

# Comparison of optical and structural characteristics of $\text{Cd}_x\text{Zn}_{1-x}\text{S}:\text{Na}, \text{Sm}/\text{Pr}$ films

AYUSH KHARE, TANDESH LAL CHANDRA<sup>a</sup>

*Department of Physics, National Institute of Technology, GE Road, Raipur – 492 010 Chhattisgarh, India*

<sup>a</sup>*State Forensic Laboratory, Raipur – 492 010 Chhattisgarh, India*

This paper reports a detailed investigation on the optical and structural properties of Sm/Pr doped  $\text{Cd}_x\text{Zn}_{1-x}\text{S}:\text{Na}$  films prepared through chemical bath deposition (CBD) technique in aqueous alkaline bath and their consequent condensation on glass substrates. Results in terms of SEM, XRD, optical absorption spectra, photoconductivity (PC) rise and decay and photoluminescence (PL) emission spectra are presented and discussed for  $\text{Cd}_x\text{Zn}_{1-x}\text{S}:\text{Na}, \text{Sm}/\text{Pr}$  films prepared on glass substrates at 60 °C in a water bath (WB). SEM studies show fibre type structures, which are related to layered growth. XRD results show prominent diffraction lines of CdS and ZnS along with lines of impurity. From results of optical absorption spectra, the band-gap values are determined, which are comparable with those obtained from PL emission spectra. Sufficiently high photo current ( $I_{pc}$ ) to dark current ( $I_{dc}$ ) ratios with a maximum value of the order of  $10^6$  are observed.

(Received January 16, 2013; accepted January 22, 2014)

*Keywords:* Chemical bath deposition, Photoluminescence, SEM, XRD, Absorption

## 1. Introduction

In the past few years, nano structured materials have drawn interest of research workers due to their potential impact in many areas such as electronics, photonics, catalysis and sensing [1]. They offer numerous applications in various fields including one-dimensional and high-density superconductors, nano wire sensor arrays, giga hertz nano mechanical resonators, high-density molecular electronic circuits [2], display devices and lasers [3]. These new materials take advantage of size-induced changes in structural, optical and electronic properties to create new or enhanced materials, whose properties deviate from the corresponding bulk phase. II-VI semiconductor nano crystals (quantum dots), whose radii are smaller than the bulk exciton Bohr radius, constitute a class of materials intermediate between molecular and bulk forms of matter. Quantum confinement of the electron-hole pair leads to an increase in the effective band-gap with decreasing crystallite size thus, offering new ways for tuning optical and photonic properties [4]. Similar relationship has been deduced for nanostructured materials prepared from the direct band-gap semiconductors e.g. ZnS, CdS, PbS etc. Nano structured zinc sulfide (ZnS) and cadmium sulfide (CdS) thin films are promising materials for their use in various optical devices. Because of the wide direct band-gap (3.7 eV), ZnS is well known as promising II-VI compound semiconductor giving a broad band luminescence from the near UV to the near IR and therefore, is of prime interest for opto-electronic devices. On the other hand CdS ( $E_g = 2.42$  eV), used as counterpart of ZnS for many years, is one of the first discovered semiconductors. CdS finds promising applications in photochemical catalysis, gas sensor detectors for laser and infrared solar cells, nonlinear optical materials, various luminescence and opto-

electronic devices [5-7]. It is well established that  $\text{Cd}_x\text{Zn}_{1-x}\text{S}$  films possess properties between those of CdS and ZnS [8, 9]. Since their addition produces a common lattice in which band structure has a larger band-gap value than CdS, it makes the material more attractive for fabricating various devices. In all the models for the light emitting mechanism and for self-compensation, point defects such as vacancies or interstitials play major role [10]. Hence to understand involved mechanism properly, it becomes imperative to extend investigations to find out the role of dopant on electro-optical properties. Role of NaF in photo conducting CdS powders, prepared by firing at 500°C for 1 hr, is found to be two fold by Bhushan and Sharma [11, 12]: (i) it acts as a flux because impurities added can not turn effective in its absence and (ii) it acts as dopant since at its particular concentration the highest photo response is noticed. Several sophisticated techniques such as molecular beam epitaxy (MBE) [13], plasma chemical sputtering [14], MOCVD [15] and MOVPE [16] have been used to produce thin films with adequate properties such as high crystalline, low resistive and high transmittance. However, CBD technique appears as an interesting technique for preparing ZnS/CdS thin films. Indeed this technique for preparation of thin films is very attractive because of being inexpensive, simple and capable of depositing optically smooth, uniform and homogeneous layers. One of the advantages of preferring CBD technique lies in Chandra's paper [17], which establishes the age of devices prepared with such films for more than two years. In recent years Bhushan and co-workers used CBD technique and reported quite high PC gain in (Cd-Pb)S and (Cd-Zn)S films doped with rare earths elements [18-22], moderate photovoltaic (PV) efficiency [23, 24], efficient PL in some of these films [25, 26] and electroluminescence (EL) in (Zn-Cd)S films using NaF as flux and Cu as impurity [27, 28]. The present paper

reports and discusses results of detailed study on optical and structural properties of  $Cd_xZn_{1-x}S: Na$  films in presence of Sm and Pr as dopants. The  $(Cd_{0.7}Zn_{0.3})S$  sample and dipping time of 60 minutes were selected on the basis of satisfactorily high PL brightness and proper band-gap value.

## 2. Experimental section

### 2.1 Sample preparation

The samples for various studies are prepared through vertically dipping the cleaned substrates of highly transparent glass plates (dimension = 75 mm × 24 mm × 2 mm) in a WB. The films are prepared at a temperature of 60°C on micro glass slide substrates, cleaned with double distilled water, acetone and ultrasonic cleaner. A 25 ml beaker is used as a container for the reaction of chemicals. This beaker is immersed into a WB and heated to the desired temperature. The aqueous solution taken into the beaker contains highly pure and analytical reagent (AR) grade 1 Molar cadmium acetate [ $Cd(CH_3COO)_2$ ], zinc acetate [ $Zn(CH_3COO)_2$ ], (zinc acetate + cadmium acetate = 7.00 ml), thiourea [ $SC(NH_2)_2$ ], triethanolamine ( $HOCH_2CH_2)_3N$  (TEA) and 30 % aqueous ammonium hydroxide ( $NH_4OH$ ) (mixture's pH ≈ 11). Thiourea and triethanolamine are two commonly used sulphiding agents [29]. In this chemical reaction, TEA acts as a complexing agent and pH balancer. For preparing the doped samples calculated proportions of 0.01 Molar solutions of sodium fluoride (NaF), samarium nitrate ( $SmNO_3$ ) and praseodymium nitrate ( $PrNO_3$ ) are also introduced in the original mixture before placing the beaker into WB. The beaker containing aqueous solution of the chemicals is well covered with another inverted bigger beaker to prevent possible ammonia loss at higher temperature.

In the beginning when precipitation starts, the solution is stirred for few minutes and no further stirring is done during the deposition. The deposition is made in the static condition by placing glass substrates inclined vertically to the walls of the beaker until the solution reaches the desired temperature. The temperature of bath is digitally controlled from outside with a timer. After desired temperature is attained, the substrate is removed from the beaker and cleaned by flushing with distilled water to remove the uneven overgrowth of grains at the surface and then dried by keeping in open atmosphere under sun light until it dries completely. The dried film is quite adherent to the substrate surface and is irremovable. Here, the subscripts to Cd and Zn represent their percentage compositions in the solution.

In the CBD process, the quality of the film is decided directly by substrate and reaction conditions. Thus, making the  $(Cd-Zn)S$  in the solution grow rather than deposit on the substrate is a serious concern. Ideally, the  $(Cd-Zn)S$  is expected to grow on the substrate in the preparation of a  $(Cd-Zn)S$  film using CBD.

### 2.2 Measuring techniques

The materials are weighed using Shimadzu ATX 224 single pan analytical balance. The excitation source for PC rise-decay studies is 100W incandescent bulb while the measurement of corresponding photocurrents is made with a digital nano ammeter (DNM-121). The PL excitation is done through 365 nm line obtained from a high pressure mercury vapour lamp filtered by Carl-Zeiss interference filter. Light output is detected by using an RCA-6217 photomultiplier tube operated by a highly regulated power supply (EHT-11 Scientific Equipment, Roorkee). For spectral studies at room temperature (RT) Hitachi F-2500 Fluorescence Spectrophotometer is used. The various X-ray analyses are made using a computerized Philips diffractometer with Cu/K-alpha radiations while SEM studies are performed using a LEO (430) scanning electron microscope. The optical absorption spectra are recorded by using a 1700 Pharmespec Shimadzu Spectrophotometer over the wavelength range 300-700 nm.

## 3. Results and discussion

### 3.1 Characterization studies

#### Scanning electron microscopy (SEM)

The luminescence efficiency of phosphor materials depends on the morphology of the film particles such as size, shape, crystallinity, defects, grain boundary and so on. SEM analysis is done to study the morphology of  $(Cd_{0.7}Zn_{0.3})S$  films and representative images at a magnification of 10 k are shown in Fig. 1. The particles in the as-prepared samples have approximately fibre shape and narrow size distribution. The SEM of NaF doped sample (Fig. 1 a) exhibits cluster of particles in form of nano fibers. In this micrograph nano wire type structures with diameter ~ 50 nm are seen. The average particle size calculated using Heyn's intercept method [30] is found to lie around 90 nm. It is supposed that upon addition of NaF, vacant spaces existing in undoped sample [31] are occupied resulting in more compact structure. Earlier workers [32] found well developed cabbage structure, which they interpreted in terms of layered growth structure forming cabbage due to overlap of different layers formed under continue growth.

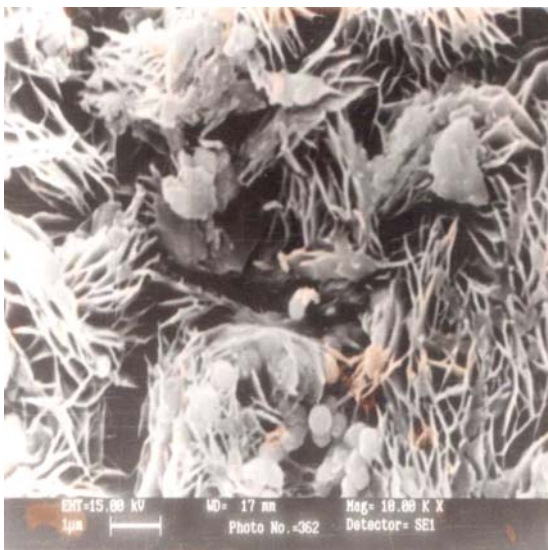
In the micrographs of Sm and Pr added samples, it is noticed that as compared to Sm, addition of Pr offers more ordered structure with fibers spreaded all over. The scattered leafy structure may also be expected when overlapping does not take place. In such samples presence of voids is also expected [33]. In the former case the particles are distributed in feather shape, which convert into wire shape in the later one.



a



b



c

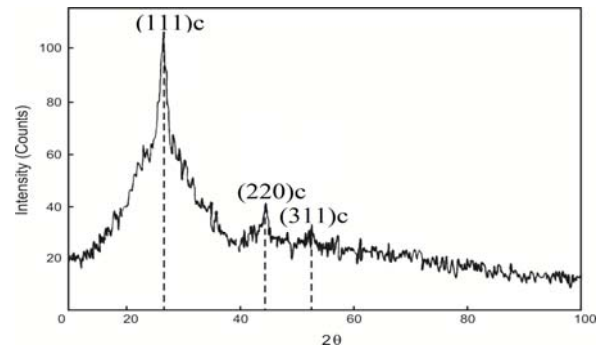
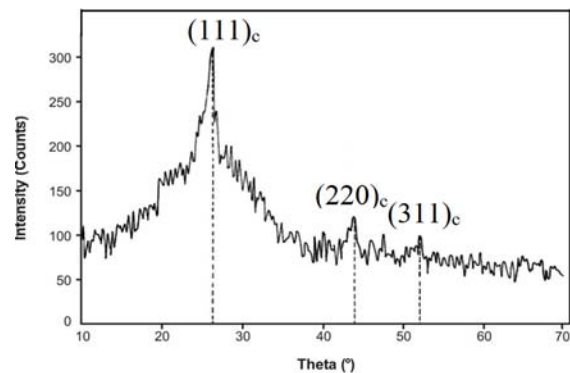
Fig. 1.

### X-ray diffraction (XRD) studies

The XRD patterns of  $(Cd_{0.7}Zn_{0.3})S$ : NaF films doped with Sm and Pr are presented in Fig. 2 (a), (b) and (c) respectively and corresponding data including lattice constant, inter planner spacing etc. are enlisted in Table 1. The assignment of diffraction lines is made by comparing with JCPDS files of ZnS (cubic, JCPDS 05-0566) and CdS (cubic, JCPDS 10-454) and the evaluated and reported values of parameters like lattice interval, lattice constant and Miller indices. The diffractograms show limited number of peaks corresponding to  $2\theta = 26^\circ C, 44^\circ C, 52^\circ$  indicating semi crystalline nature of tested material. There is a small shift of the observed peak positions to the lower angles. The presence of dopants does not disturb the crystalline structure of samples but certainly modifies the lattice parameters due to the difference in the ionic radii between the dopant and the substituted Sm/Pr [34]. The average crystallite size (c.s.) of the nano crystalline film is estimated using Scherrer's formula [35, 36]

$$c. s. = K\lambda / \beta \cos\theta \quad (1)$$

where  $\lambda$  is the wavelength of X-rays employed,  $\beta$  the full width at half maxima (FWHM) of the peak measured in radians,  $K$  a constant, which ranges between 0.87 and 1.1 for different crystalline shapes and  $\theta$  is the Bragg's angle. The observed peaks are quite broad in both the cases, which again is an indicative [37] of nano sized particles.

Fig. 2. (a) X-ray diffractograms of  $(Cd_{0.7}Zn_{0.3})S$ : NaF film.Fig. 2. (b) X-ray diffractograms of  $(Cd_{0.7}Zn_{0.3})S$ : NaF, Sm film.

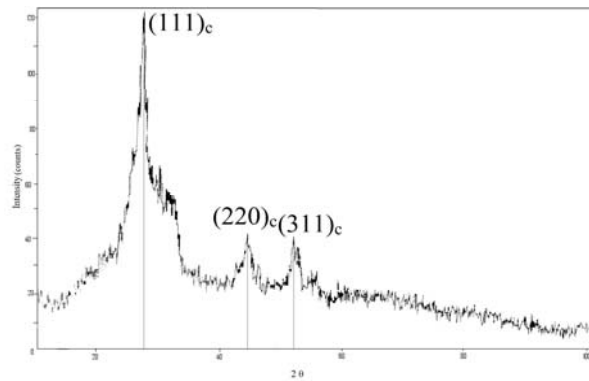


Fig. 2. (c) X-ray diffractograms of  $(\text{Cd}_{0.7}\text{-Zn}_{0.3})\text{S: NaF, Pr}$  film.

Table 1. XRD data of  $(\text{Cd}_{0.7}\text{-Zn}_{0.3})\text{S}$  films.

Preparation temperature –  $60^\circ\text{C}$ , Time of deposition – 1 hr

System	d ( $\text{\AA}$ )	Miller Indices (h k l)	Intensity	Lattice constant ( $\text{\AA}$ )
$(\text{Cd}_{0.7}\text{-Zn}_{0.3})\text{S: NaF}$	3.3135	$(111)_c$	126	5.739
	2.0560	$(220)_c$	43	5.829
	1.7670	$(311)_c$	34	5.875
$(\text{Cd}_{0.7}\text{-Zn}_{0.3})\text{S: NaF, Sm}$	6.481	$(111)_c$	304	5.216
	3.329	$(220)_c$	127	5.482
	1.761	$(311)_c$	92	5.501
$(\text{Cd}_{0.7}\text{-Zn}_{0.3})\text{S: NaF, Pr}$	3.334	$(111)_c$	121	5.775
	2.044	$(220)_c$	43	5.796
	1.772	$(311)_c$	42	5.823

### Optical absorption studies

It is reported that the band-gap of a specific material does not only depend on its structure but the size also is a controlling factor. Once the particles reach nano-meter size, quantum effects come into play and the effective band-gap increases [38]. Absorption measurements are made at RT over the wavelength range of 400-700 nm. The absorption spectra of prepared  $(\text{Cd}_{0.7}\text{-Zn}_{0.3})\text{S}$  films exhibit the films to have a high absorption in the visible region (fig.3). Chandra and Bhushan [23] also obtained a high absorption in the visible range for the  $(\text{Cd-Zn})\text{S}$  films prepared using CBD method [39]. For direct band-gap materials, the optical energy-gap is determined by extrapolating the straight line segment of the  $(\alpha h\nu)$  vs  $(\alpha h\nu)^2$  graphs to the  $h\nu$ -axis according to following relation [40].

$$\alpha h\nu = (\alpha h\nu - E_g)^{1/2} \quad (2)$$

where 'A' is a constant and ' $E_g$ ' is the band-gap value of the semiconductor material. Thus, as shown in Fig. 4, the band-gap values of materials are determined from the Tauc's plots  $[(\alpha h\nu)^2 \text{ vs } h\nu]$ . Shift in absorption ages are

observed in all the cases. Otherwise no other major changes are observed. The different band-gap values as determined from Tauc's plots are presented in Table 2.

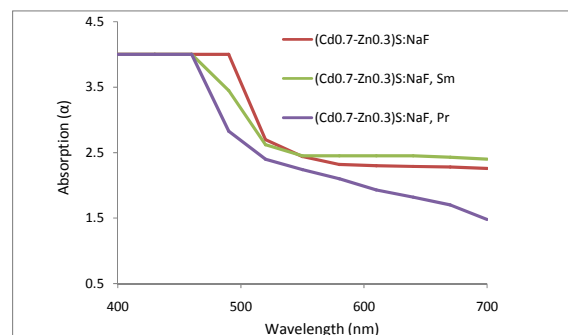


Fig. 3.

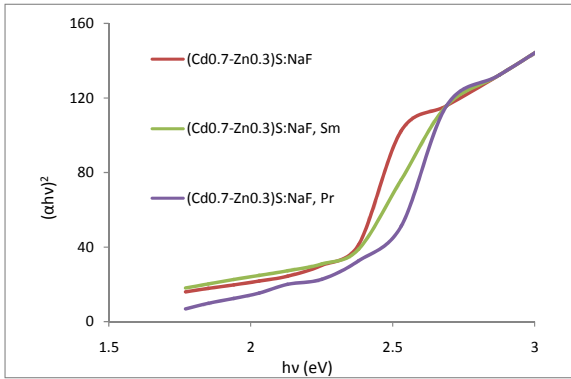


Fig. 4.

Table 2. Band-gap values of different  $(Cd_{0.7}Zn_{0.3})S$ : NaF, Sm/Pr films.

System	Band-gap value (eV)
$(Cd_{0.7}Zn_{0.3})S$ : NaF	2.31
$(Cd_{0.7}Zn_{0.3})S$ : NaF, Sm	2.24
$(Cd_{0.7}Zn_{0.3})S$ : NaF, Pr	2.42

### 3.2 PC studies

Fig. 5 shows the rise and decay curves of different  $(Cd_{0.7}Zn_{0.3})S$  films using NaF as the flux and Sm or Pr as impurities. The corresponding data of dark current ( $I_{dc}$ ),

photo current ( $I_{pc}$ ) and their ratio ( $I_{pc}/I_{dc}$ ) are summarized in Table 3. The general nature of rise and decay curves is similar in different cases: the rise consists of a fast increase in the beginning followed by saturation due to the net effect of the generation and recombination phenomena. Finally, due to balance between two processes saturation appears, further initial part of decay curves consists of fast decrease followed by very low decrease. Similarly, the decay curves show a fast decay due to recombination and a slow variation arising from trapping. It has been reported earlier that  $CdCl_2$  is a better flux as compared to NaF because  $CdCl_2$  is known to promote recrystallization of CdS [41, 42]. In this case using NaF as the flux the values of ratio  $I_{pc}/I_{dc}$  are quite similar to those obtained with  $CdCl_2$  as the flux, thus NaF can be taken as a replacement of  $CdCl_2$ . Values of instantaneous lifetime, mobility and trap depth are summarized in Table 4.

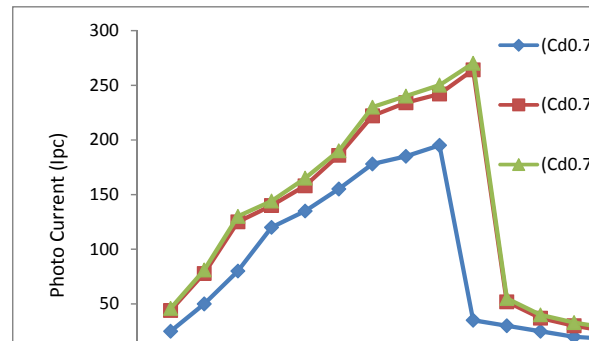


Fig. 5.

Table 3. Values of  $I_{PC}$ ,  $I_{DC}$  and the ratio  $I_{PC}/I_{DC}$  for different doped films.

Preparation temperature – 60°C, Time of deposition – 1 hr

Systems	$I_{DC}$ (nA)	$I_{PC}$ ( $\mu$ A)	$I_{PC}/I_{DC}$
$(Cd_{0.7}Zn_{0.3})S$ : NaF	0.61	75	$2.91 \times 10^5$
$(Cd_{0.7}Zn_{0.3})S$ : NaF, Sm	0.1	111	$1.11 \times 10^6$
$(Cd_{0.7}Zn_{0.3})S$ : NaF, Pr	0.1	881	$8.81 \times 10^5$

Table 4. Values of trap depth, life time and mobility for different  $(\text{Cd}_{0.7}\text{-Zn}_{0.3})$  films.

Preparation temperature – 60°C, Time of deposition – 1 hr

System	Trap depth	Trap depth	Life time ( $\tau$ )	Mobility ( $\mu$ )
	$E_1$ (eV)	$E_2$ (eV)	(in seconds)	( $\text{cm}^2/\text{Volts-sec}$ )
$(\text{Cd}_{0.7}\text{-Zn}_{0.3})\text{:NaF}$	0.729	0.728	18.78	48.93
$(\text{Cd}_{0.7}\text{-Zn}_{0.3})\text{:NaF, Sm}$	0.722	0.723	25.38	120.12
$(\text{Cd}_{0.7}\text{-Zn}_{0.3})\text{:NaF, Pr}$	0.738	0.726	23.76	95.23

### 3.3 PL spectra

The PL emission spectra of different Sm and Pr doped  $(\text{Cd}_{0.7}\text{-Zn}_{0.3})\text{S:NaF}$  films are presented in Fig. 6. Changes in band-gap values due to addition of Sm and Pr are already reported in absorption spectra. Similar changes are observed in the PL emission spectra. Maximum emission intensity is observed in Pr added  $(\text{Cd}_{0.7}\text{-Zn}_{0.3})\text{S:NaF}$  sample. It is found that spectrum of  $(\text{Cd}_{0.7}\text{-Zn}_{0.3})\text{S:NaF}$  film peaks at 520 nm, which changes to 492 nm and 489 nm in presence of Sm and Pr respectively. It is noticed that the intensities in presence of dopants Sm and Pr improve and peak positions shift towards lower wavelength side.

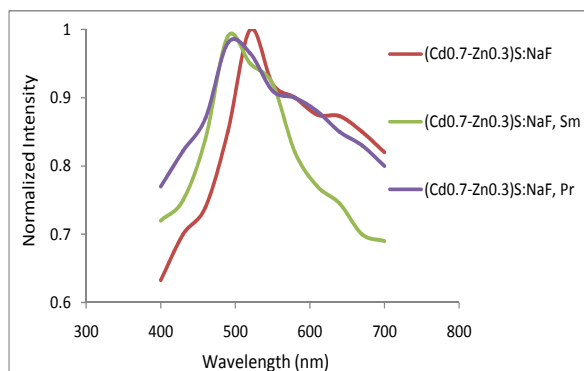


Fig. 6.

### 4. Conclusions

The CBD technique is a simple and suitable method for obtaining smooth, uniform, high reflecting and strong adherent CdZnS thin films. The SEM studies present the particles to be distributed in fiber shape while XRD results exhibit peaks corresponding to CdS and ZnS. These studies reveal the average particle size to lie in nano order. Optical absorption spectra help in determining the band-gap values of different films, which are supported by PL emission spectra. In summary, homogenous and compact CdZnS nano crystalline films are grown on glass substrate

by means of CBD technique with cadmium acetate/zinc acetate as Cd/Zn ion and thiourea as S ions source.

### References

- [1] P. F. Barbara, *Nanoscale Materials (A special issue)*. *Acc. Chem. Res.*, **32**, 87 (1999).
- [2] J. R. Heath, M. A. Ratner, *Phys. Today* **56** (5), 43 (2003).
- [3] G. Blasse, B.C. Grabmair, *Luminescence Materials*, Springer, Berlin (1994).
- [4] V.V. Nimesh, S. Mahamuni, *Semicond. Sci. Technol.* **16** (8), 687 (2001).
- [5] R. Agrawal, C. Barrelet, C. M. Lieber, *Nano Lett.* **5**(5), 917 (2005).
- [6] J. S. Jie, W. J. Zhang, Y. Jiang, X. M. Merag, Y. Q. Li, S.T. Lee, *Nano Lett.* **6**, 1887 (2006).
- [7] R. Ma, L. Dai, G. Qin, *Nano Lett.*, **7**, 868 (2007).
- [8] A. Banerjee, P. Nath, V. D. Vankar, K. L. Chopra, *Phys. Stat. Sol. (a)* **46**(2), 723 (2006).
- [9] R. Xie, U. Kolb, J. Li, T. Basche, A. Mews, *J. Am. Chem. Soc.*, **127**(20), 7480 (2005).
- [10] W. F. Zhang, Z. Yin, M. S. Zhang, Z. L. Du, W. C. Cheng, *J. Phys.: Cond. Matt.* **11**, 5655 (1999).
- [11] S. Bhushan, S. K. Sharma, *J. Mat. Sc. (Mat. in Electronics)* **1**, 165 (1990).
- [12] S. Bhushan, S. K. Sharma, *J. Phys.: Cond. Matt.* **2**(7), 1827 (1990).
- [13] H. K. Min, L. Sung-Nam, P. Nae-Man, P. Seong-Ju, *Jpn. J. Appl. Phys.* **39**, 6170 (2000).
- [14] S. Maraki, H. Nakanishi, M. Sugiyama, S. Chichibu, *Phys. Stat. