Chapter-III
The performance and usefulness of electron beam evaporated thin films mainly depend on the process parameters such as substrate temperature, thickness, type of substrates, annealing temperature, target to substrate distance, and film thickness etc. Proper choice of the deposition parameters is very crucial in obtaining stoichiometric, crystalline films with better electrical properties. Hence a systematic procedure was adopted in the preparation of La$_{0.7}$Ba$_{0.3}$MnO$_3$ (LBMO) thin films using electron beam evaporation technique and the properties of these films were systematically studied.

### 3.1. PREPARATION OF LBMO TARGET

La$_{0.7}$Ba$_{0.3}$MnO$_3$ materials with varying particle size were prepared by solid state reaction method employing polyvinyl alcohol (PVA) as a capping agent. Stoichiometric amounts of high purity (99.99%) La$_2$O$_3$, BaCO$_3$ and Mn$_2$O$_3$ were taken, uniformly mixed and ground using mortar and pestle. Calcination was done for 10 h at 873 K. The resultant mixture was reground, sieve and pressed into pellets at a pressure of 10MPa/cm$^2$. Pellets were sintered at 1173, 1273, and 1373 K in air for 16 h. The structure of the samples was characterized by X-Ray Diffraction (XRD) using a CuK$\alpha$ radiation at room temperature. Scanning Electron Microscope (SEM) of model EVO MA 15 manufactured by Carl Zeiss, for which an EDS is attached of model Inca Penta FETx3 manufactured by Oxford Instruments was used for microstructure and composition analysis. Four-probe technique was used for the measurement of temperature and current dependence of resistance of the samples.

#### 3.1.1. Structural properties

X-ray diffraction (XRD) measurements of all the samples have been carried out and the data were analyzed using JCPDS data. A typical XRD pattern of 1173, 1273, and 1373 K sintered samples was shown in Fig.3.1.1. It is clear from the analysis that all the samples are well crystallized with rhombohedral structure. At sintering temperature of 1173 K, the films exhibited impurity phases, along with LBMO phase. This indicates that the sintering temperature was not enough for the formation of stoichiometry of the films. As the sintering temperature increases, the impurity phases vanished and stoichiometric LBMO was formed. These results suggested that the complete reaction occurs when the sintering temperature was higher than 1173 K.
3.1.2. Microstructure and Composition Analysis

Fig. 3.1.2 shows the SEM images of LBMO samples sintered at different temperatures. In all the samples, significant pores were observed. At lower sintering temperature (1173 K) small grains with irregular shape were observed, resulting in many grain boundaries. This was due to the formation of impurities phases. As the sintering temperature increased, the grains become larger and resulting a substantial reduction of grain boundaries. These microstructural results were supported by the XRD results. The average grain size observed for LBMO was 20-40 nm. Energy dispersive analysis of X-rays (EDS) studies revealed that the samples were nearly stoichiometric at higher temperatures. This suggests that single phase formation is preferable at higher temperature.
Fig. 3.1.2: SEM and EDAX images of LBMO target sintered at (a) 1173 (b) 1273 (c) 1373 K.
Fig. 3.1.3: AFM images of LBMO targetsintered at (a) 1173 (b) 1273 (c) 1373 K.
Fig. 3.1.3 shows the atomic force microscope images of LBMO samples. The surface roughness of the samples was decreased with increasing of the sintering temperature, which was due to increasing of the grain size.

3.1.3. Electrical properties

The electrical resistance of the samples was measured from 213 K to 333 K. The resistivity of the samples decreased with increasing of temperature. The increase of sintering temperature promotes the grain size and microstructural densification. It enhances the conduction of charge carriers and thus responsible for the improvement of the conductivity. From this observation, the conduction is semiconducting in the whole temperature region. However in the literature, the variation of resistance of La$_{0.7}$Ba$_{0.3}$MnO$_3$ (LBMO) bulk samples at low temperature was reported by Kumar et al. [1], they observed that the conduction is metallic in the low temperature region and semiconducting for higher temperature region.

La$_{0.7}$Ba$_{0.3}$MnO$_3$ material has been prepared by solid state reaction method and their structure, morphology, composition analysis and electrical properties were investigated as a function of sintering temperature. The samples exhibited single phase rhombohedral structure. From the XRD, SEM, EDS and electrical properties, it was observed that, stoichiometric and single phase samples were observed at higher sintering temperature 1373 K. From the above analysis we find that the samples, sintered at a temperature 1373 K are used for growing the films.
Preparation of LBMO Films

In the present study, LBMO thin films were deposited on different substrates using electron beam evaporation under various substrate temperatures, thickness, and annealing temperature on various substrates by keeping the other deposition parameters as constant.

Characterization of LBMO Films

The deposited films were characterized by studying the crystallographic structure, composition, surface morphology and electrical properties, and the deposition parameters were optimized to obtain better quality films for possible applications in bolometer.

