 2 \times 1 \) \( \mu \text{m}^2 \) to \( \sim 5 \times 1.5 \) \( \mu \text{m}^2 \) with a small number of elongated (\( \sim 23 \times 2.5 \) \( \mu \text{m}^2 \)) grains. The number of elongated grains increased with increase in value of \( x \) (i.e. for \( x = 4 \) and 5) indicating second phase formation.
4.2.5 Dielectric properties at low frequencies

The dielectric properties of the compositions sintered at 1500°C for 2h were better (in spite of forming multi-phase ceramics) due to their relatively higher densities than those sintered at 1400°C, 1450°C and 1550°C. The variation in the dielectric constant ($\varepsilon_r$) and loss tangent (tanδ) with temperature measured at 1kHz-1MHz for Sr$_{5-x}$Ca$_x$Nb$_4$TiO$_{17}$ ($x = 0$-5) ceramics sintered at 1500°C/2h is shown in Figures 4.11 and 4.12 respectively. Strong anomaly in $\varepsilon_r$ and tanδ was observed for the composition with $x = 0$ at ~567°C probably due to the ferroelectric to paraelectric phase transition. Similar behavior has been reported in $\varepsilon_r$ and tanδ measured for Ba$_{5-x}$Sr$_x$DyTi$_3$V$_7$O$_{30}$ (with $x = 0$ to 5) ceramics at 435°C, 355°C, 326°C, 82°C and 46°C respectively [14]. The lower $\varepsilon_r$ observed for Sr$_5$Nb$_4$TiO$_{17}$ (composition with $x = 0$) than the compositions with $x = 1$-3 was due to its relatively lower density. The observed decrease in $\varepsilon_r$ with increase in frequency may be due to the vanishing of the contribution from interfacial and ionic polarizations. Furthermore, a decrease in $\varepsilon_r$ was observed with increase in Ca$^{2+}$ content due to the lower ionic dielectric polarizability (3.16 Å$^3$) of Ca$^{2+}$ substituted for the higher ionic dielectric polarizability (4.24 Å$^3$) of Sr$^{2+}$ ions [15]. The observed increase in tanδ with increase in temperature at frequencies 1 kHz and 10 kHz may be due to the increase in the conductivity of the compounds [14]. The loss tangent was observed to be the lowest for the composition with $x = 5$, consistent with the quality factor measured for Ca$_3$Nb$_4$TiO$_{17}$ as given in Table 4.2.
Figure 4.11. Plots of $\varepsilon_r$ versus temperature for the $\text{Sr}_{5-x}\text{Ca}_x\text{Nb}_4\text{TiO}_{17}$ ($0 \leq x \leq 5$) ceramics at 1kHz-1MHz, showing anomaly $\sim 567^\circ\text{C}$ for $x = 0$ and a decrease in $\varepsilon_r$ with increase in Ca$^{+2}$ content.
Figure 4.12. Plots of $\tan \delta$ versus temperature for $\text{Sr}_{5-x}\text{Ca}_x\text{Nb}_4\text{TiO}_{17}$ ($0 \leq x \leq 5$) compounds at 1 kHz-1MHz, showing a decrease in $\tan \delta$ with increase in Ca$^{2+}$ content from $x = 0$ to 5.

### 4.2.6 Microwave dielectric properties

The microwave dielectric properties of $\text{Sr}_{5-x}\text{Ca}_x\text{Nb}_4\text{TiO}_{17}$ ($x = 0$-5) ceramics are given in Table 4.2. The unexpected low dielectric constant ($\varepsilon_r \sim 48$) observed for the pure $\text{Sr}_5\text{Nb}_4\text{TiO}_{17}$ (the composition with no Ca$^{2+}$ substitution) may be due to the lowest density of this compound and the formation of $\text{Sr}_6\text{Nb}_4\text{Ti}_2\text{O}_{20}$ as a secondary phase in the present study. Previous studies reported $\varepsilon_r \sim 57$ [1], and $\sim 80$ [10] for the same composition. It is evident from Table 4.2 that the substitution of Ca$^{2+}$ decreased the dielectric constant and temperature coefficient of resonant frequency ($\tau_f$); however, the unloaded quality factor multiplied by the resonant frequency ($Q_u \times f_o$) did not improve to the required level for practical applications under the processing conditions employed in the present study. $\tau_f$ for the composition with $x = 1$ was positive (+12.9 ppm/°C) when sintered at 1400°C while negative (i.e. -2.5 ppm/°C and -14.5 ppm/°C) when sintered at
1450°C and 1500°C respectively. The nature of the negative $\tau_f$ is not known in the present study. The substitution of Ca$^{2+}$ ions for Sr$^{+2}$ ions increased the $Q_u \times f_o$ (GHz) value from 447 GHz to 3087 GHz, probably due to distribution of cation at the A site of the perovskite structure and the reduction in volume of the cation sites. The volume of cation sites reduces with a decrease in ionic radius, and as a result, the movement of cations decreases [16].

The dielectric constant measured at microwave frequencies was observed to decrease from 62 to 37.6 as the Ca$^{2+}$ concentration was increased from 1 to 5 due to lower ionic dielectric polarizability (3.16 Å$^3$) of Ca$^{2+}$ ions substituted for the higher ionic dielectric polarizability (4.24 Å$^3$) Sr$^{2+}$ ions [15]. Similarly, the smaller ionic radius (1.34 Å) of Ca$^{2+}$ ions than Sr$^{+2}$ (1.44 Å) ions for coordination no.12 [17] may have tilted the (Nb,Ti)O$_6$ octahedra [18] which may be responsible for the observed decrease in $\tau_f$ from +162.4 ppm/°C for to -132.5 ppm/°C with increase in the Ca content from 0 to 5 with the exception at x = 1 (Table 4.2). The dielectric constants and quality factors for Sr$_{5-x}$Ca$_x$Nb$_4$TiO$_{17}$ compounds measured at MW frequencies (Table 4.2) were found consistent with the results of dielectric constants and loss tangent at 1MHz for Sr$_{5-x}$Ca$_x$Nb$_4$TiO$_{17}$ as shown in Figure 4.11-4.12.

Table 4.1. Structural data calculated for Sr$_{5-x}$Ca$_x$Nb$_4$TiO$_{17}$ (x =0-5) ceramics.

<table>
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<th>A (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>Z</th>
<th>Structure</th>
<th>V$_{\text{unit}}$ (Å$^3$)</th>
<th>V$_{\text{m}}$(Å$^3$)</th>
</tr>
</thead>
<tbody>
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<td>32.515</td>
<td>3.9525</td>
<td>2</td>
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<td>363.788</td>
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<tr>
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<td>3.9365</td>
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<td>Orthorhombic</td>
<td>721.21</td>
<td>360.605</td>
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<tr>
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<td>32.444</td>
<td>3.9229</td>
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<tr>
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Table 4.2. Processing conditions, apparent, theoretical and relative densities, and MW dielectric properties of Sr$_{5-x}$Ca$_x$Nb$_4$TiO$_{17}$ (x =0-5) ceramics.

<table>
<thead>
<tr>
<th>x</th>
<th>C.T (°C)</th>
<th>S.T (°C)</th>
<th>$\rho_{ap}$ (g/cm$^3$)</th>
<th>$\rho_{th}$ (g/cm$^3$)</th>
<th>$\rho_{rel}$ (%)</th>
<th>$\varepsilon_r$</th>
<th>$Q_{o}\times\nu_o$ (GHz)</th>
<th>$\tau_f$ (ppm/°C)</th>
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<td>-14.5</td>
</tr>
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<td>1500/2h</td>
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$\rho_{ap}$ = apparent density, $\rho_{th}$ = theoretical density = $Z \times M_w/V_N = \rho_{rel}$ = relative density = ($\rho_{ap}/\rho_{th}$) ×100, S.T = sintering temperature. C.T = calcination temperature

### 4.3 References

1. Iqbal, Y.; Reaney, I M. *Ferroelectrics*, 2004, 302, 259-263.
10. Levin, I.; Leonid, A.; Bendersky A.; Vanderah, T A. *Phil. Mag, A*, 2000, 80(2), 411-45
CHAPTER 5

5. CHARACTERIZATION OF Sr$_{5-x}$La$_x$Nb$_{4-x}$Ti$_{1+x}$O$_{17}$

5.1 Introduction

La based dielectric ceramics have been reported to have good MW dielectric properties, e.g. investigating the MW dielectric properties of Ba$_x$La$_{4}$Ti$_{3+x}$O$_{12+3x}$ ($x = 0.0$-$1.0$) ceramics, Yamada et al. [1] reported $\varepsilon_r = 42$, $\tau_f = -17$ ppm/$^\circ$C and $Q_u \times f_0 = 86,000$ GHz for $x = 2$. Similarly, Sr$_4$La$_2$Ti$_3$Nb$_2$O$_{18}$ was reported to exhibit $\varepsilon_r = 47$, $Q_u \times f_0 = 34,423$ GHz and $\tau_f \sim -2$ ppm/$^\circ$C [2]. Fang et al. [3] investigated hexagonal perovskites in the Ba$_5$La$_x$Nb$_{4+x}$Ti$_x$O$_{15}$ ($1 \leq x \leq 3$) composition series and observed that the substitution of La$^{3+}$ for Ba$^{2+}$ at the A site and Ti$^{4+}$ for Nb$^{5+}$ at the B site of the hexagonal perovskite structure increased the $Q_u \times f_0$ from 16,936 GHz to 35277 GHz and decreased the $\tau_f$ from +69 ppm/$^\circ$C to -3 ppm/$^\circ$C. Therefore, the present study was aimed to investigate the effect of La$^{3+}$ substitutions for Sr$^{2+}$ on the microwave dielectric properties of compounds in the Sr$_{5-x}$La$_x$Nb$_{4-x}$Ti$_{1+x}$O$_{17}$ composition series.

5.2 Results and discussion

5.2.1 X-ray diffraction

The room temperature XRD patterns recorded from Sr$_{5-x}$La$_x$Nb$_{4-x}$Ti$_{1+x}$O$_{17}$ ($0 \leq x \leq 4$) compositions with $x = 0$-$4$ sintered at 1500$^\circ$C for 4h are shown in Figure 5.1. The inter-planar spacings (d-values) and relative intensities corresponding to the XRD peaks from Sr$_{5-x}$La$_x$Nb$_{4-x}$Ti$_{1+x}$O$_{17}$ with $x = 0$ matched PDF# 87-1170 for Sr$_5$Nb$_4$TiO$_{17}$. There was no evidence of the formation of any secondary phase in this composition within the in-house XRD detection limit. In previous studies [4-5], a mixture of Sr$_5$Nb$_4$TiO$_{17}$ and Sr$_6$Nb$_4$Ti$_2$O$_{20}$ had been reported in the composition with $x = 0$ (i.e. Sr$_5$Nb$_4$TiO$_{17}$) after sintering at 1500$^\circ$C/2h (also discussed in Chapter 4). This may be probably due to the low calcination temperature (990$^\circ$C/2h) employed in the previous studies and second phase formation during calcination [4-5]. The d-values and relative intensities of the XRD peaks observed for the compositions with $x = 1$-$2$ matched PDF# 87-1170 for Sr$_5$Nb$_4$TiO$_{17}$ and were indexed accordingly. The XRD patterns from the compositions...
with $x = 3$ and 4 were similar and matched PDF# 27-1059 for CaLa$_4$Ti$_5$O$_{17}$ and were indexed. The Lattice parameters “$a$”, “$b$” and “$c$” for the unit cells of Sr$_{5-x}$La$_x$Nb$_{4-x}$Ti$_{1+x}$O$_{17}$ ($x = 0$-4) compounds were refined using least squares method and the observed variation in them with increase in the La$^{3+}$ content is shown in Figures 5.2-5.4 respectively. The lattice parameters “$a$”, “$b$” and “$c$” decreased from 5.6638(4) Å to 5.5211 Å, 32.5353(24) Å to 31.287(17) Å and 3.9516(3) Å to 3.9056(19) Å respectively with increase in $x$ from 0 to 4. Each peak in the XRD patterns from the compositions with $x$ =1-4 appeared shifted towards a relatively higher diffraction angle, probably due to the substitution of smaller La$^{3+}$ (1.36 Å) ions for larger Sr$^{2+}$ (1.44 Å) ions [7]. This resulted in the shrinkage of the unit cell with decreased inter-planar spacings in accordance with the Bragg’s law $\lambda = 2d \sin \theta$. The variation in the molar cell volume ($V_m = V_{unit}/Z$) of Sr$_{5-x}$La$_x$Nb$_{4-x}$Ti$_{1+x}$O$_{17}$ ($x = 0$-4) compounds with increasing $x$ is shown in Figure 5.5. The molar volume was observed to decrease from 364.07 Å$^3$ to 337.3 Å$^3$ with increase in $x$ from 0 to 4. The variation in the theoretical density of Sr$_{5-x}$La$_x$Nb$_{4-x}$Ti$_{1+x}$O$_{17}$ ($x$ =0-4) compounds (calculated from XRD data) with increase in $x$ is shown in Figure 5.5. The theoretical density was observed to increase from 5.15 g/cm$^3$ to 5.66 g/cm$^3$, obviously due to increase in the molecular weight per volume accompanied by a simultaneous decrease in the unit cell volume with an increase in the value of $x$ from 0 to 4 (Table 5.2).
Figure 5.1. XRD patterns recorded from crushed $\text{Sr}_{5-x}\text{La}_x\text{Nb}_{4-x}\text{Ti}_{1+x}\text{O}_{17}$ ($0 \leq x \leq 4$) samples sintered at 1500°C/4h, indicating single phase formation for each composition.

