# STRUCTURAL, MORPHOLOGICAL AND OPTICAL PERFORMANCE OF SYNTHESIZED Co, Mn/ZnO NANOCOMPOSITES

K. RATHIDEVI [a,b*], N.VELMANI [c], D.TAMILSELVI [a,d].
[a]*Research & Development Centre, Bharathiar University, Coimbatore – 641 046, Tamilnadu, India*
[b]*Assistant Professor, Department of Science and Humanities, Kumaraguru College of Technology, Coimbatore – 641 049, Tamilnadu, India*
[c]*Assistant Professor, Department of Chemistry, Government arts College, Coimbatore -641 018, Tamilnadu, India*
[d]*Assistant Professor, Department of Science and Humanities, Rathinam Technical Campus, Coimbatore – 641 021, Tamilnadu, India*

The pure Zinc Oxide, Cobalt doped Zinc Oxide and Manganese doped Zinc oxide nanoparticles were synthesized using Co-precipitation method. This work aims to study the effect of doping on the structural, morphological, and optical properties of the synthesized pure and doped ZnO nanoparticles. The structural and morphological change of the nanoparticles were examined by using X-ray Diffraction analysis (XRD), Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). The elemental analysis was studied with Energy Dispersive X-ray analysis (EDAX). The optical property of the particles were analysed using UV-Visible Spectroscopy (UV) and Photoluminescence Spectroscopy (PL). The XRD results shows all the nanoparticles are crystalline and pure in nature. The doping effect found to decrease the particle size of the ZnO nanoparticles. The SEM images also show the doping has significant change on the morphology of the ZnO nanoparticles. The functional groups present in the nanoparticles were confirmed using Fourier Transform Infrared Spectroscopy. The optical property of UV-Vis spectrum shows red shift and the band gap also found to decrease for doped nanoparticles. The presence of dopants in the nanoparticles was confirmed with the EDAX spectrum. The results of above characterization techniques confirmed the doping has significant influence on the structure, morphology, and optical property of the ZnO nanoparticles.

(Received August 21, 2020; Accepted October 23, 2020)

*Keywords*: ZnO, Co-ZnO, Mn-ZnO, Nanocomposites

## 1. Introduction

The emerging technology requires innovation of materials with distinctive properties. The invention of nanoparticles with unique properties is paved a new way for the world with diversified opportunities in industries and scientific endeavours. As nanotechnology is essentially a set of technique which allows manipulation of properties at a very small scale, it can have many applications. The particles of size between 1-100 nm are the basic elements of nanostructures. The physical and chemical properties of the bulk metals can also be modified when it is changed into nanoparticles [1-4]. This is due to its change in greater surface area per weight than larger particles; so that they are more reactive compared to bulk molecules. Depending upon the applications there are variety of nanoparticles can be synthesized like semiconductor, metal, and non-metal. Metal oxide nanoparticles have received wide attention of researchers because of their unique electronic and optical properties. Nowadays electronic circuits, sensors, piezoelectric devices are fabricated with the metal oxide nanoparticles [5-8]. The semiconductor oxide particles are intensively used as photo-catalysts in oxidation process. Among metal oxide nanoparticles zinc oxide nanoparticles are most promising materials having diversified applications due its

* Corresponding author: krd.kay104@gmail.com

remarkable chemical properties like photo-stability, chemical stability, and broad range of radiation adsorption [9]. Some of the properties of intrinsic zinc oxide nanoparticles can be enhanced by using suitable dopants, among which transition metals are most widely used for improving the property of ZnO nanoparticles [10-13]. Several attempts are also made to synthesis transition metal doped ZnO nanoparticles such as hydrothermal process [14], ball milling method [15], solid state reaction method [16], and co-precipitation method[17].Various researchers have reported the enhanced properties like band gap, optical, electrical and magnetic properties of ZnO nanoparticles doped with transition metals. The transition metal like $Cu^{2+}$, $Co^{2+}$, $Mn^{2+}$, $Fe^{2+}$, $Ni^{2+}$ are most widely used as a dopant for ZnO nanoparticles[18,19]. Recent studies show that transition metal doped ZnO nanoparticles are used in spintronic applications [20, 21]. It is reported that the magnetic behaviour of ZnO nanoparticles are enhanced by doping with transition metals like Mn and Co. In this present work pure ZnO and Co-ZnO and Mn-ZnO doped nanoparticles were synthesised by Co-precipitation method. The structural analysis was studied using X-ray Diffraction analysis (XRD), Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). The optical property of the particles was analysed using UV-Visible Spectroscopy (UV) and Photoluminescence Spectroscopy (PL).