The LBMO films deposited during the present study were pin-hole free, uniform and highly adherent to the substrate surface.
3.2. Effect of substrate temperature

In order to study the effect of substrate temperature on the properties of LBMO films, the films were deposited at various substrate temperatures ranging from 823 to 1023 K by keeping the other deposition conditions as constant. The deposition parameters used during the formation of LBMO thin films were given in Table 3.2.1.

Table 3.2.1: Deposition parameters of LBMO films during deposition.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposition method</td>
<td>electron beam evaporation</td>
</tr>
<tr>
<td>Power source</td>
<td>e-beam power supply (3 kW)</td>
</tr>
<tr>
<td>Target</td>
<td>( \text{La}<em>{0.7}\text{Ba}</em>{0.3}\text{MnO}_3 ) (10 mm dia and 3 mm thick)</td>
</tr>
<tr>
<td>Substrates</td>
<td>Si (100)</td>
</tr>
<tr>
<td>Target to substrate distance</td>
<td>50 mm</td>
</tr>
<tr>
<td>Ultimate pressure ((P_U))</td>
<td>(5 \times 10^{-6}) mbar</td>
</tr>
<tr>
<td>Evaporation pressure ((P_W))</td>
<td>(2 \times 10^{-4}) mbar</td>
</tr>
<tr>
<td>Substrate temperature ((T_s))</td>
<td>823 - 1023 K</td>
</tr>
<tr>
<td>Accelerating voltage</td>
<td>5 kV</td>
</tr>
<tr>
<td>Filament current</td>
<td>50 mA</td>
</tr>
<tr>
<td>Deposition time</td>
<td>15 min</td>
</tr>
</tbody>
</table>
3.2.1. Structural properties

Fig. 3.2.1 shows the XRD pattern of the LBMO films deposited at various substrate temperatures. All the films exhibited single phase and showed characteristics of a pseudocubic perovskite structure.

![X-ray diffraction patterns of LBMO films deposited at various substrate temperatures.](image)

The films deposited at a substrate temperature of 823 K showed a weak peak at $2\theta = 22.8^\circ$ corresponding to (100) orientation of LBMO. It was found that the intensity of (100) orientation was weak for the films grown at 823 K but increased with the increase of the substrate temperature. The films deposited at 823 K and 923 K showed small impurity phases near (200). These impurity phases disappeared when the substrate temperature was increased to 1023 K and a small peak at $2\theta = 31.76^\circ$ corresponding (110) orientation was appeared. The increased intensity of the (100) peak with increasing the substrate temperature 1023 K may be due to the increase in the size of grains. The lattice parameter of the films was also influenced by the substrate temperature. The lattice parameter of the films increased from 0.388 to 0.391 nm with increasing the substrate temperature from 823 to 1023 K. The variation in the lattice parameter with substrate
temperature was due to the stresses developed in the films. The stress developed in the films was obtained by the shift in the inter planar spacing hence change in the lattice parameter. In general, the atomic kinetic energy is mainly determined by the substrate temperature. At relatively higher temperature, the atoms on the film surface moved quickly towards the lowest energy sites and formed the low energy structure. As a result, the structural quality of the LBMO films deposited at higher substrate temperature was better than the films deposited at lower temperature. The crystallite size was determined for the (100) peak using Debye Scherer’s formula and was found to increase with the increase of the substrate temperature (Table 3.2.2) and the lattice parameter decreased with increasing the substrate temperature.

Table 3.2.2: Structural information of electron beam evaporated LBMO films at various substrate temperatures.

<table>
<thead>
<tr>
<th>Substrate temperature (K)</th>
<th>Lattice parameter (a) (nm)</th>
<th>Crystalline size (d) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>823</td>
<td>0.391</td>
<td>7.4</td>
</tr>
<tr>
<td>923</td>
<td>0.389</td>
<td>19.2</td>
</tr>
<tr>
<td>1023</td>
<td>0.388</td>
<td>34.5</td>
</tr>
</tbody>
</table>

When the substrate temperature increased from 823 to 1023 K, the crystalline size was increased from 7.4 nm to 34.5 nm. The increase in the crystalline size of the LBMO films deposited at a substrate temperature of 1023 K may be due to increase in the crystallinity of (100) peak. The average film thickness of all the deposited samples was around 100 nm.

3.2.2. Composition analysis

The EDS spectra of the LBMO films deposited at different substrate temperatures were shown in Figs. 3.2.2 – 3.2.4. From the figures, it was observed that the elements of La, Ba, and Mn were observed in the LBMO films without any impurities. The films grown at higher substrate temperatures (1023 K) showed the optimal stoichiometric ratio (La, Ba, Mn = 0.7, 0.3, 1).
Fig.3.2.2: EDS pattern of the LBMO film formed at 823 K.

