Chapter II

Target preparation, thin film deposition and compositional characterization

2.1 Introduction:

As discussed in chapter 1, tunable applications, which require high tunability and low loss, barium strontium titanate (BST) in the paraelectric phase is preferred to that in the ferroelectric phase. BST with Ba:Sr ratio of 50:50 [(Ba$_{0.5}$, Sr$_{0.5}$)TiO$_3$, BST5] with its Curie temperature $T_c$, just below room temperature is found to be paraelectric and hence is the material of study in this work. This chapter describes the methodology for the synthesis of BST ceramic targets by solid-state reaction technique and deposition of BST thin films by RF magnetron sputtering. The phase purity, crystallinity and crystallite size of the target material were determined using X-ray diffraction (XRD) technique and the surface morphology of these targets was characterized by scanning electron microscopy (SEM). The target fabrication steps were optimized for obtaining BST5 targets of high density with good surface finish, suitable for sputtering. These targets were used for depositing thin films by RF magnetron sputtering. It is well known that the structural, microstructural, optical and electrical properties of BST thin films depend on the Ba/Sr, (Ba+Sr)/Ti ratio and oxygen stoichiometry. Hence, it is essential to determine the composition of the deposited films. The composition of the films was analyzed by Rutherford Backscattering Spectrometry (RBS) and X-ray Photoelectron Spectroscopy (XPS). RBS allows precise determination of the thin film stoichiometry without calibration standards required in contrast to methods like wavelength dispersive and energy dispersive X-ray spectrometries (WDS and EDS). For probing the surface composition of the BST5 thin films, X-ray Photoelectron Spectroscopy (XPS) measurements were performed.
2.2 Target fabrication:

Detailed optimization of conditions for the preparation of ceramic targets of BST5, which was used for deposition of BST thin films by RF magnetron sputtering, was carried out.

The main objectives of this part of the work were the following:

1. To synthesize Barium Strontium Titanate powder with Ba/Sr ratio 50/50 \([(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3, \text{BST5}]\) without any secondary phases.

2. Optimize sintering conditions i.e., sintering time and temperature to obtain high density sputtering targets with good surface finish, suitable for sputtering.

3. To estimate the shrinkage and to obtain 2” diameter targets after sintering.

2.2.1 Powder preparation:

Several methods can be used for the preparation of ceramic powders. The methods can be divided into two categories: mechanical methods and chemical methods\(^2,3,4\). In the mechanical methods, small particles are produced from larger ones by mechanical forces, a process referred to as comminution. The process of comminution involves operations such as crushing, grinding and milling. In some cases, a mechanical milling step forms a part of the process. A wide range of chemical methods exist for the preparation of ceramic powders. The methods can be divided into three broad categories: (i) solid state reactions, (ii) precipitation from solution and (iii) vapor phase reactions. In our case the powders were prepared using the solid state reaction method.

Target preparation using the solid state reaction method (otherwise known as ceramic method) involves the following steps: (a) Stoichiometric weighing of the starting reagents, (b) Uniform mixing, (c) Calcination, (d) Particle size reduction, (e) Uni-axial pressing and (f) Sintering. Cost effectiveness, ease of processing and the abundant availability of starting reagents are the major advantages of this process. The main disadvantage for this method is the need of high processing temperatures in order to achieve best properties. In the present study, BST5 targets were prepared using carbonates of Barium and Strontium and Titanium dioxide as the starting materials. The simple reaction is given as,

\[
\text{M}^\text{I} \text{CO}_3 + \text{M}^\text{II} \text{O}_2 \rightarrow \text{M}^\text{I} \text{M}^\text{II} \text{O}_3 + \text{CO}_2 \uparrow
\]
where, $M^I \rightarrow $Ba, Sr  \\ $M^{II} \rightarrow $Ti

### 2.2.2 Stoichiometric weighing of reagents:

The chemical reaction considered for preparation of $(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3$ powder is given in equation 2.1.

$$0.5 (\text{BaCO}_3) + 0.5 (\text{SrCO}_3) + \text{TiO}_2 \rightarrow (\text{Ba}_{0.5}, \text{Sr}_{0.5})\text{TiO}_3 + \text{CO}_2 \uparrow \quad (2.1)$$

The molecular weights of BaCO$_3$, SrCO$_3$ and TiO$_2$ are 197.35, 147.6 and 79.9 gms respectively. On adding the molecular weights according to equation 2.1, we get the total weight of the sample as 252.375 gms.