## 2. Experimental procedures

### 2.1. Materials

The reagents used were Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$- Merck, India), Sodium hydroxide (NaOH-Himedia, India), Cobalt nitrate ($Co(NO_3)_2.6H_2O$-Himedia, India), Manganous Nitrate ($Mn(NO_3)_2$), Hydrochloric acid (HCl, 37%, Loba chemicals, India) of high purity with AR grade.

### 2.2. Synthesis of Pure ZnO, Co-ZnO and Mn-ZnO Nanoparticles

To prepare pure ZnO, the following steps were involved. 1M of ($Zn(NO_3)_2.6H_2O$) was added in 100 ml distilled water in a beaker which forms a solution. 2M of 100 ml NaOH solution was dropwise to the above solution under vigorous stirring, until the pH is 12. The stirring action was continued for almost 12 hours. During the preparation of nanoparticles, the solution pH is maintained at 12 because this pH seems to be the optimum value for the formation of ZnO particles. The formed precipitate was then filtered and washed with distilled water, ethanol, dried in oven at 100°C for 2hrs. The dried precipitates were collected and ground in an agate mortar. The collected nanopowder was annealed at $500^0$C for two hours followed by stepwise cooling. Similarly, the Co doped ZnO and Mn doped ZnO nanoparticles were also synthesized using the same procedure with using doping source materials.

### 2.3. Characterization Techniques

The structural analysis of synthesized pure and doped ZnO nanoparticles were recorded at room temperature using X-ray powder diffraction (XRD) with Philips Analytical Model: X'Pert PRO equipped with CuKα radiation λ = 1.54187 Å and operating rate of 1°/min at 40 kV/30mA. The Scanning angle range 2θ between 30 - 90° was maintained. The functional group analysis of the nanoparticle samples was investigated with Fourier Transform Infrared Spectrometer (FTIR) with the measurements range recorded in the region 400 – 4000 $cm^{-1}$. The absorption studies were recorded by UV-visible spectrophotometer from 100 to 900 nm. The optical studies of Photoluminescence (PL) spectrum were recorded from 350 nm to 500 nm. The surface morphology of the synthesized nanoparticles was analysed by using (HR-SEM) HR-field emission scanning electron operated at 10kV. The elemental composition analysis of nanoparticles was examined by using Energy-Dispersive X-ray Spectrometer (EDAX).

## 3. Results and discussion

### 3.1. XRD Analysis

The structural analysis of pure ZnO, Co-ZnO and Mn-ZnO doped nanoparticles were examined by using X-Ray Diffraction analysis (XRD). The results were shown in Fig 1.The well-defined sharp XRD diffraction peaks corresponding to (100), (002), (101), (102), (110), (103), (200), (112), and (201) planes of the synthesized nanoparticles clearly shows that they are crystalline in nature. The absence of secondary phase confirms there is no impurity in the nanoparticles. The peak value of the nanoparticles corresponds to a JCPDS database of card number 36-1451. The XRD pattern of all nanoparticles reveals the single crystal of hexagonal wurtzite structure [22]. The average crystallite size of the nanoparticles were calculated by using De-bye-Scherrer formula (1),

$$D=0.94\lambda / \beta\cos\theta \quad (1)$$

where D is the average crystallite size, $\lambda$ is the wavelength ($1.5406A^0$), $\beta$ is the Full-Width Half Maximum of Intensity and $\theta$ is the Bragg angle. The crystallite size of pure ZnO, Co-ZnO and Mn-ZnO doped nanoparticles are 89nm, 66nm and 71nm, respectively.

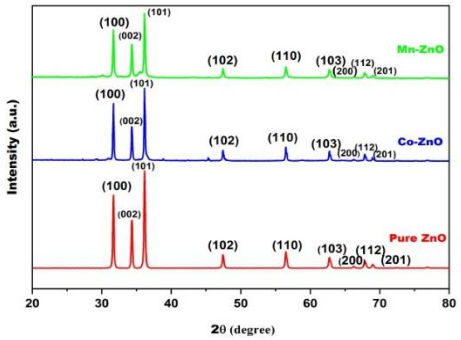


*Fig. 1. XRD pattern of Pure ZnO, Co-ZnO and Mn-ZnO nanoparticles.*

### 3.2. FTIR Analysis

The functional group analysis of the synthesized pure ZnO, Co-ZnO and Mn-ZnO nanoparticles were examined by using FTIR spectrum and the results are shown in Fig 2. The spectrum analysis of all the samples has been recorded in the wave number range from 400 to 4000$cm^{-1}$ using the KBr method at room temperature. The broad peak around 3410$cm^{-1}$ and 1632.83$cm^{-1}$ are assigned to the stretching and bending vibrations of hydroxyl group of water molecules [23, 24].A peak at around 577.56$cm^{-1}$ corresponding to the formation of Zn-O bond [25]. The sharp peak at 1396.08$cm^{-1}$ has confirmed the presence of cobalt in Co-ZnO nanoparticle. In Mn-ZnO nanoparticles, the peak at around 534 $cm^{-1}$ corresponds to stretching vibration of Mn-O. The sharp peak around 1110$cm^{-1}$ in Mn-ZnO may be due to presence of carbonyl moieties on the surface of the nanoparticles. The slight change in band position is observed in Co, Mn doped ZnO nanoparticles band can be related to the substitution of the dopants into the ZnO matrix [26].

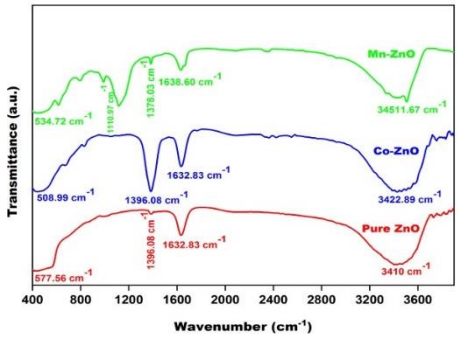


*Fig. 2. FTIR Spectrum of Pure ZnO, Co-ZnO and Mn-ZnO nanoparticles.*

### 3.3. SEM Analysis

The morphological analysis of pure ZnO, Co-ZnO and Mn-ZnO doped ZnO nanoparticles were examined by using Scanning Electron Microscopy (SEM) and the results are shown in Fig 3. The image of the pure ZnO nanoparticle shows that hexagonal nanoparticles with noticeable amount of nanorods like structure whereas the Co-ZnO nanoparticles show few nanorods along with nanoparticles. The morphology of Mn-ZnO nanoparticles are found to be in flower like structure. The results reveal that the dopants have influenced the structure of the ZnO nanoparticles.

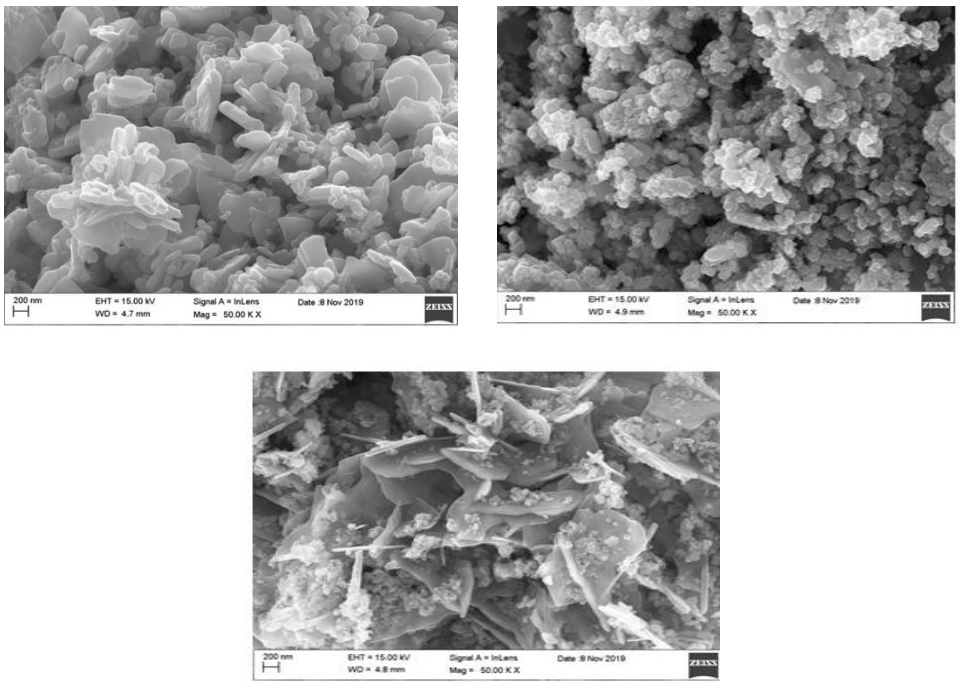

*Fig. 3. SEM image of (a) Pure ZnO (b) Co-ZnO and (c) Mn-ZnO nanoparticles.*

### 3.4. EDAX Analysis

The elemental composition of the synthesized pure ZnO, Co-ZnO and Mn-ZnO nanoparticles were measured by EDAX spectrum and the results are represented in Fig. 4.

