Bi-doped SnO₂ transparent conducting thin films deposited by spray pyrolysis: structural, electrical, optical, and photo-thermoelectric properties

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Abstract
In this research, light and heavy Bi-doped SnO₂ thin films were prepared on glass substrates by spray pyrolysis technique. The effect of heavy doped-Bi on the structural, morphological, electrical, photo-thermo-electrical, optical properties of SnO₂ thin films has been investigated. The Bi/Sn atomic ratios (x=[Bi/Sn]) were varied from 0 to 0.30 in the spray solution. X-ray diffraction analysis showed the formation of SnO₂ tetragonal rutile structure in low doped deposited thin films and amorphous structure for heavy Bi-doped SnO₂. Also, the SnO₂-Bi₂O₃ binary thin films were formed for x=[Bi/Sn]=0.05. Scanning electron microscopy images indicated that the nanostructure of the condensed thin films has a rectangular-particle growth toward particle-spherical growth. The Hall effect measurements have shown n-type conductivity in all deposited thin films. The lowest sheet resistance of 39.3 MΩ/□ and highest carrier concentration of n=4.53×10¹⁸ cm⁻³ was obtained for the thin film deposited with x=0.10. The maximum of the Seebeck coefficient (S)=325 μVK⁻¹ and figure of merit (ZT)=1.85 was obtained for the thin film deposited with x=0.20. The average transmittance of thin films varied over the range of T=72–84%. The bandgap values of samples were obtained in the range of E₉=3.52–3.88 eV for the direct band gap. From the photoconductivity studies, the sample prepared with x=0.20 exhibited the highest photoconductivity among the SnO₂:Bi thin films.

Keywords SnO₂ · Bi-doping · Spray deposition · Thermoelectric properties

1 Introduction

Research and innovation in the field of semiconductor physics to achieve new properties and applications for the construction of advanced and modern devices has always been a topic of interest to researchers and has allocated the largest volume of research annually.

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The new solid-state components, which have very high speeds in the transmission of audio and video, as well as transistors and multiple semiconductor quantum junctions, solar cells, memory components, and processing in quantum information, owe much to this research. One of these advanced and widely used materials is transparent conducting oxides (TCOs) (He et al. 2020; Li et al. 2021; Zinchenko et al. 2019; Afre et al. 2018; Dawar et al. 1995).

Transparent conducting oxides (TCOs) have been widely studied in recent years since they have shown concurrently high optical transparency in the visible region and high electrical conductivity. According to the reported results, the best n-type TCOs are In$_2$O$_3$: Sn (ITO), SnO$_2$: F (FTO), ZnO: Al (AZO) films. Optical transparency of more than 90% and resistivity in the order of $10^{-4}$ $\Omega$ cm has been found for these films (Afre et al. 2018; Dawar et al. 1995).

Among the transparent conductive thin films, SnO$_2$: F (FTO) has special importance and received more attention due to its low cost of synthesis, abundance and solidity of processes, and high chemical stability. For example, they have been used in, flat-panel displays, electrochromic devices, solar cells, electromagnetic shielding, functional glasses, and gas sensors. In heat-efficient window applications, the TCOs are used as filters that reflect in the infrared region and remain transparent in the visible region (Zinchenko et al. 2019; Afre et al. 2018).

Conventional n-type TCO materials are prepared by various deposition methods such as physical vapor deposition (PVD), thermal evaporation, chemical vapor (CVD), and spray pyrolysis. However, among these deposition methods, the spray pyrolysis (SP) technique is an inexpensive method for the deposition of transparent conducting oxides and other materials such as optical selective coating, magnetic oxide materials, superconductors, and semiconductor thin films. It is a relatively simple and inexpensive technique for large-scale coatings on glass and special substrates at atmospheric pressure (Dawar et al. 1995; Ma et al. 2021). The microstructure of the thin films can be affected by deposition parameters such as the substrate temperature, spray rate, and solution concentration. Lower temperatures lead to more disordered i.e. polycrystalline and amorphous structures, while higher temperatures lead to increased polycrystalline grain sizes and more condensation. This technique is compatible with other conventional processes like physical vapor deposition in fabricating detectors, thin film sensors, electrochromic devices, solar cells, transparent p–n junctions, and other optoelectronic devices (Dawar et al. 1995).

Recently, binary transparent oxides of n-type and p-type TCO materials have been developed such as n-Zn$_2$SnO$_4$ (Xueai et al. 2020; Sung et al. 2020), n-MgIn$_2$O$_4$ (Chang et al. 2021), n-CdSb$_2$O$_6$:Y (Yanagawa et al. 1994), n-ZnSnO$_3$ (Fujiwara et al. 2019), p-CuAlO$_2$ (Gour et al. 2021), p-CuGaO$_2$ (Duinong et al. 2019), p-SrCu$_2$O$_2$ (Yu et al. 2021), p-ZnO:Ga, N (Shet et al. 2011) and p-NiO: Li (Kumar and Sahay 2021; Azimi Juybari et al. 2010). Therefore, the use of n-type and p-type TCOs in the fabrication of active elements in optoelectronic devices as transparent p–n junctions is possible (Chiu et al. 2008; Ahmed et al. 2006; Bagheri-Mohagheghi and Shokooh-Saremi 2004, 2010; Al-Saadi et al. 2019; Filippatos et al. 2021; Hasan Zadeh Maha et al. 2013; Indira Gandhi et al. 2013).

In addition, the new impurities for the study of modified properties of tin oxide thin films such as Al (Ahmed et al. 2006; Chinappa et al. 2011), Li (Bagheri-Mohagheghi and Shokooh-Saremi 2004), Co, Ni (Bagheri-Mohagheghi and Shokooh-Saremi 2010), Cr (Al-Saadi et al. 2019; Indira Gandhi et al. 2013), B (Filippatos et al. 2021), Cu (Hasan Zadeh Maha et al. 2013), co-doped P and F and Sb (Mokaripoor and Bagheri-Mohagheghi 2015; Muruganantham et al. 2011; An and Kim 2014; Sushant Gupta et al. 2013; Yang et al. 2013; Tsubota et al. 2014a) have been investigated; but there are few reports in our
knowledge on the Bi-doping in SnO₂ transparent conducting thin films deposited by spray pyrolysis.

Bismuth is a metallic element with atomic number of 83, pentavalent with electron configuration \([\text{Xe}] 4f^{14} 5d^{10} 6s^2 6p^3\), atomic radius \(r = 1.56 \text{ Å}\) and rhombohedral structure \((a = b = c; \alpha = \beta = \gamma \neq 90^\circ)\). It has long been considered as the element with the highest atomic mass that is stable similar to lead. Additionally, bismuth has the highest Hall coefficient and when deposited in a sufficiently thin film on a substrate, bismuth is a semiconductor, rather than other metals. The most Bi-compounds in oxide and sulfide phases are Bi₂O₃, Bi₂O₅, and Bi₂S₃ (Indira Gandhi et al. 2013).

SnO₂ is known as a semiconductive oxide and is used as one of the thermoelectric base materials. The mobility of the carrier in the SnO₂ is high and increases/decreases with the addition of some impurities. In order to reduce the conductivity and increase the thermal conductivity, which plays an important role in the figure of merit, heavy elements such as bismuth, antimony, etc. can be used. Since SnO₂ ceramic has a porous structure, so the thermoelectric performance of the SnO₂ system can be improved with a dense structure because the value of the electrical conductivity must be significantly improved. The addition of heavy metals has been reported to improve the thermoelectric properties of SnO₂ (Tsubota et al. 2014a). The thermoelectric properties of Sb-doped SnO₂ have been extensively studied (Tsubota et al. 2014a, b; Yanagiya et al. 2012, 2011; Rubenis et al. 2016), but Bi-doped SnO₂ has rarely been studied. Bismuth and antimony are known to have similar chemical properties due to their similar positions in the periodic table of elements.

The Bi³⁺ doping together increases the electrical conductivity and the Seebeck coefficient because of the combined effects of decreasing the carrier concentration and increasing the carrier mobility. In addition, the use of heavy elements, such as antimony, bismuth, and tellurium, can reduce the frequency of atomic vibration, and since bismuth is heavy element, so expected to add bismuth to SnO₂ as impurity, thermoelectric properties of SnO₂: Bi thin films improve. Also, heavy elements doping can effectively reduce thermal conductivity, which is important for increasing the figure of merit (Wang 2018). Since the photoconductive and thermoelectric properties of SnO₂: Bi thin films have been less studied, in this study, after the synthesis of SnO₂ transparent conducting thin films by spray pyrolysis, the effect of bismuth concentration with different percentages on structural, optical, electrical, photoconductive, and thermoelectric properties of SnO₂: Bi thin films have been studied.

The thin films were studied using X-ray diffraction (XRD), Scanning electron microscopy (SEM) analysis, Hall measurement, Seebeck effect, Photoconductive effect, and UV–Vis absorption spectroscopy.

2 Experimental procedures

2.1 Preparation of SnO₂: Bi thin films

Bi-doped SnO₂ thin films were deposited on glass substrates by spray pyrolysis technique. The details of this method have been reported elsewhere (Azimi Juybari et al. 2010). For the preparation of thin films, the spray solutions were prepared by dissolving 0.1 mol of tin chloride: SnCl₄, 5H₂O, and bismuth nitrate: Bi₅O₅(NO₃)₄ with \(x = [\text{Bi/Sn}]\) atomic ratio = 0, 0.05, 0.10, 0.15, 0.20, 0.30 in a solvent containing double distilled water, and ethanol with a volume ratio of 1:1. For more solvability of bismuth nitrate in distilled
water a few drops of nitric acid and chloric acid were added to the spray solution. In any step, 20 ml of the starting solutions were sprayed on glass substrates, using compressed air \((3 \times 10^5 \text{ Pa})\) as the carrier gas with a solution flow rate of 10 ml/min and a nozzle to substrate distance of \(d = 35\) cm. The substrate temperature was fixed at \(T = 480\) °C. It should be noted that the bismuth solution is a corrosive solution, therefore, spray processes were done with a glassy nozzle. The steps for preparing \(\text{SnO}_2: \text{Bi}\) thin films by spray pyrolysis are shown in Fig. 1.

### 2.2 Characterization

The deposited thin films were characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM), UV–Vis spectroscopy, and electrical, optical, and thermoelectric, and photoconductivity properties of thin films have been studied. The XRD patterns of thin films were recorded by D8 Advance Bruker system with Ni filtered using Cu Kα \((\lambda = 0.15406\) nm) radiation at an operating voltage of 35 kV and a current of 30 mA.

Dissolving 0.1 mol \(\text{SnCl}_4 \cdot 5\text{H}_2\text{O} + \text{Bi}_5\text{O}(\text{OH})_9(\text{NO}_3)_4\) with \(x = [\text{Bi}/\text{Sn}]\) atomic ratio = 0, 0.05, 0.10, 0.15, 0.20, 0.30 in a double distilled water + ethanol with a volume ratio of 1:1

Use a few drops of nitric acid for more solubility of \(\text{Bi}_5\text{O}(\text{OH})_9(\text{NO}_3)_4\) in distilled water and hydrochloric acid in spray solution

Adjust spray nozzle distance 35 cm, spray rate 10 (ml/min), \(T = 480\) °C for glass substrates and compressed air \((3 \times 10^5 \text{ Pa})\) as the carrier gas

Spraying \(\text{SnO}_2: \text{Bi}\) thin films with different molar ratios = 0, 0.05, 0.10, 0.15, 0.20, 0.30 on the glass substrates

Measuring the sheet resistance and the average thickness of the thin films, and studying the structural, electrical, optical, photoconductive and thermoelectric properties of \(\text{SnO}_2: \text{Bi}\) thin films

**Fig. 1** Flowchart of synthesis thin films of \(\text{SnO}_2: \text{Bi}\) thin films with different ratios of Bi
Surface morphology of the thin films was observed using a Philips XL-30 SEM system with an acceleration voltage of 20 kV.

The sheet resistance ($R_S$) of the thin films was measured by the two-point probe method using thermally evaporated aluminum electrodes in vacuum technique using the Edwards E-306 coating system. Then, by measuring the sheet resistance ($R_S$) and the average thickness of the thin films ($t$), the electrical resistivity of the samples was calculated using the following relation:

$$\rho = R_S \times t.$$  \hspace{1cm} (1)

A Hall effect experiment was performed at room temperature $T = 300$ K by applying a magnetic field ($B = 130$ mT) perpendicular to the plane of the thin films to determine the concentration and the type of the majority carriers and also, resistivity ($\rho$) of the thin films. A schematic view of the Hall effect experiment is shown in Fig. 2.