Figure 5.2. Plot of the lattice parameter “$a$” versus $\text{La}^{3+}$, $\text{Ti}^{4+}$ content ($x$) calculated for the unit cell of $\text{Sr}_{5-x}\text{La}_x\text{Nb}_{4-x}\text{Ti}_{1+x}\text{O}_{17}$ ($0 \leq x \leq 4$) compounds, showing an almost linear decrease in “$a$” with increase in $x$. 
Figure 5.3. Plot of the lattice parameter “$b$” versus La$^{3+}$, Ti$^{4+}$ content (x) calculated for the unit cells of Sr$_{5-x}$La$_x$Nb$_{4-x}$Ti$_{1+x}$O$_{17}$ ($0 \leq x \leq 4$) compounds, showing an almost linear decrease in “$b$” with increase in x.

Figure 5.4. Plot of the lattice parameter “$c$” versus La$^{3+}$, Ti$^{4+}$ content (x) calculated for the unit cell of Sr$_{5-x}$La$_x$Nb$_{4-x}$Ti$_{1+x}$O$_{17}$ ($0 \leq x \leq 4$) compounds, showing an almost linear decrease in “$c$” with increase in x.
Figure 5.5. Plot of $V_m$ and $\rho_{th}$ versus La$^{3+}$, Ti$^{4+}$ content (x) calculated for the unit cells of Sr$_{5-x}$La$_x$Nb$_{4-x}$Ti$_{1+x}$O$_{17}$ (0 $\leq$ x $\leq$ 4) compounds, showing a linear decrease in $V_m$ and an almost linear increase in $\rho_{th}$ with increase in x.

5.2.2 Microstructural analysis

The secondary electron SEM images from thermally etched and gold-coated Sr$_{5-x}$La$_x$Nb$_{4-x}$Ti$_{1+x}$O$_{17}$ (x = 0-4) samples sintered at 1500°C/4h are shown in Figure 5.6. The sintered microstructure of the composition with x = 0 consisted of grains of average size $\sim$4×1 μm$^2$. Consistent with the measured relatively higher density (Figure 5.8) for Sr$_5$Nb$_4$TiO$_{17}$ (i.e. x = 0), the microstructure of this sample also appeared less porous than Sr$_4$LaNb$_3$Ti$_2$O$_{17}$ (i.e. x = 1). The sintered microstructure of the composition with x = 1 consisted of elongated and plat-like grains with no sharp edges along with pores and voids, consistent with its relatively poor measured density (Figure 5.8). In the microstructure of the compound with x = 2, elongated, needle shaped grains ($>20×1\mu m^2$ in size), typical morphology of the layered perovskite microstructures, were observed [4]. The microstructure of the compounds with x = 3 comprised of apparently more densely packed plate-like grains in comparison to the microstructure of compounds with x = 0, 1, 2, and 4, consistent with the higher density measured for this sample. Similarly, the microstructure of the composition with x = 4 also consisted of elongated and plate-like grains with the average grain size of $\sim$5×2 μm$^2$. 
Figure 5.6. SEIs from thermally etched and gold coated surfaces of Sr$_{5-x}$La$_x$Nb$_{4-x}$Ti$_{1+x}$O$_{17}$ (x = 0-4) samples sintered at 1500°C/4h, indicating highly dense (~97.6%) microstructure comprising grains with plate-like morphology for the compound with x = 3.

5.2.3 Low frequency dielectric properties

Figure 5.7 shows the variation in the dielectric constant of Sr$_{5-x}$La$_x$Nb$_{4-x}$Ti$_{1+x}$O$_{17}$ (x = 0-4) ceramics as a function of temperature at 1 kHz-1 MHz. Phase transition that might be from ferroelectric to paraelectric [8] phase was observed for the composition with x = 0.
at ~531°C which is lower than the phase transition temperature (~5.67°C) observed for the same composition in the previous study (chapter#4). This difference might be due to the formation of a secondary phase and lower density of Sr₅Nb₄TiO₁₇ in the previous study (chapter#4). The transition became less pronounced with increase in x (e.g. for the composition with x =1), and finally disappeared with further increase in the La³⁺ content (i.e. for x ≥ 2). The dielectric constant increased with increase in temperature, probably due to the contribution from space charge polarization at low frequency. The observed decrease in εᵣ with increase in frequency to 1 MHz may be due to the vanishing of the contributions from the space charge and dipolar polarizations [8].
Figure 5.7. Plots of $\varepsilon_r$ versus temperature for $\text{Sr}_{5-x}\text{La}_x\text{Nb}_{4-x}\text{Ti}_{1+x}\text{O}_{17}$ ($0 \leq x \leq 4$) ceramics at 1kHz to 1MHz, showing a phase transition at ~531°C for $x = 0$ and a decrease in $\varepsilon_r$ with increase $x$ from 0 to 2, then increase from with further increase in $x$ to 3 and again decrease with further increase in $x$ to 4.

5.2.4 Microwave dielectric properties

The variation in the dielectric constant ($\varepsilon_r$) and relative density ($\rho_r$) with an increase in the La$^{3+}$ and Ti$^{4+}$ content ($x$) for compounds in the $\text{Sr}_{5-x}\text{La}_x\text{Nb}_{4-x}\text{Ti}_{1+x}\text{O}_{17}$ ($x = 0 - 4$) composition series, sintered at 1500°C/4h are shown in Figure 5.8. The dielectric constant was observed to follow the relative density and was almost constant because of the small difference in the total ionic dielectric polarizability of the $\text{Sr}_{5-x}\text{La}_x\text{Nb}_{4-x}\text{Ti}_{1+x}\text{O}_{17}$ ($x = 0-4$) compounds. In this study, $\varepsilon_r \sim 74.6$ was obtained for the ~96.6% dense ceramics with $x = 0$, which was much higher than the previously reported $\varepsilon_r \sim 48$ for 86.7% dense $\text{Sr}_5\text{Nb}_4\text{TiO}_{17}$ ceramics (discuss in section 4.2.6). The observed high $\varepsilon_r$ (~74.6) can be attributed to the higher relative density (4.97 g/cm$^3$) achieved in the present study as compared to the lower relative density (4.46 g/cm$^3$) reported in the previous study (section 4.2.6). The reason for the higher density in the present study may be due its high calcination temperature (1400°C), single phase formation during calcination, longer sintering time (4h) and slow heating rate (5°C/min) in comparison to the shorter sintering time (2h), faster heating / cooling rate (10°C/min), lower calcination temperature (990°C) employed in the previous studies which resulted in second phase formation during calcination [4-5]. Iqbal and Reaney [6] and Levin et al. [9] reported $\varepsilon_r \sim 57$ and 80 for $\text{Sr}_5\text{Nb}_4\text{TiO}_{17}$ respectively. A dielectric constant ($\varepsilon_r$) in the range 74.6 to 60.8 was obtained.
as the value of \( x \) was increased from 0 to 4. The \( \varepsilon_r \) measured for \( \text{Sr}_{5-x}\text{La}_x\text{Nb}_{4-x}\text{Ti}_{1+x}\text{O}_{17} \) (0 ≤ \( x \) ≤ 5) ceramics at microwave frequencies was consistent with \( \varepsilon_r \) measured at 1 MHz for \( \text{Sr}_{5-x}\text{La}_x\text{Nb}_{4-x}\text{Ti}_{1+x}\text{O}_{17} \) (0 ≤ \( x \) ≤ 4) ceramics as shown in Figure 5.7.

![Figure 5.8. Plot of \( \rho_{rel} \) and \( \varepsilon_r \) versus La\(^{3+}\), Ti\(^{4+}\) content (\( x \)) for \( \text{Sr}_{5-x}\text{La}_x\text{Nb}_{4-x}\text{Ti}_{1+x}\text{O}_{17} \) (0 ≤ \( x \) ≤ 4) compositions sintered at 1500°C/4h, showing an almost linear relationship between the \( \rho_{rel} \) and \( \varepsilon_r \) with increasing \( x \).](image)

The variation in \( Q_u\times f_o \) (GHz) and \( \tau_f \) measured for \( \text{Sr}_{5-x}\text{La}_x\text{Nb}_{4-x}\text{Ti}_{1+x}\text{O}_{17} \) (\( x = 0-4 \)) ceramics with increase in La\(^{3+}\) and Ti\(^{4+}\) content (\( x \)) is shown in Figure 5.9. Encouragingly, the substitution of La\(^{3+}\) ions for Sr\(^{2+}\) ions and Ti\(^{4+}\) ions for Nb\(^{5+}\) ions increased the \( Q_u\times f_o \) value from 1313 GHz to 9969 GHz with increase in \( x \) from 0 to 4. The increase in \( Q_u\times f_o \) value might be due to the distribution of cations at different A and B sites of the perovskite structure and the reduction in the volume of cation sites. The volume of cation sites reduces with decrease in ionic radius, and as a result, the movement of cations decreases and hence it increases the \( Q_u\times f_o \) value [10, 11]. The increase in \( Q_u\times f_o \) value for \( \text{Sr}_{5-x}\text{La}_x\text{Nb}_{4-x}\text{Ti}_{1+x}\text{O}_{17} \) with increase in La and Ti contents was similar to that reported for \( \text{Ba}_{5-m}\text{La}_m\text{Nb}_{4-m}\text{Ti}_m\text{O}_{15} \) [12-13] and \( \text{Ba}_{6-m}\text{La}_m\text{Nb}_{4-m}\text{Ti}_{m+1}\text{O}_{18} \) [14-15] systems.

Initially, \( \tau_f \) was observed to decrease from +332.9 ppm/°C to 54.8 ppm/°C with increase in \( x \) from 0 to 2 and then increased to +117 ppm/°C upon further increase in \( x \) to 4 as shown in Figure 5.9. In the present study, the optimum dielectric properties i.e. \( \varepsilon_r \sim 60.8, Q_u\times f_o \sim 9969 \text{ GHz and } \tau_f \sim +117 \text{ ppm/°C} \) were achieved for the composition with \( x = 4 \).
[Table 5.2]; however, a previous study reported $\varepsilon_r \sim 39$, $\tau_f \sim +58$ ppm/°C and $Q_x f_o \sim 14200$ GHz for SrLa$_4$Ti$_5$O$_{17}$ [16]. The difference in the properties of SrLa$_4$Ti$_5$O$_{17}$ in the present and the previous studies might be due to different processing conditions employed heating rate of 5°C/min up 600°C, followed by 0.9°C/min to 1580°C/20h in the previous study and 5°C/min up to 1500°C/4h in the present study for SrLa$_4$Ti$_5$O$_{17}$). The observed increase in $Q_x f_o$ value and decrease in $\tau_f$ for Sr$_{5-x}$La$_x$Nb$_{4-x}$Ti$_{1+x}$O$_{17}$ with increase in the value of x in the present study, were consistent with the dielectric properties reported for Ba$_{5-x}$La$_x$Nb$_{4-x}$Ti$_x$O$_{15}$ [3]. The microwave dielectric properties of Sr$_{5-x}$La$_x$Nb$_{4-x}$Ti$_{1+x}$O$_{17}$ (0 ≤ x ≤ 4) ceramics measured for the optimally sintered compounds are summarized in Table 5.2.

![Plot](image)

Figure 5.9. Plot of $Q_x f_o$ and $\tau_f$ versus La$^{3+}$ and Ti$^{4+}$ content (x) for Sr$_{5-x}$La$_x$Nb$_{4-x}$Ti$_{1+x}$O$_{17}$ (0 ≤ x ≤ 4) ceramics, showing an increase in $Q_x f_o$ value with increase in x from 0 to 4, and an initial decrease in $\tau_f$ with increase in x from 0 to 2 and then increase upon further increase in x to 4.
Table 5.1. Structural data of Sr$_{5-x}$La$_x$Nb$_{4-x}$Ti$_{1+x}$O$_{17}$ (0 ≤ x ≤ 4) ceramics.

<table>
<thead>
<tr>
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<th>b (Å)</th>
<th>c (Å)</th>
<th>Z</th>
<th>Structure</th>
<th>$V_{\text{unit}}$ (Å$^3$)</th>
<th>$V_m$ (Å$^3$)</th>
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<td>3.9516(3)</td>
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<td>364.07</td>
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<td>32.163(5)</td>
<td>3.9421(5)</td>
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<td>712.0(3)</td>
<td>356.0</td>
</tr>
<tr>
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<td>31.857(7)</td>
<td>3.9301(8)</td>
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<td>699.2(3)</td>
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</tr>
<tr>
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<td>31.526(3)</td>
<td>3.9239(5)</td>
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<tr>
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<td>31.299(9)</td>
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Table 5.2. Processing conditions, apparent, theoretical and relative density, and microwave dielectric properties of Sr$_{5-x}$La$_x$Nb$_{4-x}$Ti$_{1+x}$O$_{17}$ (0 ≤ x ≤ 4) ceramics.

