

BANDGAP RENORMALIZATION AND PROPERTY ENHANCEMENT DUE TO Fe-DOPING IN LASER ABLATED BaSnO₃ FILMS

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Abstract

Nano-structured materials exhibit exciting physical and chemical behaviors different from their bulk counterpart, and their exotic behaviors are due to their increased relative surface area and spatial confinement of charge carriers. Pulsed laser deposition (PLD) is a straightforward, simple, thin film preparation approach with which one can deposit films with atomic layer precision. Using the PLD, we deposited BaSn_{1-x}Fe_xO₃ films with $x = 0, 0.01, 0.02, 0.3, 0.05$ and 0.07 mol% and investigated their structural, microstructural, and optical properties in detail. We observed an increase in XRD intensity and a reduction in FWHM in the most preferred direction of crystalline growth $\langle 110 \rangle$ with enhanced iron-doping levels, and these suggest the crystallinity enhancement in the films. We observed an unprecedented film thickness enhancement with Fe-doping level enhancement (from 640 nm for undoped film to 1,158 nm for seven mol% Fe-doped film). We proposed this to induced Magnetic field-assisted Particle Convergence effect. FESEM and AFM analysis shows a pin-hole-free uniform surface for 5 mol% Fe-doped film. Films exhibit high transmittance values (71 to 91% range), even under heavy doping levels, revealing their exemplary optical quality. We have observed bandgap renormalization in films under Fe-doping ($E_g = 3.18$ eV for pristine film and $E_g = 2.72$ eV for 7 mol% Fe-doped film). XPS analysis of the films suggests +3, +2, and +4 oxidation states for the Fe, Ba, and Sn ions. The high crystalline nature, high transmittance, suitable bandgap values, and good surface morphology of the Fe:BaSnO₃ films make them suitable for optoelectronic applications.

Keywords: Barium Stannate; Perovskite; Laser Ablation; Bandgap Tuning; Induced Magnetic Field-Assisted Particle Convergence Effect

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Introduction

BaSnO₃ a perovskite oxide, receives much attention among the scientific community owing to its excellent properties, and it finds applications in diverse fields. Smith *et al.* reported certain mixed metal oxides of ABO₃ type, including BaSnO₃ with perovskite structure (Smith and Welch, 1960), and Cerda *et al.* (2002) reported BaSnO₃ synthesis by sol-gel process (Cerda *et al.*, 2002). Manju *et al.* (2016) observed the ferromagnetic performance of Co/Fe-doped BaSnO₃ (Manju *et al.*, 2016). Cubic perovskite oxide semiconductor BaSnO₃ has a bandgap of 3.1 eV (Larramona *et al.*, 1989; Manju *et al.*, 2016). Jeon *et al.* (2023) prepared La-doped BaSnO₃ films on MgAl₂O₄ substrates. They observed that 5% La-doped film exhibited a low sheet resistance of $\sim 8.7 \Omega/\text{sq}$, high transparency of $\sim 85\%$, and good electromagnetic shielding effectiveness = $\sim 25.9 \text{ dB}$ in the X-band, thus making it a suitable transparent conductor (Jeon *et al.*, 2023). Paramagnetic epitaxial Ru:BaSnO₃ films by PLD technique was reported by Lindgren and Suzuki (2022). Alaan *et al.* (2016) reported the preparation of paramagnetic transparent conducting Gd-doped BaSnO₃ films by PLD (Alaan *et al.*, 2016). BaSn_{0.5}Co_{0.5}O₃ film with a low optical bandgap of 1.94 eV was reported by Gao *et al.* (2019).

Sobahi *et al.* (2018) observed photocatalytic efficiency enhancement of barium stannate doped with In for C₄H₈S degradation (Sobahi *et al.*, 2018). Barium Stannate found applications as gas sensors for sensing CH₃CH₂OH, carbon monoxide, hydrogen, petrol, and LPG (Tao *et al.*, 2000). It also finds important applications in developing DSSC (Kim *et al.*, 2013; Shin *et al.*, 2013). The Er³⁺/Yb³⁺ co-doping on BaSnO₃ increases the efficiency of DSSC based on BaSnO₃ (Kumar *et al.*, 2018). Luo *et al.* (2015) reported a smaller bandgap and more considerable Urbach tail energy for lanthanum-doped BaSnO₃ (Luo *et al.*, 2015). Balamurugan *et al.*, (2009) and Rajamanickam *et al.* (2018) reported ferromagnetism at room-temperature in Fe-doped barium stannate systems. Rajamanickam *et al.* (2017) observed enhancing conversion efficiency by iron-doping on barium stannate-based DSSCs (Rajamanickam *et al.*, 2017). Jayavelu *et al.* (2024) reported a photocatalytic water purification study using tungsten-incorporated BaSnO₃ nanoparticles (Jayavelu *et al.*, 2024). We have analyzed the properties of Fe-doped BaSnO₃ powder samples and revealed the formation of hexagonal nanorods, ferromagnetic order, and optical limiting behavior (John *et al.*, 2021b). We found a regular increase in third-order reverse saturable absorption coefficient

and an orderly diminution in saturation intensity with Fe-doping enhancement. A similar analysis on Mn-doped and Ni-doped BaSnO₃ powders, reveals magnetic and nonlinear optical limiting behavior for them (John *et al.*, 2020; 2021). We noticed a regular increase in third-order reverse saturable absorption coefficient with dopant level enhancement in both cases due to the reduction in bandgap. We also reported the supercapacitor performance of Mn:BaSnO₃ (John *et al.*, 2020).

