IOSR Journal of Electronics and Communication Engineering (IOSR-JECE)
e-ISSN: 2278-2834, p- ISSN: 2278-8735.Volume 21, Issue 2, Ser. 1 (Mar – Apr 2026), PP 14-19
www.iosrjournals.org

Structural And Optical Characterization Of Molar Dependent Synthesized Nzns Thin Films

M. Dinendra Singh And K. Kunjabali Singh
Department Of Physics, Thambal Marik College, Oinam-795135, Manipur, India
Department Of Physical Science
Khongnangthaba University, Khurai-795010, Manipur, India.

Abstract
ZnS thin films were synthesized on varying molar concentrations (MC) (0.05-0.20M) using Chemical Bath Deposition (CBD) technique and studied the growth surface morphology, crystal structures and optical properties using FESEM, XRD and UV-vis-spectrophotometer. The surface structures were observed with regular distribution of ZnS nanoparticles with particle sizes 6.7nm – 11.54nm and were confirmed with XRD results. The crystal growth showed depended on molar concentration of Zn^{+2} and S^{-2} ions. Maximum peak in the XRD spectra was shown at 0.20m with preferred reflection along (211). Two types of phase symmetrical structures -cubic f.c.c. zinc blend and hexagonal (wurtzite) were observed, both were characterized by single bonds between each atom with 1: 1 zinc to sulphate ratio. The evaluated lattice parameters a_{cal} were observed higher than the corresponding standard values while the same were reduced in hexagonal structure. The d_{cal} – values in each molar films were observed to decrease with increase of molars. The optical photon absorption coefficient in the samples was found enhancing with increase of molar concentrations within 300 – 800nm wavelengths. The study of optical absorption spectra in the host films showed maximum peak absorption at 300nm wavelength in the lower blue spectral side. The blue shift (BS) indicates the quantum dot size effect in the nZnS thin films. The optical band gap was observed increasing with molars as a result of reduction the crystallite sizes.

Keywords: *ZnS thin films, molars, XRD, FESEM, optical absorption*

Date of Submission: 05-03-2026 Date of Acceptance: 15-03-2026

I. Introduction

Synthesis and characterization of new materials from metallic and non-metallic ions by different techniques for fabrication of new useful devices and applications has been the most fascinating field of research in all branches of material science. In this way, nanoscience (NS) and nanotechnology (NT) play initiative roles in all branches of material science, biological science and other branches of sciences world-wide during the last decades. In general, particles with 1-100nm in diameter are called nanomaterials which may have structures like globular, rode-like, plate-like, flower-like or more complex structures depending on the deposition method. Spherical particles with size < 10nm are called clusters or quantum dots (QD) [1]. In nanoscience, diameter of materials is of the order **of d-Broglie wavelength** of the electron wavefunction[1]. Therefore, the electronic and optical properties of matter are changed and new properties are expected.

ZnS is one of the prominent compound semiconductors of II-VI group with a wide direct band gap (E_g = 3.7eV) which makes it suitable for fabrication of blue light emitting diodes (BLEDs) [2,3] and other opto-electronic devices, electroluminescence [4], cathodoluminescent displays, multilayer dielectric filters [5,6]. Therefore, considerable efforts have been given towards the synthesis of ZnS nanocrystals, using techniques such as electrodeposition, SILAR method, thermal evaporation, spray pyrolysis, molecular beam epitaxy etc. Most of the researchers have used equal concentration of Zn^{+2} and S^{-2}-ion precursors in the synthesis works. However, reports on variation of Zn^{+2} and S^{-2}-ions concentration in synthesis of ZnS nanoparticles are rare cases.

II. Materials And Method

Chemical Bath Deposition (CBD) technique was used for deposition of ZnS nanocrystalline thin films. In the synthesis process, we used AR grade Zinc acetate [$Zn(CH_3COO)_2$], (ZA) for Zn^{+2}-ions source, thiourea [$CS(NH_2)_2$] for S^{-2}-ions source in presence of hydrazine hydrate (HH) as reducing agent, ammonium hydroxide [$NH_4(OH)$] , (AH) as catalyst to adjust the base solution at pH value 10 and polyvinyl alcohol (PVA) as matrix in the ionic solution relative to the substrates. In the process, 10ml of ZA was mixed with 10ml of HH in 100ml glass beaker and stirred for 1/2hr till it turns into clear solution. Then, 10ml of thiourea was added to the