Fig.3.2.3: EDS pattern of the LBMO film formed at 923 K.
3.2.4. EDS pattern of the LBMO film formed at 1023 K.

3.2.3. Surface morphology

Fig. 3.2.5: AFM image of LBMO film deposited at 823 K.
The surface morphology of the films was clearly altered by the substrate temperature. Figs.3.2.5-3.2.7 shows typical AFM images (in 3D and 2D) of LBMO thin films deposited on Si at 823 K, 923 K and 1023 K substrate temperatures.

An obvious improvement in grain size with the increase of the substrate temperature due to the enhanced mobility of atoms diffusing to lower energy sites on the surface was observed. The RMS values were found to be 1.7, 1.3 and 0.6 nm for thin films deposited at 823 K, 923 K and 1023 K respectively. The surface roughness was decreased with the increase of the substrate temperature. This indicates that the enhancement in adatom
mobility in higher substrate temperature deposited films reduced the surface roughness. These morphology results are nearly equal to the XRD results.

3.2.4. Electrical properties

The electrical resistivity of LBMO thin films has a strong dependence on the microstructural defects existing in LBMO crystallites. Fig.3.2.8. shows the electrical resistivity of LBMO films as a function of substrate temperature.

![Fig.3.2.8: Variation of electrical resistivity of LBMO films deposited different substrate temperatures.](image)

It was clear that the electrical properties of LBMO thin films were greatly affected by the substrate temperature. The films showed high electrical resistivity of 69.8 mΩcm at a substrate temperature of 823 K. The electrical resistivity of the films gradually decreased to 12.6 mΩcm with increasing the substrate temperature to 1023 K. The resistivity decreased with the increase of the substrate temperature and was explained using the Petritz barrier model [2]. According to this model, the crystallites do not grow sufficiently large at lower temperatures and the larger inter-crystalline regions offer high resistance for the movement of the charge carriers. At high substrate temperatures, the
formation of fewer nucleation centers result in larger crystallite size, which may ultimately decrease the inter-crystalline barriers, hence decreasing the electrical resistivity.

One of the main factors for the bolometric application is the temperature-coefficient of resistance (TCR) defined as \((1/R*(dR/dT)*100)\) %. The variation of TCR as a function of temperature is shown in Fig.3.2.9.

**Fig.3.2.9:** Temperature dependence of TCR of LBMO films deposited at different substrate temperatures.

The maximum values of TCR vary from 3.72 to 4.09%/K by varying the substrate temperature from 823 K to 1023 K respectively. The maximum value of TCR of 4.09%/K is obtained at a temperature around 295 K. Therefore, for bolometric applications, the LBMO based devices should be cooled at 295 K for better sensitivity. These values of TCR and operating temperature are relatively better than those obtained for the films grown by pulsed laser deposition (PLD) at different substrate temperatures [6]. It is useful to note that in commercially available bolometers based on VO\(_2\) or semiconducting YBCO, TCR values vary from 1.5 to 3% /K at room temperature [3-6]. The LBMO films showed a better TCR value nearer to the room temperature.
3.3. Effect of film thickness

In order to know the effect of film thickness on the properties of LBMO films, the films were prepared with different thickness ranging from 20 to 100 nm by varying the deposition time. The deposition parameters used during the formation of LBMO thin films were given in Table 3.3.1.

Table 3.3.1: Deposition parameters of LBMO films during deposition.

<table>
<thead>
<tr>
<th>Deposition method</th>
<th>electron beam evaporation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power source</td>
<td>e-beam power supply (3 kW)</td>
</tr>
<tr>
<td>Target</td>
<td>La$<em>{0.7}$Ba$</em>{0.3}$MnO$_3$(10 mm dia and 3 mm thick)</td>
</tr>
<tr>
<td>Substrates</td>
<td>Si (100)</td>
</tr>
<tr>
<td>Target to substrate distance</td>
<td>50 mm</td>
</tr>
<tr>
<td>Ultimate pressure (P$_U$)</td>
<td>5x10$^{-6}$ mbar</td>
</tr>
<tr>
<td>Evaporation pressure (P$_W$)</td>
<td>2x10$^{-4}$ mbar</td>
</tr>
<tr>
<td>Substrate temperature (T$_s$)</td>
<td>1023 K</td>
</tr>
<tr>
<td>Accelerating voltage</td>
<td>5 kV</td>
</tr>
<tr>
<td>Filament current</td>
<td>50 mA</td>
</tr>
<tr>
<td>Deposition time</td>
<td>3 – 15 min</td>
</tr>
<tr>
<td>Thickness</td>
<td>20 - 100 nm</td>
</tr>
</tbody>
</table>

3.3.1. Compositional analysis

The composition of the as grown films was analyzed by energy dispersive spectroscopy (EDS). The EDS spectra of the LBMO films deposited at different thicknesses were shown in Figs.3.3.1-3.3.3. From the figures, it was observed that the elements of La, Ba, Mn and O were observed in the LBMO films without any impurities. All the deposited films showed nearly stoichiometric ratio.
Fig.3.3.1: EDS spectra of the LBMO film with 20 nm thickness.