<table>
<thead>
<tr>
<th>x</th>
<th>C.T (°C)</th>
<th>S.T (°C)</th>
<th>$\rho_{\text{ap}}$ (g/cm$^3$)</th>
<th>$\rho_{\text{th}}$ (g/cm$^3$)</th>
<th>$\rho_{\text{rel}}$ (%)</th>
<th>$\varepsilon_r$</th>
<th>$Q_u\times f_o$ (GHz)</th>
<th>$\tau_f$ (ppm/°C)</th>
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<td>74.3</td>
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$\rho_{\text{ap}}$ = apparent density, $\rho_{\text{th}}$ = theoretical density, $\rho_{\text{rel}}$ = relative density, S.T = sintering temperature and C. T = calcination temperature

5.3 References

6. CHARACTERIZATION OF SrLa$_{4-x}$Ln$_x$Ti$_5$O$_{17}$ (Ln = Nd, Sm x =1, 2, 3, 4) CERAMICS

6.1 SrLa$_{4-x}$Nd$_x$Ti$_5$O$_{17}$

6.1.1 Introduction

SrLa$_4$Ti$_5$O$_{17}$ has high $\varepsilon_r$ (~60.8), moderate $Q_u\times f_o$ (~9969 GHz) and high positive $\tau_f$ (~117 ppm/°C) as discussed in chapter 5. The high positive $\tau_f$ renders its use unsuitable for practical applications in telecommunication devices. La based materials have been reported to have positive $\tau_f$ which could be lowered by substituting Nd and Sm for La. Gao et al. [1] reported that when Sm was substituted for La in Ba$_4$La$_{9.33}$(Ti$_{0.95}$Zr$_{0.05}$)$_{18}$O$_{54}$, its $\tau_f$ decreased from 80.9 ppm/°C to -30.4 ppm/°C. Solomon et al. [2] reported a lower $\tau_f$ for Nd- and Sm-containing compounds in the BaRE$_2$Ti$_4$O$_{12}$ and BaRE$_2$Ti$_5$O$_{14}$ composition series (where RE = rare earths) than the La-based compositions. The decrease in $\tau_f$ due to Nd- and Sm-substitutions for La has been ascribed to the smaller ionic radii of Nd and Sm as compared to La. Yue et al. [3] reported that Nd substitution for La in CaLa$_4$Ti$_4$O$_{15}$ improved the temperature stability of the resonant frequency i.e. $\tau_f$ decreased from -17.1 ppm/°C to -5.77 ppm/°C as the Nd concentration was increased from 0 to 0.5. They also observed the formation of Ca(La$_{1-x}$Nd$_x$)$_{4}$Ti$_5$O$_{17}$ ceramics as secondary phases in the CaLa$_{4-x}$Nd$_x$Ti$_4$O$_{15}$ series. Rejini et al. [4] reported La$_4$NdCrTi$_4$O$_{17}$ and La$_4$SmCrTi$_4$O$_{17}$ to have $\varepsilon_r = 53$, $Q_u\times f_o = 8800$ GHz, $\tau_f = -27.6$ ppm/°C and $\varepsilon_r = 50$, $Q_u\times f_o = 6900$ GHz and $\tau_f = -39.5$ ppm/°C respectively. These compounds were observed to crystallize in orthorhombic crystal structure. They also observed the formation of La$_4$NdCrTi$_4$O$_{17}$ and La$_4$SmCrTi$_4$O$_{17}$ as secondary phases in La$_4$NdCrTi$_{3}$O$_{15}$ and La$_4$SmCrTi$_{3}$O$_{15}$ ceramics. In this chapter, we have investigated the effect of Nd$^{3+}$ and Sm$^{3+}$ substitutions for La$^{3+}$ in SrLa$_4$Ti$_5$O$_{17}$ for the first time in an attempt to reduce its $\tau_f$ to zero and get temperature stable microwave ceramics.
6.1.2 Results and discussion

6.1.2.1 X-ray diffraction analysis

XRD patterns recorded at room temperature from SrLa$_{4-x}$Nd$_x$Ti$_5$O$_{17}$ (0 ≤ x ≤ 4) compositions sintered at their optimum sintering temperatures for 4h are shown in Figure 6.1. The inter-planar spacings (d-values) and the corresponding XRD peak intensities from the compositions with x = 0, 1, and 2 were identical and matched PDF# 27-1059 for CaLa$_4$Ti$_5$O$_{17}$ while those from the compositions with x = 3 and 4 matched PDF# 49-256 for SrPr$_4$Ti$_5$O$_{17}$. Both SrPr$_4$Ti$_5$O$_{17}$ and CaLa$_4$Ti$_5$O$_{17}$ compositions crystallize into orthorhombic crystal structure. This showed that all compositions investigated in SrLa$_{4-x}$Nd$_x$Ti$_5$O$_{17}$ series have an orthorhombic crystal structure. The unit cell parameters “a”, “b” and “c” for each composition were refined by least squares method and the patterns were indexed accordingly. Within the XRD detection limits, there was no evidence of second phase formation which indicated that all the compositions formed single phase ceramics. The lattice parameters ‘a’, ‘b’, and ‘c’ calculated for all the studied compositions refined by the least squares method are shown in Figure 6.2-6.4 and compared in Table 6.2. As evident from Figure 6.3, the lattice parameter ‘b’ first increased with an increase in the Nd$^{3+}$ content from 0 to 1, and then decreased with further increase in the Nd$^{3+}$ content to 4.

The lattice parameters ‘a’ and ‘c’ (Figures 6.2 and 6.4) were observed to decrease almost linearly with increase in Nd$^{3+}$ content from 0 to 4 due to the smaller ionic radius (1.27 Å) of Nd$^{3+}$ substituted for the larger ionic radius (1.36 Å) of La$^{3+}$ in the orthorhombic unit cell [5]. Previous studies [6-7] regarding substitution of smaller radii ions for larger ionic radii ions in other perovskite related structures have also been reported to cause a decrease in the lattice constants [6-7]. The first increase in the lattice parameter ‘b’ might be due to some internal stresses developed in the structure of the composition with x = 0 as compared to x = 1, 2, 3, and 4, however, the exact nature of the decrease is not known and it needs high resolution TEM study to elucidate the reason. With increase in Nd$^{3+}$ content, the position of the XRD peaks shifted towards higher diffraction angles (smaller d-values), resulting in a decrease in the lattice constants.

The variation in the molar volume ($V_m = V_{cell}/Z$) of compounds in the SrLa$_{4-x}$Nd$_x$Ti$_5$O$_{17}$ (0 ≤ x ≤ 4) composition series as a function of Nd$^{3+}$ content is shown in Figure 6.5. The
molar volume of the unit cell was observed to decrease with an increase in Nd$^{3+}$ content ($x$). This demonstrated the shrinkage of the unit cell due to the incorporation of smaller Nd$^{3+}$ for the larger La$^{3+}$ ions. The unit cell volume decreased from 339.5 Å$^3$ to 331.6 Å$^3$ with increase in Nd$^{3+}$ concentration from 0 to 4. The decrease in the molar volume was consistent with the previously reported data for Ca(La$_{1-x}$Nd$_x$)$_4$Ti$_4$O$_{15}$, where the molar volume had been reported to decrease from 285.32 Å$^3$ to 280.13 Å$^3$ with increase in the Nd$^{2+}$ content from 0 to 0.5 [3]. The theoretical density ($\rho_{th}$) of SrLa$_{4-x}$Nd$_x$Ti$_5$O$_{17}$ ($0 \leq x \leq 4$) ceramics increased from 5.66 g/cm$^3$ to 5.89 g/cm$^3$ as the Nd$^{3+}$ content was increased from 0 to 4 as shown in Figure 6.6. The increase in the theoretical density may be due to the associated increase in the Mw : V$_{cell}$ ratio with increasing Nd$^{3+}$.

Figure 6.1. XRD patterns recorded from crushed/pulverized pellets of SrLa$_{4-x}$Nd$_x$Ti$_5$O$_{17}$ ($0 \leq x \leq 4$) ceramics sintered at optimum sintering temperatures i.e. 1550 °C for $x = 0$ and 4, and 1580 °C for the compositions with $x = 1-3$, showing single phase formation for each composition within the detection limit of in-house XRD.
Figure 6.2. Plot of the lattice parameter “a” versus Nd$^{3+}$ content (x) for SrLa$_{4-x}$Nd$_x$Ti$_5$O$_{17}$ (0 ≤ x ≤ 4) ceramics, showing an almost linear decrease in “a” with increase in x from 0 to 4.

Figure 6.3. Plot of the lattice parameter “b” versus Nd$^{3+}$ content (x) for SrLa$_{4-x}$Nd$_x$Ti$_5$O$_{17}$ (0 ≤ x ≤ 4) ceramics, showing an increase in “b” with increase in x from 0 to 1 and then decrease upon increase in x to 4.
Figure 6.4. The plot of lattice parameter “c” versus Nd$^{3+}$ content (x) for SrLa$_{4-x}$Nd$_x$Ti$_5$O$_{17}$ (0 ≤ x ≤ 4) ceramics, showing an almost linear decrease in “c” with increase in x from 0 to 4.

Figure 6.5. The plot $V_m$ versus Nd$^{3+}$ content (x) for the unit cell of SrLa$_{4-x}$Nd$_x$Ti$_5$O$_{17}$ (0 ≤ x ≤ 4) ceramics, showing an almost linear decrease in $V_m$ with increase in x from 0 to 4.
Figure 6.6. The plot of $\rho_{th}$ versus Nd$^{3+}$ content ($x$) for SrLa$_{4-x}$Nd$_x$Ti$_5$O$_{17}$ ($0 \leq x \leq 4$) ceramics, showing an almost linear increase in $\rho_{th}$ with increase in $x$ from 0 to 4.

Table 6.1. X-ray diffraction data for SrNd$_4$Ti$_5$O$_{17}$ refined by least squares method.

<table>
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<th>h k l</th>
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### 6.1.2.2. Density measurements

The observed variation in the apparent density \( (\rho_{ap}) \) of SrLa\(_{4-x}\)Nd\(_x\)Ti\(_5\)O\(_{17}\) (0 ≤ x ≤ 4) ceramic pellets with increase in the sintering temperature is shown in Figure 6.7. The density was observed to increase with increase in the sintering temperature from 1500°C to 1580°C for SrLa\(_3\)NdTi\(_5\)O\(_{17}\), SrLa\(_2\)Nd\(_2\)Ti\(_5\)O\(_{17}\), and SrLaNd\(_3\)Ti\(_5\)O\(_{17}\) ceramics. Unlike the other compounds forming in the SrLa\(_{4-x}\)Nd\(_x\)Ti\(_5\)O\(_{17}\) (0 ≤ x ≤ 4) composition series, the density of SrNd\(_4\)Ti\(_5\)O\(_{17}\) increased from 5.11 g/cm\(^3\) to 5.64 g/cm\(^3\) with an increase in sintering temperature from 1500°C to 1550°C but then decreased to 5.62 g/cm\(^3\) upon further increase in the sintering temperature to 1580°C. Maximum densities of ~5.42 g/cm\(^3\) (95.2%), 5.40 g/cm\(^3\) (93.9%), and 5.57 g/cm\(^3\) (95.5%) were achieved for SrLa\(_3\)NdTi\(_5\)O\(_{17}\), SrLa\(_2\)Nd\(_2\)Ti\(_5\)O\(_{17}\), and SrLaNd\(_3\)Ti\(_5\)O\(_{17}\) ceramics sintered at 1580°C for 4h. The maximum density achieved for SrNd\(_4\)Ti\(_5\)O\(_{17}\) was 5.64 g/cm\(^3\) (95.7%) at 1550°C in the present work respectively (Table 6.3).

![Figure 6.7](image)

**Figure 6.7.** The plot of \( \rho_{ap} \) versus sintering temperature for compounds formed in the SrLa\(_{4-x}\)Nd\(_x\)Ti\(_5\)O\(_{17}\) (0 ≤ x ≤ 4) composition series.

### 6.1.2.3 Microstructural analysis

The secondary electron images from thermally etched, gold-coated surfaces of SrLa\(_{4-x}\)Nd\(_x\)Ti\(_5\)O\(_{17}\) (0 ≤ x ≤ 4) ceramic samples sintered at their optimum sintering temperatures are shown in Figure 6.8. In general, the microstructure of all the investigated samples comprised densely packed (\( \rho_{rel} > 94\% \)) elongated and plate-like grains, typical of layered
perovskites with orthorhombic structure [8]; however, some non-uniform grain growth could be seen in all the samples. The average grain size for the compositions with $x = 0$, 1, or 2 was $\sim 5 \mu m$ but elongated grains of size larger than $15 \mu m$ could be also observed in the sintered microstructure of composition with $x = 0$. Similarly, the average grain size in the compounds with $x = 3$ and 4 was $\sim 7 \mu m$ but relatively large size grains could be also observed in the sintered microstructure of these compositions.