precursor. Next, de-ionized water was added to obtain 50ml of the solution. A few drops of AH solution was added to it to alkaline the solution at pH value 10. Then, 20ml of pre-dissolved 2wt.% PVA matrix solution was added to the precursor solution and stirred continuously at 70^0C for 2hrs till PVA dissolved. The chemically And ultrasonically cleaned ITO glass (40 x 25 x 2mm^2) substrates were immersed in the matrix solution for 120hrs. The ZnS thin films deposited on the substrates were then washed with de-ionized water several times for removal of any course grains to obtain fine ZnS nanocomposite matrix films. The ZnS films were annealed at 300^0C in electronic oven for 3hrs in- situ and off for 24hrs for crystal growth. The as deposited ZnS thin films were characterized X-ray diffraction (XRD) and Field Emission Electron Microscope (FESEM) techniques. The optical properties were characterized by UV-vis visible absorption spectroscopy.

III. Results And Discussion

XRD Analysis: The X-ray diffraction (XRD) spectra of the chemically synthesized ZnS thin films grown at varied molars at room temperature have been shown in the adjoining Figures 1 (a-d). The study of the grown films reveal that the crystallinity of the films were found improving with increase of molars.

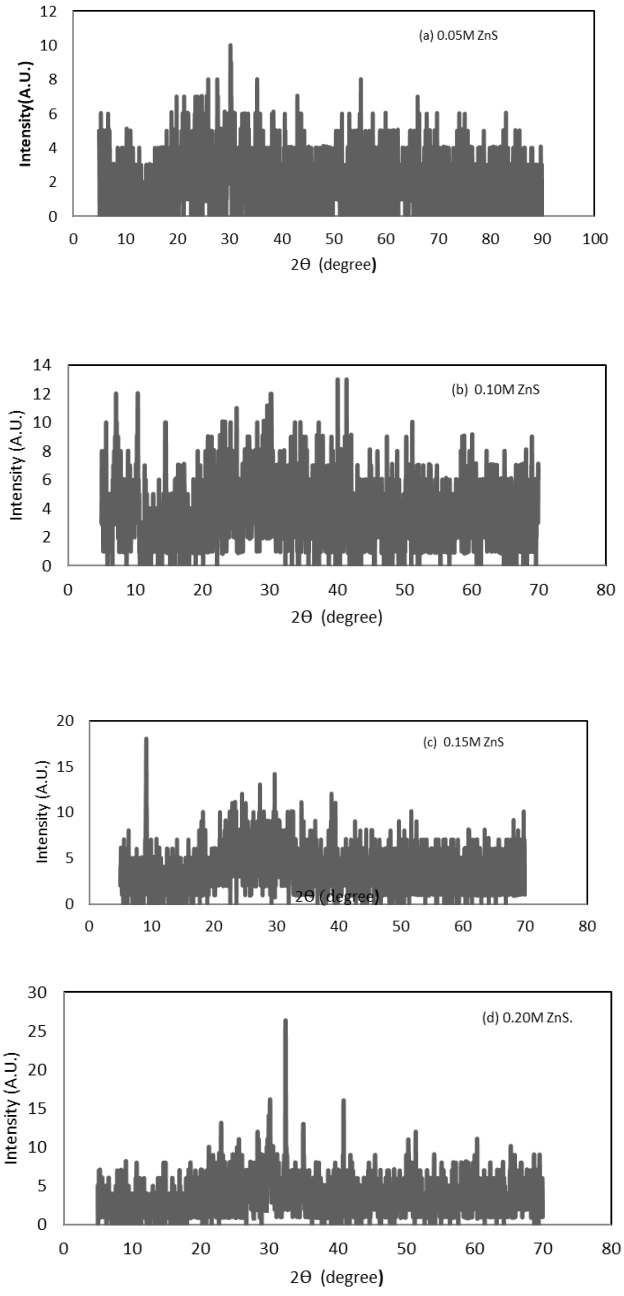


Figure 1 (a-d). X-ray diffraction spectra of ZnS thin films at varied molars.

In the present investigation, the phase structures of the host ZnS sample films were determined by a method of comparison of the peak position of the samples with the standard JCPDS values of X-ray powder data file. For cubic system, corresponding to each (hkl) plane, the lattice parameter *a*-values are determined from the relation,

$a = d_{cal}\sqrt{(h^2 + k^2 + l^2)}$ -(1)

while the X-rays diffraction planes (hkl) –values corresponding to each peak intensity in the X-rays spectra are determined from the relation were calculated from the Bragg's relation [7,8]

$\mathrm{Sin}^2\Theta = (\boldsymbol{\lambda}^2/4a^2) \times m$ ($\because 2d\mathrm{Sin}\Theta = n\boldsymbol{\lambda}$) - (2)

where $m = h^2 + k^2 + l^2$ and $\boldsymbol{\lambda}$ = 1.54Å for X-rays. The crystal lattice parameters ***d*** –values were determined from the relation

$d = \boldsymbol{\lambda}/2\mathrm{Sin}\Theta$ - (3)

The grain or particle diameters were calculated at 100% X-rays intensity from the Scherrer relation [9, 10]

$$D = k\boldsymbol{\lambda}/\beta_{2\Theta}\ \mathrm{Cos}\Theta \qquad (4)$$

where the shape factor k is taken 0.94 and for X-ray, $\boldsymbol{\lambda}$ = 1.54Å, $\beta_{2\Theta}$ is the full-width half maximum peak intensity. The particle size was calculated from the maximum peak corresponding to ZnS film at 0.20M from FWHM , $\beta = 0.86^0$ at $\Theta = 33^0$ and was found to be 11.54nm.

Table-1. Crystal parameters in ZnS films at varied molars

Molars (M)	(hkl)-values	JCPDS a-value (Å)	Cal. a_{cub} – value (Å)	a_{hex}.-value (Å)	JCPDS-d-value (Å)	Cal. c_{hex}-value (Å)	Cal. d_{hex}-value (Å)
0.10	100	5.410	8.852	6.259	3.123	10.220	5.428
	211		6.458	4.567		7.457	1.129
0.15	100		8.852	6.259		10.220	5.428
	200		5.774	4.083		6.667	1.767
0.20	210		6.455	4.565		7.453	1.614
	211		6.654	4.705		7.683	1.509
	221		6.315	4.465		7.300	1.078

D_{hkl} = 11.54nm

The lattice parameters ***a, c*** and ***d*** for hexagonal structures can be evaluated from the relation [11]

$$\frac{1}{d^2} = \frac{4}{3}\left[\frac{h^2 + hk + k^2}{a^2}\right] + \frac{l^2}{c^2} \qquad (4)$$

and $$\sin^2\theta = \frac{\lambda^2}{3a^2}(h^2 + hk + k^2) + \frac{\lambda^2}{4c^2}l^2 \qquad (5)$$

The lattice parameters for hexagonal unit cell are closely related to cubic lattice parameters of the same material by Vegard's law [12]

$$a_{hex.} = \left[\frac{1}{2}\right]^{\frac{1}{2}} a_{cubic} \quad \text{and,} \quad c_{hex} = \left[\frac{4}{3}\right]^{\frac{1}{2}} a_{cubic} \qquad (6)$$

For an ideal wurtzite structure, the relation between two identical lattice parameters is given by [13,14]

$c_{hex.} = (1.633)\, a_{hex.}$ (7)

The eqn. (4) is used for evaluating the values of lattice parameter ***d*** of hexagonal system on the basis of known (*h* k l) values of the reflecting planes with their ***a*** and ***c*** values given by eqn. (6) as shown in **Table**-1 .

Optical Properties: The optical properties of the host ZnS sample films were studied with the help of UV-vis spectrophotometer (**LS 35 Lamda PARKIN ELMER 2008**) in the visible wavelength 300nm – 800nm. The absorption coefficient, α in the films can be correlated to the photon energy as [15,.16]

$\alpha h\nu = A(h\nu - E_g)^{n/2}$ (8)

where E_g is the energy band gap between the valence and the conduction bands, α is a constant being different for different transitions, and n is a constant being equal to 1 for direct band gap semiconductor, A is a constant being different for different transitions. The absorption vs. wavelength curves of ZnS nanocrystalline thin films grown at different molarity as shown in Figures 1 (a,b,c & d) reveal that the absorption coefficient , α of photon energy enhances linearly with increase of molarity of ZnS thin films within 300-800nm wavelengths.

The enhancement of the absorption in lower wavelength site may be attributed due to increase of Zn^{+2} and S^{-2} ion concentrations in the films under controlled of quantum confinement effect [15]. The optical absorption spectra in the films showed absorption peak at 300nmwhich existed in the lower blue spectral site. The optical edge blue shift

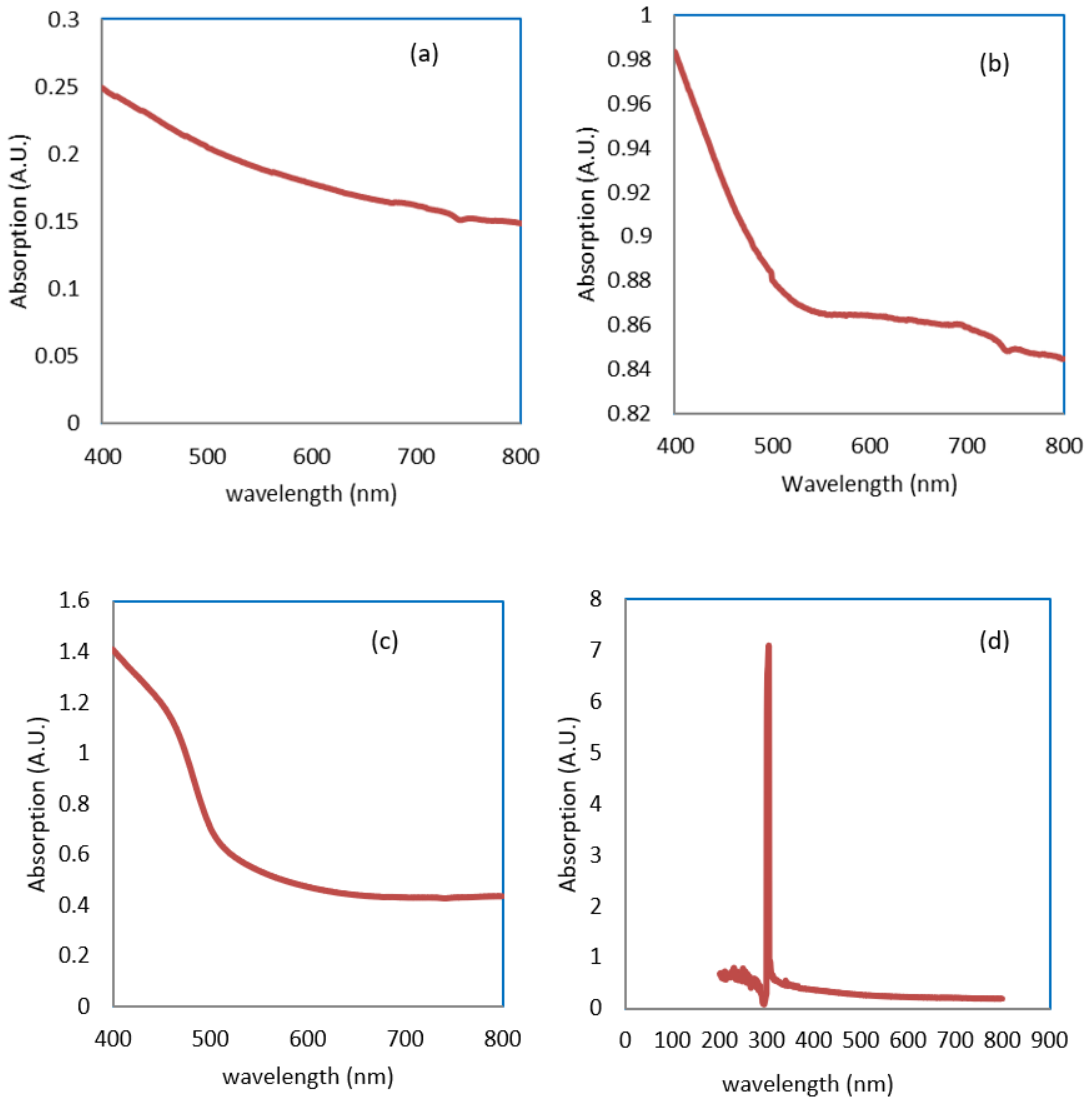
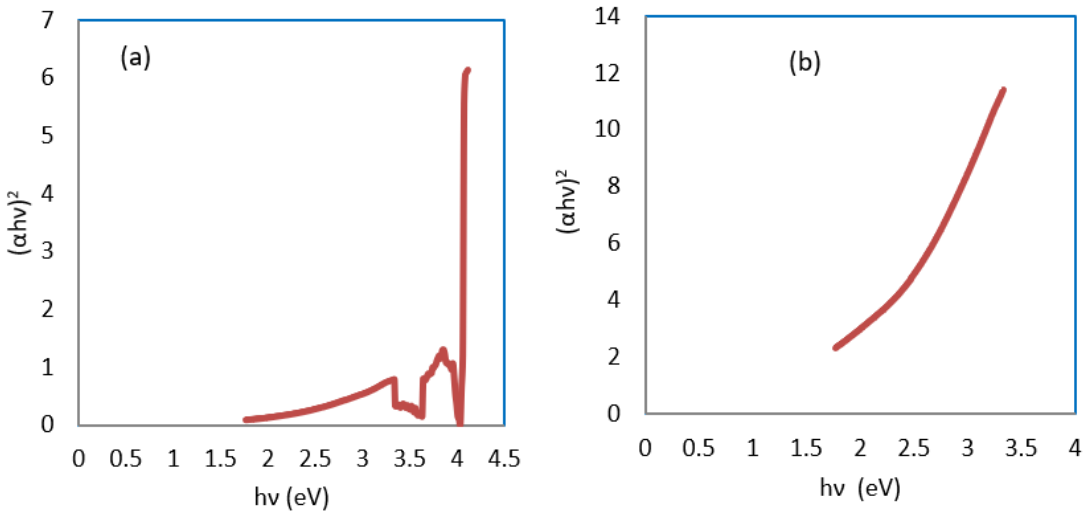


Fig. 1. Abs. vs. wavelength of light in nZnS thin films-(a) 0.05M, (b) 0.10M, (c) 0.15M & (d) 0.20M.



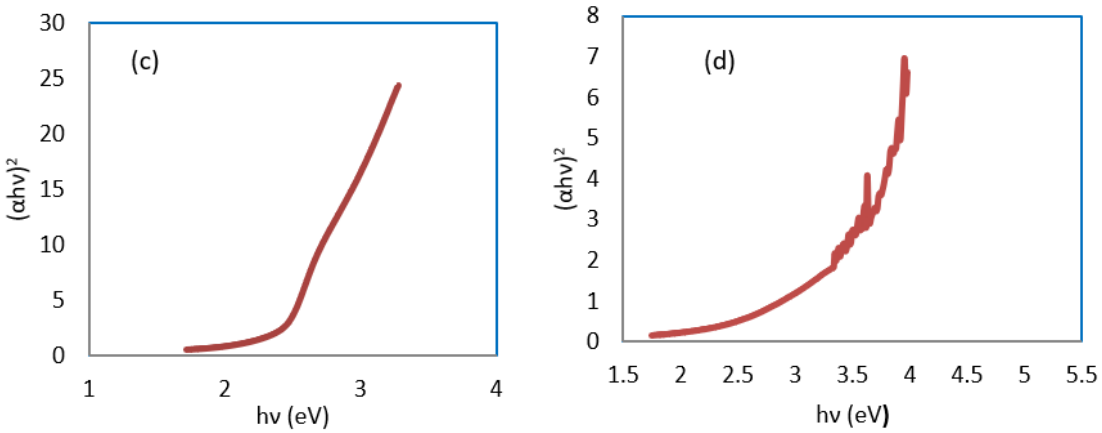


Fig.2 . $(\alpha h\nu)^2$ vs. hν curve of ZnS films - (a) 0.05M, (b) 0.10M, (c) 0.15M and (d) 0.20M.

indicated quantum dot size of the ZnS nanoparticles [8]. The band gaps determined from the $(\alpha h\nu)^2$ *vs.* $h\nu$ (photon energy) curves of the films with extrapolation to zero absorption are shown in Table-2.

Table-2. Observed extrapolated Band gaps in ZnS thin films.

Bulk Energy band gap E_g (eV)	Molars (M)	Observed energy band gap (eV)
3.70	0.05	1.90
	0.10	2.20
	0.15	2.40
	0.20	3.90

The optical variation of energy gaps vs. molars is shown in Figure 3.

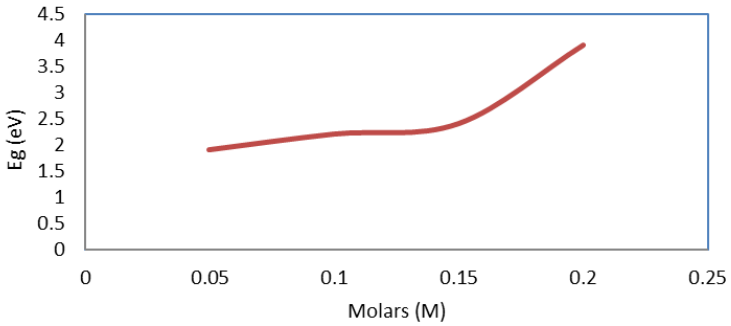


Fig.3. Variation in band gap vs. molars

The study shows that the optical energy band gap has linear relationship with the molar concentrations in the grown host ZnS thin films. This may be interpreted as on account of decrease in crystallite sizes driven by quantum confinement effects in the films. The mechanism of the study of the optical analysis of the chemically synthesized ZnS films will also find significant contributions in the photoelectrical transport mechanisms for different nano based device and applications.

IV. Conclusions

The crystal growth of the molar dependent ZnS thin films synthesized by CBD technique under control of p^H of the solution and the deposition time is found improving with increasing of Zn^{+2} and S^{-2} ions in the solution. The phase analysis in the crystalline ZnS thin films is found to possess f.c.c. cubic zinc sulphide with prominent orientation along (211) phase. The analysis of the results showed that the grain sizes were in the range of quantum dots with twi crystal phase structures cubic f.c.c. zinc sulphide spharalite and hexagonal (wurtzite) structures. The optical results showed maximum photon absorption co-efficient with blue shift but with wider optical band gap as a result of quantum confinement effect.

Acknowledgements

The authors are thankful to SAIF centre, Guwahati University for providing XRD results and Centre of Nanotechnology, IIT, Guwahati for FESEM and NIT, Manipur for UV-vis spectroscopy facility in the work.

References

[1]. Email Roduner, Nanoscopic Materials-Size Dependent Phenomena, Institute Of Physical Chemistry, University Of Stuttgari, Germany, Royal Society Of Chemistry, 2006, 1.1
[2]. Pawan Kumar, Arvind Kumar, P N Dixit And T P Sharma, Optical, Structural And Electrical Properties Of Zinc Sulphide Vacuum Evaporated Thin Films, Indian Journal Of Pure & Applied Physics, 2006, 44 690
[3]. D K Gupta, M Verma, K B Sharma And N S Sexena, Synthesis, Characterization And Optical Properties Of Cdse/Cds And Cdse/Zns Core Shell Nanostructures, Indian Journal Of Pure & Applied Physics, 2017, 55 113-121
[4]. Jyoti P Borah, J Barman, K C Sarma, Structural And Optical Properties Of Zns Nanoparticles, Chalcogenide Letters, 2008, 5 (9) 201
[5]. Jones P L, Moore D And Smith D C, A Technique For The Growth Of Single Crystal Films Of Zinc Sulphide On (100) Gallium Arsenide By Radio Frequency Sputtering, Journal Of Physics E 1976, 312
[6]. Sujver J F, Weister S F, Kelly J J And Meejerenk A, Synthesis And Photoluminescence Of Nanocrystalline Zns:Mn^{+2}, Nano. Lett., 2001, 1: 429
[7]. H P Klug, L E Alexander, X-Ray Diffraction Procedures, John & Sons, Inc, New York, 1954, 324
[8]. H Jamuna Devi, Ksh Nandini Devi, M Rasmani Devi And K Kunjabali Singh, Synthesis And Characterization Of Structural And Intergrain Nanocxrystallites In Chemically Prepared Bas:Ce^{+3}-Ions Thin Films IOSR Journal Of Applied Physics (IOSR-JAP) Vol. 16, Issue 4 Ser 1 (Jul-Aug.,2024) Pp 01-07
[9]. H P Klug And L E Alexander, X-Ray Diffraction Procedures, New York, John Willey & Sons Inc., (1954) 490
[10]. K. Kunjabali Singh And H. L. Das, Microstructures, Stress, Strain And Surface Characterization Of TD Polycrystalline Cds Thin Films, Indian J. Phys. 82 (6) (2008)685-693 .
[11]. H P Klug, L E Alexander, X-Ray Diffraction Procedures, John & Sons, Inc, New York, 1954, 346
[12]. W L Roth In M Aven And J S Prener (Eds), Physics And Chemistry Of II-VI Compounds, North Holand Publishing Co., Amsterdam, (1967) Pp-124
[13]. G A Jeffrey, G S Parikh And R L Mozzi, J Chem, Phys. 25 (5) (1956) Pp-1024
[14]. N G Dhere, N R Parikh And A Ferreir, Thin Solid Films, 44 (1977) Pp-83
[15]. Walced E Mahmood, H M EI-Mallah, J Phys. D Appl. Phys. 42(2009) 035502 2
[16]. M Rasmani Devi, S Jogita Devi And K Kunjabali Singh, IOSR Journal Of Applied Physics (IOSR-JAP) Vol.10 Issue 6 Ver. II (Nov.-Dec., 2018) Pp 24-31