

Structural and optical properties of Zn doped Bi₂O₃ thin films prepared by chemical route with effect of bath temperatures

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The present work attempts to synthesize Zn doped Bismuth Oxide thin films deposited effectively on to micro glass substrates at different bath temperatures by Chemical Bath Route. The films were characterized by XRD, SEM, EDAX and optical analysis. XRD analysis reveals that all the films belong to monoclinic in polycrystalline structure with preferred orientation along (012). The optical energy gap values of Zn doped Bi₂O₃ thin films were in the range 2.21- 2.81 eV which depend on deposition temperatures. Zn - Bi₂O₃ thin films can be used in photo voltaic cells, gas sensors, optical coatings, flat-panel displays, micro electronics, light emitting diodes, batteries, super capacitors and fuel cell industries.

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1. Introduction

Zn doped Bismuth oxides (Bi₂O₃) have been broadly studied because they acquire fascinating properties such as bandgap involving 1.6 and 2.8 eV depending on the crystalline phase, high refractive index (>2.4), dielectric permittivity, photoconductivity, and photoluminescence, as well as high oxygen conductivity (~1-1.5 Scm⁻¹). A variety of applications ranging from optical and electrochromic coatings to photovoltaic cells, photo catalysts, MIS capacitors, microwave integrated circuits, sensors, and ionic conductors in micro solid oxide cells [1-5]. On the other hand, the attainment of these applications depends on the control over the reproducible nature of the material, since the properties are connected to the crystalline structure and composition. In the past, many researchers have used a variety of methods to obtain bismuth oxide thin films. For example, Switzer et al. synthesized single crystalline d-Bi₂O₃ film on gold substrates via electrodeposition, Lokhande et al. obtained Bi₂O₃ films by spray pyrolysis. Shimanoe et al. prepared Bi₂O₃ films by RF sputtering and evaluated their electrochromic properties. Leontie et al. deliberated over the optical and electrical transport properties of Bi₂O₃ films obtained by thermal oxidation of vacuum evaporated bismuth films, while Takeyama et al. prepared Bi₂O₃ films by means of atmospheric pressure halide chemical vapor deposition (CVD) using BiI₃ and oxygen as source materials. Armelao et al. reported the synthesis of Bi₂O₃ of thin films by dipping silica slides in solutions of ethyl alcohol (C₂H₅OH) and tris (2,20-6,60 - tetramethylheptane-3, 5- dionato) bismuth (III) [Bi(dpm)₃]. However, like most of other metal alkoxides, bismuth alkoxides suffer from high cost, unavailability, toxicity and fast hydrolysis rate [6]. Various methods employed for depositing Zn doped Bi₂O₃ thin films are chemical vapour transport, vacuum evaporation, spray pyrolysis, electrodeposition, pulsed laser deposition, sputtering and chemical bath deposition (CBD) technique. Among the various methods, CBD technique has many advantages such as simplicity, non necessity of sophisticated instruments, bare minimum material wastage, reasonable way of large area deposition, and no threat of handling poisonous gases [7]. CBD is a slow route which facilitates the superior orientation of crystallites with improved grain structure. It is observed that the deposition parameters at which Zn doped

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Bi_2O_3 thin films are grown play a crucial role in deciding the uniformity of thin films and its spectral response. Hence, an attempt has been made to prepare thin films on glass substrates from chemical baths of different pH values after optimizing other deposition parameters such as temperature, dipping time and concentration of ions in the bath. This article deals with the structural and optical analysis of CBD Zn doped Bi_2O_3 thin films prepared from three different chemical baths.

2. Experimental

Zn- Bi_2O_3 thin films were deposited on the micro glass slides using chemical route. The precursor solution was equipped with Bismuth (III) nitrate dissolved in 50 ml of deionized water with a concentration of 0.2 M, then 50 ml solution of Zinc nitrate was arranged with a concentration of 0.2 M and both the solution were mixed to make up 100 ml of precursor solution. Then 8 ml of triethonamine was added to the solution to maintain the acidity of the solution so as to dissolve the Bismuth (III) nitrate with constant stirring at room temperature further. To regulate the pH value NaOH solution was added. For prior to deposition, the micro glass substrate were cleaned using deionized water, NaOH solution and acetone. The substrate was positioned perpendicularly in the bath for deposition time of 1 hour 30 minutes at bath temperatures 50°C , 60°C and 70°C . While depositing the films at 70°C and pH value 12, uniform and compact films were obtained. Thus deposition parameters such as concentration of ions, the bath temperature, pH and dipping time have been optimized suitably.

2.1. Characterization techniques

X-ray diffraction (XRD) patterns of the samples were carried out on a D/MAX 2250 V diffractometer (Rigaku, Japan), using monochromatized $\text{Cu K}\alpha$ (0.15418 nm) radiation under 40 kV and 100 mA and scanning over the range of 10-70. The morphologies and microstructures of as-prepared samples were characterized by SEM (JEOL JSM-6700F). Elemental analysis of the prepared Bi_2O_3 compacts was performed using energy dispersive X-ray spectra (EDX) (JEOL JSM-6510 LA, Japan). The optical absorbance of these films was measured within the wavelength range 300-800 nm using a Shimadzu UV-2550 spectrophotometer.

3. Results and discussion

3.1. Structural characterization

The structure of the Zn doped Bi_2O_3 films is determined from XRD analysis as shown in figure 1. The structure of Bi_2O_3 is affected, i.e., intensities vary after doping with transition metals ions Zn. The diffraction peaks due to transition metal Zn appear in XRD pattern. The peaks corresponding to (020), (012), (022), (102) and (131) are clearly seen with increasing Zn-dopant density as evinced from EDAX (6 % to 9%) for the Bi_2O_3 films, which indicates the presence of Bi_2O_3 or (α - Bi_2O_3) with monoclinic structure.

Table 1. Orientation factor of Zn - Bi₂O₃ thin films.

Bath temperatures °C	Hkl Plane	Orientation factor (f)
50	(020)	f(020)=0.1400
	(012)	f(012)=0.5616
	(022)	f(022)=0.1703
	(102)	f(102)=0.4615
	(131)	f(131)=0.0556
60	(020)	f(020)=0.1479
	(012)	f(012)=0.5255
	(022)	f(022)=0.1730
	(102)	f(102)=0.4646
	(131)	f(131)=0.0661
50	(020)	f(020)=0.1375
	(012)	f(012)=0.6633
	(022)	f(022)=0.1033
	(102)	f(102)=0.5395
	(131)	f(131)=0.0376

It is further confirmed by the JCPDS Card No (76-1730). It can be concluded that the crystal structure of Bi₂O₃ is changed from body centred cubic to monoclinic after doping with Zn. The structure peak with regard to (012) faster than the other peaks (020), (022), (102), (131) indicate a relatively preferred structural orientation along (012). The usual method that calculates the magnitude of the preferred orientation factor 'f' for a given plane relative to other planes in material was employed here [8-10]. According to this process the preferred orientation factor f (012) for the Zn doped Bi₂O₃ thin films has been calculated by the fraction of (012) plane intensity over the sum of intensities of all peaks surrounded, for the given measuring 2θ range (20°-80°). The orientation factor of all peaks has been used for the Zn-Bi₂O₃ films at different temperature 50°C, 60°C, and 70°C respectively.

It is apparent from the results obtained that f (012) is larger compared to the other orientation factor values for all the prepared films [7]. Figure 1. shows the diffraction peaks of 50°C formed at 2θ=21.55°, 29.10°, 33.79°, 36.54° and 42.84° corresponding to (020), (012), (022), (102) and (131) planes respectively. The peaks with respect to 60°C parameter formed at 2θ = 21.90°, 29.24°, 33.85°, 36.69°, and 41.46° can be seen corresponding to (020), (012), (022), (102), and (131) planes respectively. Also for 70°C, the peaks formed at 2θ =21.90°, 29.23°, 33.84°, 36.79° and 41.23° corresponding to (020), (012), (022), (102) and (131) planes respectively. The average crystallite size of the films is calculated by Debye-scherrer formula. The average Grain sizes of Zn-Bi₂O₃ for 50°C, 60°C and 70°C films were determined as 66.32 nm, 69.36 nm and 94.03 nm, respectively. The structural parameter of Zn doped Bi₂O₃ are calculated by following relation.

$$\frac{1}{d^2} = \frac{1}{\sin^2\beta} \left(\frac{h^2}{a^2} + \frac{k^2 \sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hlc \cos\beta}{ac} \right) \quad (1)$$

where, d_{hkl} is the lattice spacing of the plane
a, b and c is the (lattice)structure parameters.

Using the crystallite sizes the dislocation density and micro strain in the films have been determined and tabulated in (Table 2).

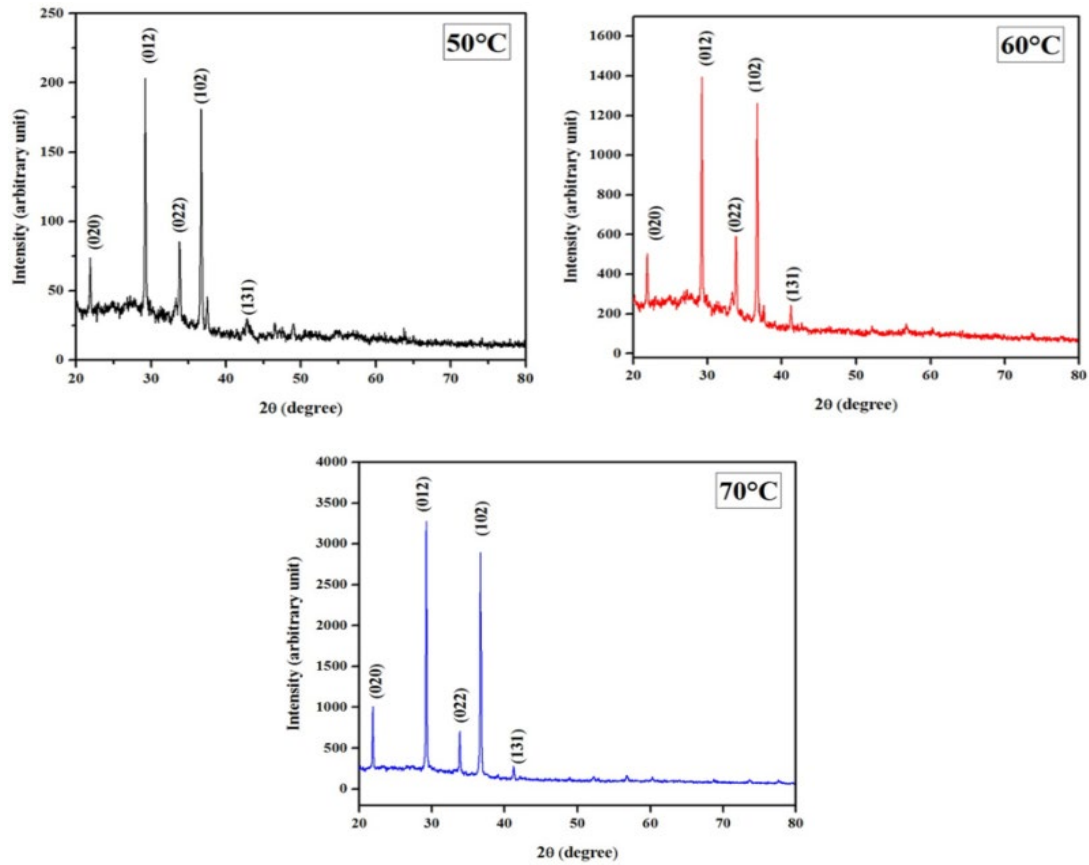


Fig. 1. XRD patterns of $\text{Zn-Bi}_2\text{O}_3$ thin films.

Table 2. Comparison of calculated and standard 'd' and '2θ' values of $\text{Zn-Bi}_2\text{O}_3$ thin films.

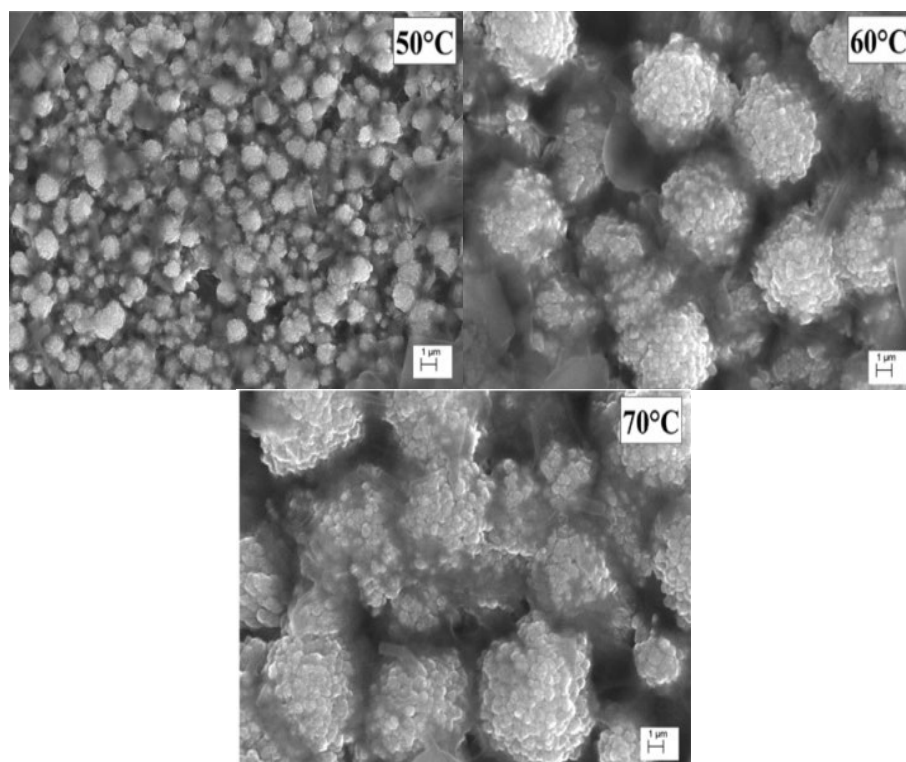
Bath Temp °C	hkl Planes	2θ Values (degree)		d-Spacing Values(Å)		FWHM (β)
		JCPDS	EXPT	JCPDS	EXPT	
50	020	21.72	21.55	4.088	4.389	0.1338
	012	28.131	29.10	3.184	3.039	0.0669
	022	33.94	33.79	2.639	2.687	0.4015
	102	36.90	36.54	2.499	2.435	0.1673
	131	41.46	42.84	2.176	2.179	0.1338
60	020	21.72	21.90	4.088	4.058	0.1338
	012	28.131	29.24	3.184	3.053	0.1506
	022	33.94	33.85	2.6390	2.647	0.1673
	102	36.90	36.69	2.499	2.449	0.0669
	131	41.46	41.25	2.176	2.188	0.2007
70	020	21.72	21.90	4.088	4.058	0.1004
	012	28.131	29.23	3.184	3.0555	0.1004
	022	33.94	33.84	2.6390	2.648	0.0836
	102	36.90	36.79	2.499	2.449	0.0669
	131	41.46	41.23	2.176	2.1893	0.1338

Table 3. Structural parameters of Zn-Bi₂O₃ thin films.

Bath Temp °C	hkl Plane	Dislocation density (Lines/m ²) 10 ¹⁰	Micro Strain (ε) (Lines ⁻² m ⁴) 10 ⁻⁴	Grain Size D (nm)	Average grain size (nm)
50	020	0.000021	0.00078	63.1098	66.32
	012	0.000005	0.00028	128.1026	
	022	0.000135	0.00147	21.5925	
	102	0.000030	0.00056	52.2150	
	131	0.000012	0.00380	66.5970	
60	020	0.000023	0.000770	63.1468	69.35
	012	0.000024	0.000627	57.0161	
	022	0.000024	0.000612	51.8277	
	102	0.000005	0.000225	130.6331	
	131	0.000028	0.000594	44.1619	
70	020	0.000013	0.000578	84.1538	94.03
	012	0.000011	0.000429	85.3844	
	022	0.000006	0.000306	103.7146	
	102	0.000005	0.000224	130.6710	
	131	0.000012	0.000396	66.2385	

3.2. Morphology and compositional analysis

From the Figure 2. the grains are found to be closely packed and reduced intergrain spacing, which refers to the films of better crystallinity, smooth and homogeneous surface with cauliflower like structure as seen in the micrograph. This is due to highly preferred orientation of films along (012) plane as exhibited by XRD. It is noteworthy to place on record that, due to the increase in film deposition temperatures, the obvious improvements of the particle size in the films are evident from the results obtained.

Fig. 2. Scanning electron micrograph of Zn-Bi₂O₃ thin films.

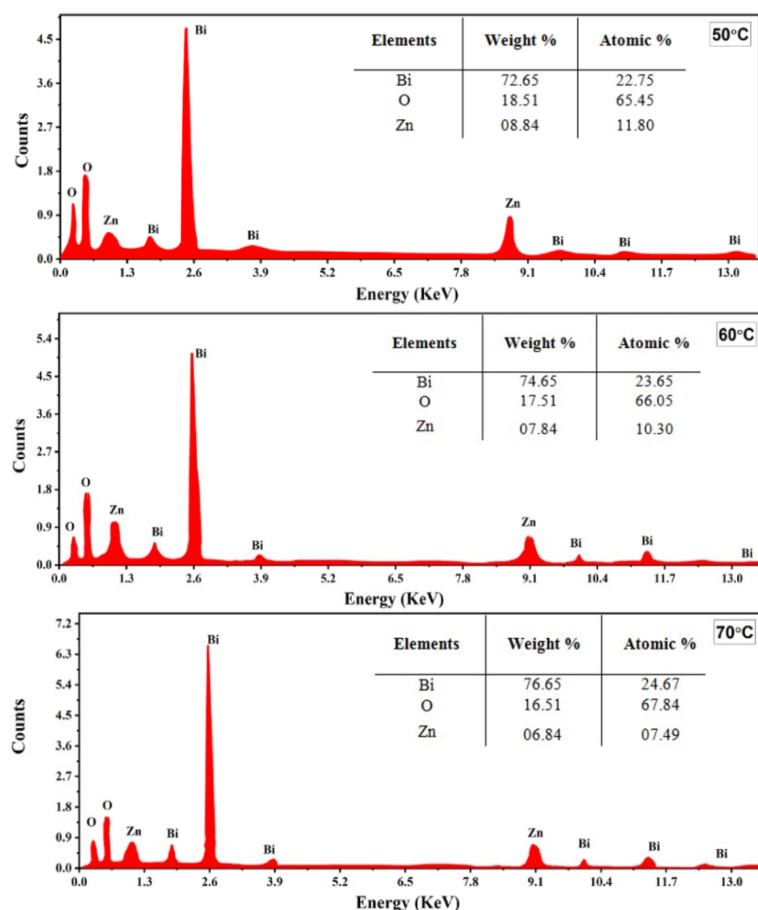


Fig. 3. EDAX Spectra of Zn - Bi₂O₃ thin films.

Figure 3. shows the EDAX spectra of Zn doped Bi₂O₃ thin films for different deposition temperatures. EDAX data that reveals the characteristic peaks associated with Bi, Zn and O. The atomic percentage and weight percentage are indicated in figure 3. This indicates that the Bi percentage is higher than the expected other nominal loading content, which could be due to the formation of precipitation of Bi during the preparation of Zn doped Bi₂O₃ films [12].

3.3. Optical analysis

Figure 4a-4b shows the absorbance and transmittance spectra to Zn doped Bi₂O₃ thin films. These spectra clearly reveal that the bismuth oxide thin film shows the best optical absorption in the range of 350-800 nm wavelength. The spectra of obtaining Zn doped Bi₂O₃ thin films also feature typical semiconductor material of good optical quality. It is found that, as the deposition temperature increases, transmittance becomes relatively higher. This can be attributed to the Zn doping Bi₂O₃, which characterizes the material as the one with by a high absorbing nature. Further, the absorption edge is not changed with increasing deposition temperature [13,16]. In addition, beyond the edge of absorption, the sum of transmittance and reflectance is found in the order unit. This confirms that there is no dispersion or absorption of incident light and that the deposited thin films surfaces are of good quality and have a soft nature [13-15]. It is obvious that the high absorbance of Zn doped Bi₂O₃ qualifies it for opto-electronic devices and electrochromic applications.

