Effect of oxygen pressure on the structural and optical properties of BaSnO₃ films prepared by pulsed laser deposition method

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Abstract
BaSnO₃ thin films were deposited on quartz substrate by pulsed laser deposition technique under different background oxygen pressures and the effects of oxygen pressure on the structural, morphological and optical properties of BaSnO₃ thin films are systematically investigated using different characterization techniques. The BaSnO₃ films deposited without and with oxygen pressures are polycrystalline in nature with cubic crystalline phase. Moderate oxygen ambience favors enhanced crystallinity of the BaSnO₃ films and 0.02 mbar is found to be optimum oxygen pressure for highest crystallinity. The surface morphology of the deposited films was strongly affected by the oxygen pressure in the deposition chamber. A systematic increase of film thickness and decrease of RMS surface roughness is observed with increase in oxygen pressure. XPS analysis reveals that barium is in the +2 oxidation state and Sn is in the +4 oxidation state in the film deposited at optimum oxygen pressure of 0.02 mbar. The deposited BaSnO₃ films have photoluminescence emissions in the visible region and have high transmittance in the visible and infrared regions. The BaSnO₃ films deposited at oxygen ambience shows a blue shift in the optical band gap. The optimized film shows high crystallinity, high value of transmittance and wide band gap energy which indicates its suitability for optoelectronic devices.

1 Introduction
Perovskites with the general formula MSnO₃ (M = Ba, Sr, Ca and Pb) have found wide variety of applications [1] in the field of optoelectronic devices. Barium stannate (BaSnO₃) is a cubic perovskite oxide compound [2] that behaves as an n-type semiconductor [3] with a wide band gap of 3.4 eV [3–6]. BaSnO₃ has three-dimensional framework of corner-sharing SnO₆ octahedra, having a linear Sn–O–Sn bonding angle 180° with ideal cubic Pm3m space group [7]. By doping, with suitable dopant materials, the properties of the BaSnO₃ can be modified in a wide range due to its high substitutional flexibility [8, 9]. BaSnO₃ is used to prepare capacitors because of its characteristic dielectric properties [10]. It is also used as a sensor material for a wide variety of gases, such as CO, Cl₂, NOₓ, O₂, CO₂, C₂H₅OH, CH₃SH and sensing humidity and liquefied petroleum gas [11, 12]. The preparation of BaSnO₃ powder by conventional solid state reaction through sintering BaCO₃ and SnO₂ at a high temperature ranging from 1200 to 1400 °C was reported [13, 14]. BaSnO₃ is a good material for future oxide electronic devices due to its high electron mobility up to 320 cm²V⁻¹ s⁻¹ in bulk single crystal [15]. It is reported that at room temperature La-doped BaSnO₃ has mobility of 183 cm²V⁻¹ s⁻¹ in epitaxial thin films and has high optical transparency in the visible region [16]. Zhao et al. [17] reported that the addition of hydrogen in the BaSnO₃ thin film at 300 K increases the conductivity carrier concentration and mobility of the films. Therefore, BaSnO₃ is a suitable material for high-mobility channels in transistors, solar cells, etc. There are various methods for the deposition of BaSnO₃ thin films such as RF sputtering [18], molecular beam epitaxy [19], pulsed laser deposition (PLD) [20], etc.

The PLD is a simple and unique technique which can be used to prepare good quality films from a large amount of materials and compounds. In this method, one can vary substrate temperature, background pressure, substrate to
target distance, laser fluence, etc. PLD has many advantages over the other deposition methods because of stoichiometry, crystallinity of the deposited material, their adherence to the substrate surface and the growth of films in different atmospheres during deposition. The preparation of lanthanum-doped BaSnO$_3$ film with substrate temperature 850 °C and oxygen partial pressure 1 × 10$^{-3}$ Torr using pulsed laser deposition is reported by Sallis et al. [20]. Febvrier et al. [21] reported the effect of oxygen pressure on the structural, optical and dielectric properties of Bi$_{1.5}$−$x$Zn$_{0.92}$−$y$Nb$_{1.5}$O$_{6.92−δ}$ thin films deposited by PLD on R-plane sapphire and LaAlO$_3$ substrates. They found that when pressure decreases, the lateral grain size increases from 37 to 77 nm and from 45 to 80 nm on sapphire and LaAlO$_3$ substrates, respectively. Zahra Saroukhani et al. [22] reported the effect of oxygen pressures of Ba$_{0.6}$Sr$_{0.4}$TiO$_3$ thin film on the SiO$_2$/Si substrate by the pulsed laser deposition (PLD) technique. Mizoguchi et al. [23] reported that the electrical conductivity of Sb-doped BaSnO$_3$ increases with increasing Sb doping concentration, showing a transition from insulating state to metallic state. Wang et al. [24] reported that the Sb-doped and La-doped BaSnO$_3$ films on SrTiO$_3$ substrates by PLD have perovskite structure and show high conductivity and high optical transmittance in the visible range. Liu et al. [25] deposited BaSnO$_3$ films on MgO substrates by PLD for various oxygen pressures ranged from 20 to 0.03 Pa. They observed that high conductivity and high transparency in visible range at low growth oxygen pressure. The heteroepitaxial deposition of La-doped BaSnO$_3$ and BaSnO$_3$ films on SmScO$_3$ and SrTiO$_3$ substrates by PLD in optimized deposition conditions is reported by Wadekar et al. [26]. They found superior electrical properties on SmScO$_3$ substrate and is due to the reduction in dislocation density from the lower lattice mismatch. During the film deposition the charge carriers generated in the substrate helps to cause changes in the electrical properties and band gap tuning of the films [27]. Zhang et al. [28] reported the effect of oxygen pressure on BaTiO$_3$ films in SrTiO$_3$ substrates and found that orientation, morphology and lattice parameter can be controlled by varying the oxygen pressure. Heterogeneous morphology of SrSnO$_3$ thin films on R-sapphire and SrTiO$_3$ substrates was reported by Alves et al. [29]. BaSnO$_3$ is a good candidate for optoelectronic applications in solar cells, gas sensors and optical devices due to high carrier concentration and wide band gap [30].

