

## **Structural and optical properties of copper doped ZnO nanoparticles and thin films**

**<sup>1</sup>Shaveta Thakur, <sup>1</sup>Neha Sharma, <sup>1</sup>Anamika Varkia and <sup>2\*</sup>Jitender Kumar**

<sup>1</sup>*Department of Physics, Arni University, Kangra (Himachal Pradesh)*

<sup>2</sup>*Department of Physics, Career Point University, Hamirpur (Himachal Pradesh)*

---

### **ABSTRACT**

*Un-doped ZnO-NPs and Zn<sub>1-x</sub>Cu<sub>x</sub>O NPs (x=0.01, 0.02, 0.03, 0.04) were synthesized using hydrothermal method and characterized by powder XRD. The effect of concentration of the precursors, on the structure, grain size and band gap energy were investigated. The XRD analysis demonstrates that the nanoparticles have the hexagonal wurtzite structure and the particle size decreases with increasing concentration of copper. From the results, the average crystallite sizes of the Zn<sub>1-x</sub>Cu<sub>x</sub>O NPs obtained from the different methods were very different, implying that the inclusion of strain in various forms has an important effect. Investigating the plots, it appears that the result of the SSP model and was more accurate than that of the Scherrer method, as the strain was considered in the calculation of crystalline size and the data were fitted more accurately in this method. SSP method was used to study the individual contributions of crystallite size and lattice strain on the peak broadening of Cu doped ZnO nanoparticles. Optical studies indicated that the band gap decreased from 3.38 eV to 3.35 eV upon Cu doping at temperature 500°C*

**Keywords:** Doping, X-Ray, Optical band gap

---

### **INTRODUCTION**

Nanotechnology is the study of manipulating matter on an atomic and molecular scale. Nanotechnology deals with developing materials, devices, or other structures possessing at least one dimension sized from 1 to 100 nanometers. Nanotechnology is the science of making or working with things that are so small that they can only be seen using a small microscope. Nanotechnology [1] includes the integration of nanoscale structures into larger material components and systems, keeping the control and construction of new and improved materials at the nanoscale [2]. Nanotechnology is very diverse, ranging from extensions of conventional device physics to completely new approaches based upon molecular self-assembly, from developing new materials with dimensions on the nanoscale to investigating whether we can directly control matter on the atomic scale. Nanotechnology entails the application of fields of science as diverse as surface science, organic chemistry, molecular biology, semiconductor physics, micro fabrication, etc. [3]. Nanotechnology may be able to create many new materials and devices with a vast range of applications, such as in medicine, electronics, biomaterials and energy production. On the other hand, nanotechnology raises many of the same issues as any new technology, including concerns about the toxicity and environmental impact of nonmaterial's and their potential effects on global economics, as well as speculation about various scenarios. Zinc oxide is a chemical compound with formula ZnO. It occurs in nature as the mineral zincite. It is an important material for a variety of practical applications. Nanoscience and nanotechnology involve studying and working with matter on an ultra small scale from sub nanometer to several

hundred nanometers . These nanosize materials have properties that are often significantly different from their counterparts with “ordinary size”[4]. ZnO is a promising material for the realization and future of nanotechnology ZnO can be utilized for electronic and photonic devices, as well as for high-frequency applications.” ZnO is a key technological material and it is a unique material. ZnO a direct band gap semiconductor with the band gap of 3.37eV [5] that is suitable for short wavelength optoelectronic applications and high exciton binding energy of 60 meV [6] . The high exciton binding energy of ZnO crystal can ensure efficient excitonic emission at room temperature. ZnO has been proposed to be a more promising UV emitting phosphor than GaN because of its larger exciton binding energy. ZnO is transparent to visible light and can be made highly conductive by doping. ZnO has a long history of usage for pigments and protective coatings on metals. The electrical, optoelectronic and photochemical properties of undoped ZnO has resulted in use for solar cells, [7-8] transparent electrode [9-10] and blue/UV light emitting devices [11]. ZnO films have low electric resistance and high transparency in the visible range. Several deposition techniques have been used to grow ZnO thin films, including sol-gel process [12], spray pyrolysis [13], molecular beam epitaxy (MBE) [14,15], chemical vapor deposition (CVD) [16] and sputtering [17, 18]. In comparison with other techniques, the solution route method has the advantage of being low cost and low substrate temperature deposition. In the present work undoped ZnO and Copper doped ZnO nanoparticles were synthesized using solution route method, which is robust and reliable to control the shape and size of particles without requiring the expensive and complex equipments]. By reducing the size of ZnO crystals to nanoscale dimensions, researchers can tailor the properties via quantum confinement and surface effects

## MATERIALS AND METHODS

### 2.1 Sample Preparation

All chemicals were purchased and used as received without further purification. Water was distilled twice/deionized. Here copper doped ZnO nanoparticle were made. First, (1M) Zinc acetate was mixed with 80 ml of deionized water and 20ml of ethanol and the mixed solution was stirred for 5 mins. Secondly (0.01M) Cupric nitrate was mixed with 80 ml of deionized water and 20ml of ethanol. Mixed all above solutions( named as solution A) .Ammonia solution was prepared by adding 44 ml of ammonia in 100 ml of deionized water (named as solution B). Then ammonia solution was added dropwise into solution A. The initial solution was blue in color. Ph value increased with the addition of ammonia solution and added into it until it becomes clear solution. NaOH solution was added into it (i.e 4.4 gm in 100 ml of deionized water) until the complete precipitation occurred. The container of the solution was placed in a water bath, and the temperature was kept at 60 °C for 1h. Filtered precipitates were dried in oven at 500°C constant temperature. Dry sample was ground for 1 hour.

### 2.2 Preparation of Cu doped ZnO thin films using Spin Coater

The deposition of doped zinc oxide by spin coating technique has seen increased research activity over the past several years as the need for high quality zinc oxide thin films has increased. Spin coating is used for the application of thin films. A typical process involves depositing a small puddle of a Fluid resin onto the center of a substrate and then spinning the substrate at high speed (typically around 3000 rpm). After preparing ZnO colloidal solution, thin films were deposited. We used 75 x 25mm square inch quartz slides of thickness 1.35mm as the substrate. Prior to processing, each quartz slides was washed sequentially in acetone and distilled water. The quartz slides were then dried. This ensures that there is no contamination on the quartz surface that could potentially interfere with deposition of ZnO thin films. The substrate is secure properly on to the spin coater, and with the aid of syringe, small amount of colloidal solution carefully dispersed on to the substrate. The spin coater is immediately spun at the rate of 3000rpm for 30 secs.

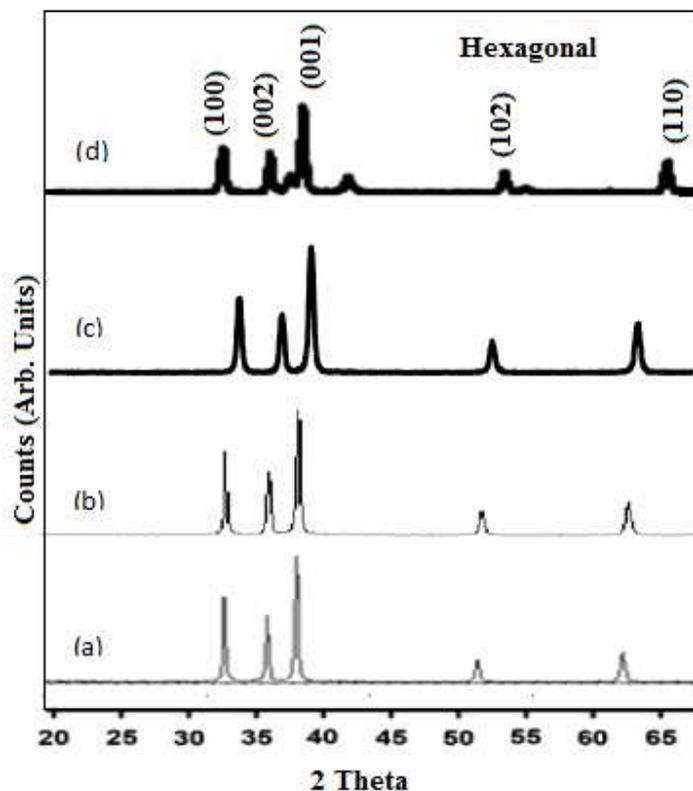
## RESULTS AND DISCUSSION

### 3.1 XRD analysis

The XRD patterns of the prepared sample are shown in Figure 1. It was clearly seen that the FWHM of the reflection peaks decreased after adding the dopant cations, indicating growth of the crystalline or changes in the crystal strains. There was also a negligible shift in peaks, and their FWHM obviously decreased for the samples that were doped with different concentration of Cu compared to the un-doped ZnO-NPs. This shift also corresponds to the strain of the compound and replacement of some Zinc cations with Cu in each compound. By replacing Cu with Zinc in the lattice, the strain changed as shown in the peak shift. The crystallite sizes of the synthesized powders are estimated from X-ray lines broadening using Scherer’s equation

$D = \frac{0.94\lambda}{\beta \cos \theta}$ , where  $\beta$  is full width at half maximum (FWHM),  $\theta$  is diffraction angle, and  $\lambda$  is wavelength of X-rays

[19]. The evaluated bond length ( $L$ ) and lattice parameters ( $a$ , and  $c$  are given in Table 1) of ZnO gradually decrease with increasing dopant concentration of Ag (by keeping  $C_o = 5.0$  mol %). To see the effect of doping on Zn-O bond length, bond length has been calculated using the following formula [20].



**Figure 1 :** The XRD pattern of Undoped ZnO -NPs and Cu doped ZnO- NPs heated at 500<sup>o</sup>C

(a) Pure ZnO- NPs, (b) Cu<sub>0.01</sub>-doped ZnO- NPs, (c) Cu<sub>0.02</sub>-doped ZnO- NPs, (d) Cu<sub>0.03</sub>-doped ZnO -NPs, (e) Cu<sub>0.04</sub>-doped ZnO NPs

$$L = \sqrt{\frac{a^2}{3} + \left(\frac{1}{2} - u\right)^2 c^2} \tag{1}$$

where  $a$  and  $c$  are the lattice parameters and

$$u = \frac{a^2}{3c^2} + 0.25 \tag{2}$$

**Table 1:** Bond Length ( $L$ ), Particle Size ( $D$ ) and lattice parameters LP ( $a$  and  $c$ ) of undoped and doped ZnO nanoparticles

Ag(mol%) Concentration	L(nm)	D(nm)	LP(nm)	
			a	c
Undoped	1.977083	51.98	3.25	5.2
0.01	1.978352	59.80	3.251	5.20802
0.02	1.881130	24.14	3.2516	5.20256
0.03	1.977083	24.59	3.25	5.2

### 3.2 Crystalline Size and Strain

#### 3.2.1 Scherrer Method

XRD can be utilized to evaluate peak broadening with crystallite size and lattice strain due to dislocation. The crystalline size of the un-doped ZnO and Cu-doped ZnO with different concentration were determined by the X-ray line broadening method using the Scherrer equation  $D = (k\lambda / \beta_D \cos\theta)$ , where D is the crystalline size in nanometers, k is a constant equal to 0.94,  $\beta_D$  is the peak width at half= maximum intensity, and  $\theta$  is the peak position. Here XRD was done by the X-Ray diffraction of the powder samples were performed using the diffractometer. X-Ray diffraction patterns were recorded with diffractometer using Cu Ka ( $\lambda = 1.542 \text{ \AA}$ ) with an accelerating voltage of 40 KV. Data were collected with a counting rate of 3<sup>0</sup>/min. Scherrer formula is given as by which we calculate the size of particle.

$$D = \frac{k\lambda}{\beta_D \cos\theta} \quad (3)$$

$$\cos\theta = \frac{k\lambda}{\beta_D} \left( \frac{1}{\beta_D} \right) \quad (4)$$

#### 3.2.2 Size- Strain Plot Method

In case of isotropic line broadening a better evaluation of the size-strain parameter can be obtained by considering an average “size-strain plot”(ssp), which has the advantage that less weight is given to data from reflections at high angles, where the precision is usually lower. In this approximation, it is assumed that the “crystallite size” profile is described by a lorentzian function and the “strain profile” by a Gaussian functions [21], accordingly, we have

$$(d_{hkl} \beta_{hkl} \cos\theta)^2 = \frac{K}{D} (d_{hkl}^2 \beta_{hkl} \cos\theta) + (\epsilon/2)^2 \quad (5)$$

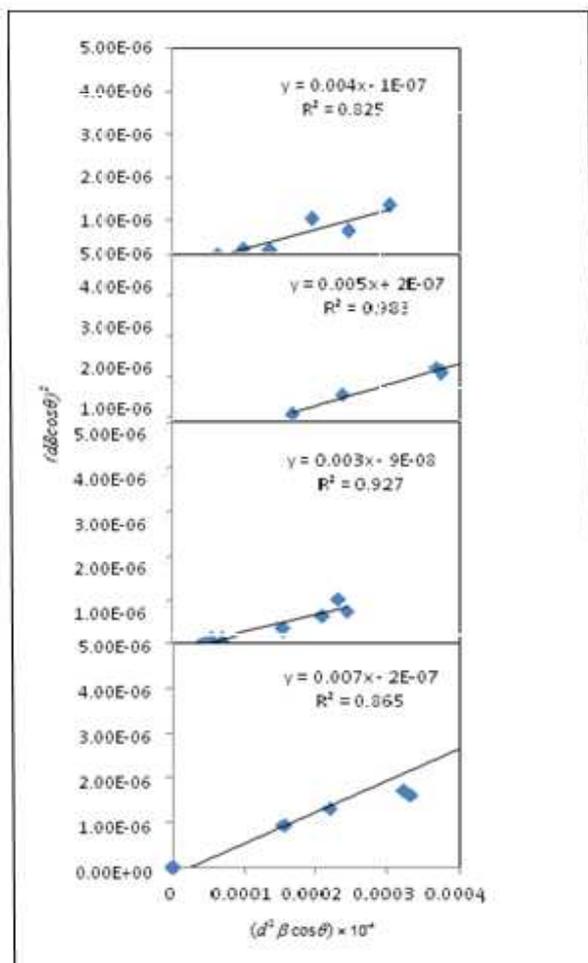
Where k is the constant that depends on the shape of the particles: for spherical particles it is given as 3/4. In Figure 2, the term  $(d_{hkl} \beta_{hkl} \cos\theta)^2$  is plotted with respect to  $(d_{hkl}^2 \beta_{hkl} \cos\theta)$  for the all orientation peaks of ZnO-NPs and Cu<sub>(0.1-0.4)</sub> doped ZnO with the wurtzite hexagonal phase from  $2\theta = 20^\circ$  to  $2\theta = 60^\circ$ . In this case the particle size is determined from the slope of the linearly fitted data and the root of the y- intercept gives the strain. According to Hook’s law, a linear proportionality between the stress and strain as given as  $\sigma = Y\epsilon$ , where  $\sigma$  is the stress of the crystal and Y is the modulus of elasticity or Young’s modulus, for a significantly small strain. This equation deviates from this linear approximation with increasing strain. For a hexagonal crystal, Young’s modulus is given by the following relation [22].

$$Y_{hkl} = \frac{[h^2 + \frac{(h+2k)^2}{3} + (\frac{al}{c})^2]^2}{s_{11}(h^2 + \frac{(h+2k)^2}{3})^2 + s_{33}(\frac{al}{c})^4 + (2s_{13} + s_{44})(h^2 + \frac{(h+2k)^2}{3})(\frac{al}{c})^2} \quad (6)$$

Where  $S_{11}$ ,  $S_{13}$ ,  $S_{33}$ ,  $S_{44}$  are the elastic compliances of ZnO with values of  $7.858 \times 10^{-12}$ ,  $-2.206 \times 10^{-12}$ ,  $6.940 \times 10^{-12}$ ,  $23.57 \times 10^{-12} \text{ m}^2 \text{ N}^{-1}$ , respectively [23]. Young’s modulus for the Ag doped ZnO-NPs was calculated. For an elastic system that follows Hooke’s law, the energy density u (energy per unit) can be calculated from  $u = (\epsilon^2 Y_{hkl})/2$ . The results obtained from the Scherrer method and the SSP models are summarized in Table 2.

**Table 2: Geometric parameters of pure and Cu doped ZnO at 500°C**

Compound	Method					
	Scherrer D(nm)	Size strain plot(nm)				
	D(nm)	$\epsilon \times 10^{-4}$	$\gamma \times 10^9$	$\sigma \times 10^6$	$\mu \times 10^3$	
ZnO	51.98	241.93	10.00	144.09	144.09	72.04
Cu <sub>0.01</sub> Zn <sub>0.99</sub> O	59.80	250	7.5	144.09	108.06	40.52
Cu <sub>0.02</sub> Zn <sub>0.98</sub> O	24.14	150	12.5	144.09	180.11	112.57
Cu <sub>0.03</sub> Zn <sub>0.97</sub> O	24.59	107.14	17.5	144.09	252.15	220.63



**Figure 2: The SSP plot of Cu–doped ZnO NPs heated at 500<sup>0</sup> C (a) Cu<sub>0.1</sub> doped ZnO NPs (b) Cu<sub>0.02</sub> doped ZnO NPs (c) Cu<sub>0.03</sub> doped ZnO NPs (d) Cu<sub>0.04</sub> doped ZnO NPs. The particle size is achieved from the slop of the linear fitted data**

**OPTICAL ANALYSIS**

Diffuse reflectance spectra were recorded to estimate the optical band gap of the pure and copper doped zinc oxide with different concentrations (Zn<sub>1-x</sub>Cu<sub>x</sub>O, where (x = 0.01 to 0.03)). Diffused reflectance spectroscopy (DRS) on powders or pallets is roughly analogous to transmission measurements on thin films. Figure 3 shows the plot for the percentage of reflection as a function of band gap energy (hν) of the nanoparticles synthesized via hydrothermal method. The optical band gaps of pure and doped zinc oxide are estimated from the plots of reflectance verses energy. The band gap estimated for pure zinc oxide 3.39 eV that is slightly higher than the bulk zinc oxide (3.37 eV). The diffused reflectance spectra of Cu doped zinc oxide (Zn<sub>1-x</sub>Cu<sub>x</sub>O), where (x = 0.01 to 0.03) shows that, as the concentrations of copper increases (x = 0.01 to 0.03), the band gaps also decreases. The band gap values were

deduced from the intersection of the two linear regions Table 3. Diffused spectra indicate that the Cu doping causes little structural disorder in zinc oxide lattice.

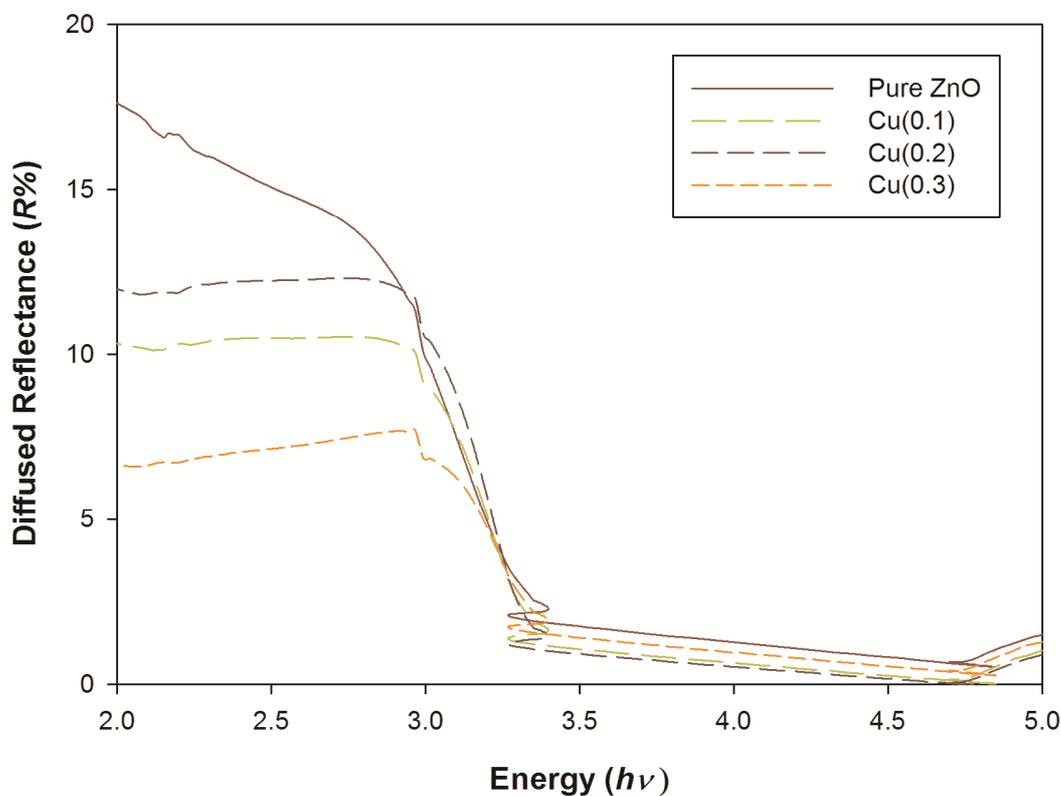


Figure 3: DRS of ZnO nanoparticles synthesized at various concentration of Copper doped ZnO (0.01M, 0.02 M, 0.03 M, and 0.04 M) at 60°C for 1 hour

Table 3: Variations of band gap with increase in concentration of Cu doped ZnO heated at 500°C

Compound	Band gap (eV)
ZnO	3.39
Cu <sub>0.01</sub> Zn <sub>0.99</sub> O	3.38
Cu <sub>0.02</sub> Zn <sub>0.98</sub> O	3.37
Cu <sub>0.03</sub> Zn <sub>0.97</sub> O	3.35

### CONCLUSION

Un-doped ZnO-NPs and Zn<sub>1-x</sub>Cu<sub>x</sub>O NPs (X= 0.01M, 0.02M, 0.03M) were synthesized by using hydrothermal method and characterized by powder XRD. The effect of concentration of the precursors, temperature and time of growth on the structure, grain size and band gap energy were investigated. The XRD analysis demonstrates that the nanoparticles have the hexagonal wurtzite structure and the particle size decreases with growth temperature with increasing concentration of the copper. From the results, the average crystallite sizes of the Zn<sub>1-x</sub>Cu<sub>x</sub>O NPs obtained from the different methods were very different, implying that the inclusion of strain in various forms has an important effect. Investigating the plots, it appears that the result of the SSP model was more accurate than that of the Scherrer method, as the strain was considered in the calculation of crystalline size and the data were fitted more accurately in this method.

**Acknowledgment**

Authors are thankful to Dr. Atul Khanna from Guru Nanak Dev University, Amritsar for his valuable suggestions and cooperation to avail X-Ray diffraction and UV-Visible Spectrophotometer facilities.

**REFERENCES**

- [1] M. Pitkethly, *NanoToday*, Dec **2004**.
- [2] S.A. Wolf, D.D. Awschalom, R.A. Buhrman, J.M. Daughton, S. Molnar Von, M.L. Roukes, A.Y. Chhetkanova and D.M., *Treger Science*, 294 (**2001**), 1488.
- [3] S. Thakur, J. Kumar, J. Sharma, N. Sharma and Praveen Kumar, “*Structural and Optical Properties of Nickel Doped ZnO Nanoparticles and Thin Films*” *J. Opt. Adv. Mater.* **15** (**2013**) 989-994
- [4] Zhong Lin Wang, *Journal of Physics: Condensed Matter*, 16 (**2004**), R829- R858.
- [5] S Pearton, T Steiner, *Progress Mater J. Sci.*, 50 (**2005**), 293.
- [6] A.E Jimenez-Gonzalez, A Jose, Soto Urueta, R Suarez-Parra, *J. Cryst. Growth*, 192 (**1998**), 430.
- [7] D. G. Baik And S. M. Cho, *Thin Solid Films*, 354(**1999**), 227
- [8] Y. Ohya, M. Ueda And Y. Takahashi, *Jpn. J. Appl. Phys.*, 35 (**1996**), 4738.
- [9] Y. Natsume, *Thin Solid Films*, 372(**2000**), 30.
- [10] G. K. Paul, S. Bandyapadhyay And S. K. Sen, *Phys. Status Solid A*, 191(**2002**), 509.
- [11] D.C. Look, D. C. Reynolds, C. W. Litton And G. Cantwell, *Appl. Phys. Lett.*, 81 (**2002**), 1830.
- [12] P Sagar, M Kumar., R.M. Mehra, *Thin Solid Films*, 489 (**2005**), 94.
- [13] Baik D.G, S.M Cho., *Thin Solid Films*, 354 (**1999**), 227.
- [14] P. Fons, K. Iwata, S. Niki, A. Yamada, K. Matsubara, *J. Cryst. Growth*, 209 (**2000**), 532.
- [15] K. Sakurai, D. Iwata, S. Fujita, S. Fujita, *Jpn. J. Appl. Phys.*, 138 (**1999**), 2606.
- [16] Y. Liu, C.R. Gorla, S. Liang, N. Emanetoglu, Y. Lu, H. Shen, *J. Electron. Mater.*, 29 (**2000**), 69.
- [17] J.L. Vossen, *Phys. Thin Films*, 9 (**1977**), 1.
- [18] P.C. Karulkar, M.E. Mc Coy, *Thin Solid Films*, 83 (**1981**), 259.
- [19] B. D. Cullity, S. R. Stock, *Elements of X-ray diffraction*, **2001**.
- [20] G. SriFvasan, R. T. Rajentra Kumar, *J. Sol-gel Technol.* 43 (**2007**), 171..
- [21] M.A. Tagliente, M. Massaro, *Nucl. Instrum Methods Phys.*, 266 (**2008**) 1055.
- [22] J. Zhang, Y. Zhang, K.W. Xu, V. Ji, *Solid State Commun.* 139 (**2006**) 87.
- [23] J.F. Nye, *Physical Properties of Crystals*, **1985**.