Figure 6.8. SEIs recorded from the thermally etched, gold-coated surfaces of SrLa$_{4-}$
$\times$Nd$_{x}$Ti$_{5}$O$_{17}$ ($0 \leq x \leq 4$) ceramics sintered at their optimum sintering temperatures, showing an elongated and plate-like grain morphologies for each composition along with some large grains-indicative of abnormal grain growth.
6.1.2.4 Microwave dielectric properties

The observed variation in $\varepsilon_r$ measured for SrLa$_{4-x}$Nd$_x$Ti$_5$O$_{17}$ ($0 \leq x \leq 4$) ceramics with increase in Nd$^{3+}$ content substituted for La is shown in Figure 6.9. $\varepsilon_r$ was observed to decrease almost linearly with increase in the Nd$^{3+}$ content. In 1993, Shannon [9] reported the ionic dielectric polarizabilities ($\alpha$) of La$^{3+}$ and Nd$^{3+}$ as 6.07 Å$^3$ and 5.01 Å$^3$ respectively. In 1996, the polarizability of La$^{3+}$ ions was revised to be 4.82 Å$^3$ [10] i.e. lower than that of Nd$^{3+}$. On the basis of this revised lower value of polarizability for La$^{3+}$, $\varepsilon_r$ of SrLa$_{4-x}$Nd$_x$Ti$_5$O$_{17}$ should increase with increase in the Nd$^{3+}$ content; however, the trend of $\varepsilon_r$ variation with Nd$^{3+}$ content indicated that Nd$^{3+}$ polarizability was less than that of La$^{3+}$. It is noticeable that the ionic dielectric polarizability ($\alpha_D$) of a compound is calculated from the sum of the ionic dielectric polarizabilities of the individual ions constituting the compound. The ionic dielectric polarizability of La$^{3+}$ ions was recalculated again by plotting the linear fit for the ionic dielectric polarizabilities verses $r^3$ (cube of ionic radius) of lanthanide ions for coordination no. 8. Using this approach, the ionic dielectric polarizability for La$^{3+}$ was reported to 5.71 Å$^3$ [11]. Thus the observed decrease in $\varepsilon_r$ from 60.8 to 44 with increase in Nd$^{3+}$ concentration from 0 to 4 may be due to the lower ionic dielectric polarizability of Nd$^{3+}$ than that of La$^{3+}$ (Figure 6.10).

The observed variation in $\tau_f$ for SrLa$_{4-x}$Nd$_x$Ti$_5$O$_{17}$ ($0 \leq x \leq 4$) ceramics with different Nd$^{3+}$ contents ($x$) substituted for La$^{3+}$ ions followed the $\varepsilon_r$ versus $x$ curve. An almost linear decrease was observed in $\tau_f$ with increase in the Nd$^{3+}$ content as shown in Figure 6.11. The substitution of smaller radius (1.27 Å) Nd$^{3+}$ ions for the larger radius (1.36 Å) La$^{3+}$ ions [5] may have caused anti-phase tilting of the TiO$_6$ octahedra [12] leading to a decrease in $\tau_f$ from +117 ppm/°C (for $x = 0$) to -142.3 ppm/°C (for $x = 4$).

The observed variation in $Q_u \times f_o$ value for SrLa$_{4-x}$Nd$_x$Ti$_5$O$_{17}$ ceramics with increase in Nd$^{3+}$ content is shown in Figure 6.12. Initially, $Q_u \times f_o$ decreased from 9969 GHz to 6030 GHz (at 5.40GHz) with increase in $x$ from 0 to 2 but upon further increase in $x$ to 4, it increased to 8678 GHz (at 5.53GHz). The decrease in $Q_u \times f_o$ value might be attributed to the different factors like, grain size, porosity, dislocations, and lattice defects that vary from sample to sample [13]. Another possible reason for the observed decrease in $Q_u \times f_o$...
may be the development of internal stresses in the crystal due to increase in the difference of ionic size at the A site of the perovskite structure [4, 14]. The difference in ionic size between Sr$^{2+}$ and La$^{3+}$ ions is smaller in comparison to that between Nd$^{3+}$ and Sr$^{2+}$ ions and may result in an increase in internal stresses in the lattice in the later compounds. The MW dielectric properties measured for the optimally sintered samples are given in Table 6.3. The ceramics designed and processed in the present study exhibited, $\varepsilon_r \sim 60.8$ to 44.1, $Q_u \times f_o \sim 9969$ GHz to 6030 GHz and $\tau_f \sim 117$ ppm/$^\circ$C to -142.2 ppm/$^\circ$C (Table 6.3). A careful analysis of the MW dielectric properties of ceramics designed and processed in the present study indicated that near zero $\tau_f$ corresponded to $\varepsilon_r \sim 54$ with $Q_u \times f_o \sim 6000$ GHz at $x \sim 1.6$ (Figure 6.11).

Figure 6.9. The plot of $\varepsilon_r$ versus Nd$^{3+}$ content ($x$) for SrLa$_{4-x}$Nd$_x$Ti$_5$O$_{17}$ ($0 \leq x \leq 4$) ceramics, showing a linear decrease in $\varepsilon_r$ with increase in $x$ from 0 to 4.
Figure 6.10. The plot of $\alpha_D$ versus Nd\textsuperscript{3+} content (x) for SrLa\textsubscript{4-x}Nd\textsubscript{x}Ti\textsubscript{5}O\textsubscript{17} ($0 \leq x \leq 4$) ceramics, showing a linear decrease in $\alpha_D$ with increase in x from 0 to 4.

Figure 6.11. The plot of $\tau_f$ versus Nd\textsuperscript{3+} content (x) for SrLa\textsubscript{4-x}Nd\textsubscript{x}Ti\textsubscript{5}O\textsubscript{17} ($0 \leq x \leq 4$) ceramics, showing an almost linear decrease in $\tau_f$ with increase in x from 0 to 4.
Figure 6.12. The plot of $Q_u \times f_o$ versus Nd$^{3+}$ content (x) for SrLa$_{4-x}$Nd$_x$Ti$_5$O$_{17}$ ($0 \leq x \leq 4$) ceramics, showing a decrease in $Q_u \times f_o$ for the compounds with $x = 0$ to 2 followed by an increase with further increase in $x$ to 4.

Table 6.2. Structural data of SrLa$_{4-x}$Nd$_x$Ti$_5$O$_{17}$ ($0 \leq x \leq 4$) ceramics refined by least squares method.

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<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>Z</th>
<th>Structure</th>
<th>$V_{\text{unit}}$ (Å$^3$)</th>
<th>$V_m$ (Å$^3$)</th>
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<td>3.9104(14)</td>
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<td>679.1(8)</td>
<td>339.55</td>
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<tr>
<td>1</td>
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<td>5.530(3)</td>
<td>31.355(12)</td>
<td>3.9052(11)</td>
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Table 6.3. Processing conditions, apparent, theoretical and relative densities, and MW dielectric properties of SrLa$_{4-x}$Nd$_x$Ti$_5$O$_{17}$ (0 ≤ x ≤ 4) ceramics.

<table>
<thead>
<tr>
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<th>C.T (°C)</th>
<th>S.T (°C)</th>
<th>$\rho_{ap}$ (g/cm$^3$)</th>
<th>$\rho_{th}$ (g/cm$^3$)</th>
<th>$\rho_{rel}$ (%)</th>
<th>$\varepsilon_r$</th>
<th>$Q\times f_o$ (GHz)</th>
<th>$\tau_f$ (ppm/°C)</th>
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<td>95.7</td>
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<td>8678</td>
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S.T = sintering temperature, C.T = calcination temperature, $\rho_{ap}$ = apparent density, $\rho_{th}$ = theoretical density, and $\rho_{rel}$ = relative density.
6.2 SrLa$_{4-x}$Sm$_x$Ti$_5$O$_{17}$

6.2.1 Results and discussion

6.2.1.1 X-ray diffraction analysis

XRD patterns recorded at room temperature for the compounds in the SrLa$_{4-x}$Nd$_x$Ti$_5$O$_{17}$ (0 ≤ x ≤ 4) composition series sintered at the corresponding optimum sintering temperatures for 4h are shown in Figure 6.13. XRD pattern recorded for SrLa$_4$Ti$_5$O$_{17}$ was similar to CaLa$_4$Ti$_5$O$_{17}$ (PDF# 27-1059); however, the unit cell parameters of SrLa$_4$Ti$_5$O$_{17}$ were refined by least squares method to incorporate the variation in cell volume due to Sm$^{3+}$ ions substitution for La$^{3+}$ ions. The crystal structure of SrLa$_{4-}$Ti$_5$O$_{17}$ is orthorhombic with lattice parameters $a = 5.549(5)$ Å, $b = 31.299(9)$ Å, $c = 3.9104(13)$ Å, $V = 679.1(8)$ Å, and $Z = 2$, having a theoretical density of 5.66 g/cm$^3$. XRD pattern from SrLa$_3$SmTi$_5$O$_{17}$ (x = 1) was similar to SrLa$_4$Ti$_5$O$_{17}$ and was indexed accordingly. The XRD patterns from SrLa$_2$Sm$_2$Ti$_5$O$_{17}$ (x = 2) and SrLaSm$_3$Ti$_5$O$_{17}$ (x = 3) ceramics were similar and matched PDF# 49-256 for SrPr$_4$Ti$_5$O$_{17}$; however, the unit cell parameters were refined by the least squares method and the patterns were indexed accordingly. The compounds with x = 0-3 crystallized into orthorhombic structure. The XRD pattern from SrSm$_4$Ti$_5$O$_{17}$ (i.e. x = 4) ceramics matched PDF#.16-400 for Sm$_2$Ti$_2$O$_7$ and PDF# 35-734 for SrTiO$_3$. This indicated that composition with x = 4 crystallized into a two phase ceramics. No Solid solution is known to exist in the SrTiO$_3$-Sm$_2$Ti$_2$O$_7$ binary system due to the large difference between the ionic radii of Sr$^{2+}$ (1.44 Å) ions and Sm$^{3+}$ (1.24 Å) ions for the coordination no. 12 [5]. Both Sm$_2$Ti$_2$O$_7$ and SrTiO$_3$ crystallize into cubic structure with lattice parameters, $a = b = c = 10.23310$ (80) Å, and $a = b = c = 3.9050$ Å with space groups $Fd\bar{3}m$ and $Pm\bar{3}m$ respectively. With the increase in Sm$^{3+}$ content from 0 to 3, the position of the XRD peaks shifted towards higher diffraction angles (smaller d-values), resulting in a decrease in the unit cell constants. The lattice parameters “$a$”, “$b$”, and “$c$” calculated for all the studied compositions refined by the least squares method are shown in Figure 6.14-6.16 and compared in Table 6.5. The lattice parameter “$b$” first increased as the Sm$^{3+}$ content was increased from 0 to 1 and then decreased with further increase in the Sm$^{3+}$ content to 3. The first increase in the
lattice parameter ‘b’ might be due to some internal stresses developed in the structure of the composition with x = 0 as compared to x = 1, 2, 3, and 4, however, the exact nature of the decrease is not known and it needs high resolution TEM study to elucidate the reason. The lattice parameters “a” and “c” were observed to decrease with increase in the Sm$^{3+}$ content from 0 to 3, due to the incorporation of smaller Sm$^{3+}$ (1.24 Å) ions for larger (1.36 Å) La$^{3+}$ ions in the unit cell of the orthorhombic structure [5]. The lattice parameters “a”, “b”, and “c” were also reported to decrease with the substitution of smaller Sm$^{3+}$ ions for larger La$^{3+}$ ions in other perovskite related structures such as La$_5$CrTi$_3$O$_{15}$ and Ba$_4$La$_{9.33}$Ti$_{18}$O$_{54}$ in the previous studies [4, 15]. Consistent with the observed decrease in lattice constants, molar volume of the unit cell also decreased from 339.5 Å$^3$ to 330.4 Å$^3$ as the value of x was increased from 0 to 3 (Figure 6.17), indicative of shrinkage of the unit cell leading to the observed decrease in the unit cell volume. The observed decrease in molar volume was consistent with the decrease in the molar volume reported for other MW ceramics with Sm$^{3+}$ substituted for La$^{3+}$ ions [15]. The theoretical density ($\rho_{th}$) of SrLa$_{4-x}$Sm$_x$Ti$_5$O$_{17}$ compounds was observed to increase with an increase in the Sm$^{3+}$ concentration from 0 to 3 due to the corresponding increase in molecular weight per molar volume (Mw/V$_{cell}$) of the unit cell. $\rho_{th}$ increased from 5.66 g/cm$^3$ to 5.98 g/cm$^3$ with an increase in Sm$^{3+}$ content from 0 to 3 as shown in Figure 6.18. $\rho_{th}$ could not be calculated due to the formation of two phases at x = 4.
Figure 6.13. XRD patterns recorded for SrLa$_{4-x}$Sm$_x$Ti$_5$O$_{17}$ (0 ≤ x ≤ 4) ceramics sintered at 1500°C for x = 0, 1550°C for x = 1, 3, or 4 and 1580°C for the composition with x = 2 for 4h, showing single phase formation for the compositions with x ≤ 3 and two phase (i.e. Sm$_2$Ti$_2$O$_7$ and SrTiO$_3$) for the composition with x = 4.
Figure 6.14. The plot of the lattice parameter “$a$” versus Sm$^{3+}$ content (x) for SrLa$_{4-x}$Sm$_x$Ti$_5$O$_{17}$ ($0 \leq x \leq 3$) compounds, showing a decrease in “$a$” with increase in x.

Figure 6.15. The plot of lattice parameter “$b$” versus Sm$^{3+}$ content (x) for SrLa$_{4-x}$Sm$_x$Ti$_5$O$_{17}$ ($0 \leq x \leq 3$) compounds, showing an increase in “$b$” with increase in x from 0 to 1 and then decrease with further increase in the value of x.
Figure 6.16. The plot of lattice parameter “c” versus Sm$^{3+}$ content (x) for SrLa$_{4-x}$Sm$_x$Ti$_5$O$_{17}$ ($0 \leq x \leq 3$) ceramics, showing an almost linear decrease in “c” with increase in x from 0 to 3.

Figure 6.17. The plot of $V_m$ versus Sm$^{3+}$ content (x) for SrLa$_{4-x}$Sm$_x$Ti$_5$O$_{17}$ ceramics, showing a nearly linear decrease in $V_m$ with increase in x from 0 to 3.
Figure 6.18. The plot of $\rho_{th}$ versus Sm$^{3+}$ content (x) for SrLa$_{4-x}$Sm$_{x}$Ti$_5$O$_{17}$ $(0 \leq x \leq 3)$ ceramics, showing a nearly linear increase in $\rho_{th}$ with increase in x from 0 to 3.

### 6.2.1.2 Density measurements

The observed variation in the apparent densities ($\rho_{ap}$) of SrLa$_{4-x}$Sm$_{x}$Ti$_5$O$_{17}$ $(0 \leq x \leq 4)$ ceramics with different amounts of Sm$^{3+}$ content substituted for La with increase in sintering temperature is shown in Figure 6.19. The observed densities of SrLa$_3$SmTi$_5$O$_{17}$, SrLaSm$_3$Ti$_5$O$_{17}$ and SrSm$_4$Ti$_5$O$_{17}$ first increased with an increase in the sintering temperature from 1500°C to 1550°C and then decreased with further increase in the sintering temperature to 1580°C; however, the observed density of SrLa$_2$Sm$_2$Ti$_5$O$_{17}$ ceramics linearly increased with increase in the sintering temperature from 1500°C to 1580°C/4h. This demonstrated that the densities of the compositions with x = 1, 3, and 4 saturated at 1550°C. Maximum apparent densities of 5.51 g/cm$^3$ (95.2%), 5.69 g/cm$^3$ (95.1%) and 5.94 g/cm$^3$ were achieved for SrLa$_3$SmTi$_5$O$_{17}$, SrLaSm$_3$Ti$_5$O$_{17}$ and SrSm$_4$Ti$_5$O$_{17}$ sintered at 1550°C for 4h while a maximum density of 5.69 g/cm$^3$ (97.2%) was achieved for SrLa$_2$Sm$_2$Ti$_5$O$_{17}$ ceramics sintered at 1580°C for 4h (Table 6.5). An increase in the apparent densities was also observed with increasing Sm$^{3+}$ content at constant sintering temperature [Figure 6.19]. The increase may be due to the higher atomic weight of Sm than La. Previous studies have also reported an increase in bulk densities of compounds upon Sm$^{3+}$ ions substitutions for La$^{3+}$ ions [15].
Figure 6.19. The plot of apparent densities ($\rho_{ap}$) versus sintering temperature for SrLa$_{4-x}$Sm$_x$Ti$_5$O$_{17}$ compounds with different amounts of Sm$^{3+}$ ions substituted for La$^{3+}$ ions.

### 6.2.1.3 Microstructural analysis

Secondary electron SEM images of SrLa$_{4-x}$Sm$_x$Ti$_5$O$_{17}$ ($0 \leq x \leq 4$) samples sintered at their optimum sintering temperatures are shown in Figure 6.20. Generally, the grains observed in the microstructure of samples with $x \leq 3$ were elongated or plate-like in shape, typical of layered perovskites with general formula $A_{n}B_{n}O_{3n+2}$ having orthorhombic structure [13]. The dimensions of the grains varied from $\sim 2 \times 1 \ \mu m^2$ to $15 \times 5 \ \mu m^2$. The grain morphology was observed to change from elongated or plate-shape to polygonal with an increase in the Sm$^{3+}$ content e.g. at $x = 4$. The microstructure of all the compositions appeared dense, consistent with the measured density of $\sim 95\%$ of the corresponding theoretical density. The average grain size of the ceramic with $x = 4$ varied from $\sim 2.6 \times 1.5 \ \mu m^2$ to $5 \times 5 \ \mu m^2$. 
Figure 6.20. SEIs from the thermally etched, gold-coated SrLa$_{4-x}$Nd$_x$Ti$_5$O$_{17}$ (0 ≤ x ≤ 4) ceramics samples sintered at their optimum sintering temperatures, showing elongated and plate-like grains for the compositions with x ≤ 3, while polygon-shaped grains for the composition with x = 4.

6.2.1.4 Microwave dielectric properties

The variation in $\varepsilon_r$ measured for SrLa$_{4-x}$Sm$_x$Ti$_5$O$_{17}$ (0 ≤ x ≤ 4) ceramics with increase in sintering temperature is shown in Figure 6.21. The relationship between the dielectric constant and sintering temperature revealed the same trend as between the observed apparent density and sintering temperature. $\varepsilon_r \sim$ 56, 42.6 and 79.1 were obtained for
SrLa₃SmTi₅O₁₇, SrLaSm₃Ti₅O₁₇ and SrSm₄Ti₅O₁₇ ceramics sintered at 1550°C and 50.3 for SrLa₂Sm₂Ti₅O₁₇ ceramics sintered at 1580°C. The variation in εᵣ of SrLa₄₋ₓSmₓTi₅O₁₇ (0 ≤ x ≤ 4) compounds with the increase in the Sm³⁺ content sintered at the relevant optimum sintering temperatures is shown in Figure 6.22. εᵣ was observed to decrease first from 60.8 to 42.6 with increase in Sm³⁺ content from 0 to 3 and then increased to 79.1 with further increase in Sm³⁺ content to 4 [Figure 6.22]. The variation in τᵣ for optimally sintered SrLa₄₋ₓSmₓTi₅O₁₇ compositions with increase in Sm³⁺ content is shown in Figure 6.24. For any MW dielectric resonator, εᵣ and τᵣ are directly proportional to each other [17]; therefore, τᵣ revealed the same behaviour as εᵣ with increasing Sm³⁺ content. τᵣ initially decreased from +117 ppm/°C to -96 ppm/°C as the Sm content was increased from 0 to 3 and then increased to +523 ppm/°C with further increase in the Sm³⁺ content to 4. The decrease in τᵣ may be attributed to the smaller ionic radius (1.24 Å) of Sm³⁺ substituted for larger (1.36 Å) La³⁺ ions for coordination no.12 which may have caused anti-phase tilting of the TiO₆ octahedra [12]. The abrupt increase in τᵣ at higher Sm³⁺ concentrations may be attributed to the structural phase transition from orthorhombic (low symmetry) to cubic structure (high symmetry structure) as a result of the formation of Sm₂Ti₂O₇ and SrTiO₃ both having cubic structure.

The variation in Qₓ × fₒ value measured for SrLa₄₋ₓSmₓTi₅O₁₇ compounds with increase in Sm³⁺ content is shown in Figure 6.25. The value of Qₓ × fₒ was observed to decrease from 9969 GHz to 3142 GHz (at 5.33 GHz) as the Sm³⁺ content (x) was increased from 0 to 2, then increased to 7332 GHz (at 5.88 GHz) with further increase in x to 3 and again decreased to 5131 GHz (at 4.08 GHz) with further increase in x to 4. The abrupt decrease in Qₓ × fₒ for x = 1 and 2 may be due to the formation of dark cores at the interior of the pellets at high sintering temperatures employed. The dark cores appear due to the reduction of Ti⁴⁺ into Ti³⁺ as a consequence of the formation of oxygen vacancies [18].

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The variation in \( Q_u \times f_o \) value might be due to various factors including grain size, porosity, dislocations, and lattice defects that vary from sample to sample [13]. Additionally, the difference in the ion size between \( \text{Sr}^{2+} \) and \( \text{La}^{3+} \) is less in comparison to that of \( \text{Sm}^{3+} \) and \( \text{Sr}^{2+} \) and thus increase in \( \text{Sm}^{3+} \) content may have caused an increase in the internal stresses of the lattice which may have adversely affected \( Q_u \times f_o \) value [4, 14].

The final decrease in the \( Q_u \times f_o \) value for \( x = 4 \) may be attributed to the structural change from orthorhombic to cubic due to the formation of \( \text{Sm}_2\text{Ti}_2\text{O}_7 \) and \( \text{SrTiO}_3 \) mentioned above. The MW dielectric properties of \( \text{SrLa}_{4-x}\text{Sm}_x\text{Ti}_5\text{O}_{17} \) (\( 0 \leq x \leq 4 \)) ceramics measured at their optimum sintering temperatures are summarized in Table 6.5. A careful analysis of the MW dielectric properties of ceramics designed and processed in the present study indicated that near zero \( \tau_f \) corresponds to \( \varepsilon_r \approx 53 \) at \( x = 1.4 \).

![Figure 6.21. The plot of \( \varepsilon_r \) versus sintering temperature for \( \text{SrLa}_{4-x}\text{Sm}_x\text{Ti}_5\text{O}_{17} \) (\( 0 \leq x \leq 4 \)) with different amounts of \( \text{Sm}^{3+} \) content (x) substituted for \( \text{La}^{3+} \), showing increase in \( \varepsilon_r \) with temperature and hence density.](image)
Figure 6.22. Plot of $\varepsilon_r$ versus Sm$^{3+}$ content (x) for SrLa$_{4-x}$Sm$_x$Ti$_5$O$_{17}$ ($0 \leq x \leq 4$) ceramics, showing a nearly linear decrease in $\varepsilon_r$ with an increase in value of $x$ from 0 to 3 and increase in $\varepsilon_r$ with further increase in the value of $x$ to 4.

Figure 6.23. The plot of $\alpha_D$ versus Sm$^{3+}$ content (x) for SrLa$_{4-x}$Nd$_x$Ti$_5$O$_{17}$ ($0 \leq x \leq 4$) ceramics, showing a linear decrease in $\alpha_D$ with increase in $x$. 
Figure 6.24. The plot of $\tau_f$ versus Sm$^{3+}$ content (x) for SrLa$_{4-x}$Sm$_x$Ti$_5$O$_{17}$ (0 ≤ x ≤ 4) compositions, showing an almost linear decrease in $\tau_f$ with increase in x from 0 to 3, and then an abrupt increase in $\tau_f$ with further increase in x to 4 due to structural phase transition.

Figure 6.25. The plot of $Q_u \times f_o$ versus Sm$^{3+}$ content (x) for SrLa$_{4-x}$Sm$_x$Ti$_5$O$_{17}$ (0 ≤ x ≤ 4) ceramics, showing variations in $Q_u \times f_o$ with increase in x.
Table 6.4. Structural data of SrLa$_{4-x}$Sm$_x$Ti$_5$O$_{17}$ (0 ≤ x ≤ 4) ceramics

<table>
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<th>b(Å)</th>
<th>c(Å)</th>
<th>Z</th>
<th>Structure</th>
<th>V$_{\text{unit}}$ (Å$^3$)</th>
<th>V$_{\text{m}}$ (Å$^3$)</th>
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<td>31.299(9)</td>
<td>3.9104(14)</td>
<td>2</td>
<td>Orthorhombic</td>
<td>679.1(8)</td>
<td>339.55</td>
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<tr>
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<td>5.5153(14)</td>
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<td>3.8940(10)</td>
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<td>336.3</td>
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<tr>
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<td>31.324(12)</td>
<td>3.8781(14)</td>
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<td>668.4(7)</td>
<td>334.2</td>
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<tr>
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<td>?</td>
<td>?</td>
<td>Cubic(Sm$_2$Ti$_2$O$_7$ and SrTiO$_3$</td>
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Table 6.5. Processing conditions, apparent, theoretical, and relative density, and MW dielectric properties of SrLa$_{4-x}$Sm$_x$Ti$_5$O$_{17}$ (0 ≤ x ≤ 4).

<table>
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<tr>
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<th>S.T (°C)</th>
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<th>$\rho_{\text{th}}$ (g/cm$^3$)</th>
<th>$\rho_{\text{rel}}$ (%)</th>
<th>$\varepsilon_r$</th>
<th>$Q_0\times f_0$ (GHz)</th>
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? --------could not be identified because of the mixed-phase nature,
S.T = sintering temperature, C.T= calcination temperature, $\rho_{\text{ap}}$ = apparent density, $\rho_{\text{th}}$ = theoretical density, $\rho_{\text{rel}}$ = relative density

6.3 References


11. Santosh, B. Structural, Lattice vibrational and microwave dielectric studies on some rare earth based complex perovskites, Department of Physics, Indian institute of technology Madrass, Chennai, India, PhD thesis, **2008**, pp-100.


CHAPTER 7

7. CHARACTERIZATION OF Sr_{1-x}Ca_xLa_4Ti_5O_{17}

7.1 Introduction

A number of dielectric ceramics with general formula $A_nB_nO_{3n+2}$ have been investigated for their possible applications as dielectric resonators. Joseph et al. [1] reported that Ca$_5$Nb$_4$Ti$_{17}$ and Ca$_5$Ta$_5$Ti$_{17}$ exhibited $\varepsilon_r = 44.9$, $Q_u \times f_o = 17600$ GHz and $\tau_f \sim -112.9$ ppm/$^\circ$C and $\varepsilon_r = 40.1$, $Q_u \times f_o = 16450$ GHz and $\tau_f \sim -53.6$ ppm/$^\circ$C respectively. Jawaher et al. [2] reported CaLa$_4$Ti$_{17}$ with $\varepsilon_r \sim 53$, $\tau_f \sim -20$ ppm/$^\circ$C and $Q_u \times f_o \sim 17359$ GHz. Similarly, SrLa$_4$Ti$_{17}$ was reported to exhibit $\varepsilon_r \sim 39.1$, $\tau_f \sim 58$ ppm/$^\circ$C and $Q_u \times f_o \sim 14200$ GHz [3]. In the present (chapter #5) SrLa$_4$Ti$_{17}$ was found to exhibit $\varepsilon_r \sim 60.8$, $\tau_f \sim 117$ ppm/$^\circ$C and $Q_u \times f_o \sim 9969$ GHz; however, the high positive $\tau_f$ makes it unsuitable candidate for use as a DR in telecommunication technology. Generally, materials with high $\varepsilon_r$ have positive $\tau_f$ [4]; however, it is possible to combine materials with identical crystal structures but with opposite $\tau_f$ in proper ratios to get tailor materials to lower the resultant $\tau_f$. A number of efforts have been made to design and process materials for temperature stable DRs by making solid solutions of materials with positive and negative $\tau_f$ [5-7], and also by using suitable dopants [8-9].

Keeping in view the opposite signs of $\tau_f$ of SrLa$_4$Ti$_{17}$ and CaLa$_4$Ti$_{17}$, the present study was aimed at designing and processing temperature stable, high dielectric constant and low loss MW dielectric materials in the CaLa$_4$Ti$_{17}$-SrLa$_4$Ti$_{17}$ composition series.

7.1.1 Results and discussion

7.1.1.1 Density measurements

The observed variation in the relative densities ($\rho_{rel}$) of Sr$_{1-x}$Ca$_x$La$_4$Ti$_{17}$ ($0 \leq x \leq 1$) ceramics with an increase in the sintering temperature from 1450°C to 1580°C for 4h is shown in Figure 7.1. The relative density was observed to increase to a maximum for the composition with $x = 0$ at 1500°C and then decreased with further increase in the
sintering temperature to 1550°C. Similarly, the relative densities for the compositions with \( x = 0.25, 0.5 \) and 0.6 were observed to increase to a maximum at 1550°C and then decreased with further increase in the sintering temperature to 1580°C. The relative densities of the compositions with \( x = 0.85 \) and 1 increased to 97.3% and 98.6% of the corresponding theoretical densities at 1580°C respectively. The maximum relative density of each composition along with its optimum sintering temperature is given in Table 7.3.

Figure 7.1. The plot of \( \rho_{\text{rel}} \) versus sintering temperature for Sr\(_{1-x}\)Ca\(_x\)La\(_4\)Ti\(_5\)O\(_{17}\) (0 ≤ x ≤ 1) ceramics.

7.1.1.2 X-ray diffraction

The room temperature XRD patterns recorded for Sr\(_{1-x}\)Ca\(_x\)La\(_4\)Ti\(_5\)O\(_{17}\) (0 ≤ x ≤ 1) compositions sintered at their optimum sintering temperatures for 4h are shown in Figure 7.2. The inter-planar spacings (d-values) and the corresponding XRD peak intensities from all the compositions were identical and matched PDF# 27-1059 for CaLa\(_4\)Ti\(_5\)O\(_{17}\). The unit cell parameters for each composition were refined by the least squares method and the patterns were indexed accordingly. Within the in-house XRD detection limits, there was no evidence of second phase formation which indicated that all the compositions formed single phase ceramics. The refined 2θ, d-values and the corresponding hkl indices calculated for the SrLa\(_4\)Ti\(_5\)O\(_{17}\) unit cell are given in Table 7.1.
All the compositions crystallized into orthorhombic structure with space group \textit{Pnnm} which was consistent with previously reported orthorhombic structures for the end members of the series i.e. \textit{SrLa_4Ti_5O_17} and \textit{CaLa_4Ti_5O_17} [3]. The lattice parameters “\textit{a}”, “\textit{b}”, and “\textit{c}” calculated for all the studied compositions refined by least squares method are compared in Table 7.2. The lattice parameters “\textit{a}”, “\textit{b}”, and “\textit{c}” were observed to decrease with increase in \textit{Ca}^{2+} content from 0 to 1, due to the smaller ionic radius (1.34 Å) of \textit{Ca}^{2+} ions substituted for larger (ionic radius = 1.44 Å) \textit{Sr}^{2+} ions for coordination no.12. With the increase in \textit{Ca}^{2+} content, the position of the XRD peaks shifted towards higher diffraction angles (smaller d-values), resulting in a decrease in the lattice constants [10-11]. Similar decrease in lattice parameters has been reported for other ceramics subjected to substitutions of smaller ions for larger ions at the A site of the perovskite structure [12-13]

The variation in the molar volume and theoretical density (calculated from XRD data) with an increase in the \textit{Ca}^{2+} content from 0 to 1 is shown in Figure 7.3. Both the molar volume and theoretical density were observed to decrease with an increase in the \textit{Ca}^{2+} content. The molar volume decreased from 339.5 Å³ to 335.9 Å³ with increase in \textit{Ca}^{2+} content from 0 to 1. This decrease was due to the smaller ionic radius of \textit{Ca}^{2+} ions substituted for the relatively larger \textit{Sr}^{2+} ions at the A site of the perovskite structure. The theoretical density decreased from 5.66 g/cm³ to 5.47 g/cm³ with an increase in \textit{Ca}^{2+} content from 0 to 1 because of the associated decrease in the “MW/V” ratio for the \textit{Sr_{1-x}CaLa_4Ti_5O_17} unit cell, where MW denotes the molar weight and V stands for the unit cell volume. The theoretical density of the compositions with \textit{x} = 0 and 1 were consistent with the previously reported theoretical densities of 5.66 g/cm³ for \textit{x} = 0 and 5.465 g/cm³ for \textit{x}=1 [3, 14]
Figure 7.2. XRD patterns from $\text{Sr}_{1-x}\text{Ca}_x\text{La}_4\text{Ti}_5\text{O}_{17}$ ($0 \leq x \leq 1$) ceramics sintered at their optimum sintering temperatures for 4h, showing single phase formation for each composition within the detection limit of in-house XRD.

Figure 7.3. The plots of $V_m$ and $\rho_{th}$ versus Ca$^{2+}$ content (x) for sintered $\text{Sr}_{1-x}\text{Ca}_x\text{La}_4\text{Ti}_5\text{O}_{17}$ ($0 \leq x \leq 1$) compositions, showing an almost linear decrease in both $V_m$ and $\rho_{th}$ with increase in the value of x.
Table 7.1. X-ray powder diffraction data of SrLa$_4$Ti$_5$O$_{17}$

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7.1.1.3 Microstructural analysis

Secondary electron images (SEIs) from thermally etched and gold-coated surfaces of Sr$_{1-x}$Ca$_x$La$_4$Ti$_5$O$_{17}$ (0 ≤ x ≤ 1) ceramics sintered at their optimum sintering temperatures are shown in Figure 7.4. Highly dense sintered microstructure was observed for each composition and visibly appeared consistent with the measured relative densities (Figure 7.1). Elongated and plate-like grain morphology, typical of layered perovskite, was observed for each composition [15]. The average grain size was observed to decrease from 7 × 3 µm$^2$ to 4 × 2 µm$^2$ with an increase in the Ca$^{2+}$ content from 0 to 1. These microstructural observations and the observed increase in the relative densities indicated that the substitution of Ca$^{2+}$ ions for Sr$^{2+}$ ions improved the sinteribility and enhanced the densification of the investigated ceramics (Table 7.3).
Figure 7.4. SEIs of \( \text{Sr}_{1-x}\text{Ca}_x\text{La}_4\text{Ti}_5\text{O}_{17} \) \((0 \leq x \leq 1)\) ceramics, showing microstructures comprising densely packed elongated and plate-like grains for each composition and a decrease in the grain size with increase in \( \text{Ca}^{2+} \) content \((x)\).

7.1.2.3 Microwave dielectric properties

The variation in \( \varepsilon_r \) of \( \text{Sr}_{1-x}\text{Ca}_x\text{La}_4\text{Ti}_5\text{O}_{17} \) \((0 \leq x \leq 1)\) ceramics sintered at their optimum sintering temperatures for 4h in air is shown in Figure 7.5. \( \varepsilon_r \) was observed to decrease from \(~60.8\) to \(52.7\) with increase in \( \text{Ca}^{2+} \) content from \(0\) to \(1\) due to the lower ionic dielectric polarizability \((3.16 \ \text{Å}^3)\) of \( \text{Ca}^{2+} \) ions than that of \( \text{Sr}^{2+} \) \((4.24 \ \text{Å}^3)\) ions [16]. A previous study reported \( \varepsilon_r \sim 39.1 \) [3] for the composition with \(x = 0\), which was lower.
than the $\varepsilon_r \sim 60.8$ for the same composition in the present study. This might be due to the different processing and sintering conditions (heating rate of $5^\circ C$/min up to $600^\circ C$, followed by $0.9^\circ C$/min to $1580^\circ C/20h$ in the previous study and $5^\circ C$/min up to $1500^\circ C/4h$ in the present study). $\varepsilon_r$ for the composition with $x = 1$ was consistent with the previously reported $\varepsilon_r (\sim 53.7)$ for CaLa$_4$Ti$_5$O$_{17}$ [2].

The variation in $Q_u \times f_o$ (GHz) with an increase in Ca$^{2+}$ content ($x$) for Sr$_{1-x}$Ca$_x$La$_4$Ti$_5$O$_{17}$ ($0 \leq x \leq 1$) ceramics is shown in Figure 7.6. $Q_u \times f_o$ (GHz) was observed to increase from 9969 GHz (at 6.07GHz) to 12700 GHz (at 5.33GHz) as the Ca$^{2+}$ content was increased from 0 to 1. The reason for improvement in $Q_u \times f_o$ value might be the size/distribution of cations at the A-site of the perovskite structure. Larger differences in the ionic radii at the A-site cause larger local distortion which degrades the quality factor as suggested by Kagomiya et al. [17]. As the Ca$^{2+}$ content was increased, the size difference of A-site cations between Ca$^{2+}$ (1.34 Å) and La$^{3+}$ (1.36 Å) became smaller compared to that of Sr$^{2+}$ (1.44 Å) and La$^{3+}$; that may have led to the improvement in the $Q_u \times f_o$ value [18].

The variation in $\tau_f$ of Sr$_{1-x}$Ca$_x$La$_4$Ti$_5$O$_{17}$ ($0 \leq x \leq 1$) ceramics with increase in the Ca$^{2+}$ content is shown in Figure 7.7. $\tau_f$ was observed to decrease with increase in the value of $x$ due to the incorporation of smaller Ca$^{2+}$ ions for the larger Sr$^{2+}$ ions at the A-site of the perovskite structure [Figure 7.7]. It has been reported [19] that such substitutions cause anti-phase tilting of the TiO$_6$ octahedra, resulting in a decrease in $\tau_f$ from +117 ppm/°C to -37 ppm/°C with the increase in Ca$^{2+}$ content from 0 to 1. Previous studies reported $Q_u \times f_o \sim 17359$ GHz and $\tau_f \sim -20$ ppm/°C for CaLa$_4$Ti$_5$O$_{17}$ [2] and $Q_u \times f_o = 14200$ GHz and $\tau_f = 58$ ppm/°C for SrLa$_4$Ti$_5$O$_{17}$ [3]. Again the difference in the properties of the end members in the present and the previous studies can be attributed to the different processing and sintering conditions (heating rate of $5^\circ C$/min up to $600^\circ C$, followed by $0.9^\circ C$/min to $1580^\circ C/20h$ in the previous study and $5^\circ C$/min up to $1500^\circ C/4h$ in the present study for SrLa$_4$Ti$_5$O$_{17}$ and 150 MPa, sintering at 1650°C to 1670°C/4h in the previous study while 80 MPa and sintering at 1580°C/4h in the present study for CaLa$_4$Ti$_5$O$_{17}$ ). Another previous study [14] reported $Q_u \times f_o \sim 12500$ GHz for CaLa$_4$Ti$_5$O$_{17}$, which was almost consistent with our $Q_u \times f_o \sim 12700$ GHz value; however, $\tau_f \sim 3$ ppm/°C was much closer to zero than $\tau_f \sim -37$ ppm/°C measured in the present study for $x = 1$ [14]. The MW dielectric properties of optimally sintered Sr$_{1-x}$Ca$_x$La$_4$Ti$_5$O$_{17}$ ($0 \leq x \leq 1$) ceramics are
summarized in Table 7.3. In the present study, $Q_u \times f_o \sim 11532$ GHz (at 5.16 GHz), $\tau_f \sim -1.4$ ppm/°C and $\varepsilon_r \sim 53.7$ were achieved for the composition with $x = 0.6$ (i.e. $\text{Sr}_{0.4}\text{Ca}_{0.6}\text{La}_4\text{Ti}_5\text{O}_{17}$).