Fig.3.3.2: EDS spectra of the LBMO film with 60 nm thickness.
3.3.2. Structural properties

X-ray diffraction patterns of LBMO films formed at various thicknesses were shown in Fig.3.3.4.

Fig.3.3.3: EDS spectra of the LBMO film with 100 nm thickness.

Fig.3.3.4: X-ray diffraction patterns of LBMO films deposited at different thicknesses.
The essential characteristic of a thin film is its thickness. Since the physical properties, especially the structural and electrical properties are dependent on the thickness of film, it is important to know the effect of this parameter with the highest possible accuracy. Fig.3.3.4 shows XRD reflection peaks of LBMO thin films with thickness ranging from 20 to 100 nm. The main phase of the film was characterized in a cubic perovskite structure. The crystallinity of LBMO films was clearly improved with the increase in the film thickness. Therefore, thickness of LBMO film is an important parameter which affects on the crystallinity of LBMO films. At lower thickness (20 nm) two small peaks at angle $2\theta = 22.7^\circ$ and $46.8^\circ$ were observed and related to the (1 0 0), (2 0 0) reflections respectively. When the thickness increased from 20 to 60 nm, same peaks were observed with increased intensity and beyond this thickness a new peak of (1 1 0) was observed. Due to the surface confinement in ultra-thin material, the crystallization process as LBMO film grows is likely to be retarded, which resulted in lower crystallinity. The hump at lower film thickness may be due to interactions of the X-rays with the underlying substrate material. The position of the diffraction peaks is independent of the film thickness; however preferential orientation improves with film thickness. The improvement in the peak intensity may be due to better alignment of crystallites with the increase in thickness. The large thickness may provide sufficient space for the thermal motion of particles; which may in turn helps for better alignment of crystallites. This causes an improvement in crystallinity with increase in film thickness. The observed XRD data were indexed by matching with the data available for LBMO. Grain or cluster sizes were determined using the Scherrer formula. Changes in the crystallite size and lattice parameter with respect to thickness are tabulated in Table 3.3.2. When thickness increased from 20 to 100 nm, the lattice parameter increased from 0.385 to 0.388 nm respectively, due to the angle relaxation which is the predominant process for relieving the strain from the substrate and weakening of tensile strain in the films, and the film lattice parameter nearly equal to LBMO bulk lattice parameter. From the preferred orientation of (100), the crystallite size values were found increase to 6.1 to 34.5 nm with increased thickness from 20 to 100 nm.
Table 3.3.2: Crystallite size and lattice parameter of the LBMO films with different thickness.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>Crystallite size d (nm)</th>
<th>Lattice parameter (a) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>6.1</td>
<td>0.385</td>
</tr>
<tr>
<td>60</td>
<td>16.9</td>
<td>0.387</td>
</tr>
<tr>
<td>100</td>
<td>34.5</td>
<td>0.388</td>
</tr>
</tbody>
</table>

3.3.3. Surface morphology

The influence of film thickness on the surface morphology of LBMO films was examined by the AFM (Figs.3.3.5-3.3.7). The AFM micrograph shows the features of structural change and grain growth for LBMO films for different thicknesses ranging from 20 to 100 nm. Root mean square surface roughness values were determined on an area of (3 × 3) µm². The AFM picture of the film grown for a thickness of 20 nm consisted of smaller crystallites that are uniformly distributed. The surface morphology of the films with thicknesses 20 and 60 nm showed a nearly similar structure. But at higher thicknesses (100nm), a significant improvement in the grain size took place. At the initial stages of the film growth, there were many nucleation centers present on the substrate surface. For a constant rate of deposition, the deposition time is very short for thinner films when compared to the thicker films. The small crystallites cannot grow into larger ones in thinner films due to the shorter deposition time, and hence the thinner films have small crystallites. With the increase of film thickness, coalescence of the small grains took place, leading to the formation of bigger crystallites in the film along with an improved crystallinity as observed from the XRD analysis. The grain size evaluated from AFM measurements varied in the range 7.4 - 35.7 nm with the increase of film thickness from 20 to 100 nm, and nearly matched the grain size evaluated from the XRD measurements.

Further-more, the root-mean-square (RMS) roughness on the surface of the films having thickness of 20, 60, and 100 nm were obtained as 2.7, 1.8, and 0.6 nm respectively. The change of roughness is associated with the change of grain size. As the
grains grew bigger, the density of grain boundaries decreased and the grain growth took place with a large variation in the height of the grains on the film surface. Therefore, it is apparent that the thickness of the film changes the grain size as well as the surface roughness. A similar changes of surface roughness with the change of film thickness was also reported by Ng et al in sputtered Ni$_{80}$Fe$_{20}$ films grown on Si substrates [7].

Fig.3.3.5: AFM images of the LBMO film with 20 nm thickness.

Fig.3.3.6: AFM images of the LBMO film with 60 nm thickness.
3.3.4. Electrical properties

The variation of resistivity of the LBMO films with different thickness is shown in Fig.3.3.8. The resistivity increases as the film thickness increases as a function of temperature and the transition temperature decreases. With increasing the thickness from 20 to 100 nm, the transition temperature (Tp) decreases from 303 K to 290 K. It is also observed that there is a clear change of resistivity values with increasing film thickness.

![Graph showing variation of resistivity with temperature for different film thicknesses.](image)

**Fig.3.3.8:** Variation of resistivity of LBMO films by different thickness as a function of temperature.
This change of the electrical resistivity values may be attributed mainly to three different contributions due to: (a) micro structural defects, (b) increase of the crystalline degree, and (c) the scattering of charge carrier by the film surface and composition. Fig. 3.3.8 shows resistivity versus temperature curves of LBMO/Si with thickness from 20 nm to 100 nm. The insulator to metal transition temperature (Tp) of the thinnest sample (20 nm) is the highest at room temperature. As the thickness of the sample increases, the Tp decreases and the resistivity increases. At lower thickness the Tp is the highest, nearly 303 K, when the thickness increases the Tp of film decreases. The resistivity of LBMO films shows a strong relation to the peak temperature.

The enhanced electrical properties of LBMO thin films on a Si substrate is well explained by double exchange theory which predicted that the epitaxial strain of the lattice by the substrate reduced the static Jahn-Teller distortion and increased the double exchange interaction. As the film thickness increases, the strain created relax and consequently an enhancement of the static Jahn-Teller, so the resistivity of the films increase as the films grows thicker. As the films grow thicker, the electrical behavior of these films tend to become similar with that of their bulk materials due to the relaxation of strain effect on the thin films. Similar behavior was also observed in magnetron sputtered LBMO/LAO films [8].

For bolometric applications, the TCR is an important parameter that should be controlled. A high TCR implies high bolometric device efficiency. The TCR of the LBMO thin films grown on the Si substrates was calculated as TCR=(1/R*(dR/dT)*100)%. The behavior of the TCR as a function of temperature for different film thicknesses is shown in Fig. 3.3.9. As seen, the TCR decreased with increasing the film thickness. The maximum values of the TCR value is high at lower thickness, when the thickness of the LBMO film increased, the TCR value decreased. The maximum values of the TCR were 4.09, 4.32 and 5.12%/K for the 100, 60 and 20 nm respectively. We conclude that the measured resistivity value of 100 nm was higher than the 20 nm thin film. Similar behavior observed by Touyama et al. [9] was reported previously; the technique was used pulsed laser deposition (PLD) on SrTiO$_3$ substrates. The compositional changes may be caused the drastic resistivity change and widened the transition area 60 nm samples. As a result, the TCR were enhanced.
Fig. 3.3.9: Variation of TCR of LBMO films by different thickness as a function of temperature.
3.4. Effect of annealing temperature

In order to know the effect of annealing temperature on the properties of LBMO films, the films were annealed at different annealing temperatures. The deposition parameters used during the formation of LBMO thin films were given in Table 3.4.1.

**Table 3.4.1: Deposition parameters of LBMO films during deposition.**

<table>
<thead>
<tr>
<th>Deposition method</th>
<th>electron beam evaporation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power source</td>
<td>e-beam power supply (3 kW)</td>
</tr>
<tr>
<td>Target</td>
<td>La₀.₇Ba₀.₃MnO₃(10 mm dia and 3 mm thick)</td>
</tr>
<tr>
<td>Substrates</td>
<td>Si (100)</td>
</tr>
<tr>
<td>Target to substrate distance</td>
<td>50 mm</td>
</tr>
<tr>
<td>Ultimate pressure (P_U)</td>
<td>5x10⁻⁶ mbar</td>
</tr>
<tr>
<td>Evaporation pressure (P_W)</td>
<td>2x10⁻⁵ mbar</td>
</tr>
<tr>
<td>Substrate temperature (T_s)</td>
<td>773 K</td>
</tr>
<tr>
<td>Accelerating voltage</td>
<td>5 kV</td>
</tr>
<tr>
<td>Filament current</td>
<td>50 mA</td>
</tr>
<tr>
<td>Deposition time</td>
<td>15 min</td>
</tr>
<tr>
<td>Annealing temperature</td>
<td>873 – 1173 K</td>
</tr>
</tbody>
</table>

3.4.1. Compositional analysis

The composition of the as grown films was analyzed by energy dispersive spectroscopy (EDS). The EDS spectra of the LBMO films annealed at different annealing temperatures were shown in Figs.3.4.1-3.4.3. From the figures, it was observed that the elements of La, Ba, Mn and O were observed in the LBMO films without any impurities. All the deposited films showed nearly stoichiometric ratio.
Fig. 3.4.1: EDS pattern of the LBMO film annealed at 873 K.

Fig. 3.4.2: EDS pattern of the LBMO film annealed at 1023 K.
3.4.2. Structural properties

Thermal annealing is one of the most important factors, since annealing temperature can improve the crystal quality and reveal structural defects in thin films. Fig.3.4.4 shows the XRD patterns of as grown film and films annealed at various temperatures. Generally, annealing increases atomic mobility, enhancing the ability of atoms to find the most energetically favoured sites; on the other hand, with the increase of the annealing temperature, the densities of the crystallographic defects including dislocations, interstitials in the LBMO thin films decreased. It was observed that all the films exhibited pseudocubic structure. All the films were annealed for 1 h. By increasing the annealing temperature from 873 to 1173 K, we noticed an increase of the (100), (110) and (200) peak intensities (Fig.3.4.4), indicating a probable improvement of the films crystallinity. The 2θ shifts towards higher angle with increasing annealing temperature. It was found that, with increasing annealing temperature, the full-width at half-maximum (FWHM) becomes smaller, which is evidence for the improvement of the crystal quality. The XRD pattern of the film annealed at 873 K exhibited a low crystallinity which is probably due to an important amount of the amorphous phase.
increasing the annealing temperature, the amorphous film is being converted to an epitaxial phase of LBMO. The percentage of the amorphous phase could play an important role in the transport properties. The out-of-plane parameters can be determined from the symmetric XRD $\theta$–$2\theta$ scans.

![X-ray diffraction patterns of LBMO films annealed at different temperatures.](image)

**Fig.3.4.4:** X-ray diffraction patterns of LBMO films annealed at different temperatures.

The average crystallite size is increased with increasing annealing temperature revealing a fine nanocrystalline grain structure. Generally, the crystallite size depends on the annealing temperature [10].

The changes in the lattice parameter, grain size and stress of the LBMO films as a function of annealing temperature were given in Table 3.4.2. With increasing the annealing temperature from 873 to 1173 K, the grain size increases from 8 to 38 nm. This indicates an improvement in the crystalline nature of the film with increase of annealing temperature. By increasing the annealing temperature from 873 to 1173 K, the calculated lattice parameter of the LBMO film increases slowly from 0.385 to 0.392 nm. The growth of granules with the increase of annealing temperature promotes the reduction of the number of non-bridging oxygen type defects favoring the formation of the LBMO grains.


### Table 3.4.2: Crystalline size, lattice parameter values of LBMO thin films annealed at different temperatures.

<table>
<thead>
<tr>
<th>Annealing temperature (K)</th>
<th>Crystalline size (d) (nm)</th>
<th>Lattice parameter (a) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>873</td>
<td>8</td>
<td>0.385</td>
</tr>
<tr>
<td>1023</td>
<td>18</td>
<td>0.389</td>
</tr>
<tr>
<td>1173</td>
<td>38</td>
<td>0.393</td>
</tr>
</tbody>
</table>

**3.4.3. Surface morphology**

The surface morphology of the films clearly altered with the annealing temperature. Figs. 3.4.5-3.4.7 shows the surface morphology of LBMO thin films annealed at different temperatures (873, 1023 and 1173 K) on Si substrates. It is evident that different surface morphologies are evolved relying on temperature during the annealing process. It was clearly seen that both the RMS roughness and grain size of the films increased as the annealing temperature increases. The increase of roughness with increasing the annealing temperature was due to increase of grain size. The density of grain boundaries decreased and the grain growth took place with a large variation in the height of the grains on the films surface[11, 12]. From the AFM images, we can conclude that the quality of the thin film annealed at 1173 K was the highest.
Fig. 3.4.5: AFM images of the LBMO film annealed at 873 K.

Fig. 3.4.6: AFM images of the LBMO film annealed at 1023 K.
3.4.4. Electrical properties

The electrical resistivity of LBMO thin films has a strong dependence on the microstructural defects and grain size. It was clear that the electrical properties of LBMO thin films were greatly affected by annealing temperature. The films showed high electrical resistivity of 34.8 mΩ cm at annealing temperature (873 K). The electrical resistivity of the films decreased to 6.3 mΩ cm with increasing the annealing temperature to 1173 K. Fig. 3.4.8 shows the temperature dependence of resistivity for the films annealed at different temperatures.
Fig. 3.4.8: Variation of electrical resistivity of LBMO films annealed at different temperatures.