Although there are enough works on the effect of oxygen pressure on various perovskites deposited on various substrates, the effect of oxygen ambience on the properties of laser-ablated BaSnO$_3$ thin films deposited on quartz substrate was not observed. Therefore, the study on the properties of the laser-ablated BaSnO$_3$ thin films prepared with and without oxygen ambience is important from the scientific point of view. The crystallization and microstructure of the films depend on the deposition parameters in the chamber. During pulsed laser deposition in a reactive gas atmosphere such as oxygen, the hydrodynamic interaction between the plume and the background gas helps to attain the same composition to that of the target [31]. The effect of oxygen pressure can alter the charge carrier concentration, oxygen vacancy, transmittance and bandgap of the developed thin films. The type of polycrystalline or epitaxial growth of films is determined by the nature of the substrate and it affects the microstructural properties of the film [32]. The polycrystalline and epitaxial thin films with different microstructures can be obtained by selecting the suitable substrates. Even though many authors reported the properties of BaSnO$_3$ thin films on MgO, Si, LaAlO$_3$, SrTiO$_3$ substrates, but the study on the properties of BaSnO$_3$ thin films deposited on quartz substrate has not yet been reported. Quartz has high working and melting temperatures. Quartz has extremely low thermal expansion coefficient and has ability for rapid changing of temperature without cracking. We have used quartz as the substrate for depositing the BaSnO$_3$ thin films as they can withstand high annealing and substrate temperatures. High temperature annealing is needed in some cases to improve crystallinity of the prepared BaSnO$_3$ thin films. The film prepared at 0.02 mbar has the highest crystallinity and has high transmittance in the visible and infrared region and hence it can be used for various optoelectronic applications.

2 Experiment

BaSnO$_3$ powder was prepared by the conventional high temperature solid state method [14, 33]. High quality (purity-99.99%, Sigma) BaCO$_3$ and SnO$_2$ powders are mixed in stoichiometric ratio and the mixture was ground well in an agate mortar for 6 h using acetone as the mixing agent. The grind powder taken in a platinum crucible was heated in a microprocessor programmable furnace for 6 h at a temperature of 1250 °C. During heating the rate of rise of temperature was kept at 5°C/min. After heating, the powder was cooled to room temperature naturally. The phase purity of the BaSnO$_3$ powder thus prepared was analyzed by the X-ray diffraction pattern and micro-Raman spectrum. The BaSnO$_3$ powder thus prepared was well-ground in an agate mortar and poly vinyl alcohol was added to the mixture as the binding agent. Pellets of 3 mm diameter and 1 mm thickness were prepared from the BaSnO$_3$ powder in a hydraulic press by applying pressure of 8 ton and the pressed pellet was sintered at temperature of 1000 °C for 6 h in a programmable furnace. The well-sintered pellet thus prepared is used as the target for film preparation. The deposition of BaSnO$_3$ films was done in a multiport chamber which was pre-evacuated to a base pressure of 10$^{-6}$ mbar using a turbo molecular pump and a rotary pump. The ablation of target
was carried out using a laser radiation at 355 nm wavelength of pulse width 7 ns and repetition frequency of 10 Hz from a Q switched (frequency tripled) Nd:YAG laser (Quanta Ray INDI Series-Spectra Physics). Cleaned quartz substrate kept at distance of 4.5 cm from the target was heater at a temperature of 600 °C. The films are fabricated on heated substrate for a deposition time of 45 min using a laser energy of 60 mJ at different back ground oxygen pressures, viz 0, 0.01, 0.015, 0.02, 0.025 and 0.03 mbar. To maintain uniform ablation during film preparation, the target was rotated (speed 33 rpm). All the films are annealed at temperature of 700 °C for 1 h. The film prepared without oxygen ambience is designated as BS 0 and the films prepared with background oxygen pressures 0.01, 0.015, 0.02, 0.025 and 0.03 mbar are designated as BS 0.01, BS 0.015, BS 0.02, BS 0.025 and BS 0.03, respectively.