Hence for the preparation of 1 gram of stoichiometric powder we take,

- **Barium Carbonate (BaCO$_3$)** → $\frac{0.5 \times 197.35}{252.375} \rightarrow 0.3910$ gms
- **Strontium Carbonate (SrCO$_3$)** → $\frac{0.5 \times 147.6}{252.375} \rightarrow 0.2924$ gms
- **Titanium dioxide (TiO$_2$)** → $\frac{79.9}{252.375} \rightarrow 0.3166$ gms

The required amount of the starting reagents with purity >99.9%, (Aldrich Chemicals) were weighed using an electronic balance (A&D technologies, Model GR-120), with an accuracy of 0.1mg.

### 2.2.3 Uniform mixing of reagents:

In order to ensure a complete chemical reaction, the starting reagents have to be mixed uniformly to increase the point of contact between the reagents. Hence, the measured starting materials along with acetone as mixing medium and zirconia grinding balls were taken in zirconia jar (vial) and were thoroughly mixed for 1 hr at 150 rotations per minute (rpm) using a planetary Ball Mill (Retsch PM 100, Germany). After mixing, the slurry was transferred to an alumina crucible and was dried at 100°C over night in an oven.
2.2.4 Calcination:  

Calcination (also referred to as calcining) is a thermal treatment which brings about thermal decomposition or removal of a volatile fraction and phase transition. In the present case, chemical reaction takes between the initial reactants by chemical decomposition reactions in which the solid reactants such as BaCO$_3$ and SrCO$_3$ decompose to form a new solid phase such as BaO and SrO respectively. During this process CO$_2$, which is commonly associated with the metal carbonates are released. BaO and SrO which are not stable phases of Ba and Sr reacts with TiO$_2$ to form (Ba,Sr)TiO$_3$. A clear illustration is given below,

$$M_i'CO_3 \xrightarrow{\Delta} M_i'O + CO_2 \uparrow \quad (2.2)$$

$$M_i'O + TiO_2 \xrightarrow{\Delta} M_i'TiO_3 \quad (2.3)$$

where, $M_i' \rightarrow$ Ba, Sr

The calcination process normally takes place well below the melting temperature of the product materials$^{5,6}$. The parameters such as temperature and duration of calcinations are important factors influencing shrinkage of the material during sintering.

The uniformly mixed and dried powders were calcined in a furnace at different temperatures and duration. The important point in the calcination process is to prepare single phase powder with no secondary phases at the lowest possible temperature and duration. The completion of reaction, phase formation and the absence of secondary phases were confirmed using XRD. The XRD patterns of some of the calcined samples are shown in figure 2.1.

It can be seen from figure 2.1 that the powders calcined at 1100°C for 5 hrs yielded single phase BST5 powder. In order to bring down the calcination temperature, the powders were calcined at 1000°C and 900°C, which did not yield single phase BST5 even after calcining to 10 hrs and 5 hrs respectively. On the other hand, calcining the starting materials at 1000°C for 10 hrs yielded single phase BST5 powder with no secondary phases. This calcination condition was therefore chosen for further processing.
2.2.5 Particle size reduction:

The particle size reduction (also known as pulverization) of the complex oxides after the calcinations stage is important. It is well known that particles with small size can be compacted well, which in turn yields higher density at lower sintering temperatures. In our case a planetary ball mill (Retsch PM 100, Germany) was used for pulverization. There are several processing variables in pulverization that determine the final size of the particles of the product. The variables include milling speed, milling time, grinding ball: powder ratio etc.\(^7\) In the present study, calcined powders were dry ground for different milling durations; The ball: powder ratio and the milling speed were fixed at 3:1 and 350 rpm respectively. The XRD pattern of pulverized BST5 powder as a function of milling time is shown in figure 2.2.

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**Figure 2.1:** X-ray diffraction pattern of BST5 powder calcined at (a) 900°C for 10 hrs, (b) 1000°C for 5 hrs, (c) 1000°C for 10 hrs and (d) 1100°C for 5 hrs.
Figure 2.2: X-ray diffraction pattern of BST5 powder pulverized at 350 rpm for (a) 1 hr (b) 2 hrs, (c) 3 hrs and (d) 4 hrs.

The variation in full width at half maxima (FWHM) and crystallite size as a function of milling time is shown in figure 2.3. It can be observed that the crystallite size decreases with increase in milling time till about 3 hrs. Further increase in the milling time causes the particles to agglomerate leading to an increase in crystallite size (decrease in FWHM). Hence, for a milling speed of 350 rpm, the optimum milling time for BST5 powder was found to be 3 hrs.
2.2.6 Uniaxial pressing:

