Facile Way of Making Hydrothermally Synthesized Crystalline SrSnO₃ Perovskite Nanorods Suitable for Blue LEDs and Spintronic Applications

Aadil Ahmad Bhat,* M. Burhanuz Zaman, Javied Hamid Malik, Khurshaid Ahmad Malik, Insaaf Assadullah, and Radha Tomar

ABSTRACT: Mn doping in SrSnO₃ perovskite material via hydrothermal process under subcritical conditions is reported for the very first time. The present article aims to carry this perovskite suitable for blue light-emitting diodes (LEDs) and spintronic applications. The influence of various Mn doping percentages on structural, morphological, compositional, optical, photoluminescent, and magnetic properties of SrSnO₃ is demonstrated. The perovskite material is grown in an orthorhombic crystal structure having a space symmetry of Pnma along with point group of mmm as determined from the Rietveld refinement. Doping is an excellent way to modify the properties of wide-band-gap perovskite nanostructures. Incorporation of Mn is the result of exact substitution. Morphological studies indicate formation of rodlike structures with thickness in nanoscale dimensions (180−280 nm), and the thickness is a function of doping concentration. The higher doping concentration resulted in enhanced growth of the nanorods. Selected area electron diffraction (SAED) results showed the single-crystal nature of the nanorods. Thermogravimetric analysis (TGA) confirmed the high stability of the material at elevated temperatures. Also, the doped perovskite material is transparent in the visible light, active in the ultraviolet region having a band gap of \( \sim 2.78 \) eV, and is tuned up to 2.25 eV as the Mn doping concentration reaches 10%. The transfer of excitonic energy from the host material to the dopant Mn²⁺ ion leads to the formation of spin-forbidden \( [4T_1 \rightarrow 6A_1] \) emission. Later on, photoluminescence study indicates an enhancement in luminescence behavior of Mn doped perovskite nanostructures. The Commission Internationale de l’Éclairage (CIE) diagram drawn to find the color coordinates of the nanorods determines their suitability for blue LEDs. In addition, Mn doping results the conversion of diamagnetic SrSnO₃ into a ferromagnetic material, making the nanorods suitable for spintronic applications.

1. INTRODUCTION

Perovskite materials of type ABO₃ have been explored extensively in the recent past due to the fact of achieving interesting optical, electronic, dielectric, and photocatalytic properties. The family of alkaline-earth stannate perovskites (ASnO₃, A = Sr, Ca, Ba) has been studied for diverse technological applications, including photocatalysis, dielectrics, high-temperature humidity sensing, etc. Moreover, the electronic structure comprising of wide-bandgap perovskites have become a fascinating topic for researchers from the last few decades because of their wide application in the field of engineering technology and scientific community. In relating to this, SrSnO₃ a wide-band-gap perovskite material exhibiting an orthorhombic crystal phase with space symmetry Pnma. Since doping is an easy way to modify the band gap of any semiconducting material, various research groups have reported rare earth metal and transition metal doping of SrSnO₃ depending on whether luminescent or photocatalytic properties were in consideration. Among such perovskite nanostructures, doped SrSnO₃ has been explored mostly as a photoluminescent and photocatalytic material. Doping of f-block elements, such as europium and samarium, has also been reported to enhance the photoluminescent properties of SrSnO₃ perovskite material. From the literature survey, it was found that doping of d block element in SrSnO₃ has been widely explored as it enhances the photoluminescence properties of the host material. When a dopant is incorporated in the SrSnO₃ host material, the dopant may occupy the A site of the host lattice. The reason for this is to maintain excessive positive charge and nonequal substitution. Transition metal doping in SrSnO₃ enhances the optical, magnetic, and photocatalytic properties. A 3d element (Cu)
as a dopant of SrSnO$_3$ is a prime candidate for reduction of NO by exhibiting extreme photocatalytic activity. Different chemical methods have been adopted for the synthesis of SrSnO$_3$ nanostructures. It is quite well known that the method of synthesis has a great influence on the physical properties, which leads to formation of different surface morphologies. Among various chemical methods, the hydrothermal process is an easy and economical method that allows for control over the growth and the size of the materials synthesized.

Various d block elements [Fe, Co, Cr, V, Cu] have been doped in SrSnO$_3$ perovskites to modify the physical properties. However, the existence of the ferromagnetic character from the diamagnetic material [SrSnO$_3$] by Mn doping is not yet investigated. The present work is on the hydrothermal synthesis of Mn-doped SrSnO$_3$, which is reported for the first time as far as Mn doping of SrSnO$_3$ is concerned. The crystal structure of the Mn-doped SrSnO$_3$ orthorhombic perovskite is shown in Figure 1.

The photoluminescent properties are enhanced by Mn doping, and the material is made suitable for blue light-emitting diodes (LEDs). The perovskite material is diamagnetic in nature, and the present work demonstrates the conversion of the diamagnetic SrSnO$_3$ into a ferromagnetic material.

2. CHARACTERIZATION TECHNIQUES

X-ray diffraction (XRD) studies were performed on Rigaku Miniflex 600 diffractometer. Scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) were performed for morphological and compositional analysis using a field emission-scanning electron microscope (FE-SEM) (Philips Model-Quanta 200 FEG). The morphology was also studied using transmission electron microscopy (TEM) (JEOL 1230 fitted with a GATAN ORIUS CCD camera). Optical properties were determined using a UV–visible spectrophotometer (UV2450 Shimadzu). For photoluminescence, a spectrofluorophotometer (RF 6000, Shimadzu) was employed. Magnetic properties were studied using a vibrating sample magnetometer (VSM).

3. RESULTS AND DISCUSSION

3.1. XRD Analysis. Initial confirmation of material formation was carried out with the help of X-ray diffraction (XRD). The XRD patterns of the synthesized samples are shown in Figure 2a. From the patterns, the crystalline nature and the crystal phase of the synthesized samples are determined. The XRD pattern of various samples consists of high-intense peaks that determine the crystalline nature. The indexed peaks show that the samples have grown in an orthorhombic crystal structure. On inclusion of different Mn doping percentages into the base perovskite material, the crystal phase is maintained and no considerable change in the peak positions is observed. The results indicate the exact substitution of the doping atoms at the vacant lattice sites. There is an extra peak at 2$\theta$ = 27° that determines trace elements of SnO$_2$ in the samples. The peak intensity was

![Figure 1. Representation of the Mn-doped SrSnO$_3$ orthorhombic perovskite.](image)

![Figure 2. (a, b) XRD patterns and lattice strain of samples A, B, C, D, and E, respectively.](image)
enhanced as the doping percentage increased, indicating improvement in the crystalline behavior. The crystallite size of the samples was determined using the famous Scherrer formula given below:

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \]

where \( D \) is the crystallite size of the synthesized material, 0.9 is the shape factor, \( \lambda \) is the wavelength of X-rays, and \( \beta \) is the full width at half-maximum (FWHM). The crystallite size for samples A, B, C, D, and E are 53.5, 53, 52.56, 49.8, and 47.47 nm, respectively. Reduction in the crystallite size of the host material is mainly due to the difference in the atomic radii of Mn and Sr. Mn doping increases the tendency of agglomeration, forming large molecules. For lattice parameter calculation, the following formula was used:

\[ \frac{1}{d_{hkl}^2} = \frac{k^2}{a^2} + \frac{l^2}{b^2} + \frac{\ell^2}{c^2} \]

The lattice parameters of the samples are summarized in Table 1.

The microstrain can be demonstrated using a Williamson Hall plot, which is used to portray the microstrain and the crystallite size of the material. The equation is given by
\[ \beta_{hkl} \cos \theta_{hkl} = \frac{K}{D} + 4\varepsilon \sin \theta_{hkl} \]

where \( \beta \) is the FWHM, \( \theta \) is the diffraction angle, \( K \) is the shape factor, which is equal to 0.9, \( \lambda \) is the XRD wavelength (1.540), \( D \) is the crystallite size, and \( \varepsilon \) is the microstrain [ref 14]. The Williamson Hall plot is a graph between \( \beta \cos \theta \) and \( 4 \sin \theta \). The slope of the graph provides information regarding the microstrain, and the intercept shows the crystallite size. It is clearly shown in Figure 2b that as the concentration of the dopant increases, the lattice strain and the slope of the graph also increase. The Rietveld refinement of the SrSnO\(_3\) perovskite is shown in Figure 3.

### 3.2. Morphological Analysis

The morphology of the synthesized nanostructures has been investigated using transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The TEM micrographs are shown in Figure 4a–c, and from the micrographs, depicts rodlike structures having a nanoscale thickness with variable lengths. All the samples exhibit almost the same morphology (rods) and indicates the growth is anisotropic. Since no additive or template is used during the synthesis, the anisotropic behavior in the growth is totally ascribed to the nature of the reaction medium (distilled water). Under the prevailing reaction conditions, an increase in the viscosity and a consequent fall in the dielectric constant of water at higher temperatures and pressure cause reactions to occur at higher rates. Therefore, under the subjected hydrothermal conditions, reactions occur at faster rates and result in anisotropic growth of the nanostructures.\(^{29,30}\) The growth is dominant along a particular crystal direction, i.e., one-dimensional growth is dominant. From the micrographs, it is clearly visible that the nanorods with higher Mn doping concentrations are thicker. Sample A nanorods are about 180 nm thick, whereas sample B nanorods are 200–250 nm thick. The nanorods of sample C are the thickest, with \( \sim 240–280 \) nm thickness. These results indicate enhancement in the growth of the nanorods with doping. The selected area electron diffraction (SAED) pattern of the samples shown in Figure 4d comprises parallel lines of bright spots along a particular direction. Thus, the SAED pattern captured at a particular rodlike structure elucidates the single-crystal nature of the rods.

Scanning electron microscopy is used to determine the surface morphology of the synthesized doped perovskite material. The SEM micrographs shown in Figure 5 also contain rodlike structures throughout the samples and support the TEM results of the samples. The samples show uniform morphology throughout, consisting of nanorods of thickness 125–400 nm with variable lengths.

Since doped SrSnO\(_3\) is a multinary perovskite, determining the stoichiometric ratio of the constituent elements is a cumbersome process. The synthesized samples were subjected to energy-dispersive spectroscopy (EDS) so as to determine the composition. The EDS spectra are shown in Figure 6.
atomic percentage tables in the insets of the corresponding spectra of the samples. The spectra showed the presence of only Sr, Sn, Mn, and O in the samples and thereby confirm the purity of the samples. The inset tables show that the constituent elements are in the stoichiometry ratio as was taken in the precursor solutions.

3.3. FTIR Analysis. The presence of biomolecules in the synthesized samples is detected with the help of Fourier transform infrared (FTIR) spectroscopy. The FTIR spectra of the samples are shown in Figure 7. A sharp dip in the spectra near 628 cm$^{-1}$ occurs because of metal oxide antisymmetric vibration (Sn–O), and this stretching is most predominant. The presence of the carbonyl group (C=O) is determined by the occurrence of a peak at 1000 cm$^{-1}$. Sn–OH vibration is also detected and is evident from the peak observed at 1492 cm$^{-1}$. The peak at 1086 cm$^{-1}$ is ascribed to SrCO$_3$. C–H stretching is observed at wavenumber 2885 cm$^{-1}$.

Figure 6. EDS spectra of samples A, B, C, D, and E with inset bar graphs determining the elemental composition.

Figure 7. FTIR spectra of samples A, B, C, D, and E.

Figure 8. TGA results of samples A, B, C, D, and E.
3.4. TGA Analysis. To investigate the thermal stability of the synthesized perovskite material, thermogravimetric analysis (TGA) was carried out and the results are shown in Figure 8. The samples were subjected to elevated temperatures (30–700 °C) under a nitrogen atmosphere, and the corresponding weight changes were recorded. The results indicate a minor weight loss in the materials, except for a maximum loss observed in sample A (see Figure 8). This weight loss observed is believed to have occurred due to the evaporation of water molecules present because of the moisture and due to some (OH) groups attached to the compound. The negligible weight loss observed indicates that the samples are quite stable at high temperatures.

3.5. Optical Investigation. Optical absorbance was observed in the wavelength range of 250–900 nm using a UV–visible spectrophotometer. The absorbance spectra are

![Figure 9. (a) Optical spectra and (b) corresponding Tauc plots for band-gap calculation.](image)

![Figure 10. (a) PL spectra and (b) the corresponding CIE diagram.](image)

![Figure 11. Schematic energy level diagram of Mn-doped SrSnO₃ perovskite.](image)

![Figure 12. Room-temperature VSM characteristics of samples A, B, C, D, and E.](image)
shown in Figure 9a, and the samples show good absorbance in the ultraviolet region of the solar spectrum. A sudden rise in absorbance is observed in all of the samples at around 350 nm. This wavelength corresponds to the band edge of the material. The direct band-gap values of the samples were determined from the absorbance spectra via the Tauc plots shown in Figure 9b. From the Tauc plots, the band-gap values of samples A, B, C, D, and E were calculated to be about 2.25 eV. The band-gap values are lower than those reported for the pristine SrSnO3 perovskite material.8 This decrease in the band gap with Mn doping occurred because of the defect levels introduced between the conduction band minima and valance band maxima.

3.6. PL Spectra. The optical properties of the nanostuctures were also determined by studying the photoluminescence (PL) behavior of the materials at room temperature. The PL spectra of the samples observed at room temperature are shown in Figure 10a. The spectra consist of two peaks when the samples were eliminated with photons of wavelength 250 nm. A wide, small peak centered at ~365 nm (3.4 eV) corresponds to the near band edge (NBE) emission, and the emitted photons are slightly lower in energy than the corresponding optical energy band gap of the materials. This is because the exciton energy levels responsible for the photoluminescence lie just below the conduction band minima between the conduction and the valance band. The emission (blue emission) at 461 nm (2.68 eV) is believed to have appeared due to the electronic Mn2+(6T_{1g}→6A_{1g}) d→d spin-forbidden transition by transfer of energy from excitons in the host SrSnO3 material.34 From the PL spectra, it is clearly visible that the emission peak intensities increase with the doping concentration and thereby enhance the photoluminescence behavior of the material. Out of the five samples, sample E has higher peak intensity and hence exhibits better photoluminescence. The reason for the enhanced photoluminescent behavior of sample E might be due to the creation of more oxygen vacancies on Mn doping. The Commission Internationale de l’Eclairage (CIE) co-ordinate is determined to find the illumination of the materials using the CIE diagram calculated using Osram software. The CIE diagram is shown in Figure 10b, and the coordinates are (x, y) = (0.19, 0.13), which lie in the blue region of the diagram. This indicates that the synthesized photoluminescent materials are suitable for blue LEDs that form the backlit display of almost all modern LCD devices, such as mobile phones, television screens, etc. (Figure 11).

3.7. Ferromagnetic Analysis. Incorporation of Mn as the dopant into the SrSnO3 diamagnetic material was carried out so as to modify the magnetic behavior of the nanorods. Magnetic properties of the nanorods were explored at room temperature using the VSM technique. The VSM results of the nanorods obtained are shown in Figure 12. The plot shows hysteresis for all of the samples having a positive slope, elucidating the ferromagnetic nature of the samples. The extent of saturation increases with an increase in the Mn content. The ferromagnetism associated with the synthesized samples is ascribed to unpaired parallel electrons.

4. EXPERIMENTAL DETAILS

The reagents and chemicals used during the synthesis were purchased from CDH Chemicals and were of analytical reagent (AR) grade. For preparation of the Mn-doped SrSnO3 perovskite material, the hydrothermal method was used, followed by a subsequent calcination process. Sr(NO₃)₂, SnCl₂·2H₂O, and MnCl₂·4H₂O were chosen as precursor sources for strontium, tin, and manganese, respectively. Transparent aqueous solutions of Sr(NO₃)₂ (0.18 M) and SnCl₂·2H₂O (0.2 M) were prepared in separate beakers using a magnetic stirrer at room temperature. After 15 min of magnetic stirring, these two solutions were mixed together. To this mixture, 0.02 M MnCl₂·4H₂O was added while stirring. Further, a 2 M NaOH solution was added to the mixture so as to maintain a basic pH, and it resulted in formation of a white precipitate. This precipitate was then transferred into a Teflon-coated autoclave. The autoclave was then kept in an oven, and the temperature was set to 160 °C. The reaction was carried out for 15 h, and after the decided reaction time, the oven was turned off and the autoclave was kept as such till room temperature was reached. Then, the autoclave was opened and the settled white (milky) material was collected, washed, dried, and ground as reported elsewhere.22,23 The powder thus obtained was then calcinated in a furnace at 900 °C for 7 h. The material thus obtained was denoted as sample A. Two more samples were prepared under similar reaction conditions with 0.06 and 0.1 M MnCl₂·4H₂O concentrations and were labeled as samples B, C, D, and E respectively.

5. CONCLUSIONS

Mn doped SrSnO₃ nanostructures were prepared for the very first time under subcritical conditions. The effect of Mn doping on the growth and properties of SrSnO₃ is studied. The structural properties confirmed that the materials grow in the orthorhombic phase. Morphological studies showed formation of nanorods. The SAED patterns represented the single-crystal nature of the nanorods. TGA confirmed that the nanomaterials are quite stable at elevated temperatures. Optical absorbance showed that the doped perovskite material is ultraviolet-active. The PL study concluded the enhancement in the luminescence behavior of the perovskite nanorods with Mn doping. The emission arising at nearly 460 nm is due to d→d transition of Mn, which results in the spin-forbidden electronic transition from the [6T₁→6A₁] transition state. The CIE diagram showed that the nanorods were suitable for blue LEDs and hence have the potential ability to serve as backlit displays for liquid-crystal display (LCD) screen-based devices. The magnetic behavior showed the ferromagnetic character of the nanorods that indicated the suitability of the perovskite for spintronic applications.

AUTHOR INFORMATION

Corresponding Author

Aadil Ahmad Bhat — School of Studies in Chemistry, Jiwaji University, Gwalior 474011, India; orcid.org/0000-0002-7510-9663; Email: nabiyaadillo78@gmail.com

Authors

M. Burhanuz Zaman — School of Studies in Physics, Jiwaji University, Gwalior 474011, India; orcid.org/0000-0003-0691-6338

Javied Hamid Malik — School of Studies in Chemistry, Jiwaji University, Gwalior 474011, India

Khursheid Ahmad Malik — School of Studies in Chemistry, Jiwaji University, Gwalior 474011, India

Insaaf Assadullah — School of Studies in Chemistry, Jiwaji University, Gwalior 474011, India
Radha Tomar – School of Studies in Chemistry, Jiwaji University, Gwalior 474011, India

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c00831

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
The authors are thankful to IIC-IIT Roorkee for providing FE-SEM/EDS facilities. They are grateful to the CIF and the Department of Physics, Jiwaji University, Gwalior, for extending the TEM, XRD, FTIR, TGA, and optical facilities. They also acknowledge Dr. Shakeel Ahmad Khanday and Prof. Poolla Rajaram for help with the discussion of the results.

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