Crystalline structure of the BaSnO₃ films was characterized by XPERT PRO diffractometer in the 2θ range 20–80° using Cu-Kα radiation of wavelength 1.5406 Å in Bragg–Brentano geometry. The measurements were carried out with a step size of 0.04000 and a scan speed of 2° min⁻¹ was maintained. Surface morphology of the films was analyzed using atomic force microscopy (AFM) and scanning electron microscopy (SEM) at nanometric scale using Bruker, Dimension Edge with Scan Assist in contact mode and Nova Nano SEM-450 Field Emission Scanning Electron Microscope (FEI-USA), respectively. The thickness of the films was measured using lateral SEM analysis. Photoluminescence spectra of the films were recorded using Horiba JobinYvonFlourolog III modular spectrofluorometer equipped with Xe-flash lamp using an excitation wavelength of 350 nm. The optical absorption, transmission spectroscopic measurements of all the films were performed in the wavelength range of 2300–250 nm using Perkin Elmier spectrophotometer. The surface composition and elemental analysis were done using X-ray photoelectron spectrometer (XPS) ESCALABX1 + A1528 using advantage software. The beam source used for the XPS measurements was aluminum Kα radiation.

3 Results and discussion

3.1 XRD analysis

XRD patterns of the laser-ablated BaSnO₃ films are shown in Fig. 1, which indicate the polycrystalline nature of the films and all the XRD pattern present peaks corresponding to cubic BaSnO₃ crystalline phase (JCPDS file 00-015-0780) [34]. The XRD pattern of BS 0 film presents two high intense peaks at 2θ values 30.76° and 44.04°, a medium intense peak at 54.67° and weak peak at 2θ value 72.72°. These peaks can be indexed to lattice planes (110), (200), (211) and (310) of cubic BaSnO₃ crystalline phase, respectively. In addition to these four peaks, a medium intense peak at 2θ value 64.05° corresponding to (220) lattice plane of cubic phase can be seen in the XRD patterns of the films prepared under background oxygen. In films prepared under background oxygen pressure (ρO₂), the intensity of (110) peak shows a systematic increase with increase in ρO₂ up to 0.02 mbar and thereafter the intensity of the peak decreases with increase in ρO₂ (Fig. 2a). The β(hkl), Full Width at Half Maximum (FWHM), of the (110) peak is estimated from the XRD data and are given in Table 1 and for the BS 0 film its value is 0.262°. The value of β(hkl) of (110) peak shows a systematic decrease with increase in background oxygen pressure up to ρO₂ = 0.02 mbar and thereafter the value of β(hkl) of this peak increases with increase in back ground oxygen pressure. From this it can be inferred that moderate oxygen ambiene will be helpful in getting good crystalline BaSnO₃ film and the film prepared at ρO₂ = 0.02 mbar possesses the highest crystalline quality. The improvement in the crystalline nature of BaSnO₃ thin films with and without oxygen pressure is similar to that reported by Chen et al. [35]. They have described the interactions of species in the plume such as plasma with oxygen. When the BaSnO₃ films were deposited in an oxygen free ambience (BS 0 film), the species ejected from the target can have large mean free path and they will arrive with little active interaction on the substrate surface and hence the crystallization was suppressed [36]. In the presence of oxygen ambiene in the chamber, the mean free path of the species ablated from the BaSnO₃ target gets reduced and it will react with oxygen which can lead to heat generation and redistribution of energy. This will result in the migration and the formation of crystallization of the species on the substrate in the chamber. Therefore, when the oxygen ambiene is increased, the species which is ablated from the target has shorter mean free path and it results in the better quality of the films. When the oxygen ambiene was further increased, excessive collisions between the species and oxygen will cause energy loss and do not have sufficient energy to undergo surface diffusion [35]. This results in the decrease of the crystallinity of the BaSnO₃ films. Thus, the highly crystalline BaSnO₃ films can be prepared by optimizing the oxygen pressure during the deposition in the chamber. From the XRD patterns of the films, it can be seen that as ρO₂ increases, both (110) and (200) peaks show large intensity enhancement up to ρO₂ = 0.02 mbar. The relative intensities, I(110) and I(200) of the peaks (110) and (200) for the films prepared under background oxygen pressure with respect to those values in BS 0 films are estimated and are plotted in Fig. 2b.

The average size of the crystallites (Dhkl) of the films can be calculated using the Debye–Scherrer’s formula [37]:

\[
D_{hkl} = \frac{k\lambda}{\beta_{hkl}\cos\theta_{hkl}},
\]  

(1)
where $\lambda$ is the wavelength of the X-ray radiation, $k$ is a constant which can be taken as 0.9 for spherical crystallites and $\theta_{hkl}$ is the diffraction angle. The average size of the crystallites of the BaSnO$_3$ films deposited under different oxygen pressure is shown in Table 1. The crystallite size increases from 30 to 34 nm with the increase of oxygen ambience. This can be due to the interaction and agglomeration of particles with each other [38]. The lattice constants for the films were calculated and found to be in agreement with the reported value 4.101 Å [39].

The factors such as the internal stress, thermal stress, strain and lattice distortion in the films can broaden the XRD peaks and hence the crystallite size estimated using the Scherrer formula can be smaller than the actual value of the crystalline size [40]. The following Williamson–Hall relation can be used to study the effect of strain-induced broadening crystallite size in the full width at half maximum (FWHM) of XRD peaks [41, 42] and it is shown in Fig. 2c:

$$\beta_{hkl} \cos \theta_{hkl} = \frac{k \lambda}{D'Y} + 2\eta \sin \theta_{hkl}. \quad (2)$$

Fig. 1 XRD patterns of laser-ablated BaSnO$_3$ thin films for different oxygen pressures
where $D\eta$ is the size of the strain free crystallite, and $\eta$ is the lattice strain. Plots of $\sin \theta$ vs. $\beta \cos \theta$ are drawn for all the films and straight line plots are obtained. The $y$-intercept of the plot is a measure of $\frac{k \lambda}{D \eta}$ from which the crystallite size can be calculated and the strain can be estimated from the slope of the plot (Table 1). From the data shown in Table 1, it can be found that all the films prepared have considerable strain in them and there is strain-induced broadening for the XRD peaks.

## Table 1 Structural parameters of BaSnO$_3$ thin films deposited under different oxygen pressures

| Sample code | $\beta$(110) (degrees) | Crystalline size (nm) | Lattice constant (nm) | Lattice strain |
|-------------|------------------------|-----------------------|-----------------------|---------------|
|             |                        | Scherrer formula $(D)$ | SEM WH plot $(D')$    |               |
| BS 0        | 0.262                  | 30                    | 89                    | 47±5          | 0.4103       | 0.00619±0.00134 |
| BS 0.01     | 0.256                  | 32                    | 83                    | 63±18         | 0.4104       | 0.00286±0.00126 |
| BS 0.015    | 0.251                  | 33                    | 84                    | 66±33         | 0.4105       | 0.00373±0.00131 |
| BS 0.02     | 0.221                  | 34                    | 68                    | 69±23         | 0.4105       | 0.00282±0.00203 |
| BS 0.025    | 0.277                  | 31                    | 65                    | 53±22         | 0.4106       | 0.00538±0.0022  |
| BS 0.03     | 0.282                  | 29                    | 66                    | 40±5          | 0.4104       | 0.00854±0.00505 |

### 3.2 XPS analysis

X-ray photoelectron spectroscopy (XPS) was used for the analysis of the chemical states and the composition of the elements present in the laser-ablated BaSnO$_3$ films deposited on the substrate. The presence of the peaks corresponding to Ba, Sn and O in the XPS spectra of the films suggests the formation of BaSnO$_3$ phase in the films. The XPS survey spectrum of a typical BaSnO$_3$ film deposited under oxygen...
ambience at ρO2 = 0.02 mbar is shown in Fig. 3a. The C1s peak is observed at 284.4 eV in all the XPS spectra of the films. Its origin can be attributed to different reasons. It can be due to the carbon contamination of film surface in the presence of air. But the high intensity of this peak observed in the present case suggests the possibility of its origin can be from other reasons. It can have contribution from the binding agent used for the preparation of PLD source pellet or from the small trace of barium carbonate phase present in the film. Since the films are sintered at high temperature the binding agent would have decomposed while the sintering process itself. Hence, the possibility of the origin of the observed C1s peak in the XPS spectra, from the binding agent used for sintering the pellet, can be ruled out.

Figure 3b–d shows the core level spectra of Ba3d, Sn3d and O1s peaks of barium, tin and oxygen, respectively, in the BS 0, BS 0.01, BS 0.02 and BS 0.03 films. We can clearly see that the core level spectra of Ba3d, Sn3d and O1s peaks in the BS 0 film exhibit considerable broadening compared to that of the films deposited with oxygen ambience. The observed broadening in the peaks of BS 0 film can be due to defects, where the film is deposited without oxygen ambience [43]. The defects cause disorder around the environment of atom, which is responsible for the corresponding broadening of the Ba3d, Sn3d and O1s peaks in the BS 0 film compared to that of the films deposited under oxygen ambiances. The films deposited in the presence of oxygen ambience in the chamber will become free of oxygen defects and thereby the peak becomes narrow. For the BS 0 film, the core level spectrum of Ba (Fig. 3b) yields two peaks at the binding energy values 795.3 and 780.0 eV, respectively, with a peak difference of 15.3 eV. These peaks can be unambiguously assigned to spin orbit doublet peaks of Ba3d3/2 and Ba3d5/2, respectively. In all the films deposited at different oxygen pressure, namely ρO2 = 0.01, 0.02 and 0.03 mbar, the Ba3d3/2 and Ba3d5/2 peaks are observed at binding energy values of ~ 795.1 and ~ 779.8 eV, respectively (with the peak difference of 15.3 eV). It is reported that Ba3d3/2 and Ba3d5/2 peaks at binding energy values 795.2 and 779.9 eV with a peak separation of 15.3 eV corresponding to Ba2+ state [44, 45]. Singh et al. [46] reported the Ba3d spin orbit doublet peaks of Ba3d3/2 and Ba3d5/2 at the binding energies 794.8 and 779.4 eV, respectively, with a peak separation of 15.4 eV. The observed peak positions suggest that Ba atom

![Fig. 3 XPS spectra of laser-ablated BaSnO3 films](image-url)
in the developed compound is in the Ba$^{2+}$ state [47]. The experimental and fitted values of BS 0 and BS 0.02 film are well matched for Ba3d peaks and are shown in Fig. 4a, b.

For the BS 0 film, the spin orbit doublet Sn3d$_{3/2}$ and Sn3d$_{5/2}$ peaks are observed at binding energy values of 486 and 494.4 eV with peak difference of 8.4 eV (Fig. 3c). For all the films deposited under different oxygen pressures, namely $p_{O_2}=0.01$, 0.02 and 0.03 mbar (BS 0.01, BS 0.02 and BS 0.03), the Sn3d peaks are observed at binding energy values of ~486.5 eV and ~495.1 eV with the peak difference of 8.4 eV. The deconvoluted and fitted values for Sn peaks in BS 0 film (Fig. 4c) have major contribution around the binding energy 485.5 eV and this suggests that it is from Sn$^{2+}$ state [48]. For BS 0.02 film (Fig. 4d), the deconvoluted spectrum of Sn has major contribution around the binding energy 486.5 eV. The observed peak positions are in good agreement with the binding energy values for Sn$^{4+}$ state reported literature [47, 48], and hence it can be seen that Sn exists in

![Graphs showing deconvoluted core level splitting of peaks Ba, Sn, and O.](image)

Fig. 4 Fitted and deconvoluted core level splitting of peaks Ba, Sn, and O. a, c, e For BS 0 film and b, d, f for BS 0.02 film
Sn$^{4+}$ oxidation state in BS 0.02 film. The deconvoluted O1s spectra for BS 0 (Fig. 4e) and BS 0.02 film (Fig. 4f) show the three peaks having the binding energy 530.0, 531.1 and 532.2 eV. Socratous et al. [49] reported that the O1s peak can be deconvoluted into low, intermediate and high binding energies corresponding to fully coordinated oxygen, oxygen species in the oxygen deficient region and OH species, respectively. The intensity of peak having binding energy representing oxygen species in the oxygen deficient region [45] is high in the case of BS 0 film (Fig. 4e) and its intensity is low for BS 0.02 film (Fig. 4f).

3.3 Morphological analysis

3.3.1 FE-SEM/EDX analysis

The FE-SEM images of the films deposited without background oxygen ambience and with oxygen ambience are shown in Fig. 5. The effect of oxygen ambience on the surface morphology of the BaSnO$_3$ films can be clearly seen in the FE-SEM images. The surface morphology of the BS 0 film (Fig. 5) shows the random distribution of isolated clusters of different sizes which are formed due to the
Effect of oxygen pressure on the structural and optical properties of BaSnO$_3$ films prepared…

Agglomeration of smaller grains. In the presence of oxygen ambience, the coalescence decreases and the particle tend to migrate and combine together with each other on the substrate surface and form high quality crystalline films (up to oxygen pressure $\rho_{O_2} = 0.02$ mbar) which agrees with the result of the XRD analysis. The microstructural property of the films deposited under different oxygen pressures can be explained by the Thornton structure zone model [50]. The change in the microstructure of BaSnO$_3$ films can be due to the properties of the species ejected from the target and appearing in the surface of the substrate [21]. The ablated species lose its kinetic energy due to scattering with the oxygen molecules. When the oxygen pressure increases beyond 0.02 mbar, the surface mobility of the species reaching the substrate decreases due to their lower kinetic energy and hence there is a decrease in the grain size which can be observed in the morphology of the deposited films. The species which are deposited on the substrate have low or high energy may lead to different stresses. Stress that occurs during film deposition is referred to as intrinsic stress. The thermal expansion mismatch between the film and substrate and grain growth in films having sufficient atomic mobility will also lead to stress in the films. The microstructural evolution during coalescence can play an important role in stress evolution. The stress generated in this case is similar to that reported by Engwall et al. [51] in which the decrease in energy between the atoms in the surface and grain boundary gives a force for adjacent grains to close the gap between and will induce stress in the film formation under oxygen ambience. The stress which is produced during the film growth may lead to crack in the film under oxygen ambience [52]. Similar crack morphology is reported by Butt et al. [53]. The grain size variation shown from the FE-SEM image is larger than the size of the crystallites obtained from XRD analysis. From the XRD analysis, we measure the mean dimension of the crystallites. But in FE-SEM images, we observe the aggregates of the crystallites and the instrument does not have much resolution for showing these crystallites clearly [54, 55]. The crystalline size due to strain-induced broadening and stress is also calculated from the W–H plot (Table 1). We can see that the crystallite size obtained by W–H analysis lies in between that obtained from Scherrer analysis and FE-SEM analysis.

EDX analysis has been carried out to find the composition of the BaSnO$_3$-deposited films. The EDX spectra of the BaSnO$_3$ films deposited at 0.02 mbar are shown in Fig. 6. The presence of peaks corresponding to Ba, Sn and O indicates the formation of BaSnO$_3$ films. The atomic percent of the elements for the BS 0.02 mbar is listed in Table 2.

FE-SEM cross-sectional images of the BaSnO$_3$ films deposited for oxygen pressures 0.15, 0.02 and 0.025 (BS 0.15, BS 0.02 and BS0.025 films) are shown in Fig. 7. From the figure, it can be seen that the thickness of the films is increasing with increasing oxygen pressure. The formation of films with uniform thickness can be seen in the cross sectional FE-SEM images of films deposited at background oxygen pressure 0.015 mbar (Fig. 7a), 0.02 mbar (Fig. 7b) and 0.025 mbar (Fig. 7c). Thus, optimum value of background oxygen pressure is helpful in getting high quality uniform films. It is found that the thickness of the film increases systematically with increase in background oxygen pressures (Fig. 7d) and is shown in Table 3. The thickness of the film is affected by different factors such as target-substrate distance, laser energy density, gas pressure and deposition temperature. Similar behavior was also seen in the reference [21, 36]. Earlier it is explained that without oxygen pressure, the ablated species from the BaSnO$_3$ target has very high energy and reach the substrate rapidly. This causes desorption of atoms from substrates due to the effect of re-sputtering and will result in low deposition rate. When oxygen pressure increases, it results in increase in the collision of ablated species and the oxygen atoms in the chamber. Thus, there is a decrease in the partial energy of the molecules reaching to the substrate and thereby the number of adatoms increases resulting in the thickness of the films [36]. These may be the reason for the observed increase in the film thickness with increase in oxygen pressure.

![Fig. 6 EDX spectra of BaSnO$_3$ films deposited at oxygen ambience of 0.02 mbar](image)

| Table 2 EDX composition of BaSnO$_3$ films deposited at oxygen ambience of 0.02 mbar |
| Element | Weight (%) | Atomic (%) | Net intensity |
|---------|------------|------------|--------------|
| O K     | 10.52      | 48.54      | 740.65       |
| SnL     | 39.98      | 24.86      | 1537.43      |
| BaL     | 49.5       | 26.6       | 983.45       |
3.3.2 AFM analysis

AFM analysis is useful for the study of the surface morphology, surface homogeneity and nanostructure of deposited films. The AFM images of two typical films, namely BS 0.015 and BS 0.02 are shown in Fig. 8a, b, respectively. The root mean square (RMS) surface roughness of the BaSnO₃ films is obtained using WSXM 5.0 Develop 6.4 software and the values are shown in Table 3. The bombarding species on the substrate and the film surface may vary with different oxygen pressures and hence the surface roughness can change with oxygen pressure. This indicates the formation of the films with more uniform surface morphology at higher oxygen pressures. The analysis on the AFM images of the BaSnO₃ films deposited at different oxygen pressures shows a decrease in the RMS surface roughness with increase in oxygen pressure. Similar feature is reported by Jayasree et al. [56]. The observed decrease in the roughness may be due to the kinetics associate with the atomic arrangements of the species which is ejected from the target in the plasma in the chamber during deposition. The profile of the line scan curves obtained from the AFM images of BS 0.015 and BS 0.02 films are shown in Fig. 8c, d, and they show an average roughness values of 7.0 and 5.9 nm, respectively.

Table 3 Optical and morphological parameters of BaSnO₃ thin films for different oxygen pressures

| Sample code | Average transmittance (%) | Band gap (eV) | RMS roughness (nm) | Thickness (nm) |
|-------------|--------------------------|--------------|--------------------|---------------|
| BS 0        | 65                       | 2.91         | 13.46              | 108           |
| BS 0.01     | 81                       | 3.04         | 12.57              | 161           |
| BS 0.015    | 77                       | 3.05         | 11.08              | 170           |
| BS 0.02     | 85                       | 3.09         | 10.11              | 240           |
| BS 0.025    | 82                       | 3.09         | 9.47               | 251           |
| BS 0.03     | 84                       | 3.06         | 9.37               | 264           |
3.4 Optical analysis

3.4.1 UV-visible analysis

The optical absorbance and transmittance spectra of the films deposited at different oxygen pressures in the wavelength range 190–2300 nm are shown in Fig. 9a, b, respectively. All the films have good transparency in the visible and near infrared range. The sharp fall of transmittance near the absorption edge observed for all the films indicates their good crystalline nature. The average transmittance of the films in the wavelength region 190–2300 nm is measured and the values are shown in Table 3. The BS 0 film present an average transmittance value of 65%, whereas the films prepared under oxygen ambience possess higher values of average transmittance. This indicates the films prepared under oxygen ambience are of superior quality compared to that prepared in oxygen-free ambience. The high transparency of the BaSnO$_3$ films prepared under oxygen pressures can be due to low value of RMS roughness as revealed in AFM analysis. Beena et al. [57] reported the higher value of transmittance in the laser-ablated indium oxide films due to smooth surface morphology and the improved crystalline quality of the films. The absorption coefficient $\alpha$, can be calculated from the transmittance spectra using the following relation:

$$\alpha = \frac{1}{d} \ln \frac{1}{T},$$

(3)

where $d$ is the thickness of the film and $T$ is the transmittance of the film. The band gap energy $E_g$ of the films can be estimated from the following relation [41]:

$$a(h\nu) = A(h\nu - E_g)^n,$$

(4)

where $h$ is the Planck’s constant, constant $A$ is the band edge sharpness which is related with the order in crystalline structure of deposited films, $\nu$ is the frequency of radiation, and the exponent $n$ is depending on the nature of band transition. The values of $n$ for direct allowed and direct forbidden transitions will be 1/2 and 3/2, respectively. For the indirect allowed and indirect forbidden transitions, $n$ can take values 2 and 3, respectively [41, 58, 59]. The band gap is determined for all the films from the plot of $(a)^{1/n}$ versus photon energy $h\nu$ on the $x$-axis (Fig. 9c). It is observed that for all the films, the best straight line is obtained for $n=2$, which corresponds to indirect allowed transition. The estimated values of the optical energy gap for the films vary from 2.91 to 3.09 eV (Table 3). The optical energy gap for the BS 0 film is 2.91 eV and its value is higher in films deposited under oxygen ambience. The optical energy gap increases systematically with increase in $p$O$_2$ up to 0.025 mbar oxygen pressure thereafter decreases slightly with increase in $p$O$_2$. The lowest value of band gap energy of the BS 0 film can be due to the presence of defects or oxygen vacancies in it, as this film is prepared...
under oxygen-free ambience. But at high oxygen ambience, the defects get reduced and the band gap energy increases [60]. In addition, it is seen that the absorption edge is shifted to the wavelength of smaller region with oxygen ambience imply a blue shift in the band gap of the films. The increase of band gap with oxygen pressure is also reported by Lethy et al. [61] for the nanostructured tungsten oxide films prepared by pulsed laser deposition technique. The reduction in the RMS surface roughness in the film deposited under oxygen ambience can also have contributed to the increase in the band gap energy. Similar results were observed in laser-ablated potassium lithium niobate films [56]. The bandgap of the films can be altered by varying the oxygen pressure and thereby reducing the oxygen vacancies in the chamber during the deposition.

### 3.4.2 Photoluminescence analysis

The photoluminescence spectra of the BaSnO$_3$ films recorded for an excitation wavelength 350 nm are given in Fig. 10. The deposited BaSnO$_3$ films have emission in the visible region. The PL spectra of these films present two intense emissions at 408, 430, and a weak emission at 580 nm. In BaSnO$_3$ films, the emissions are caused by the transitions between energy levels of constituent elements.
barium and tin of the compound [62]. The emission at 408 nm is due to the transition $^2P^0_{1/2} - ^2D_{5/2}$ of barium and 430 nm is due to the transition of $^1S_{0} - ^1P^0_{1}$ of tin [62]. The emission around 580 nm is due to transition of $^2D - ^2F_0$ of tin [63]. It is reported that green–yellow–red emission (low energy) is due to deep defects and violet–blue emission (high energy) is due to shallow defects [32]. The PL intensity is associated with degree of order–disorder in the structure that changes the localised states in the band gap [29]. It can be seen that intensity of the emission peaks undergoes considerable reduction in the films prepared under oxygen ambience. The reduction in the PL intensity of the films prepared under oxygen ambience may be due to the reduction of defects or oxygen vacancies present in the sample.

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References

1. E. Moreira, J.M. Henriques, D.L. Azevedo, E.W.S. Caetano, V.N. Freire, U.L. Fulco, E.L. Albuquerque, J. Appl. Phys. 112, 043703 (2012). https://doi.org/10.1063/1.4745873
2. S. Upadhyay, O. Parkash, D. Kumar, J. Phys. D. Appl. Phys. (2004). https://doi.org/10.1088/0022-3727/37/10/011
3. J. Cerda, J. Arbiol, R. Díaz, G. Deranneau, J.R. Morante, Mater. Lett. 56, 131–136 (2002)
4. B. Ostrick, M. Fleischer, U. Lampe, H. Meixner, Sens. Actuators. B 44, 601–606 (1997)
5. C. Dorothee, P.D. Popa, F. Iacomi, J. Optoelectr. Adv. Mater. 13(4–5), 413–417 (2012)
6. Q. Liu, J. Dai, Z. Liu, X. Zhang, G. Zhu, G. Ding, J. Phys. D. Appl. Phys. 43, 455401 (2010). https://doi.org/10.1088/0022-3727/43/45/455401
7. R.M. Katiliute, P. Seibutus, M. Ivanov, R. Grigalaitis, A. Stanulis, J. Banys, A. Kareiva, Ferroelectrics. 464, 49–58 (2014)
8. W.J. Lee, H.J. Kim, J. Kang, D.H. Jang, T.H. Kim, J.H. Lee, K.H. Kim, Annu. Rev. Mater. Res. 47, 391–423 (2017)
9. B. Liu, Q. Liu, Y. Zhang, Z. Liu, L. Geng, J. Alloys. Compd. 680, 343–349 (2016). https://doi.org/10.1016/j.jallcom.2016.04.157
10. S.A. Salehizadeh, H.M. Chenari, M. Shahani, H.A. Ahangar, R. Zamiri, A. Rehaei, J.S. Kumar, M.P.F. Graca, J.M.F. Ferreira, RSC. Adv. 8, 2100 (2018). https://doi.org/10.1039/c7ra12442b
11. M.J. Ansaree, S. Upadhyay, I. Nyoges, Sens. Actuators. B 21, 2825–2838 (2015). https://doi.org/10.1007/s11581-015-1476-1
12. J. U.Lampe, H. Gerblinger, Meixner, Sens. Actuators. B 24–25, 657–660 (1995)
13. W. Lu, H. Schmidt, J. Mater. Sci. 42, 10007–10013 (2007). https://doi.org/10.1080/0022-3727/43/45/455401
14. S. Upadhyay, O. Parkash, J. Mater. Sci. Lett. 16, 1330–1332 (1997)
15. H.J. Kim et al., Appl. Phys. Express 5, 061102 (2012)
16. S. Raghavan, T. Schumann, H. Kim, J.Y. Zhang, T.A. Cain, S. Stenner, APL. Mater. 4, 016106 (2016)
17. C.W. Zhao, B.C. Luo, C.L. Chen, RSC. Adv. 7, 19492 (2017)
18. M. Wu, S. Yu, L. He, L. Yang, W. Zhang, Sci. Rep. 7, 103 (2017). https://doi.org/10.1038/s41598-017-00178-9
19. H. Yun, M. Topskal, A. Prakash, K. Ganga, B. Leitmann, B. Jalan, R.M. Wentzovciovitch, K.A. Khoyan, J.S. Jeong, J. Vac. Sci. Technol. A 36, 031503 (2018). https://doi.org/10.1116/1.5026298
20. S. Sallis, D.O. Scanlon, S.C. Chae, N.F. Quackenbush, D.A. Fischer, Appl. Phys. Lett. 103, 042105 (2013). https://doi.org/10.1063/1.4816511
21. A.L. Febvrier, A.C. Galca, ACS. Appl. Mater. Interfaces. 4, 5227–5233 (2012)
22. Z. Saroukhani, N. Tahmasebi, S.M. Mahdavi, A. Nemati, Bull. Mater. Sci. 38, 1645–1650 (2015)
23. H. Mizoguchi, P. Chen, P. Boolchand, V. Ksenofontov, C. Felser, P.W. Barnes, P.M. Woodward, Chem. Mater. (2013). https://doi.org/10.1021/cm4019309
24. H.F. Wang, Q.Z. Liu, F. Chen, G.Y. Gao, W. Wu, X.H. Chen, J. Appl. Phys. 101, 106105 (2007). https://doi.org/10.1063/1.2736629
25. Y. Liu, J. Dai, Y. Zhang, H. Li, B. Li, Z. Liu, W. Wang, J. Alloys. Compd. 655, 389–394 (2016)
26. P.V. Wadekar, J. Alaria, M. O’Sullivan, N.L.O. Flack, T.D. Manning, L.J. Phillips, K. Durose, O. Lozano, S.Lucas, J.B. Claridge,