The next step in the process is to compact the pulverized powders into cylindrical discs (referred as green pellets) by uniaxial pressing. The compaction of the powder should be done slowly to facilitate the escape of the entrapped air. To make green pellets of the ceramic powder, a rigid die which is rust free is to be used. The die and plunger used in the present study is shown in figure 2.4a and the uniaxial press is shown in figure 2.4b. Prior to every pressing of the BST5 green pellet, dummy discs of stearic acid are made to ensure that the walls of the die and plunger are free of dust, rust and other contaminations. The inner diameter of the die used in the present study is 57 mm, which is also the diameter of the green pellets. The thickness of the green pellet is determined by the amount of material (BST5 powder) used and the force applied. Depending up on the amount of material used, the force was varied between 10 and 15 ton to make green pellets of BST5. At this stage (prior to the sintering process) the density of the green pellet would be between 50 and 55% of the theoretical density of bulk BST5 ($\rho_c=5.58$ g/cm$^3$). In order to increase the strength of the green pellets, binding agents such as polyvinyl alcohol (PVA) are generally used. These binding agents are volatile and get removed during sintering process. Though it looks advantageous, it has its own short
comings, such as formation of pores, dents and crevice, which would lead to higher porosity, poor density and inferior quality of the end product. So, in the present study no such binding agents were used.

**Figure 2.4a:** Photograph of the die and plunger used in this study.

**Figure 2.4b:** Photograph of the uniaxial press used in this study.
2.2.7 Sintering:

Sintering is the final stage of the target preparation process\(^9\). The objective of sintering in the present study is to reduce porosity in the compact target material and also to realize targets of the required diameter and thickness. The elimination of porosity and densification of the target material in this stage is determined by the sintering temperature and duration.

In the present study, the green pellets were subjected to various sintering treatments as shown in table 2.1 below, \(\frac{\rho}{\rho_0} \times 100\) is the percentage of the measured density relative to theoretical density (term as “relative density” from here on).

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Sintering Temperature (°C)</th>
<th>Sintering Duration (hrs)</th>
<th>Volume Shrinkage (%)</th>
<th>(\frac{\rho}{\rho_0}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green pellet</td>
<td>none</td>
<td>none</td>
<td>-</td>
<td>55.15</td>
</tr>
<tr>
<td>BST1a</td>
<td>1100</td>
<td>1</td>
<td>5.89</td>
<td>70.37</td>
</tr>
<tr>
<td>BST1b</td>
<td>1100</td>
<td>2</td>
<td>5.97</td>
<td>70.43</td>
</tr>
<tr>
<td>BST1c</td>
<td>1100</td>
<td>3</td>
<td>6.21</td>
<td>70.61</td>
</tr>
<tr>
<td>BST1d</td>
<td>1100</td>
<td>4</td>
<td>6.32</td>
<td>70.7</td>
</tr>
<tr>
<td>BST2a</td>
<td>1200</td>
<td>1</td>
<td>11.59</td>
<td>74.91</td>
</tr>
<tr>
<td>BST2b</td>
<td>1200</td>
<td>2</td>
<td>14.85</td>
<td>77.77</td>
</tr>
<tr>
<td>BST2c</td>
<td>1200</td>
<td>3</td>
<td>17.14</td>
<td>79.92</td>
</tr>
<tr>
<td>BST2d</td>
<td>1200</td>
<td>4</td>
<td>18.24</td>
<td>81.00</td>
</tr>
<tr>
<td>BST3a</td>
<td>1300</td>
<td>1</td>
<td>17.24</td>
<td>80.00</td>
</tr>
<tr>
<td>BST3b</td>
<td>1300</td>
<td>2</td>
<td>20.18</td>
<td>82.97</td>
</tr>
<tr>
<td>BST3c</td>
<td>1300</td>
<td>3</td>
<td>22.04</td>
<td>84.94</td>
</tr>
<tr>
<td>BST3d</td>
<td>1300</td>
<td>4</td>
<td>22.53</td>
<td>85.78</td>
</tr>
<tr>
<td>BST4a</td>
<td>1400</td>
<td>1</td>
<td>30.27</td>
<td>94.98</td>
</tr>
<tr>
<td><strong>BST4b</strong></td>
<td><strong>1400</strong></td>
<td><strong>2</strong></td>
<td><strong>31.05</strong></td>
<td><strong>96.05</strong></td>
</tr>
<tr>
<td>BST5a</td>
<td>1350</td>
<td>1</td>
<td>22.04</td>
<td>85.01</td>
</tr>
<tr>
<td>BST5b</td>
<td>1350</td>
<td>2</td>
<td>26.39</td>
<td>89.96</td>
</tr>
<tr>
<td>BST5c</td>
<td>1350</td>
<td>3</td>
<td>27.96</td>
<td>91.93</td>
</tr>
<tr>
<td>BST5d</td>
<td>1350</td>
<td>4</td>
<td>28.80</td>
<td>93.01</td>
</tr>
</tbody>
</table>

**Table 2.1:** Sintering behavior for BST5 target material.
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The plot in figure 2.5 shows the variation in shrinkage with sintering temperature of the BST5 green pellets.