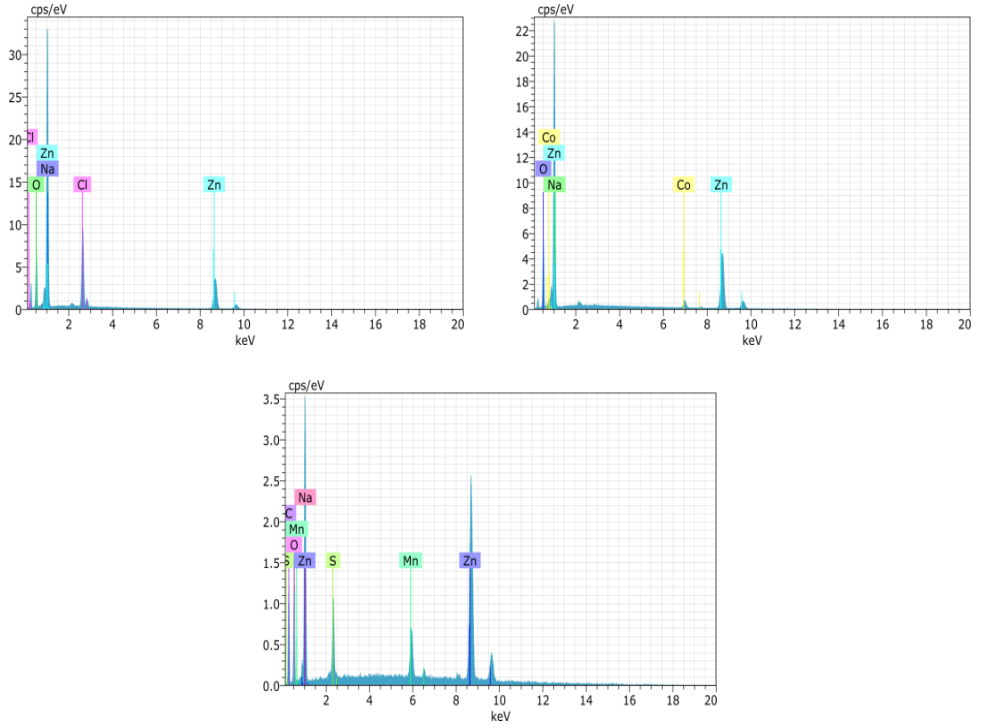


*Fig. 4. EDAX spectra of Pure ZnO, Co-ZnO and Mn-ZnO nanoparticles.*

From the figure, the presence of the elements Zn, O, Co and Mn samples are confirmed. The C peaks correspond to their origin in copper grid. EDAX spectrum shows no impurities present in the synthesized pure ZnO, Co-ZnO and Mn-ZnO nanoparticles. The data of weight and atomic percentage of element were also confirmed by EDAX spectrum and presented in Table 1.

*Table 1. Weight percentage of synthesized nanoparticles from EDAX spectrum.*

| **Samples** | **Wt. %** | | | **Co/Mn /Zn Wt. % ratio** |
|---|---|---|---|---|
| | **Zn** | **Co/Mn** | **O** | |
| ZnO | 66.23 | - | 21.50 | - |
| Co-ZnO | 55.10 | 3.09 | 18.14 | 0.056 |
| Mn-ZnO | 51.61 | 3.25 | 12.70 | 0.062 |

### 3.5. UV Spectral Analysis

The optical properties of the samples were analysed by using UV-Visible absorption spectroscopy and results are shown in Fig 5.The absorption spectrum of the synthesized pure and doped nanoparticles shows a broad absorption band at 370 nm, 368 nm and 366 nm for ZnO, Co-ZnO and Mn-ZnO respectively. From the figure it is clear that the peaks are shifted to longer wavelength doped nanoparticles shows red shift. The photoexcitation of electrons from valence band to conduction band produces the absorption band and shifts the band slightly towards longer wavelength. In addition, the indirect band gap energies (Eg) were calculated according to the formula (2),

$$\alpha h\nu = A\,(h\nu - Eg)^{n/2} \qquad (2)$$

where α, h, v, A and Eg stand for the absorption coefficient, Planck's constant, the frequency of light, a constant and the band gap energy, respectively. The term n is determined by the characteristic optical transition of a metal oxide (n = 1 and n = 4 for a direct transition and an