To measure the thermoelectric effect, a system is used in which a temperature difference ($\delta T$) is applied to both ends of the sample using a heat source (electric heater) and a cold source (water and ice). Then, with increasing temperature, a difference in thermoelectric potential ($\delta V$, emf) appears at the two ends of the sample, which is called the thermoelectric effect. Then the Seebeck coefficient is obtained from the ratio of the difference in electrical voltage to the temperature difference. The Seebeck coefficients were determined by calculating the slope of the thermoelectric (emf) versus temperature difference ($\delta T$) at the temperature range $T = 300$–$500$ K (Hasan Zadeh Maha et al. 2013).

A schematic view of the thermoelectric apparatus is shown in Fig. 3. The open circuit voltage generated by the sample was measured using a digital microvoltmeter.

The temperature difference between the two ends of the sample causes the transport of carriers from the hot to the cold end, thus creating an electric field, which gives rise to thermoelectric across the ends. The generated thermoelectric is directly proportional to the temperature gradient applied to the two ends of semiconductor thin films.

The optical measurements were carried out in the range of $\lambda = 190$–$1100$ nm using Unico 4802 double beam spectrophotometer system. The thickness of the thin films ($t$) was controlled by deposition parameters and determined from transmission interference fringes by the Swanepoel method (Azimi Juybari et al. 2010). To study the photoconductive properties...
of thin films, samples were exposed to light radiation with a fixed intensity (4200 Lux) at a fixed distance (20 cm) using a normal light source (a tungsten fiber lamp). Then, the electrical resistance change of the prepared thin films was recorded.

3 Results and discussion

3.1 Structural properties

The XRD patterns of thin films with different values of $x$ from 0 to 0.30 are shown in Fig. 4a–e. As seen, for $x=0$ and $x=0.05$, thin films are polycrystalline corresponding to SnO$_2$ phase and have tetragonal rutile structure and show preferred orientation along (211) which changes into the only plane (200) at $x=0.05$. Other orientations such as (110), (310), and (301) are shown, but with lower intensities. At doping level of $x=0.05$, the $\gamma$-Bi$_2$O$_3$ phase is also shown.

By adding Bi impurity more than $x=0.05$ toward $x=0.30$, the intensities of peaks decreased considerably, and thin film structure close to amorphous nature with a higher background. As seen in Fig. 4c–e as the Bi-concentration is increased gradually, the SnO$_2$ phase disappeared and unstable phases of tin oxides such as beta-SnO, Sn$_3$O$_4$, and Sn$_5$O$_6$, and also tin–bismuth oxides combined phases such as Bi$_2$SnO$_7$, and Bi$_7$SnO are indicated.

Regarding atomic radius of Bi$^{5+}$ (1.56 Å) and Sn$^{4+}$ (0.71 Å), in doping levels lower than $x=0.10$, the substitution of Bi$^{5+}$ ions in lattice positions of Sn$^{4+}$ is possible which results in increasing the intensities of the peaks. Indeed, we knew that at a low doping level this is possible, even if the atomic radius of impurity becomes more than the atomic radius of the host atom (Remsen 2012). However, in doping level $x=0.10$ and higher, bismuth ions occupy the interstitial sites, therefore, lead to lattice disorder and defect in BTO thin film structure and decreasing of crystallinity of thin films. This suggests there is a solubility limit for Bi in SnO$_2$ lattice in about $x=0.10$. The estimated crystallite size ($D$) is calculated using Debye–Scherrer’s formula (Azimi Juybari et al. 2010).

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (2)$$
where $\beta$ is the full width at half maximum of the corresponding XRD peak, $k$ is a constant ($\sim 1$) and $\theta$ is the Bragg angle. XRD parameters such as crystallite size (D) and the phases identified along (211) plane have been summarized in Table 1.