![Graph showing variation of shrinkage with sintering temperature and duration.](image)

**Figure 2.5:** Percentage of shrinkage in BST5 ceramics sintered at various temperatures and durations.

It can be observed from the above plot that the shrinkage increases with increase in temperature and duration. The increase is attributed to the densification of the samples. Figure 2.6 confirms the increase in relative density of the samples with increase in sintering temperature and duration.
The optimized sintering condition for BST5 target preparation in the present study is 1400°C for 2hrs. This sintering condition yielded the maximum relative density of 96%. The SEM micrograph of the sintered target is shown in figure 2.7.

The samples sintered between 1100°C and 1300°C did not yield the required density even after sintering for 4 hrs. A sintering condition of 1350°C for 2hrs and above
was required to achieve relative density of >90%. The green pellets which were subjected to a sintering condition of 1400°C for 3 hrs and 4 hrs resulted in cracks propagating through the thickness of the material, reaction with the alumina supporting plate and black colored surface (indicating oxygen deficiency) and hence cannot be used as target material in sputtering process. The photographs of some of the targets prepared are shown in figure 2.8.

Figure 2.8: Photographs of the BST5 targets prepared.

2.3 Thin film deposition by RF magnetron sputtering:

RF magnetron sputtering has been widely accepted as one of the versatile techniques for the deposition of high quality BST thin films by several research groups. It has been employed for the following reasons: any solid material (metals, insulators and semiconductors) can be sputtered, complex compounds can be sputtered stoichiometrically, use of low gas pressure for sputtering, appreciable rates of deposition and uniformity over large area is possible. The parameters such as the RF power density (in W/cm²), substrate temperature, sputter gas mixture i.e, the Ar/O₂ ratio (from here on referred as oxygen mixing percentage, OMP), working/sputtering gas pressure and substrate to target distance can be controlled to influence the material properties of the sputtered films. It is important to note that the control over parameters that influence the physical properties is in general, greater during deposition (in situ) than it is after deposition (ex situ). Therefore, in situ treatment of thin films is always preferred over ex situ treatments. However, some of the thermal processes in the device fabrication procedure could amount to an ex situ annealing treatment as far as the film is concerned.
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Hence, it is important to study the influence of each type of processing (in situ or ex situ) and optimize for ideal device behavior.

The schematic of the RF magnetron sputtering system used in this work is shown in figure 2.9. It consists of a 30 liter stainless steel vacuum chamber (VC) which houses 3 cathodes and a substrate holder. Out of the 3 cathodes, 2 are RF powered while the other one is dc powered. One of the RF powered cathodes was used for the deposition of BST5 thin films.

During deposition of thin films, the vacuum chamber is continuously cooled by flow of water through the water cooling jackets fitted on the exterior to the vacuum chamber. The vacuum chamber is evacuated through the electro-pneumatic roughing valve (RV) from atmospheric pressure to \(\leq 2 \times 10^{-3}\) Torr using a rotary vane mechanical pump (RP, DS-102, Varian, Italy), with an approximate pumping speed of 6.84 m\(^3\) h\(^{-1}\). The vacuum chamber is isolated from the turbo molecular pump (TMP, Turbo-V 301, Varian, Italy) through a mechanical screw driven gate valve (GV) which is attached to the VC by a 6” conflat flange with copper gasket. The pumping speed of the TMP is about 15 m\(^3\) h\(^{-1}\). Once the chamber pressure reaches \(\leq 2 \times 10^{-3}\) Torr, the RV is closed and the TMP is evacuated through electro-pneumatic backing valve (BV). As the fore-line pressure reaches \(\leq 2 \times 10^{-3}\) Torr, the TMP is switched on and the GV is opened. The pressure in the vacuum chamber can now be brought into the high vacuum regime. The pressure is monitored using a cold cathode gauge (Pfeiffer vacuum, Germany). A base pressure of 2 x 10\(^{-6}\) Torr can be achieved in about 2 hrs. Two mass flow controllers (MFC, Bronckhurst Hi-tech, Ruurlo-Holland) which can independently control flows of argon (Ar, 99.9% purity) and molecular oxygen (O\(_2\), 99.999% purity) are connected to the VC through a solenoid valve. The use of a gas mixture of inert argon and reactive oxygen helps to achieve the same stoichiometry as that of the target in the film. The working pressure during sputtering is controlled partly by adjusting the total input gas flow and by reducing the throughput of the TMP by partially closing the manual gate valve. The working pressure is monitored by a capacitance manometer (CMM, Inficon, USA). Once the predetermined working pressure and deposition temperature is achieved, the sputter deposition process is started by initiating the plasma using the RF power generator (RF-
VII Inc, USA) coupled with the matching network. The VC walls and substrate holding stage form the grounded electrode.