Figure 7.5. The plot of $\varepsilon_r$ versus $\text{Ca}^{2+}$ content ($x$) for $\text{Sr}_{1-x}\text{Ca}_x\text{La}_4\text{Ti}_5\text{O}_{17}$ ($0 \leq x \leq 1$) ceramics, showing a decrease in $\varepsilon_r$ with increase in $\text{Ca}^{2+}$ content.

Figure 7.6. The plot of $Q_u \times f_o$ versus $\text{Ca}^{2+}$ content ($x$) for $\text{Sr}_{1-x}\text{Ca}_x\text{La}_4\text{Ti}_5\text{O}_{17}$ ($0 \leq x \leq 1$) ceramics, showing increase in $Q_u \times f_o$ (GHz) value with increase in $\text{Ca}^{2+}$ content.
Figure 7.7. The plot of $\tau_f$ versus Ca$^{2+}$ content ($x$) for compounds in the $\text{Sr}_{1-x}\text{Ca}_x\text{La}_4\text{Ti}_5\text{O}_{17}$ ($0 \leq x \leq 1$) composition series, showing a decrease in $\tau_f$ with increase in Ca$^{2+}$ content.

Table 7.2. Structural data of $\text{Sr}_{1-x}\text{Ca}_x\text{La}_4\text{Ti}_5\text{O}_{17}$ ($0 \leq x \leq 1$) ceramics

<table>
<thead>
<tr>
<th>$x$</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$Z$</th>
<th>Structure</th>
<th>$V_{\text{unit}}$ (Å$^3$)</th>
<th>$V_m$ (Å$^3$)</th>
</tr>
</thead>
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<tr>
<td>0</td>
<td>5.549(5)</td>
<td>31.299(9)</td>
<td>3.9104(13)</td>
<td>2</td>
<td>Orthorhombic</td>
<td>679.1(8)</td>
<td>339.55</td>
</tr>
<tr>
<td>0.25</td>
<td>5.5326(16)</td>
<td>31.342(7)</td>
<td>3.9082(18)</td>
<td>2</td>
<td>Orthorhombic</td>
<td>677.7(5)</td>
<td>338.8</td>
</tr>
<tr>
<td>0.5</td>
<td>5.5293(6)</td>
<td>31.313(4)</td>
<td>3.9031(9)</td>
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<td>Orthorhombic</td>
<td>675.78(14)</td>
<td>337.8</td>
</tr>
<tr>
<td>0.6</td>
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<td>31.310(4)</td>
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<td>675.19(11)</td>
<td>337.6</td>
</tr>
<tr>
<td>0.85</td>
<td>5.5201(11)</td>
<td>31.293(7)</td>
<td>3.8967(7)</td>
<td>2</td>
<td>Orthorhombic</td>
<td>673.1(3)</td>
<td>336.56</td>
</tr>
<tr>
<td>1</td>
<td>5.5170(14)</td>
<td>31.275(7)</td>
<td>3.8942(13)</td>
<td>2</td>
<td>Orthorhombic</td>
<td>671.93(23)</td>
<td>335.9</td>
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Table 7.3. Processing conditions, apparent, theoretical and relative densities and MW dielectric properties of $\text{Sr}_{1-x}\text{Ca}_x\text{La}_4\text{Ti}_5\text{O}_{17}$ ($0 \leq x \leq 1$) ceramics

<table>
<thead>
<tr>
<th>$x$</th>
<th>C.T (°C)</th>
<th>S.T (°C)</th>
<th>$\rho_{ap}$ (g/cm$^3$)</th>
<th>$\rho_{th}$ (g/cm$^3$)</th>
<th>$\rho_{rel}$ (%)</th>
<th>$\varepsilon_r$</th>
<th>$Q_\mu f_0$ (GHz)</th>
<th>$\tau_f$ (ppm/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1250/6h</td>
<td>1500/4h</td>
<td>5.36</td>
<td>5.66</td>
<td>94.5</td>
<td>60.8</td>
<td>9969</td>
<td>117.0</td>
</tr>
<tr>
<td>0.25</td>
<td>1300/6h</td>
<td>1550/4h</td>
<td>5.46</td>
<td>5.60</td>
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<td>56.5</td>
<td>10966</td>
<td>39.0</td>
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<td>1550/4h</td>
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<td>5.55</td>
<td>98.0</td>
<td>55.8</td>
<td>11782</td>
<td>8.5</td>
</tr>
<tr>
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<td>1300/6h</td>
<td>1550/4h</td>
<td>5.34</td>
<td>5.54</td>
<td>96.3</td>
<td>53.7</td>
<td>11532</td>
<td>-1.4</td>
</tr>
<tr>
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<td>1580/4h</td>
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<td>5.498</td>
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<td>52.4</td>
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</tr>
<tr>
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<td>1580/4h</td>
<td>5.39</td>
<td>5.473</td>
<td>98.6</td>
<td>52.7</td>
<td>12700</td>
<td>-37.0</td>
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C.T = calcination temperature, S.T = sintering temperature, $\rho_{ap}$ = apparent density, $\rho_{th}$ = theoretical density, $\rho_{rel}$ = relative density
7.2 CHARACTERIZATION OF SrLa$_4$Ti$_{5-x}$Zr$_x$O$_{17}$

7.2.1 Introduction

Zr-doped BaTiO$_3$ i.e. BaZr$_x$Ti$_{1-x}$O$_3$ received much attention due to its improved electrical properties as a result of partial replacement of Ti$^{4+}$ with Zr$^{4+}$ [20-21]. Chen et al. [22] reported $\varepsilon_r = 55.9$, $Q_u\times f_o = 15,600$ GHz and $\tau_f = 4.6$ ppm/°C for CaLa$_4$Ti$_{4.95}$Zr$_{0.05}$O$_{17}$ (i.e. for Zr = 0.05) sintered at 1500°C for 4h. In the present study, the effect of partial replacement of Ti$^{4+}$ by Zr$^{4+}$ on the phase, microstructure and MW dielectric properties of SrLa$_4$Ti$_3$O$_{17}$ was investigated in an attempt to design and process materials with high $\varepsilon_r$, $Q_u\times f_o$ and near zero $\tau_f$.

7.2.2 Results and discussion

7.2.2.1 Density measurement

The relative densities ($\rho_{rel}$) of SrLa$_4$Ti$_{5-x}$Zr$_x$O$_{17}$ (0 ≤ x ≤ 0.1) ceramics with different amounts of Zr$^{4+}$ substitutions after sintering at 1450 to 1580°C for 4h are shown in Figure 7.8. The theoretical density of SrLa$_4$Ti$_3$O$_{17}$ calculated from the XRD data was 5.66 gcm$^{-3}$. $\rho_{rel}$ for each SrLa$_4$Ti$_{5-x}$Zr$_x$O$_{17}$ composition exceeded 81% of its theoretical density at all the sintering temperature used in the present study. $\rho_{rel}$ of SrLa$_4$Ti$_3$O$_{17}$ (x = 0) first increased from 85.5% to 94.7% as the sintering temperature was increased from 1450 to 1500°C and then decreased 94.5% of its theoretical density with further increase in the sintering temperature to 1550°C. Similarly, $\rho_{rel}$ of the composition with x = 0.05 initially increased from 87.6% to 92.4% as the sintering temperature was increased from 1450 to 1550°C and then decreased to 89.6% of its theoretical density with further increase in the sintering temperature to 1580°C. This showed that saturation of the $\rho_{rel}$ for the composition with x = 0 and 0.05 occurred at some temperature below 1550°C. The relative density ($\rho_{rel}$) of the compositions with x = 0.01, 0.07 and 0.1 increased from 81.4% to 96.6%, 83.1% to 95.7% and 83.9% to 97.3% of its theoretical density respectively as the sintering temperature was increased from 1450°C to 1580°C.
Figure 7.8. The plot of \( \rho_{rel} \) versus sintering temperature for SrLa\(_4\)Ti\(_{5-x}\)Zr\(_x\)O\(_{17}\) (\(0 \leq x \leq 0.1\)) ceramics, showing an increase in \( \rho_{rel} \) with increasing sintering temperature.

### 7.2.2.2 X-ray diffraction

Figure 7.9 shows the XRD patterns recorded from SrLa\(_4\)Ti\(_3\)O\(_{17}\), SrLa\(_4\)Ti\(_{4.99}\)Zr\(_{0.01}\)O\(_{17}\), SrLa\(_4\)Ti\(_{4.95}\)Zr\(_{0.05}\)O\(_{17}\), SrLa\(_4\)Ti\(_{4.93}\)Zr\(_{0.07}\)O\(_{17}\) and SrLa\(_4\)Ti\(_{4.90}\)Zr\(_{0.1}\)O\(_{17}\) ceramics sintered at their optimum sintering temperatures for 4h. All the patterns were similar and were indexed on the basis of the refined unit cell of SrLa\(_4\)Ti\(_3\)O\(_{17}\). Within the detection limit of in-house XRD, each compound crystallized into a single phase ceramics with no evidence of any second phase formation. The crystal structure of SrLa\(_4\)Ti\(_3\)O\(_{17}\) is known to have orthorhombic structure with \( Pnnm \) space group. The lattice parameters of SrLa\(_4\)Ti\(_3\)O\(_{17}\) refined by the least squares method are \( a = 5.549(5) \) Å, \( b = 31.299(9) \) Å, and \( c = 3.9104(13) \) Å. X-ray diffraction peaks shifted towards lower angles (high d-values) as the value of \( x \) was increased from 0 to 0.1 due the larger ionic radius of Zr\(^{4+}\) (0.83 Å) than Ti\(^{4+}\) (0.604 Å) for coordination no.6 [23].
Figure 7.9. XRD patterns recorded for SrLa₄Ti₅₋ₓZrₓO₁₇ (0 ≤ x ≤ 0.1) ceramics sintered at their optimum sintering temperatures, showing formation of single phase ceramics for each composition.

7.2.2.3 Microstructural analysis
The secondary electron SEM images from thermally etched and gold-coated surfaces of SrLa₄Ti₅₋ₓZrₓO₁₇ (0 ≤ x ≤ 0.1) compositions sintered at their optimum sintering temperatures are shown in Figure 7.10. The sintered microstructure of each composition comprised elongated and plate-like grains, which is the typical morphology observed in the microstructure of layered perovskites as reported for CaLa₄Ti₅₋ₓZrₓO₁₇ (0 ≤ x ≤ 0.1) ceramics [22]. The microstructure of SrLa₄Ti₄.₉₅Zr₀.₅O₁₇ appeared visibly cracked at the interior (not shown in Figure 7.10) which may be a possible reason for its lower density than the other compositions in the SrLa₄Ti₅₋ₓZrₓO₁₇ (0 ≤ x ≤ 0.1) series. Highly dense microstructure was observed for the composition with x = 0.1, consistent with the measured high relative density (~97.7%) for this composition.
Figure 7.10. SEIs from thermally etched and gold-coated surfaces of SrLa$_4$Ti$_{5-x}$Zr$_x$O$_{17}$ (0 ≤ x ≤ 0.1) ceramics, showing highly dense microstructure for each composition.

7.2.2.4 Microwave dielectric properties
The variation in $\varepsilon_r$ of SrLa$_4$Ti$_{5-x}$Zr$_x$O$_{17}$ (0 ≤ x ≤ 0.1) ceramics with increasing sintering temperature is shown in Figure 7.11. The relationship between the dielectric constant and sintering temperature revealed the same trend as between the relative density and sintering temperature. There was a small decrease in $\varepsilon_r$ from 60.8 (x = 0) to 57.3 (x =0.1) with increase in Zr$^{4+}$ content from 0 to 0.1. The relatively lower $\varepsilon_r$ (~ 54.5) observed for
the composition with \( x = 0.05 \) may be due to its low relative density (~ 92%) in comparison to the other compositions.

Figure 7.11. The plot of \( \varepsilon_r \) versus sintering temperature for \( \text{SrLa}_4\text{Ti}_{5-x}\text{Zr}_x\text{O}_{17} \) \((0 \leq x \leq 0.1)\) ceramics with different amount of \( \text{Zr}^{4+} \) substitutions, showing an increase in \( \varepsilon_r \) with temperature and a decrease in \( \varepsilon_r \) with increase in \( \text{Zr}^{4+} \) content. The variation in \( \varepsilon_r \) for \( \text{SrLa}_4\text{Ti}_{5-x}\text{Zr}_x\text{O}_{17} \) \((0 \leq x \leq 0.1)\) ceramics as a function of increasing \( \text{Zr}^{4+} \) content is shown in Figure 7.12.