The films annealed at 1173 K shows the lower resistivity at the transition temperature (Tp). The increase of the transition temperature and the decrease in the resistivity under annealing is not surprising, since it is well known that this conventional treatment can often improve the microstructure and the electrical transport properties of the film [13,14]. This decrease in electrical resistivity was due to the increase in crystallite size, decrease in grain boundary density and increase in the mobility of the films.

The temperature coefficient of resistance (TCR), which is a significant quantity characterizing the electrical transport of CMR manganites, is a key figure of merit for uncooled or moderately cooled infrared imaging (bolometric) applications, and is calculated by TCR = \((1/R*(dR/dT)*100)\)% . Achieving high TCR values at room temperature is the ultimate goal for bolometric application.

The temperature dependence of the TCR for films annealed at different temperatures is plotted in Fig. 3.4.9. In the film annealed at 873, the TCR (TCRmax) is 3.5% /K at 260 K, and shifts to 5.14%/K at 295 K by increasing the annealing
temperature to 1173 K and it is nearer to room temperature. In general, higher TCR values are obtained at low temperatures in CMR materials, such as La$_{0.67}$Ca$_{0.33}$MnO$_3$ (8% at 250 K) and Nd$_{0.7}$Sr$_{0.3}$MnO$_3$ (11% at 200 K) [15]. High Curie temperature with a low TCR value is achieved in La$_{0.67}$Sr$_{0.33}$MnO$_3$ (2% at 327 K) [16]. However, a higher TCR max value of 5.4% /K was observed at 296 K for the films annealed at high temperatures. This means that bolometric devices based on such LBMO films can operate at room temperature.

![Variation of TCR of LBMO films annealed at different temperatures.](image)

*Fig.3.4.9: Variation of TCR of LBMO films annealed at different temperatures.*

The TCR value of the films annealed at 1173 K is significantly higher than that of other bolometric materials such as amorphous silicon germanium alloys (SiGe, −1.8% /K), vanadium oxide (VOx , −1.7% /K) and YBa$_2$Cu$_3$O$_{7-x}$ superconducting materials (−3.2% /K).

3.5. Effect of Substrates
In order to study the effect of substrate material on the properties of LBMO thinfilms, the films were depositedon different substrates such as silicon, MgO and c-ZrO₂, keeping theotherdeposition conditions constant. The deposition parameters maintained during the formation of LBMO thin films were given in Table 3.5.1.

**Table 3.5.1: Deposition parameters of LBMO films during deposition.**

<table>
<thead>
<tr>
<th>Deposition method</th>
<th>electron beam evaporation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power source</td>
<td>e-beam power supply (3 kW)</td>
</tr>
<tr>
<td>Target</td>
<td>La₀.₇Ba₀.₃MnO₃(10 mm dia and 3 mm thick)</td>
</tr>
<tr>
<td>Substrates</td>
<td>Si (100), MgO (100) and c-ZrO₂</td>
</tr>
<tr>
<td>Target to substrate distance</td>
<td>50 mm</td>
</tr>
<tr>
<td>Ultimate pressure (PU)</td>
<td>5x10⁻⁶ mbar</td>
</tr>
<tr>
<td>Evaporation pressure (PW)</td>
<td>2x10⁻⁴ mbar</td>
</tr>
<tr>
<td>Substrate temperature (Ts)</td>
<td>1023 K</td>
</tr>
<tr>
<td>Accelerating voltage</td>
<td>5 kV</td>
</tr>
<tr>
<td>Filament current</td>
<td>50 mA</td>
</tr>
<tr>
<td>Deposition time</td>
<td>15 min</td>
</tr>
</tbody>
</table>

**3.5.1. Structural properties**

The X-ray diffraction patterns of the films formed on different substrates were shown in Fig.3.5.1. The peaks in the spectra of LBMO thin films deposited on Si, MgO and c-ZrO₂ substrates confirm the pseudocubic structure. The absence of impurity peaks in the XRD patterns of all the films indicates that the films are single phase. The films prepared on Si substrate exhibited (100), (110) and (200) preferred orientations. The films prepared on c-ZrO₂ substrate exhibited (100) and (200) orientations and the films prepared on MgO substrate exhibited (100), (111), (200) and (211) orientations.
Furthermore a small angular shift of the (100) and (200) peaks is observed with changing substrates. On MgO substrate additional peaks belonging to LBMO are observed. The crystallinity of LBMO films determined from the full width at half maximum (FWHM) values of (200) diffraction peak. Since FWHM is one of the measurements of crystallinity, smaller FWHM values indicate the higher crystalline films. The values of grain sizes given in Table 3.5.2 are found to be in the range from 28 to 39 nm. It is observed that the smallest one corresponds to the LBMO thin films deposited on c-ZrO₂ substrate.

![X-ray diffraction patterns of LBMO films deposited on different substrates.](image)

Fig.3.5.1: X-ray diffraction patterns of LBMO films deposited on different substrates.