Figure 2.9: Schematic of the sputtering system used in this study.
The substrate holding stage (AJA International, USA) is placed on the top plate of the VC and is capable of rotating on its own axis and at the same time allows the deposition of oxide films at temperatures ranging from room temperature up to 800°C. Prior to every sputter deposition, the target was conditioned by pre-sputtering\textsuperscript{15} for an hour by closing the shutter. The system is vented to atmosphere after closing all valves to isolate the pumps from the VC. The photographs of the sputter deposition unit, inner view of the vacuum chamber and RF plasma generated during sputtering of BST5 are shown in figure 2.10.

\textbf{Figure 2.10}: Photograph of (a) the sputtering system, (b) inner view of the vacuum chamber and (c) RF plasma generated during BST5 deposition.

As mentioned earlier, parameters such as RF power density, substrate temperature, OMP, working gas pressure, substrate to target distance, type of substrate used and post-deposition annealing treatments influence the properties of the sputtered films. Optimization of all the sputtering conditions for the best material properties in the deposited film can be very cumbersome and time consuming. Initial studies indicated that
the power densities < 2.5 W/cm² resulted in very low rates of sputtering where as power densities > 3.5 W/cm² resulted in target damage. Hence, the power density was fixed at 3W/cm². The substrate to target distance was fixed at 5cms because higher distances led to lower deposition rates and lower distances led to damage of the vacuum seals near the cathode due to heat radiating from the substrate heater at higher temperatures. The working pressure was fixed at 20 mTorr. The different deposition parameters used in the current study are given in table 2.2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power density (W/cm²)</td>
<td>3.0 W/cm²</td>
</tr>
<tr>
<td>Substrate to target distance (cms)</td>
<td>5 cms</td>
</tr>
<tr>
<td>Working pressure (mTorr)</td>
<td>20 mTorr</td>
</tr>
<tr>
<td>Oxygen mixing percentage, OMP (%)</td>
<td>Varied from 0-100 in steps of 25%</td>
</tr>
<tr>
<td>Substrate Temperature (°C)</td>
<td>RT and 400°C to 800°C</td>
</tr>
<tr>
<td>Substrate Type</td>
<td>Fused silica and Pt/Si as the primary substrates. Single crystal substrates: LaAlO₃, MgO, c-plane sapphire. Si for RBS and XPS analysis.</td>
</tr>
<tr>
<td>Post-deposition annealing treatment</td>
<td>900°C for 1 min (Quasi rapid thermal annealing). 400°C to 1000°C for 1 hour</td>
</tr>
</tbody>
</table>

Table 2.2: Sputter deposition parameters used in the current study.

Out of the above mentioned parameters, substrate temperature and post-deposition annealing treatments highly influences the crystalline property of BST5 thin films where as the influence of OMP i.e., Ar:O₂ ratio, during sputtering appear to be complex; the ambient oxygen partial pressure not only influences the oxygen incorporation into the films, but also the titanium non-stoichiometry and the A/B site ratio which are strongly linked to the zero bias field dielectric permittivity and loss. The exact OMP in sputter deposition of oxides is always under considerable scrutiny in any oxide system.16,17,18. There is a tradeoff between the ideal level of energetic impingement in an oxide containing plasma, and the risk of anion deficiency that can occur under low OMP. Hence, it is important to systematically vary OMP and study its impact on the cation and anion stoichiometry.

2.4 Compositional characterization:

For compositional analysis, BST5 thin films were deposited on RCA¹⁹ cleaned Si substrates. The OMP was varied from 0-100% in steps of 25% while keeping the other
parameters fixed. Deposition and characterization of BST5 thin films deposited at 100% oxygen ambient has been carried out and reported for the first time by our group.

The composition and rate of deposition (derived from the thickness) of BST5 films deposited at 800°C was determined using Rutherford backscattering spectroscopy (RBS). X-ray photoelectron spectroscopy (XPS) provided information about the chemical bonds present near the surface. The important objective of the RBS and XPS experiments was to establish the composition of the films sputtered from a stoichiometric target of Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ and to establish the OMP that yields the composition of the sputtered film close to that of the target. The results of these analyses are provided below; in each case, a brief introduction to the technique is also given.

2.4.1 Rutherford Backscattering Spectroscopy:

The apparatus for Rutherford backscattering analysis of thin films consist of three major components:

1. A helium ion source.
2. An accelerator to deliver mono-energetic helium ions.
3. A solid state detector to measure the energy of scattered ions.

A schematic representation of the system is shown in figure 2.11.

![Figure 2.11: Schematic diagram of a Rutherford Backscattering Spectroscope.](image)

In Rutherford backscattering, the sample under study is bombarded with mono-energetic beam of $^4$He$^+$ particles, which travel hundreds of nanometers or even microns
into the sample. The scattering processes which the ions undergo are influenced by the constituent atoms present in the sample. This allows determining the composition of the sample. The backscattered particles are detected by the solid-state detector system which measures the energies of the particles. During the collision, energy is transferred from the incident particle to the atoms of the target specimen. The change in energy of the scattered particle depends on the masses of incoming and target atoms. If, incident particle of mass \( M_1 \) and energy \( E_0 \) bombard on a target atom of mass \( M_2 \), the residual energy \( E \) of the particle scattered at angle \( \theta \) after collision can be expressed as\(^{20}\):

\[
E = k \, E_0 \tag{2.4}
\]

\[
k = \left[ \frac{M_1 \cos \theta + \sqrt{M_2^2 - M_1^2 \sin^2 \theta}}{M_1 + M_2} \right]^{1/2} \tag{2.5}
\]

where, \( k \) is known as the kinematic scattering factor, which is actually the energy ratio of the particle before and after the collision.

Since \( M_1 = 4 \) for He, \( E_0 \) is determined by the accelerator and \( E \) is measured by the detector, \( k \) is simply determined by the mass of the target atoms.

In the present study, the RBS experiments were carried out at IIT Kanpur, using 2MeV \(^4\)He\(^+\) particles delivered from 1.7MV Tandetron accelerator. The scattered particles were detected at an angle of 155\(^0\) with a surface barrier detector having resolution of 18keV.

The spectra were theoretically fitted using SIMNRA software\(^{21}\). The measured and fitted RBS spectra are shown in figure 2.12. The fit between the measured and calculated data is reasonably good for the Ba, Sr, Ti and O atoms in the films.
Figure 2.12: Measured and simulated RBS (\(^{4}\text{He}\)) data for BST5 films deposited from a Ba\(_{0.5}\)Sr\(_{0.5}\)TiO\(_3\) target as a function of OMP.
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Figure 2.13 provides the stoichiometry information and rate of deposition determined by SIMNRA.

![Figure 2.13](image)

**Figure 2.13:** Compositional analysis of BST5 thin films as a function on OMP (a) Rate of deposition and oxygen incorporation as a function of OMP (b) Ba/Sr ratio and (Ba+Sr)/Ti ratio of BST5 films as a function of OMP.

From figure 2.13a, it can be observed that the rate of deposition decreased with increase in OMP. The decrease in deposition rate with increase in OMP is due to lower molecular weight of oxygen (O₂, 31.998) when compared to that of Ar (39.948). Figure 2.13 also shows the variation in film composition with OMP. Note that the ideal composition of Ba₀.₅Sr₀.₅TiO₃ is 10 at.% Ba, 10 at.% Sr, 20 at.% Ti and 60 at.% oxygen. It can be noted that the films deposited at 0 and 25 % OMP are found to be significantly oxygen deficient. Oxygen vacancies are undesirable, because they increase the optical and microwave loss of the BST thin films²²,²³,²⁴. The films deposited at 50% OMP and above show improved oxygen stoichiometry.

As discussed earlier, the Ba/Sr ratio influences the Curie point of the film. In the present case, the Ba/Sr ratio remains rather constant at a value close to the nominal target composition. This indicates that for these set of conditions, OMP has low impact on the A-site stoichiometry.
On the other hand, it is found that Ti stoichiometry in the films is highly influenced by OMP. The films deposited at 0 and 25% OMP are Ti-rich, while BST5 films deposited at 75 and 100% OMP are Ti-deficient. In general, BST thin films with a (Ba+Sr)/Ti ratio close to 1 have shown the highest permittivity and tunability. The excess Ti in the Ti-rich samples can be accommodated in the grains and/or grain boundaries depending on their concentration. High concentration of Ti can lead to precipitations of amorphous TiO$_{2-x}$ between the grains.

Close replication of the target stoichiometry was achieved for films sputter deposited at 800°C with working pressure of 20 mTorr using 50% OMP.

The same set of samples, which were used for RBS analysis were used for X-ray Photoelectron Spectroscopy (XPS) also. XPS provides information about the chemical bonds present near the surface of films.