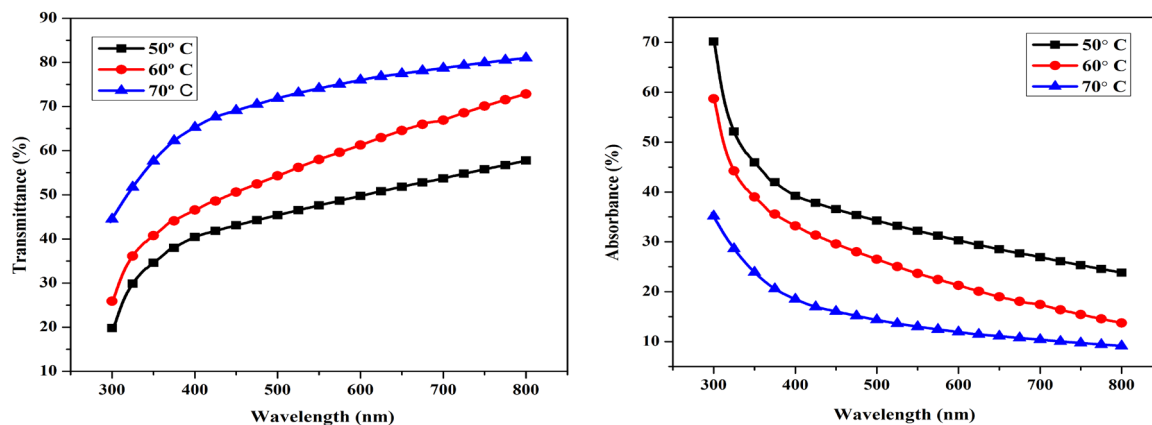


Fig. 4. (a), (b) UV-vis Absorbance and Transmittance of Zn-Bi₂O₃ thin films.

The optical band gap transition was calculated using the Tauc's relation in the high semiconductor absorption region according to the relationship between the absorption coefficient (α) and photon energy ($h\nu$), as follows

$$\alpha h\nu = \alpha_0 (h\nu - E_g)^n \quad (2)$$

where E_g is the optical energy gap and α_0 is constant which is independent of energy and is sometimes called the band tailing parameter and equal $\left(\alpha_0 = \frac{4\pi\sigma_{\min}}{nc\Delta E}\right)$; where σ_{\min} is the minimum metallic conductivity, n is the refractive index and c is the velocity of light. In addition, according to the Davis and Mott model, the high density of states located at the near mobility edge is associated with neutral dangling bonds in an amorphous part of Zn doped Bi₂O₃. [17, 18,]. In order to estimate the direct energy gap, E_g^d of the investigated Zn doped Bi₂O₃ thin films, $(\alpha h\nu)^2$ are plotted against the photon energy ($h\nu$) as shown in Figure (5). The optical direct band gap energy is given by extrapolating the linear part of the plot to intercept the $h\nu$ axis ($h\nu = 0$). The estimated values of the direct energy gap are shown in figure 5. It was observed that the optical energy gap increases with increasing deposition temperatures. This result is due to the process of recrystallization of Zn doped Bi₂O₃ with increasing deposition temperatures which agree with earlier reports [17-19].

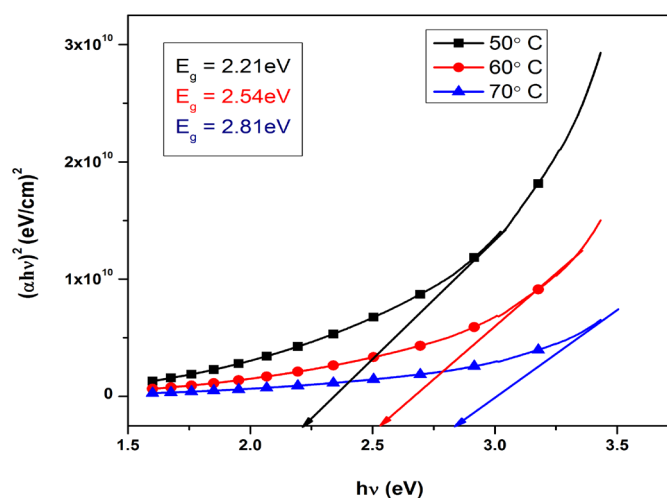


Fig. 5. Tauc plot of Zn - Bi₂O₃ thin films.

4. Conclusion

Zn doped Bismuth oxide thin films mainly belong to monoclinic structure for the films formed at different bath temperatures. The dislocation densities and micro strains of the samples under study are found to decrease with thickness, indicating reduction in film imperfections. From the EDAX analysis, the compositions of the Zn doped Bi₂O₃ thin films for different baths are studied as it confirms the presence of Zn, Bi and O. Surface morphological studies carried out by means of SEM analysis reveals that the size of the particles increases with the increase in bath temperatures. From the absorbance spectra, the material in the present study is found to be highly absorbant in nature.

Transmittance studies witnesses the decrease in the film transmittance decrease with increase in bath temperatures, which leads to a decrease in light scattering losses. The band gap energy values determined for the films are directly proportional to bath temperatures, offering themselves promising candidates for various technological applications.

References

- [1] Osmary Depabloe Rivera, Ana Martinez, Sandra. and Rodil, Journal of alloys and compounds, **853** (2021) 157245, 1-14; <https://doi.org/10.1016/j.jallcom.2020.157245>.
- [2] Rui Chen, Zhu Rui Shen, Hu Wang, Hui Jing Zhou, Yu Ping Liu, Da Tong Ding, and Tie Hong Chen, Journal of alloys and compounds, **509(5)** (2011) 2588-2596; <https://doi.org/10.1016/j.jallcom.2010.11.102>.
- [3] Waseem. Raza, Haque, Muneer, Harada, and Matsumura, Journal of Alloys and Compounds, **648** (2015) 641-650; <https://doi.org/10.1016/j.jallcom.2015.06.245>.
- [4] Wei Qin, Jing Qi, and Xiaohong Wu, "Vacuum", **107** (2014) 1-4; <https://doi.org/10.1010/j.vacuum.2014.02.003>.
- [5] Guo Liu, Shuai Li, Yuanyuan Lu, Jing Zhang, Zhaochi Feng, and Can Li, Journal of Alloys and Compounds, **689** (2016) 787-799; <https://doi.org/10.1016/j.jallcom.2016.08.047>.
- [6] Timonah Soitah, Yang Chunhui, Yu Yong, Niu Yinghua, and Sun Liang, "Properties of Bi₂O₃ thin films prepared via a modified Pechini route", Current Applied Physics, **10** (2010) 1372-1377; <https://doi.org/10.1016/j.cap.2010.04.006>.
- [7] S. Prabahar, and M. Dhanam, Journal of Crystal Growth, **285** (2005) 41-48; <https://doi.org/10.1016/j.jcrysgro.2005.08.008>.
- [8] T.V.L Thejaswini, D. Prabhakaran, and M. Akhila Maheswari, Photochemistry and Photobiology, (2016), 217-229; <https://dx.doi.org/10.1016/j.jphotochem.2016.12.001>.
- [9] P.Malathy, K.Vignesh, M.Rajaraman, and A.Suganthi, Ceramics International, **40** (2014), 101-07; <http://dx.doi.org/10.1016/j.ceramint.2013.05.109>.
- [10] M.J.Jabeena Fatima, C.V. Niveditha, and S.Sindhu, Royal Society of Chemistry (2013) 1-8; <http://dx.doi.org/10.1039/C5RA12760B>.
- [11] K.Thirumalai, E.T. Deva Kumar, R.Aravindhan, J.Raghava Rao, and M.Swaminathan, Surfaces and Interfaces, **5** (2016) 30-38; <https://dx.doi.org/10.1016/j.surfin.2016.09.005>.
- [12] Samia Kausar, Ataf Ali Altaf, Muhammad Hamayun, Muhammed Danish, Muhammed Zubair, Sumbal Nz, Shabbir Muhammed, Muhammed Zaheer, Shafiq Ullah, and Amin Badshah, Inorganica Chimica Acta, **502** (2020), 1-12; <https://doi.org/10.1016/j.ica.2019.119390>.
- [13] J. Song, Y. He, J. Chen, D. Zhu, Z. Pan, Y. Zhang, J.-a. and Wang, J. Electron. Mater. **41** (2012) 431-436; <https://doi.org/10.1007/s11664-011-1783-x>.
- [14] S.A. Mahmoud, A.A. Akl, and S.M. Al-Shomar, Physica B **404** (2009) 2151-2158; <https://doi.org/10.1016/j.physb.2009.04.003>.
- [15] G. Du, W. Liu, J. Bian, L. Hu, H. Liang, X. Wang, A. Liu, and T. Yang, Appl. Phys. Lett. **89** (2006), 052113-1 – 052113-3; <https://doi.org/10.1063/1.2245217>.
- [16] F. Urbach, Phys. Rev. **92** (1953) 1324-1324; <https://doi.org/10.1103/PhysRev.92.1324>.
- [17] H. Fritzsche, J. Tauc, New York, 1974, 254; <http://dx.doi.org/10.1007/978-1-4615-8705-7>.
- [18] A. Ashour, H.H. Afifi, S.A. Mahmoud, Thin Solid Films **248** (1994) 253-256; [http://dx.doi.org/10.1016/0040-6090\(94\)90020-5](http://dx.doi.org/10.1016/0040-6090(94)90020-5).
- [19] J. Melsheimer, D. Ziegler, Thin Solid Films, **129** (1985) 35-47; [https://doi.org/10.1016/0040-6090\(85\)90092-6](https://doi.org/10.1016/0040-6090(85)90092-6)