The lattice parameter of LBMO films formed on Si, MgO and c-ZrO₂ are 0.388, 0.392 and 0.387 nm respectively. Electronic properties of thin epitaxial films are influenced by the nature of the substrate which largely controls the film growth morphologies, defect structure and the level of stress. In general, if the difference between the lattice parameters of the film and substrate is within 1±2%, film growth takes place in a layer by layer mode accommodating the difference through expansion or contraction of the in-plane lattice parameter. However, if the difference in the lattice parameter is significantly large, an island-type growth starts at the beginning of film deposition.
lattice parameter of bulk $\text{La}_{0.7}\text{Ba}_{0.3}\text{MnO}_3$ is 0.391 nm, whereas for the cubic crystals of Si, MgO, and c-ZrO$_2$ it is 0.5431, 0.4312 and 0.5214 nm respectively. The crystallite size and lattice parameter of the LBMO films are given in Table 3.5.2.

Table 3.5.2: Crystalline size and lattice parameter values of LBMO thin films formed on different substrates.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Orientation (hkl)</th>
<th>Crystalline size (d) (nm)</th>
<th>Lattice parameter (a)(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(100)</td>
<td>(200)</td>
<td>34.5</td>
<td>0.388</td>
</tr>
<tr>
<td>MgO(100)</td>
<td>(200)</td>
<td>39</td>
<td>0.394</td>
</tr>
<tr>
<td>c-ZrO$_2$</td>
<td>(200)</td>
<td>28</td>
<td>0.387</td>
</tr>
</tbody>
</table>

3.5.2. Compositional analysis

The composition of the as LBMO films deposited on different substrates was analyzed by energy dispersive spectroscopy (EDS) and shown in Figs. 3.5.2-3.5.4. From the figures, it was observed that the elements of La, Ba, Mn and O were observed in the LBMO films without any impurities. All the deposited films showed nearly stoichiometric ratio.
Fig. 3.5.2: EDS pattern of the LBMO film deposited on Si substrate.

Fig. 3.5.3: EDS pattern of the LBMO film deposited on MgO substrate.
Fig. 3.5.4: EDS pattern of the LBMO film deposited on c-ZrO$_2$ substrate.

3.5.3. Surface morphology

Fig. 3.5.5: AFM image of the LBMO film deposited on Si substrate.
Figs. 3.5.5-3.5.7 show the AFM images of the LBMO thin films deposited on Si, MgO and c-ZrO₂ substrates. The mean roughness (RMS) of the surfaces is calculated for a 3 μm² scan area. It was clearly seen that both the RMS roughness and grain size of the films changed with substrate. It is found that the mean roughness of films deposited on Si, MgO and c-ZrO₂ is 0.6, 3.4 and 4.9 nm respectively. It is known that the change in surface roughness may cause deterioration of the electrical properties. These results,
together with the XRD analysis, clearly indicated that the crystallinity is influenced by the nature of substrates.

3.5.4. Electrical properties

The electrical resistivity of LBMO thin films depend on the microstructural and lattice mismatch between the substrate and films. It is also observed that there is a clear change of resistivity values with changing the substrate material. The films showed high electrical resistivity of 27.8 mΩ cm when deposited on c-ZrO₂ and low electrical resistivity of 4.37 mΩ cm for the films deposited on MgO substrate. Fig. 3.5.8 shows the temperature dependence of resistivity for the films deposited on different substrates. The electrical resistivity for LBMO films deposited on MgO substrate has lower resistivity with low transition temperature, whereas LBMO films deposited on Si substrate, exhibited high transition temperature nearer to the room temperature.

![Fig.3.5.8: Variation of electrical resistivity of LBMO films deposited on different substrates.](image)
In Fig.3.5.9 we plotted the TCR as a function of temperature for the films deposited on Si, MgO, and c-ZrO$_2$ substrates. The TCR values are; 5.32% /K at 245 K for the MgO sample; 4.09%/K at 295 K for the Si sample, and; 3.2%/K at 268 K for c-ZrO$_2$ sample.

Fig.3.5.9: Temperature dependence of TCR of LBMO films deposited on different substrates.

From the above result we conclude that the films deposited on MgO have high TCR value with low transition temperature, but our aim is uncooled bolometers. By comparing the above result, we observed that the films deposited on Si substrate are useful for uncooled bolometer operations.
References

[1] R. Kumar, A.K. Gupta, V. Kumar, G.L. Bhalla, and N. Khare,

[2] R.L. Petritz,


R. Sobolewski,


[8] Soong, and Ngai-shek,
The University of Hong Kong (Pokfulam, Hong Kong)b2663683 (2002).

102504.

[10] A.F. Khan, M. mehmood, A.M. Rana, and T. Muhammad,


T. Venkatesan, R. Hiskes, and J.L. MacManus-Driscoll,