Figure 7.12. The plot of \( \varepsilon_r \) versus \( \text{Zr}^{4+} \) content \((x)\) for \( \text{SrLa}_4\text{Ti}_{5-x}\text{Zr}_x\text{O}_{17} \) \((0 \leq x \leq 0.1)\) ceramics, showing a decrease \( \varepsilon_r \) with an increase in the \( \text{Zr}^{4+} \) content \((x)\). The abnormal decrease in \( \varepsilon_r \) at \( x = 0.5 \) is due to the relatively lower density of this sample.
Keeping in view the higher ionic dielectric polarizability (3.25 Å³) of Zr⁴⁺ ions than Ti⁴⁺ (2.93 Å³), εᵣ of SrLa₄Ti₅₋ₓZrₓO₁₇ (0 ≤ x ≤ 0.1) ceramics should increase with increase in the Zr⁴⁺ content. Contrastingly, εᵣ was observed to decrease with increase in Zr⁴⁺ content which could be explained as follows: The larger ionic radius of Zr⁴⁺ compared to Ti⁴⁺ leads to an increase in the bond length and hence weakens the bonding strength between oxygen and the B-site ion. This increases the band valance of the B site of the compounds in the SrLa₄Ti₅₋ₓZrₓO₁₇ (0 ≤ x ≤ 0.1) series and it is known that εᵣ decreases with increase in the bond valance [17]. The observed decrease in εᵣ with increase in the Zr⁴⁺ content from 0 to 0.1 can also be explained on the basis of the smaller (8.71) value of the (α/rₗₐₙ³) ratio of Zr⁴⁺ than Ti⁴⁺ (13.27), where α and rₗₐₙ³ are the ionic dielectric polarizability and cube of the effective ionic radius respectively [23-25].

The observed variation in the temperature coefficient of resonant frequency (τᵣ) of SrLa₄Ti₅₋ₓZrₓO₁₇ compositions as a function of increasing Zr⁴⁺ content (x) sintered at their optimum sintering temperatures is shown in Figure 7.13. It can be seen from Figure 7.13, that τᵣ decreased abruptly from +117 ppm/°C to +86.4 ppm/°C as the x value was increased to 0.01, and then decreased slowly to 70.1 ppm/°C with further increase in the value of x to 0.1. The decrease in τᵣ may be due to the increased tilting of the BO₆ octahedra caused by the Zr⁴⁺ substitution for Ti⁴⁺ [26] resulting in an increase in the band valence of the B site [27]. The Qₐ×fₒ values for SrLa₄Ti₅₋ₓZrₓO₁₇ (0 ≤ x ≤ 0.1) ceramics sintered at their optimum sintering temperatures are given in Table 7.4, showing no significant improvement in the Qₐ×fₒ value with increase in the Zr⁴⁺ content. Generally, Qₐ×fₒ values are significantly influenced by the porosity, grain size, impurities, and second phase formation [28]. The observed decrease in τᵣ with increase in Zr⁴⁺ content suggests that further increase Zr⁴⁺ content may be required for further decrease in τᵣ value to nearly zero.
Figure 7.13. The plot of $\tau_f$ versus Zr$^{4+}$ content ($x$) for SrLa$_4$Ti$_{4-x}$Zr$_x$O$_{17}$ ($0 \leq x \leq 0.1$) compositions, showing a decrease in $\tau_f$ with increase in Zr$^{4+}$ content.

Table 7.4. Processing conditions, relative densities and MW dielectric properties of SrLa$_4$Ti$_{4-x}$Zr$_x$O$_{17}$ ($0 \leq x \leq 0.1$) ceramics.

<table>
<thead>
<tr>
<th>$x$</th>
<th>C.T ($^\circ$C)</th>
<th>S.T ($^\circ$C)</th>
<th>$\rho_{rel}$ (%)</th>
<th>$\varepsilon_r$</th>
<th>$Q_u \times f_o$ (GHz)</th>
<th>$\tau_f$ (ppm/$^\circ$C)</th>
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<td>57.3</td>
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</table>

7.3 References


11. Bijumon, P V; Sebastian, M T; Dias, A; Moreira, R L; Mohanan, P. J. Appl. Phys., 2005, 97, 104108.


CHAPTER 8

8. CONCLUSIONS

The aim of the present study was to design and process compositions in the Sr$_{5-x}$Ca$_x$Nb$_4$TiO$_{17}$, Sr$_{5-x}$La$_x$Nb$_4$-$x$Ti$_{1+x}$O$_{17}$, SrLa$_{4-x}$Nd$_x$Ti$_{5-x}$O$_{17}$, SrLa$_{4-x}$Sm$_x$Ti$_{5-x}$O$_{17}$, Sr$_{1-x}$Ca$_x$La$_4$Ti$_5$O$_{17}$ and SrLa$_4$-$x$Zr$_x$O$_{17}$ series for possible microwave applications such as DRs in telecommunication technology. All the compositions were prepared through solid state sintering route. The compositions were characterized using XRD and SEM for phase and microstructural analysis, and LCR and vector network analyzer (VNA) were used for electrical properties measurements. The main conclusions are summarized below:

8.1 Ca substituted Sr$_2$Nb$_4$TiO$_{17}$

At temperatures $\leq$1450°C, Sr$_{5-x}$Ca$_x$Nb$_4$TiO$_{17}$ compositions with $x$ = 1, 2, 3 and 4 formed single phase Sr$_5$CaNb$_4$TiO$_{17}$, Sr$_5$Ca$_2$Nb$_3$TiO$_{17}$, Sr$_2$Ca$_3$Nb$_4$TiO$_{17}$ and SrCa$_4$Nb$_3$TiO$_{17}$ ceramics respectively. At $x$ = 0 and 5, Sr$_5$Nb$_4$TiO$_{17}$ and Ca$_5$Nb$_4$TiO$_{17}$ formed but along with Sr$_2$Nb$_2$O$_7$ (for $x$ = 0), and CaNbO$_3$ and CaNb$_2$O$_6$ (for $x$ = 5) as second phases. Above 1450°C, all the compositions crystallized into two-phase ceramics. At low frequencies, phase transition that might be from ferroelectric to paraelectric was observed in the composition with $x = 0$ at $\sim$ 567°C. Both the molar volume and theoretical density decreased with increase in the Ca$^{2+}$ content. For the Ca$^{2+}$ substituted Sr$_2$Nb$_4$TiO$_{17}$ compositions sintered at 1500°C for 2h, $\varepsilon_r$ in the range 62.5 to 37.6, $\tau_f$ in the range $+162.4$ ppm/°C to $-132.5$ ppm/°C and $Q_u \times f_0$ in the range $\sim$ 447 to 3087 GHz were achieved.

8.2 La substituted Sr$_2$Nb$_4$TiO$_{17}$

XRD revealed single phase formation for all the compositions in the Sr$_{5-x}$La$_x$Nb$_4$-$x$Ti$_{1+x}$O$_{17}$ (0 $\leq x \leq 4$) series sintered at 1500°C for 4h. A phase transition that might be from ferroelectric to paraelectric was observed for the composition with $x = 0$ at temperature $\sim$531°C. The lattice parameters and molar volume of the unit cell decreased with increase in the La$^{3+}$ content. The theoretical density of the compounds increased
with increase in the La$^{3+}$ content due to the increased MW/V ratio. The dielectric constant was observed to follow the relative density. The $Q_u \times f_o$ was observed to increase from 1313 GHz to 9969 GHz as the La$^{3+}$ content was increased from 0 to 4. In the present study, $\varepsilon_r \sim 72.6$, $Q_u \times f_o \sim 5830$ GHz, $\tau_f \sim 78.7$ ppm/°C and $\varepsilon_r \sim 60.8$, $Q_u \times f_o \sim 9969$ GHz and $\tau_f \sim +117$ ppm/°C were achieved respectively for the Sr$_2$La$_3$NbTi$_4$O$_{17}$ ($x = 3$) and SrLa$_4$Ti$_5$O$_{17}$ ($x = 4$) compounds sintered at 1500°C/4h.

8.3 Nd substituted SrLa$_4$Ti$_5$O$_{17}$

XRD revealed the formation of single phase ceramics for all the compositions in the SrLa$_{4-x}$Nd$_x$Ti$_5$O$_{17}$ ($0 \leq x \leq 4$) series sintered in the temperature range 1500°C to 1580°C for 4h. The theoretical density was observed to increase from 5.66 g/cm$^3$ to 5.89 g/cm$^3$ with increase in Nd$^{3+}$ content ($x$) from 0 to 4. The molar volume ($V_m$) decreased from 339.5 Å$^3$ to 331.6 Å$^3$ as the Nd$^{3+}$ content was increased from 0 to 4. The ceramics in the SrLa$_{4-x}$Nd$_x$Ti$_5$O$_{17}$ ($0 \leq x \leq 4$) system have $\varepsilon_r$ in the range 60.8 to 44.1, $Q_u \times f_o$ in the range 9969 to 6030 GHz and $\tau_f$ in the range 117 ppm/°C to -142.2 ppm/°C. A near zero $\tau_f$ corresponds to $\varepsilon_r \sim 54$ at $x = 1.6$.

8.4 Sm substituted SrLa$_4$Ti$_5$O$_{17}$

XRD revealed the formation of single phase ceramics for the SrLa$_{4-x}$Sm$_x$TiO$_{17}$ ($0 \leq x \leq 4$) compositions with $x = 0$ to 3 and a mixture of Sm$_2$Ti$_2$O$_7$ and SrTiO$_3$ for the composition with $x = 4$ sintered at temperatures ranging from 1500°C to 1580°C for 4h. The molar volume ($V_m$) decreased from 339.5 Å$^3$ to 330.6 Å$^3$ with increase in $x$ from 0 to 3. The theoretical density increased from 5.66 g/cm$^3$ to 5.98 g/cm$^3$ as the value of $x$ value was increased from 0 to 3. The ceramics in the SrLa$_{4-x}$Sm$_x$TiO$_{17}$ ($0 \leq x \leq 4$) series exhibited $\varepsilon_r$ in the range 79.1 to 42.1, $Q_u \times f_o$ in the range 9969 to 3142 GHz and $\tau_f$ in the range +523 ppm/°C to -142.2 ppm/°C. An analysis of results suggested that near zero $\tau_f$ corresponded to $\varepsilon_r \sim 53$ at $x = 1.4$.

8.5 Ca substituted SrLa$_4$Ti$_5$O$_{17}$

XRD revealed the formation of single phase ceramics (within the detection limit of in-house XRD) for all the compositions in the Sr$_{1-x}$Ca$_x$La$_4$Ti$_5$O$_{17}$ ($0 \leq x \leq 1$) sintered in air.
for 4h in the temperature range 1500-1580°C. Theoretical density and molar volume decreased due to the substitution of smaller Ca\(^{2+}\) (1.33 Å) ions for larger Sr\(^{2+}\) (1.44 Å) ions. The molar volume (\(V_m\)) decreased from 339.5 Å\(^3\) to 335.9 Å\(^3\) as the Ca\(^{2+}\) content was increased from 0 to 1. The theoretical density decreased from 5.66 g/cm\(^3\) to 4.47 g/cm\(^3\) as the x value was increased from 0 to 1. \(\varepsilon_r\) decreased from 60.8 to 52.7, the \(\tau_f\) decreased from +117 ppm/°C to -37.0 ppm/°C, and \(Q_u\times f_o\) value increased from 9969 GHz to 12700 GHz with increase in Ca\(^{2+}\) content from 0 to 1. The analysis of results indicated that high \(\varepsilon_r\) (~53.7), high \(Q_u\times f_o\) (~11532 GHz) and near zero \(\tau_f\) (~-1.4 ppm/°C) corresponded to the composition with x = 0.6 (i.e. Sr\(_{0.4}\)Ca\(_{0.6}\)La\(_4\)Ti\(_5\)O\(_{17}\)).

8.6 Zr substituted SrLa\(_4\)Ti\(_5\)O\(_{17}\)

XRD revealed the formation of single phase ceramics for each composition in the SrLa\(_4\)Ti\(_5\)-xZr\(_x\)O\(_{17}\) (0 ≤ x ≤ 0.1) series sintered in air for 4h in the temperature range 1500-1580°C. \(\varepsilon_r\) decreased from 60.8 to 55.5, \(\tau_f\) decreased from +117 ppm/°C to 71.5 ppm/°C, however, no significant change was observed in the \(Q_u\times f_o\) value with the increase in Zr\(^{4+}\) content from 0 to 0.1.
CHAPTER 9

PLAN FOR THE FUTURE WORK

1. Attrition mill can be used for mix-milling of the starting raw powders to get relatively smaller particle size powder and improve density of ceramics in the investigated systems.

2. Detailed transmission electron microscopy of samples can be carried out to study the relationship between the MW dielectric properties and octahedral tilting.

3. Other rare earth elements such as Pr$^{3+}$, Dy$^{3+}$, Gd$^{3+}$, Er$^{3+}$, Tb$^{3+}$ and Ho$^{3+}$ ions can be substituted for La$^{3+}$ ions to study their effects on the MW dielectric properties of modified SrLa$_4$Ti$_5$O$_{17}$ compositions.

4. Sn$^{4+}$, Mn$^{4+}$, and Te$^{4+}$ can be substituted for Ti$^{4+}$ to study their effects on the MW dielectric properties of modified SrLa$_4$Ti$_5$O$_{17}$ compositions.

5. Sintering additives such as CuO, or ZnO can be added to lower the sintering temperature and / or improve the density of e.g. Sr$_{0.4}$Ca$_{0.6}$LaTi$_5$O$_{17}$ to further enhance its quality factor.

6. Raman spectroscopy in the temperature range 25 to 800°C of the studied compositions can be carried out to investigate structural phase transitions (if any) in the investigated compositions.