We analyzed remarkable property enrichment in PLD prepared BaSnO₃ films on Mn-doping and observed unusual thickness enhancement of about two folds with a 7 mol% Mn-doping owing to induced magnetic field-assisted particle convergence mechanism (John *et al.*, 2024a). Similarly, we have observed excellent property enhancement and uncommon thickness increase in Ni-doped BaSnO₃ films (John *et al.*, 2024b). Interestingly, in both these cases, all the deposition parameters remain the same for pure and doped films, and are annealed at identical temperature. Only parameter that varied was the dopant level in the PLD target. In both cases, the dopants used are magnetic. We have not observed such a film thickness enhancement in our earlier investigations on non-magnetic dopants in various materials deposited using PLD (Lethy *et al.*, 2008; Rani *et al.*, 2008; Krishnan *et al.*, 2010; Vinodkumar *et al.*, 2010a; 2010b; Pillai *et al.*, 2011). It becomes curious that the unusual thickness enhancement due to the IMPC effect exhibited for Mn/Ni:BaSnO₃ films possibly owing to magnetic nature of the dopants. To ascertain whether this unusual film thickness enhancement during PLD owing to the IMPC mechanism is solely owing to the magnetic nature of the dopant material, we extended the study with another important magnetic dopant, Fe. Thus, in the present investigation, we fabricated BaSn_{1-x}Fe_xO₃ films with $x = 0, 0.01, 0.02, 0.03, 0.05$, and $0.07 \text{ mol\%}$ using PLD and analyzed their structural/topographical/optical behaviors.

Experimental Methods

We have synthesized the pure and Fe-doped BaSnO₃ (BaSn_{1-x}Fe_xO₃, $x = 0, 0.01, 0.02, 0.03, 0.05$, and $0.07 \text{ mol\%}$) powder samples using a solid-state reaction approach from ultra-purity BaCO₃, SnO₂, and Fe₂O₃ (John *et al.*, 2021a). The PLD pellets are prepared (diameter- 3 mm and thickness- 1 mm) from the powder samples (supplementary information (SI)). In our earlier studies, we prepared

good-quality BaSnO_3 films on fused silica substrates using PLD with frequency-doubled laser radiation at 532 nm under optimized deposition conditions and annealing (John *et al.*, 2019a; 2019b). We have found that 600°C-temperature at the substrate, 60 mJ-laser energy, and 900°C-annealing is suitable for yielding highly crystalline BaSnO_3 films (John *et al.*, 2019b). Also, 0.02 mbar oxygen pressure is suitable for preparing good quality films (John *et al.*, 2019a).

In the present study, we deposited the pure and Fe: BaSnO_3 films using 532 nm laser radiation on fused quartz plates under the above optimized deposition conditions for a 45 min duration. The films thus prepared were annealed for 1 h at 900°C, and films having Fe-doping levels 0, 1, 2, 3, 5, and 7 mol% are labeled as BSF0, BSF1, BSF2, BSF3, BSF5, and BSF7, respectively. We explored the different properties of the pure and Fe-doped barium stannate films using different techniques (for details see in (SI)).

Analysis of Results

Using the XRD technique, we investigated the crystal structure of laser-ablated pristine and iron-doped BaSnO_3 films, and Figure 1 presented the XRD diffractograms of the films. The X-ray diffractograms of the films show a polycrystalline nature with characteristic peaks related to the cubic phase of barium stannate (ICDD 15-0780 Card) (Upadhyay, 2013). Peaks obtained at 2θ values 30.24°, 43.62°, 54.25°, 63.63°, and 72.32° in BSF0 are due to <110>, <200>, <211>, <220>, and <310> crystal orientations, respectively. The peak at

$2\theta = 30.24^\circ$ confirms that the (110) orientation shows the maximum intensity, suggesting <110> the favored crystal growth direction in BSF0. In the XRD diffractogram of the powder sample (ICDD 15-0780) also, the (110) peak bears 100% intensity. We also observed the highest intensity for the doped films for the (110) peak, indicating that Fe-doping does not modify the favored direction of crystal growth. In the doped films, (110) peak intensity shows an enhancement with increased doping concentration. The (110) peak intensity for Fe-doped films BSF1, BSF2, BSF3, BSF5, and BSF7 are 1.71, 1.83, 2.32, 2.45, and 1.99 times that in BSF0. Thus, 5 mol%, Fe-doped film shows the highest intensity for the most intense peak, indicating its superior crystalline quality. In the Mn: BaSnO_3 films also we observed very high crystallinity enhancement for the preferred <110> direction and the highest XRD intensity is obtained at 5 wt% Mn-doping (John *et al.*, 2024a). In the Ni: BaSnO_3 films also very high XRD intensity enhancement with Ni-doping was observed and 3 mol% Ni-doped films show the superior crystalline quality (John *et al.*, 2024b).