indirect transition). The optical band gap values are shown in Fig 5. The band gap value is found to be 3.59 eV, 3.55 eV and 3.53 eV for ZnO, Co-ZnO and Mn-ZnO nanoparticles, respectively. From this value it is clear that the band gap of pure ZnO nanoparticles increases by adding dopants. The decrease in band gap may be related to the decrease in crystallite size of the dopants [27]. The analogue decrease in the band gap was also observed and it may be revealed that this shift asserts the uniform substitution of $Co^{2+}$ and $Mn^{2+}$ ions in the ZnO lattice

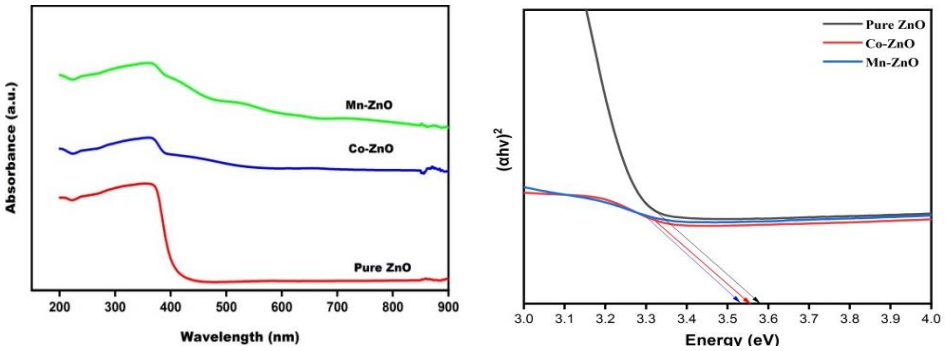


*Fig. 5. UV-Vis Spectrum and Band-gap Spectrum of Pure ZnO, Co-ZnO and Mn-ZnO nanoparticles.*

### 3.6. PL Spectral Analysis

The effect of doping on the structure of the ZnO nanoparticles has been analysed by using PL spectrum. The emission spectrum of pure ZnO and Co-ZnO and Mn-ZnO doped nanoparticles has been recorded at room temperature are shown in Fig 6. From the graph a broad emission peak is observed around 466 nm for pure ZnO and Co-ZnO and Mn-ZnO nanoparticles. The peaks are found to be in blue range [28]. The results of PL studies confirmed that the doping of ZnO nanoparticles with Co and Mn has suppressed the emission peak of pure ZnO nanoparticles at 390 nm in ultraviolet range and strengthened the emission peak in blue range [29,30].

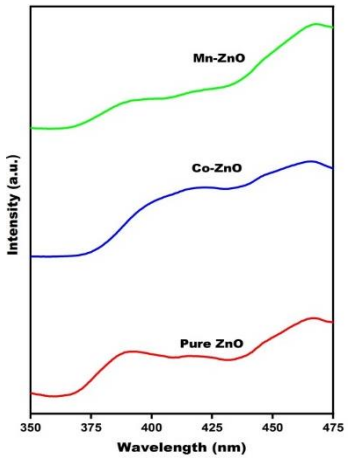


*Fig. 6. PL Spectrum of Pure ZnO, Co-ZnO and Mn-ZnO nanoparticles.*

## 4. Conclusion

The pure ZnO, Co-ZnO and Mn-ZnO doped nanoparticles were synthesized by chemical precipitation method. The XRD analysis confirmed the hexagonal wurtzite structure for ZnO nanoparticles with crystalline nature. The particle size of Pure ZnO, Co-ZnO and Mn-ZnO doped nanoparticles were found to be 89nm, 66nm and 71nm, respectively. The results from optical

studies reveal that the peaks are shifted to longer wavelength for doped nanoparticles shows red shift. The band gap values were found to be 3.59 eV, 3.55 eV and 3.53 eV for ZnO, Co-ZnO and Mn-ZnO nanoparticles, respectively.

These values show that the band gap of pure ZnO nanoparticles decreases by adding dopants and the decrease in band gap may be related to the decrease in crystallite size of the dopants. The SEM image confirms different structures like nanorods for pure ZnO nanoparticle, nanoparticles with noticeable amount of nanorods for Co-ZnO nanoparticles and flower like structure for Mn-ZnO doped nanoparticles. The purity of the synthesized nanoparticles was confirmed by EDAX spectrum. The findings of structural, morphological and optical property of the ZnO nanoparticles has strongly influenced by the dopants.

## References


[1] A. K. Sharma, A. K. Tiwari, A. R. Dixit., Mater. Today Proc, **2**, 3539 (2015).
[2] P. K. Singh, P. Kumar, M. Hussain, A. K. Das, G. C. Nayak, Bull. Mater. Sci, **39**, 469 (2016).
[3] P. Kumar, P. K. Singh, D. Kumar, V. Prakash, M. Hussain, A. K. Das, Mater. Manuf. Process, 1 (2016).
[4] O. Lupan, V. Cretu, V. Postica, M. Ahmadi, B. R. Cuenya, L. Chow, I. Tiginyanu, B. Viana, T. Pauporté, R. Adelung, Sensors Actuators B Chem,**223**, 893 (2016).
[5] W. Dongting, Z. Xuehong, F. Yuzhen, S. Jianhong, Z. Cong, Z. Xianxi, Nano- Structures & Nano-Objects,**10**(1), (2017).
[6] A. Tomchenko, A. Harmer, G. P. Marquis, B. T. Allen, Sens. Actuators B, **93**(126), (2003).
[7] G. Marcě, V. Augugliaro, López-Muñoz, M. J. Martín, C. Palmisano, L. Rives, V. Schiavello, M. Tilley, R. J. D. Venezia., J. Phys. Chem. B, **105**(1033), (2001).
[8] S. Singh, M. Joshi, P. Panthari, B. Malhotra, A. C. Kharkwal, H. Kharkwal, Nano- Structures & Nano-Objects,**11**(1), (2017).
[9] H. R. Ghorbani, F. P. Mehr, H. Pazoki, B. M. Rahmani, Orient J. Chem, **31**(2), (2015).
[10] S. Kumaresan, K. Vallalperuman, S. Sathishkumar, M. Karthik, P. Siva Karthik, J. Mater. Sci. Mater. Electron, 1 (2017).
[11] T. C. Bharat, Shubham, S. Mondal, H. S. Gupta, P. K. Singh, A. K. Das, Mater. Today Proceedings, **11**(Part 2), 767 (2019).
[12] K. Sato, H. Katayama-Yoshida, Semiconductor Science and Technology, **17**(367), (2002).
[13] Jinbo Cao, Junqiao Wu, Mater.Sci. Eng. R. Rep, **71**, 35 (2011).
[14] S. Baruah, J. Dutta., Sci. Technol. Adv. Mater, 013001 (2009).
[15] S. Suwanboon, P. Amornpitoksuk, A. Sukolrat, N. Muensit, Ceram Int, **39**, 2811 (2013).
[16] S. Han, T. Jang, Y. Kim, B. Park, J. Park, Y. Jeong, Appl. Phys. Lett, **83**, 920 (2003).
[17] O. Jayakumar, H. Salunke, R. Kadam, M. Mohapatra, G. Yaswant, S. Kulshreshtha, Nanotechnology,**17**, 1278 (2006).
[18] F. Pan, C. Song, X. Liu, Y. Yang, F. Zeng., Mater Sci. Eng, R: Reports,**62**, 1 (2008).
[19] D. Tamilselvi, N. Velmani, K. Rathidevi, J. Ovonic Res,**16**(2), 123 (2020).
[20] A. A. Azab, S. A. Esmail, M. K. Abdelamksoud, Silicon,**11**, 165 (2019).
[21] T. J. Castro et al., J. Appl. Phys. **121**, 013904 (2017).
[22] A.T. Ravichandran, R. Karthick, Results in Materials, **5**, 100072 (2020).
[23] T. Thangeeswari, Ann Tresa George, A. Arun Kumar, Indian J. Sci., and Technol,**9**(1), (2016).
[24] Suwanboon, S. Sci. Asia, **34**, 31 (2008).
[25] Arya Rajan, G. Baskar, International Journal of Modern Science and Technology, **1**(1), 17 (2016).
[26] M. Faraz et al. Mater. Chem. Phys,**211**, 137 (2018).
[27] M. Nirmala, A. Anukaliani, Physica B**,406**, 911 (2011).
[28] M. Jay Chithra, K. Pushpanathan, M. Loganathan, Mater. Manuf. Process, **29**, 771 (2014).
[29] S. Satheeskumar, V. Jeevanantham, D. Tamilselvi, J. Ovonic Res,**14**(1), 9-15 (2018).
[30] S. Srivastavaa, A. Agarwal, J. Ovonic Res, **14**(5), 395-404 (2018).