### 3.2 Surface morphology by SEM analysis

SEM micrographs of thin films are shown in Fig. 5. As seen, the surface morphology of the thin films is dependent upon the Bi doping level. In the low doping level of Sn ($x \leq 0.10$), the micrographs show that the nanostructure of the condensed thin films has separate single spherical crystallite and grain growth morphology, and further increasing the Bi content up to $x = 0.20$ trend to spherical grain growth type, but with very

![Fig. 4 a–f XRD patterns of Bi-doped SnO$_2$ with various concentrations of $x = \text{[Bi/Sn]}$ at.\%](image-url)
These results agree with XRD results which showed that with increasing the Bi-content the grain size of crystalline particles decreases. However, at $x \geq 0.20$ again crystallite size is increased.

Table 1 XRD parameters for Bi-doped SnO$_2$ thin films at (211) orientation

| Sample               | 20 (°) | Lattice distance (Å) | FWHM (°) | Mean grain size (nm) |
|----------------------|--------|----------------------|----------|----------------------|
| Un-doped SnO$_2$     | 51.761 | 1.7647               | 0.547    | 17.95                |
| SnO$_2$:Bi ($x = 0.05$) | 51.764 | 1.7646               | 0.411    | 23.90                |
| SnO$_2$:Bi ($x \geq 0.10$) | -     | -                    | -        | -                    |

Fig. 5 The SEM images of the morphology of Bi-doped SnO$_2$ thin films with various Bi-concentrations of $x = \text{[Bi/ Sn]}$ at.\

smaller size. These results agree with XRD results which showed that with increasing the Bi-content the grain size of crystalline particles decreases. However, at $x \geq 0.20$ again crystallite size is increased.
3.3 Electrical properties

The results of electrical measurements for SnO$_2$: Bi thin films have been summarized in Table 2. Also, variation of resistivity ($\rho$) and carrier concentration ($n$) as a function of $x$ is shown in Fig. 6. The resistivity of undoped SnO$_2$ thin film is $5 \times 10^{-3}$ (Ω cm). Apart from pure SnO$_2$ thin film, at first, the resistivity of thin films was decreased with Bi-doping up to $x \leq 0.10$ and reached to about 2.3 Ω cm at $x = 0.10$ and then it is increased in the range $0.10 < x \leq 0.20$ to about 22.7 Ω cm at $x = 0.20$.

The initial decrease in electrical resistance is due to the substitution of Bi$^{5+}$ ions at the Sn$^{4+}$ lattice sites. This substitution leads to the creation of donor levels that increase the density of free electrons. Then, the electrical resistance is increased which relate to creating new combined bonds from Bi–Sn–O in the SnO$_2$ lattice and creation of unstable phases, including Sn$_3$O$_4$ and Sn$_5$O$_6$. The formation of these phases increases resistance, because Bi is substituted in interstitial locations, the SnO$_2$ lattice. But, again in $x > 0.20$, resistivity decreased and reached about 3.6 Ω cm which is related to energy band structure due to the formation of Sn–O–Bi mixed phases or decrease of the $E_g$.

However, the intrinsic oscillation of resistivity is related to phase structure change of thin films due to Bi-doping. This tendency in the change of carrier concentration is seen, too.

The majority carrier concentration was calculated using the following equation by the Hall effect measurements (Azimi Juybari et al. 2010):

**Table 2** Electrical and thermoelectric measurement results of Bi-doped SnO$_2$ thin films

| x   | Sheet resistance ($R_s$, kΩ/□) | Resistivity ($\rho$, Ω cm) | Carrier concentration ($n$, cm$^{-3}$) | Carrier type (Hall effect) | Energy gap ($E_g$, eV) | Thickness (t, nm) | Δt = ± 50 |
|-----|-------------------------------|-----------------------------|---------------------------------------|-----------------------------|-----------------------|------------------|-----------|
| 0.00| 0.225                         | $1.25 \times 10^{-2}$       | $4.86 \times 10^{19}$                | (–)                         | 3.88                  | ~ 500            |           |
| 0.05| 120.0                         | 0.70                        | $2.67 \times 10^{17}$                | (–)                         | 3.58                  | ~ 650            |           |
| 0.10| 39.3                          | 2.35                        | $4.53 \times 10^{18}$                | (–)                         | 3.56                  | ~ 600            |           |
| 0.15| 81.2                          | 5.68                        | $4.83 \times 10^{16}$                | (–)                         | 3.55                  | ~ 700            |           |
| 0.20| 264.0                         | 22.44                       | $1.50 \times 10^{16}$                | (–)                         | 3.52                  | ~ 850            |           |
| 0.30| 51.8                          | 3.62                        | $1.35 \times 10^{18}$                | (–)                         | 3.52                  | ~ 700            |           |

**Fig. 6** Variation of electrical resistivity and carrier’s concentration of SnO$_2$: Bi thin films as a function of $x = \text{[Bi/Sn]}$ at.%
where $I$, $B$, $t$, $q$, and $V_H$ are the measured current, magnetic flux density, thin film thickness, electron charge, and Hall voltage, respectively. From the Hall effect experiment at room temperature ($T = 300$ K), it was found that the majority carriers were electrons for all doping levels (n-type conductivity).

### 3.4 Optical properties

The optical transmittance of the SnO$_2$: Bi thin films in the wavelength range of $\lambda = 300$–1100 nm is shown in Fig. 7. Totally, the average transparency of thin films relatively decreased from ~84 to ~72% when $x$ increases from 0 to 0.30. This behavior is due to the presence of Bi-ions in SnO$_2$ lattice and scattering in grain boundaries and decreasing the crystalline size as is expected from XRD analysis and SEM images. The doped sample deposited with $x = 0.10$ exhibits the highest transparency of about 80% in the visible region.

The optical energy gap ($E_g$) of the prepared thin films was determined from the optical measurements. The absorption coefficient for the thin films was found to follow the relation:

$$\alpha = A (\hbar \nu - E_g)^m / \hbar \nu$$

where $A$ is constant, $\hbar \nu$ is the incident photon energy, $m$ depends on the nature of band transition; $m = 1/2$ or 3/2 for direct allowed and direct forbidden transitions, and $m = 2$ or 3 for indirect allowed and indirect forbidden transitions (Azimi Juybari et al. 2010; Bagheri-Mohagheghi and Shokooh-Saremi 2010). From the $(\alpha \hbar \nu)^2$ versus $\hbar \nu$ plots, the intercept obtained by the extrapolation of the linear region to $\alpha = 0$ gives the direct bandgap ($E_g$) of the thin films (Fig. 8). The values of $E_g$ were obtained in the range of 3.52–3.88 eV (Table 2). $E_g$ gradually decreased with increasing Bi-doping level from $x = 0$ to $x = 0.30$.

This change of $E_g$ attributed to many-body effects so that with decreasing carrier concentration, the energy gap is also decreased (Bagheri-Mohagheghi and Shokooh-Saremi 2010).

**Fig. 7** Optical transmittance of Bi-doped SnO$_2$ thin films with different values of $x = [\text{Bi/Sn}]$ at.%
3.5 Photoconductive properties

To investigate the photoconductivity of semiconductor thin films, the sample is exposed to light at a certain wavelength. Then, pair of electrons and holes are produced by absorbing light energy in semiconductors and exciting the electrons to the conduction band. Therefore, the density of free electron carriers (holes) increases and as a result, the electrical conductivity increases. This phenomenon is known as photoconductivity in semiconductor physics. In this experiment, the resistance of the prepared thin films was obtained (under lighting) at specified time intervals at room temperature. The variation of the relative resistance of the thin films ($\Delta R/R$) with illumination versus exposure time and Bi-doping are shown in Fig. 9. As seen, the photoconductivity of the thin films is increased with increasing exposure time. Resistance of SnO$_2$: Bi thin films decrease immediately after exposure to light. Photoconductivity increases when the Bi-doping level increases from $x = 0$ to $x = 0.20$ and then it decreases. Thus, the exposure time and doping level have significant influence on the photoconductivity of the thin films. The thin film deposited with

Fig. 8 Plots of $(\alpha h\nu)^2$ versus $h\nu$ for SnO$_2$: Bi thin films with different values of $x = [\text{Bi/Sn}]$ at.%

Fig. 9 The relative change of sheet resistance versus exposure time for SnO$_2$: Bi thin films with different values of $x = [\text{Bi/Sn}]$ at. %
\( x = 0.20 \) exhibited more photoconductivity than the other prepared thin films. This effect is due to the presence of impurity levels and the band tail that is created near the edge of the conduction band. By absorbing photon energy, electrons are excited at these levels and easily transferred to the conduction band with the least energy available (Mokaripoor and Bagheri-Mohagheghi 2015).

### 3.6 Thermoelectric properties

Thermoelectric materials transform thermal energy into electrical energy. Although n or p-type metal oxides with acceptable electrical conductivity (Wang et al. 2010) are found for use in thermoelectric applications, studies are still needed to develop these materials.

The figure of merit of a thermoelectric material is expressed according to Eq. 5:

\[
ZT = \frac{S^2 \sigma}{\kappa T},
\]

where \( S \) is the Seebeck coefficient, \( \sigma \) is the electrical conductivity, \( \kappa \) is the thermal conductivity, and \( T \) is the temperature. The value of \( S^2 \sigma \) is the power factor that can be used to approximate the thermal performance. According to Eq. 5, to produce high-quality thermoelectric composites, materials must have high electrical conductivity and low thermal conductivity. Therefore, to increase the thermoelectric efficiency of composite material, it is necessary to consider high \( S \) and \( \sigma \) values and low \( \kappa \) values. However, one of the problems related to the efficiency of thermoelectric materials is the coordination of electrical and thermal conductivity due to the \( ZT \) relationship, which affects the capabilities of thermoelectric materials (Chen et al. 2018). In general, the scattering of phonons in the lattice reduces the thermal conductivity, and the addition of n or p-type semiconductors to the oxide material can be effective in increasing/decreasing the electrical conductivity of the composite material. In other words, due to the complex relationship between conductivity and thermal parameters, it is difficult to increase the value of \( ZT \) by adjusting these parameters.

To improve the thermoelectric properties, factors such as effective mass, charge carrier density, and carrier mobility play an important role. Because of increasing temperature, the mobility of carriers also increases. Therefore, the carrier moves from a higher temperature site to a lower temperature and a greater thermoelectric potential occurs (Xa et al. 2015).

Wiedemann–Franz law was used to calculate the \( ZT \) coefficient. According to Wiedemann–Franz’s law, in a semiconductor the relationship between thermal conductivity (\( k \)) and electrical conductivity (\( \sigma \)) is according to Eq. 6 (Xa et al. 2015; Lan et al. 2010):

\[
L = \frac{K}{\sigma T}
\]

where \( L = \frac{\pi^2 k_B^2}{3e^2} = 2.45 \times 10^{-8} \text{W} \Omega^{-1} \text{K}^{-2} \), \( k_B \) Boltzmann constant, and e electron charge are often used for thermoelectric materials (Lan et al. 2010).

Figure 10 presents the variation of the Seebeck coefficient versus temperature for \( \text{SnO}_2: \text{Bi} \) thin films. The slope of these diagrams determines the conduction type. If the temperature difference \( \Delta T \) between the two ends of a material is small, then the Seebeck coefficient of material is defined as:

\[
S = \frac{\Delta V}{\Delta T}
\]
where $\Delta V$ is the thermoelectric voltage seen at the terminals. As a result, in p-type semiconductors (which have only holes in mobile charges), $S$ is positive. Likewise, in n-type semiconductors (which have only negative mobile charges or electrons), $S$ is negative.

As seen in Fig. 10, thermoelectric power (emf) increases in the negative direction (n-type conductivity) for all thin films apart from $x = 0.30$ in agreement with Hall’s experiment at room temperature. In 0.30 Bi-doping level, initially, thermoelectric (emf) increases in negative direction and then increases in the positive direction (p-type conductivity) at temperature difference equal to $\Delta T = 80$ K. Indeed, we expect that with applying a thermal field to the thin film, trapped holes in lattice become free and majority carriers change from electron to hole. This problem related to creating holes in temperature difference more than $\Delta T = 80$ K, through oxygen vacancy due to releasing the $O^{2-}$ ions at high temperature (Al-Saadi et al. 2019; Filippatos et al. 2021). The highest Seebeck coefficient was obtained equal to 325 $\mu$VK$^{-1}$ for a prepared thin film with $x = 0.20$. Also, values of $\sigma$, $K$, Seebeck coefficient, and of the figure of merit are reported in Table 3. The results in Table 3 show that when Bi is doped in SnO$_2$ thin film, the electrical conductivity as well as the thermal conductivity calculated using Widmann-Franz’s law has the lowest value for the sample $x = 0.20$ and the maximum value without the doped sample, and the value of the figure of merit for $x = 0.20$ is 1.85, which is higher than the other samples. We know that the thermal conductivity of the samples depends mainly on the lattice contribution. Since the atomic