The enhanced XRD intensity with Fe-doping enhancement can result from the increase in film thickness (Figure 2(a)), as revealed by lateral FSEM analysis and stylus profilometry. The slight dip in (110) peak intensity in BSF7 compared to that of BSF5 can result from disorders/defects caused due to Fe-dopants in BaSnO_3 cubic lattice due to the Fe-segregation on the boundaries of grains. The intensity of (200), (211), and (220) peaks also varies with Fe-doping concentration. The (220) and (211) peaks show the highest intensity at BSF2, whereas (220) shows the highest intensity at BSF3. In pure film and films with lesser Fe-doping

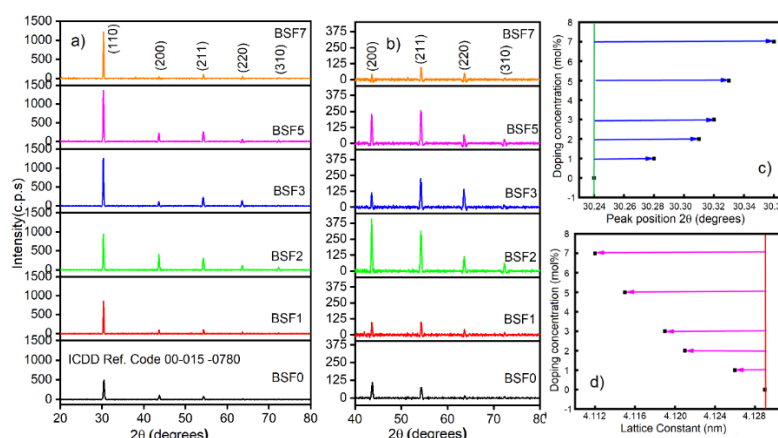


Figure 1. a) X-ray diffractograms of the $\text{BaSn}_{1-x}\text{Fe}_x\text{O}_3$ ($x = 0, 0.01, 0.02, 0.03, 0.05$, and 0.07 mol%) films, b) magnified view of selected 2θ range 40° to 80° , c) and d) shift in (110) peak position and corresponding lattice constant reduction with Fe-doping levels

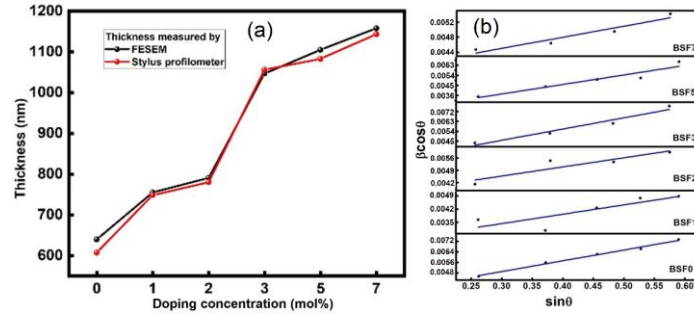


Figure 2. a) Film thickness variation with Fe-doping, b) Williamson-Hall plots of the BaSn_{1-x}Fe_xO₃ films ($x = 0, 0.01, 0.02, 0.03, 0.05$, and 0.07 mol%)

Table 1. Structural parameters of the BaSn_{1-x}Fe_xO₃ films deposited on quartz substrate

Sample code	FWHM $\beta(110)$ (degrees)	Crystallite size (nm)		Lattice parameter (nm)	Lattice strain
		Scherer formula	WH plot		
BSF0	0.271	29	57 ± 40	4.129	0.00409 ± 0.000214
BSF1	0.228	34	71 ± 21	4.126	0.00747 ± 0.000945
BSF2	0.207	35	78 ± 39	4.121	0.00429 ± 0.00074
BSF3	0.175	40	80 ± 46	4.119	0.00241 ± 0.00114
BSF5	0.169	44	86 ± 45	4.115	0.00213 ± 0.00115
BSF7	0.201	37	65 ± 60	4.112	0.00372 ± 0.00042

concentration, the films exhibit a random growth of crystallites. As the doping concentration increases, this randomness in crystallite growth turns to be more oriented along $\langle 110 \rangle$.

$\beta(110)$, the (110) peak's FWHM decreases regularly from 0.271° in BSF0 to 0.169° in BSF5 and then increases to 0.201° in BSF7. The variation of β_{110} with different doping levels also supports crystallinity enhancement in the doped films and indicates that in barium stannate, the optimum doping is 5 mol%.

The (110) peak presented the peak position shift regularly towards higher 2θ side (Figure 1(c)) on Fe-doping enhancement. This peak shift can be due to the slight ionic radii variance of dopant (Fe^{3+} (0.645 Å)) and host (Sn^{4+} (0.69 Å)) and fortifies the belief that Fe ion is incorporated into the BaSnO₃ lattice. No peaks corresponding to Fe₂O₃ or any other oxides of Fe in the XRD pattern indicate the replacement for Sn in the BaSnO₃ host lattice by Fe or the segregation of Fe in the non-crystalline grain boundary. The slight decrease in the lattice parameter value with Fe-doping concentration increase (Table 1 and Figure 1(d)) indicates a slight lattice contraction due to tensile stress (Vinodkumar *et al.*, 2010a; 2010b). We have observed a comparable peak shift towards the higher 2θ side for (110) peak and a consequent reduction in lattice constants in Mn:BaSnO₃ and Ni:BaSnO₃

films with doping concentration enhancement (John *et al.*, 2024a; 2024b).

We estimated the crystallite size (Table 1) in deposited films using the Scherer Equation (Stock, 2014):

$$D_{hkl} = \frac{k\lambda}{\beta_{hkl} \cos \theta_{hkl}}, \quad (1)$$

where $\lambda = 1.5406$ Å, and k is the shape factor constant of crystallites (k is 0.9 for spherical size). The crystallite size in BSF0 is 29 nm, and it regularly increases with an increase in Fe-doping level until 5 mol% (crystallite size in BSF5 is 44 nm) and after that decreases slightly (crystallite size in BSF7 is 37 nm). The slight reduction in crystallite size observed in BSF7 can be due to a small decline in its crystallinity owing to the defects and disorders introduced in this film due to heavy doping. Moreover, in BSF7 film, the number of nucleation centers are higher than in BSF5 as evidenced by FESEM & AFM images. This can also be a reason for the reduced crystallite size in BSF7.