### 2.4.2 X-ray Photoelectron Spectroscopy:

X-ray Photoelectron Spectroscopy (XPS, also known as Electron Spectroscopy for Chemical Analysis, ESCA) is a surface analytical technique, which is based upon the photoelectric effect. The core level shift provides information about the chemical bonding and valence states in a thin surface layer (~15Å) of the sample. Each atom in the surface has core electrons with a characteristic binding energy that is conceptually, not strictly, equal to the ionization energy of that electron. When the sample surface is irradiated using a monochromatic x-ray beam, the energy of the x-ray photon is absorbed by the core electron of the atom. If the photon energy, $h\nu$, is large enough, the core electron will then escape at a takeoff angle, $\theta$, from the surface plane of the sample. The emitted electron with kinetic energy of $E_k$ is referred to as the photoelectron. The binding energy, $E_b$, of the core electron is given by the relation:

$$E_b = h\nu - E_k - \phi$$  \hspace{1cm} (2.6)

where $h\nu$ is the energy of the x-ray photon. $E_k$ is measured by the energy analyzer of the instrument. As, the work function, $\phi$, induced by the analyzer can be compensated artificially, the above equation can be given as,

$$E_b = h\nu - E_k$$  \hspace{1cm} (2.7)
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The photoemission process is shown in figure 2.14. Unlike RBS, XPS does not provide accurate compositional information without the use of appropriate reference standards. The X-ray Photoelectron Spectroscopy (XPS) measurements described in this section were performed at Indian Institute of Chemical Technology (IICT), Hyderabad using a Kratos Axis 165 Spectrometer with Mg Kα radiation (1253.6 eV) and a takeoff angle of θ=45°. The X-ray power supply was run at 15 kV and 5 mA. The pressure in the analysis chamber during the scans was ~10⁻⁹ Torr.

![Figure 2.14: Photoemission process.]

For samples such as BST which are highly insulating, a positive charge zone will be formed on the surface as the photoelectrons are emitted out of the sample surface. The positive potential can vary from few volts to tens of volts and this would result in a shift in the XPS peak position. In such a case, the binding energy of adventitious Carbon, C 1s peak with a characteristic binding energy of 284.8 eV is used as the reference for calibration. A low-energy electron flood gun is used to deliver the electrons to the sample surface, in order to neutralize the surface charge during data acquisition. The electron flood gun can be tuned to provide the right current to push the XPS peaks back to the real position.

The core electron of any element has a unique binding energy, which is like a “fingerprint” and is sensitive to the chemical environment of the element. The core electron of the same atom bonded to different chemical species can exhibit a change in the binding energy. This variation in the binding energy results in the shift of the corresponding XPS peak, which would range from 0.1 eV to 10eV. This effect is called
the “chemical shift”, which is useful in identifying the chemical state of surface elements\(^3\).

For the samples deposited as a function of OMP, a complete spectrum (survey scan) of data for ejected photoelectrons with energies in the range 0 to 1100 eV was gathered, with a 2 eV step size. A typical survey spectrum on BST5 is shown in figure 2.15.

![XPS survey spectrum of BST5 thin film deposited at 50% OMP.](image)

Refined spectra with a 100 meV step size were also gathered and fitted with a Lorentzian function for the constituent elements in BST5. The Ba 3d, Sr 3d, Ti 2p and O1s spectrum were recorded in the binding energies ranging from \(~775\) to \(800\) eV, \(~129\) to \(139\) eV, \(~440\) to \(480\) eV and \(~524\) to \(540\) eV, respectively.

Traces of carbon were detected at 284.6 eV in all the BST5 films deposited at different OMP as shown in figure 2.16 Compensation for sample charging was performed by comparison of the C 1s peak in each of the wide spectra with the known value (284.6 eV) of the C 1s peak.
Figure 2.16: C 1s photoemission spectra of BST5 films deposited at different OMP.

The above photoelectron spectra show a prominent peak at 284.6 eV. This peak is attributed to the adsorbed hydrocarbon (adventitious carbon) having a general formula C\textsubscript{x}H\textsubscript{x}.\textsuperscript{31} Apart from the adventitious hydrocarbon no other signal pertaining to any other additional component is observed. It is noted that the binding energy of C (1s) electron in metallic carbonates is between 289.6 -290.5eV. Since none of the above spectra show any components in this energy range, it can be concluded that all the samples are devoid of contaminations in the form of metallic carbonates on the surface.

The Ti (2p) photoelectron spectra of BST5 films deposited at different OMP is shown in figure 2.17. It can be seen that the spectra are identical in shape and the binding
energy of $2p_{1/2}$ and $2p_{3/2}$ in all the samples are centered around $463.5 \pm 0.2$ and $458 \pm 0.2$ eV respectively.

Figure 2.17: Ti 2p photoemission spectra of BST5 films deposited at different OMP.

The valance state of Ti in all the films were confirmed to be Ti$^{4+}$, because it is known that the binding energy of Ti $2p_{3/2}$ electrons in 3+ and 2+ states shifts to lower binding energies by 2.0 and 3.6 eV respectively. The difference in binding energies of the two peaks is about 5.7eV, which is very close to the reported value of 5.8 eV for Ti-O in the perovskite lattice$^{32}$. The difference in $2p_{1/2}$ and $2p_{3/2}$ in metallic Ti is about 6.7eV. So, it could be concluded that the Ti in the present case corresponds to Ti in the oxide
perovskite lattice and does not have any metallic chemical state even for films deposited at 0 and 25% OMP.

![Figure 2.18: O1s photoemission spectra of BST5 films deposited at different OMP.](image)

The O (1s) spectra in figure 2.18 show two components; the peak at 529 eV correspond to the binding energy of the O in the BST lattice while the other centered about 531.5 eV is indicative of defects. These defects can arise due to strongly chemisorbed moisture, metallic hydroxides or carbonates ($\text{CO}_3^{2-}$)\textsuperscript{33}. The existence of metallic carbonates can be completely neglected as the C (1s) spectra do not show any signal pertaining to metallic carbonates in the energy range of 289.6 -290.5eV. Hence, the defect peak might arise due to formation of metallic hydroxides on the surface.
The other observation which could be made from the above spectra is that the intensity of the higher binding energy component of O 1s decreases with increase in OMP. This shows that the BST5 films deposited at 0 and 25% OMP have oxygen vacancies which were confirmed by RBS analysis also. As the oxygen percentage (OMP) during sputtering is increased, the density of oxygen vacancies decrease and thus the intensity of the higher binding energy component of the O 1s decreases.

Figure 2.19: Ba 3d photoemission spectra of BST5 films deposited at different OMP.

XPS spectra of the Ba (3d) of BST5 films deposited at different OMP are shown in figure 2.19. Each of the Ba 3d_{3/2} and Ba 3d_{5/2} peaks can be fitted with two peaks separated by around 1.5±0.1 eV. The lower binding-energy peaks, i.e., 795.3 and 778.5 eV can be assigned to Ba atoms in the BST perovskite lattice\(^{34}\) where as the high binding
energy peaks at 795.7 and 780.5 eV are assigned to defects. Since the formation of a carbonate on the surface is neglected, the most probable reason for this high energy component would be the formation of hydrides.

Figure 2.20: Sr 3d photoemission spectra of BST5 films deposited at different OMP.

It could also be seen that the BST5 films deposited at 0% and 25% OMP has two distinct high binding energy components each in Ba 3d3/2 and Ba 3d5/2. But as the OMP increases the high energy components merges with that of the low energy peak, indicating the reduction in the defect density of Ba on the film surface. This can be observed even more clearly in Sr (3d) spectra shown in figure 2.20, where the high energy components of Sr 3d3/2 and Sr 3d5/2 vanished completely for the films deposited at higher OMP.
2.5 Summary:

In summary, this chapter has presented a study on the fabrication of ceramic targets of Ba\textsubscript{0.5}Sr\textsubscript{0.5}TiO\textsubscript{3} (BST5) by solid-state reaction method. First, the calcination process was optimized to obtain single phase BST5 powders at 1000\degree C. The calcined powder was then pulverized in a planetary ball mill for 3 hrs. The pulverized powder was then pressed into cylindrical discs and sintered at different conditions. The sintering conditions i.e., sintering time and temperature were optimized to obtain high density sputtering targets with good surface finish, suitable for sputtering. The percentage of volume shrinkage and the relative density of the material after sintering were estimated. A sintering condition of 1400\degree C for 2 hrs yielded high quality target material with 96% relative density. The crystallite size and phase purity was confirmed by X-ray diffraction technique. The surface morphology was studied using scanning electron microscopy.

Thin films of BST5 were deposited by RF magnetron sputtering technique from a single stoichiometric target of BST5. RF magnetron sputtering has been widely accepted as one of the versatile techniques for the deposition of high quality BST thin films.

The influence of oxygen mixing percentage (OMP) on the composition of BST5 film was estimated by RBS and XPS techniques. The total working pressure was fixed at 20 mTorr. The results obtained from RBS analysis indicate that OMP not only influences the oxygen incorporation into the films, but also the (Ba+Sr)/Ti ratio. The effect of OMP on Ba/Sr ratio was found to be marginal. The films deposited at 0 and 25% OMP were oxygen deficient and had excess Ti. A close replication of the target stoichiometry was achieved for films sputter deposited at 50% OMP.

The XPS results clearly indicated the presence of oxygen vacancies in the films deposited at 0 and 25% OMP, complementing the RBS results. The oxygen vacancy chemisorbs moisture, forming metal hydroxides on the surface of the film. An increase in OMP shows decrease in oxygen defect density.

An introduction to other characterization techniques used in this study to determine the structural, microstructural, optical and electrical properties have been discussed in the next Chapter.
References:

Target preparation, thin film deposition and compositional characterization