![Behavior of thermoelectric voltage against temperature difference for SnO$_2$: Bi thin films with different values of $x = [\text{Bi/ Sn}]$ at. %](image)

### Table 3: Results of measurement of thermoelectric properties of Bi-doped SnO$_2$ thin films

| $X$ | $\sigma (\Omega \text{ cm})^{-1} \times 10^{-2}$ | $K (\text{W m}^{-1} \text{ K}^{-1}) \times 10^{-6}$ | $S (\mu \text{V/ K})$ | $S^2\sigma (\text{W m}^{-1} \text{ K}^{-2}) \times 10^{-10}$ | $ZT (S^2\sigma T/k) (T = 300 \text{ K})$ |
|-----|---------------------------------|---------------------------------|-----------------|---------------------------------|-----------------------------|
| 0.00 | 80.00                           | 13.72                           | −198.00         | 313.63                          | 0.68                        |
| 0.05 | 12.82                           | 2.2                             | −98.18          | 12.41                           | 0.17                        |
| 0.10 | 42.55                           | 7.3                             | −86.1           | 31.54                           | 0.13                        |
| 0.15 | 17.6                            | 3                               | −124.00         | 27.1                            | 0.27                        |
| 0.20 | 4.45                            | 0.76                            | −325.00         | 47                              | 1.85                        |
| 0.30 | 27.62                           | 4.74                            | +5.71           | 0.09                            | 0.003                       |
weights and atomic radii of Sn and Bi are different (atomic weight Sn:Bi = 118.71:208.98 amu, and atomic radii Sn:Bi = 140:156 pm), the reduction in thermal conductivity in sample x = 0.20 can be mainly attributed to the increase in phonon scattering in the crystal lattice.

4 Conclusions

In this paper, the preparation and characterization of Bi-doped SnO2 thin films are reported. These thin films have been deposited on glass substrates by the spray pyrolysis technique. The structural, morphological, electrical, optical, thermoelectric, and photoconductive properties of prepared thin films have been investigated. The results are characterized as follows:

(a) It is observed that the physical properties of thin films strongly depend on the [Bi/Sn] concentrations in the deposition solution. The prepared low Bi-doped thin films exhibited a preferential growth along the (211) direction with a tetragonal rutile SnO2 phase. The thin films deposited with x = 0.05 exhibited better crystallinity than the other prepared thin films.
(b) The SEM images indicated that the nanostructure of the condensed thin films has a particle-cluster growth type with a nearly uniform surface.
(c) The minimum sheet resistance (Rs) and maximum carrier concentration (n) were obtained equal to 39.3 (KΩ/□) and 4.53 × 10^{18} cm⁻³, respectively, for the thin film deposited with x = 0.10. The majority carrier concentration (n) was obtained in the order of 10^{16}–10^{18} cm⁻³, using Hall effect measurements for Bi-doped SnO2 thin films.
(d) The thermoelectrical measurements showed that thermoelectric (emf) continuously increased in the negative direction (n-type conductivity) for all thin films except for x = 0.30 Bi-doped SnO2 thin film. The film deposited with x = 0.20 exhibited the best thermoelectric properties than the other samples. The Seebeck coefficient and figure of merit was obtained equal to 325 μVK⁻¹ and 1.85, respectively, for x = 0.20 Bi-doped SnO2 thin film.
(e) The transparency of the thin films decreased about 10%, as x increased from 0 to 0.30. The prepared thin film with x = 0.02 exhibited the highest optical transparency in the visible region.
(f) The band gap values were obtained in the range of 3.52–3.88 eV for direct allowed transitions.
(g) Photoconductivity studies showed that exposure time and Bi-doping play a very important role in the photoconductive property. Also, the best photoconductive property was obtained for the thin film deposited with x = 0.20.

These results showed that Bi doping modified the physical properties of the SnO2 thin films and made them suitable for solid state devices applications such as photoconductor, photo- thermoelectric, and sensor devices.

Declaration

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.
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