The obtained crystallite size shows the nanostructured nature of films.

The peaks get broadened due to strain in films. However, Scherer analysis cannot account for this broadening during calculation of size of crystallites. Using the Williamson-Hall (W-H) relation, we can

estimate the defect-induced microstrain (η) and strain-free crystallite size (Williamson and Hall, 1953):

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

here D' - size of the crystallite, and η - strain in film. From plot between $\sin \theta$ and $\beta \cos \theta$, slope and intercept on the y-axis give the values of η and D' . Figure 2(b) shows the W-H plot for pristine and Fe:BaSnO₃ films, and Table 1 shows the η and D' values.

The higher values of D' estimated from W-H plot than those obtained from the Scherrer formula suggest the peak broadening due to strain in films.

Morphological Analysis

Figure 3 presents FESEM images of pure and Fe-doped BaSnO₃ films. The FESEM image BSF0 presents smooth surface morphology with a dense distribution of grains with imprecise boundaries. However, with 1 mol% of Fe incorporation, the grain boundaries became explicit and continually visible on the entire surface, albeit with varying sizes. In BSF2, the morphology remains almost similar to that of BSF1 but with a tendency to form larger grains with precise boundaries. This tendency continues, forming large isolated particles distributed

randomly on the surface of a continuous film after the doping concentration becomes 3 mol%. This grain size enhancement very well supports the enhancement of crystallinity (revealed by XRD) with Fe-doping.

Interestingly, a beautiful pin-hole-free surface morphology with larger grains well-separated with boundaries emerged in BSF5. This kind of morphology is well-suited when used as an electron-blocking layer in excitonic solar cells for efficient charge transfer and for getting a good fill factor (Suresh *et al.*, 2017; 2018). In BSF7, the morphology changes more or less similar to that of BSF3 with randomly distributed larger and smaller grains with definite boundaries. However, the grains are slightly larger in BSF7 as compared to BSF3. The grain size variation with Fe-doping follows almost a similar pattern for crystallite variation.

In laser ablation techniques of film growth, possibly three ways of nucleation prevails, namely 3D-island growth (Volmer-Weber), layer by layer growth (Frank-Van der Merwe) and intermediate growth (Stranski-Krastnov) (Kumar *et al.*, 2014). The formation of a continuous film with successive discrete larger islands in BSF5 film points towards the possibility of intermediate growth (Stranski-Krastnov) dominating over the other two ways

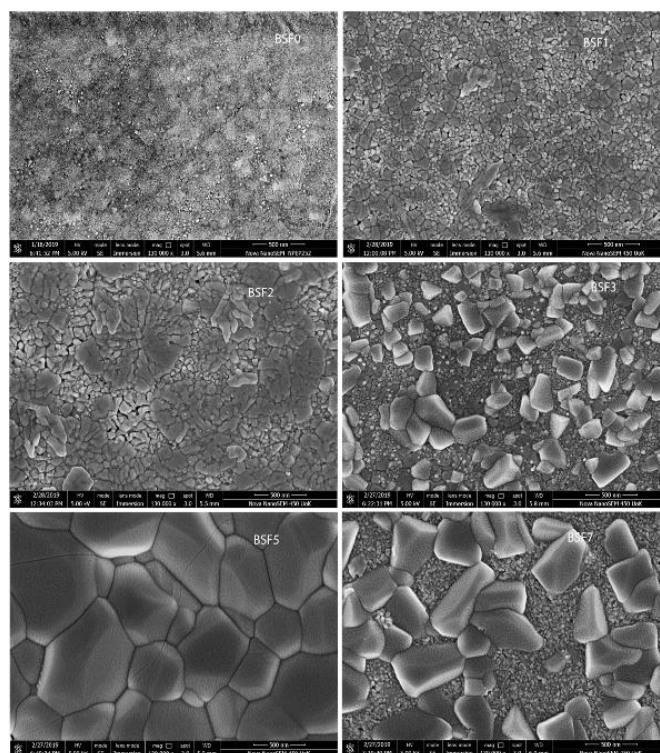


Figure 3. FESEM images of the BaSn_{1-x}Fe_xO₃ films (x = 0, 0.01, 0.02, 0.03, 0.05, and 0.07 mol%)

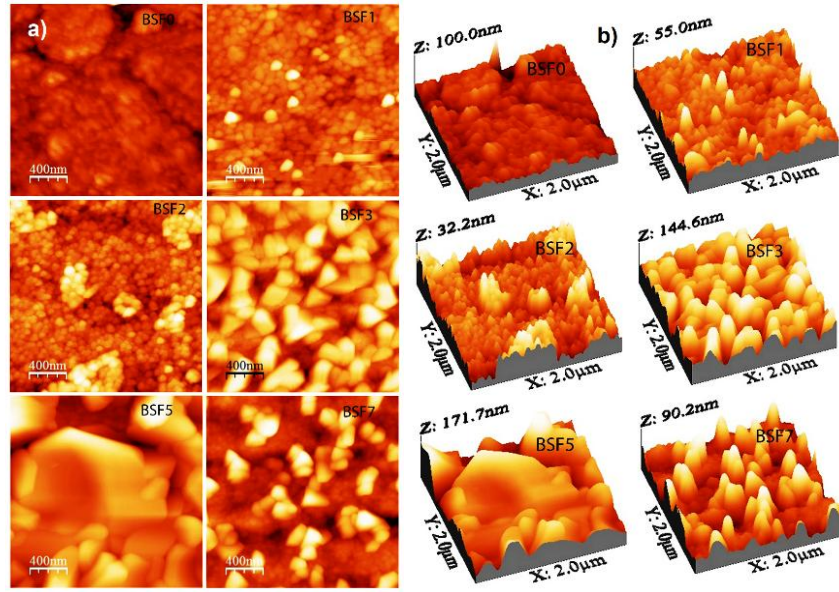


Figure 4. AFM images: (a) 2D and (b) 3D of pristine and Fe-doped BaSnO₃ films

Table 2. Thickness, roughness and optical constants of pristine and Fe:BaSnO₃ films

Sample code	RMS surface roughness (nm)	Thickness (nm)		Average transmittance (%)	Optical constants at wavelength $\lambda = 550$ nm		Bandgap (eV)
		FESEM	Stylus profilometer		Refractive index (n)	Dielectric constant (ϵ_r)	
BSF0	17.21	640	652	91	1.93	3.85	3.18
BSF1	15.78	755	764	90	2.15	4.73	3.14
BSF2	10.34	791	798	83	1.75	3.08	3.03
BSF3	11.45	1047	1095	82	1.83	3.32	2.91
BSF5	23.65	1105	1124	76	1.98	4.01	2.87
BSF7	21.59	1158	1189	71	1.64	2.68	2.72

(John *et al.*, 2024a). Also, BSF5 film shows improved crystallinity compared to other films.

AFM Analysis

Figures 4(a) and 4(b) respectively presents the 2-dimensional and 3-dimensional AFM micrographs of pristine and Fe: BaSnO₃ films. BSF0 depicts small grains with imprecise boundaries, as seen in its FESEM image. The surface morphology revealed by the AFM images follows a similar pattern as shown in FESEM images. As in FESEM, AFM pictures also reveal that the surface morphology of BSF1 is similar to that of BSF2, whereas the surface morphology of BSF3 has a similar pattern as in BSF7. In both FESEM and AFM images, BSF5 film presents a unique better surface morphology with bigger grains compared to that of other films. We estimated the roughness (RMS) for the deposited films employing WSXM software (Table 2), and its values are in the range of 10.34 nm to 23.65 nm.

We estimated the thickness of pristine and doped films employing lateral FESEM analysis, which shows a drastic increase with doping concentration (Figure 5). We also measured the film thickness using a Stylus Profilometer, which also agrees well (Figure 2(a)) with that estimated from the vertical FESEM analysis (Table 2). BSF0 shows a film thickness of 640 nm from FESEM analysis and 652 nm from the Stylus Profilometer measurement. The film thickness increases systematically in a drastic manner with dopant level increase. BSF7 shows a film thickness of 1,158 nm from FESEM analysis (Figure 5) and 1,189 nm from Stylus Profilometer measurement. All the parameters for deposition, like energy, wavelength and spot size of laser radiation, deposition time, background oxygen pressure, nature of the substrate, substrate temperature, and target-to-substrate distance, remain the same during the films' deposition. Also, all the films are subjected to identical annealing conditions, and the only factor

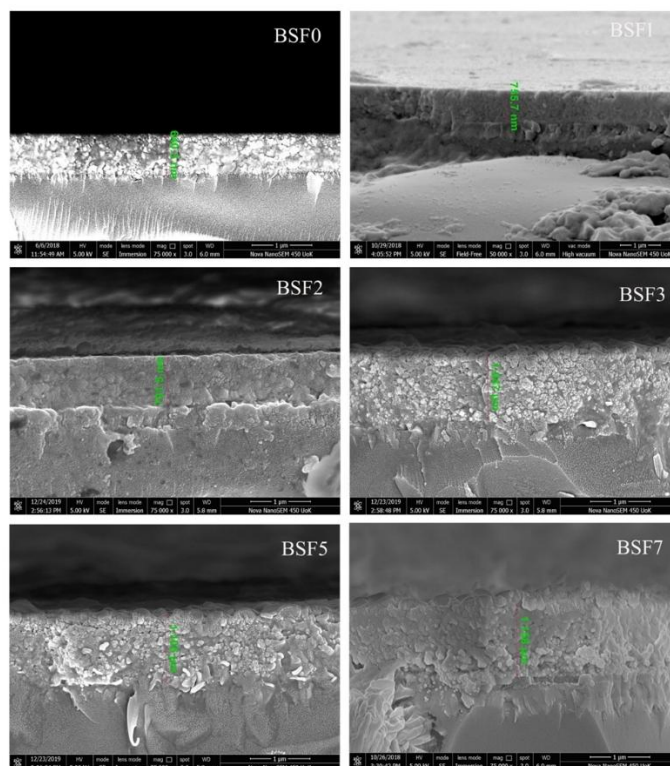


Figure 5. Lateral FESEM images of the pristine and Fe-doped barium stannate films

varying is the Fe-doping concentration. Interestingly, it is to be mentioned that a similar drastic film thickness enhancement was observed in our earlier studies with laser-ablated BaSnO_3 films on both Ni and Mn-doping (John *et al.*, 2024a; 2024b). On Mn-doping the thickness of the film increases steadily from 606.1 ± 0.5 nm in pristine film to $1,128.0 \pm 2.4$ nm in 7 wt% Mn-doped films (ellipsometric method). Similarly, on Ni-doping the thickness of the film rapidly raises from 606.12 ± 0.7 nm in pristine film to $1,303 \pm 1.3$ nm in 7 mol% (ellipsometric method).

Since we have not applied any external magnetic field during deposition, this unusual film thickness enhancement cannot be ascribed to the PLD Aurora effect (Kobayashi *et al.*, 2002). The only reason for the increase in thickness is the presence of Fe ions in the laser-ablated plasma plume. To explain this interesting observation, an induced magnetic field-assisted particle convergence growth mechanism is suggested (John *et al.*, 2024a; 2024b).

In the PLD process of preparing $\text{Fe}:\text{BaSnO}_3$ films, the plasma plume contains BaSnO_{3-x} , Ba^{2+} , Sn^{4+} , FeO_{1-x} , Fe^{3+} , and electrons (John *et al.*, 2024a; 2024b). As explained in our earlier studies (John *et al.*, 2024a; 2024b), these particles are removed from the target surface due to the quick expansion

of the plume, and moves outwards to the surface. A net displacement between the heavy positive ions and electrons occurs due to their kinetic energy gradient resulting the formation of an electric field and magnetization of iron nanoparticles. The magnetic field induced nearby iron nanoparticles attracts the paramagnetic BaSnO_{3-x} particles near to the magnetic field leading to a convergence effect. The morphological and XRD analysis shows the formation of larger grains with precise boundaries in the Fe-doped films, supporting this assumption. Thus, the observed film thickness rise can be ascribed to the IMPC effect.

Surprisingly, this effect in the PLD process of preparation of BaSnO_3 film observed in the case of three dopants which are happened to be magnetic in nature. As explained in the introduction section we never observed such a thickness enhancement in PLD deposited films with different non-magnetic dopants (Lethy *et al.*, 2008; Rani *et al.*, 2008; Krishnan *et al.*, 2010; Vinodkumar *et al.*, 2010a; 2010b; Pillai *et al.*, 2011). Hence, it can be concluded that the unusual film thickness rise obtained in the present case can be ascribed to IMPC mechanism due to the magnetic nature of the dopant material.

The elemental analysis of the pristine and doped films has been done using EDS spectra and is

displayed in Figure 6 and it shows the presence of Fe in the doped films and the oxygen deficient nature of the films. The actual amount of Fe incorporated in to the deposited films is less than

the Fe-doping concentrations in the PLD pellets (Figure 6(d)). However, the Fe content in the film bears good linear relationship with the Fe-doping concentrations in the PLD pellet (Figure 6(e)).

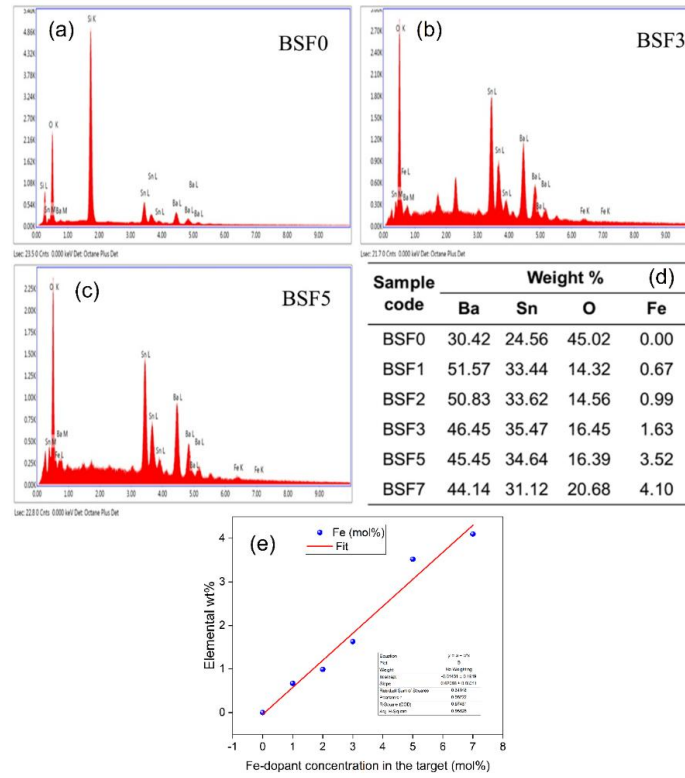


Figure 6. (a) to (c): EDS spectra of typical films, (d) elemental composition in the films, and (e) graphical representation of the films' Fe- content vs. Fe-doping concentrations in the PLD pellet

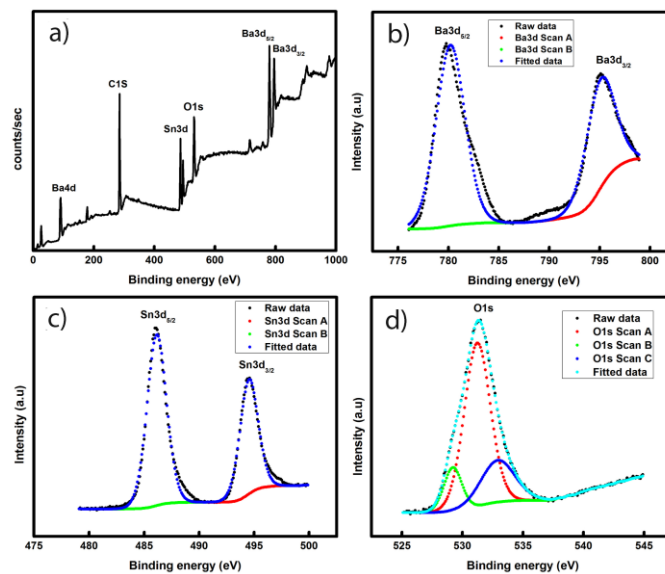


Figure 7. XPS Spectra of BSF0 film (a) Survey spectrum, (b) to (d) Core level spectra of Ba, Sn and O, respectively

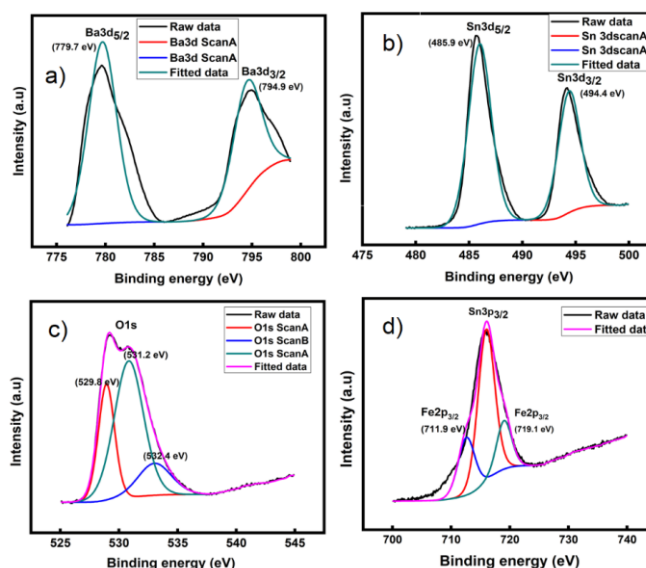


Figure 8. XPS spectra of BSF5, (a) to (d) Core level spectra of Ba, Sn, O and Fe

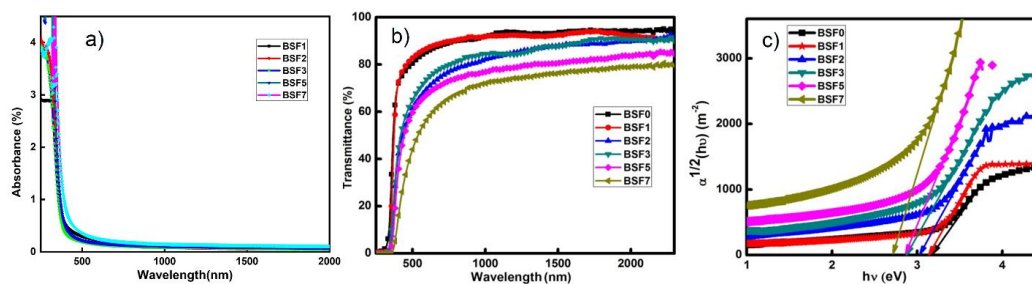


Figure 9. (a) and (b) Absorbance and Transmittance spectra, (c) Tauc plot of the films

XPS Analysis

A carbon peak in the XPS survey spectrum (Figure 7(a)) of BSF0 indicates the possible contamination of the film surface when exposed to air. The fitted and deconvoluted Ba $3d_{5/2}$ and Ba $3d_{3/2}$ doublet peaks, respectively, at BE = 780 and 795.3 eV (peak separation = 15.3 eV) and these values denotes the Ba²⁺ oxidation state of BSF0 (Figure 7(b)) (Nithyadharseni *et al.*, 2016). The peaks observed at BE = 486.1 and 494.52 eV (peak difference = 8.4 eV) label the Sn $3d_{5/2}$ and Sn $3d_{3/2}$ doublets of Sn⁴⁺ in the film (Figure 7(c)) (Kwoka *et al.*, 2005). The deconvoluted O1s spectrum (Figure 7(d)) has three peaks. The peak at BE = 529.27 eV related to the lattice oxygen, and that at BE = 531 eV relates to the oxygen vacancies, and the peak at BE = 532 eV represents the adsorbed oxygen in the film surface (Chen *et al.*, 2018).

Figure 8 represents the XPS spectral components of BSF5. The Ba core-level spectrum presents a doublet at BE = 779.7 and 794.9 eV

(peak difference = 15.2 eV) related to Ba $3d_{5/2}$ and Ba $3d_{3/2}$ of Ba²⁺ state (Nithyadharseni *et al.*, 2016). The 485.9 and 494.4 eV peaks (peak separation = 8.5 eV) of core-level spectra of Sn represents Sn $3d_{5/2}$ and Sn $3d_{3/2}$ doublets of Sn⁴⁺ state (Kwoka *et al.*, 2005). The peaks at 529.8, 531.2, and 532.4 eV in the O1s core-level spectrum relate respectively to lattice oxygen, oxygen vacancies, and adsorbed or loosely bound oxygen ions on the deposited film surface (Chen *et al.*, 2018). The deconvoluted Fe spectrum (Figure 8(d)) presents Fe $3p_{3/2}$ and Fe $3p_{1/2}$ peaks at 711 eV and 719.8 eV (separation = 8.8 eV) indicating Fe³⁺ state in the film (Lee *et al.*, 2017; Yan *et al.*, 2018).

UV-visible Analysis

Figures 9(a) and 9(b) show the absorbance and transmittance spectra of pristine and Fe:BaSnO₃ films. All the deposited films display low values of absorbance and high values of transparency in the visible and IR region, indicating their high

optical quality. This can be ascribed to the expansive bandgap energy of host material and the films' good crystalline quality. Thickness enhancement with increased Fe-doping concentration can cause a reduction in transmittance. All the films show sharp absorption edges near the bandgap energy region. The films' absorption edge gradually shifts towards the longer wavelength region with Fe-doping level enhancement indicating a red shift in the bandgap values.

The films' absorption coefficient (α) is associated to the transmittance and thickness (d) by (Pankove, 1971):

$$\alpha = \frac{1}{d} \ln \left(\frac{1}{T} \right) \quad (3)$$

The optical bandgap energy E_g is determined using the Tauc plot relation:

$$\alpha(h\nu) = A(h\nu - E_g)^n \quad (4)$$

where A is a constant, and the exponent n indicates the nature of transition. The E_g is estimated by extrapolating $(\alpha)^{1/n}$ plot on the y-axis vs. $h\nu$ on the x-axis (Figure 9(c)). In the present case $n = 2$ yields the straight line plot indicating indirect allowed transition for the films. We observed a systematic reduction in the bandgap with increased doping concentration. The reduction in bandgap energy can be due to the energy distribution between the intra-energy levels on Fe-doping. Above the VB there can be an increase in the density of states, causing the creation of intermittent energy states in the region of bandgap of barium stannate (Zhang *et al.*, 2019). Therefore, iron doping in the BaSnO₃ host lattice is vital in reducing the bandgap or tuning the bandgap towards the visible region of the deposited films.

Refractive index (n) and extinction coefficient (k) are useful for the design of optical materials and fabrication of new optical devices (Khan *et al.*, 2010) and therefore, it is important to determine them. They can be considered as the fingerprint of the material and are related to the interaction between material and incident light. The refractive index (n) and extinction coefficient (k) of the pure and Fe:BaSnO₃ films are estimated (Table 2) from the optical spectra using the following equations (Khan *et al.*, 2010):

$$n = \frac{(1+R) + \sqrt{4R - (1-R^2)k^2}}{1-R}, \quad (5)$$

where R is the reflectance of the film, and

$$k = \frac{\alpha\lambda}{4\pi}. \quad (6)$$

Conclusions

We investigated the structural, morphological, and optical behaviour of BaSn_{1-x}Fe_xO₃ films deposited by PLD. The polycrystalline nature with BaSnO₃ cubic phase is identified from the XRD studies. A modest Fe-doping of 5 mol% in BaSnO₃ enhances its crystalline quality. The FESEM and AFM studies presents a unique pin-hole free surface morphology for 5 mol% Fe:BaSnO₃ films. A drastic film thickness enhancement is observed with increase in Fe doping concentration owing to the IMPC mechanism owing to the Fe-dopant which is magnetic in nature. The XPS spectra indicates the presence of Ba²⁺, Sn⁴⁺ and Fe³⁺ oxidation states in the films. The films exhibit good transparency in the VIS - IR region and we observed a bandgap renormalization with increasing doping concentration. Hence, the high crystallinity, smooth pinhole-free surface morphology, high transmittance, low extinction coefficient, and bandgap tuning of the deposited material suggest the possibility of using them for various optoelectronic devices.

Supplementary Information

Sample Preparation and Characterization

We have synthesized the pure and Fe-doped BaSnO₃ (BaSn_{1-x}Fe_xO₃, $x = 0, 0.01, 0.02, 0.03, 0.05$, and 0.07 mol%) powder samples using a solid-state reaction approach. The high-purity BaCO₃, SnO₂, and Fe₂O₃ were mixed in an agate mortar and pestle for six hours using acetone as the mixing agent. The mixed powder was heated in a platinum crucible in a programmable furnace at 1,250°C for six hours with a 5°C/min temperature rise. The powder sample thus prepared was mixed with poly-vinyl alcohol (binding agent) and ground again in an agate mortar. The pellets, with a diameter of 3 mm and a thickness of 1 mm, were prepared from the mixture by applying a pressure of 5 tons. The pressed pellets were sintered again in the furnace at a temperature of 1,000°C for 6 h and used for preparing films using pulsed laser deposition (PLD). We employed frequency-doubled 532 nm laser radiation (pulse width-7 ns) from a Q-switched Nd:YAG laser (Quanta-Ray INDI-series, Spectra-Physics, USA) for film preparation. We maintained a base pressure of 6×10^{-6} mbar in the chamber using a diffusion pump and rotary pumps. We mounted the pellets (target) on a rotating target holder and

rotated them at a uniform speed to avoid pitting on the surface of the target and to ensure uniform deposition of BaSnO₃ films. We deposited the pure and Fe-doped BaSnO₃ films on a quartz substrate under the optimized deposition conditions (deposition duration = 45 min., laser energy = 60 mJ, background oxygen pressure = 0.02 mbar, substrate target distance = 5 mm, and substrate temperature = 600°C). The films thus prepared were post-annealed at a temperature of 900°C for 1 h, and the films with Fe-doping levels 0, 1, 2, 3, 5, and 7 mol% are labeled as BSF0, BSF1, BSF2, BSF3, BSF5, and BSF7, respectively.

We used the X-ray diffraction technique for analyzing the crystalline nature of the films using CuK α X-ray radiation (X-ray wavelength 1.54060 Å and 2 θ range of 20-80°, Bruker Advance 8 in Bragg-Brantano geometry). We used NOVA NANOSEM 450 (FEI, Bruker, USA) and Bruker Dimension Edge with Scan Assist in contact mode for the morphological analysis of the films and Quantax 200 Energy Dispersive X-ray spectrometer for their elemental composition analysis. We used Perkin-Elmer Lambda 950 spectrophotometer for the optical absorption and transmission spectral measurements in the 2,300-250 nm wavelength range. We studied the samples' surface composition and elemental analysis using X-ray Photoelectron Spectrometer (XPS) ESCALABX1+A1528 employed with Advantage software. We estimated the film thickness using lateral FESEM images and stylus-profilometer [Veeco Dektak-6M)].

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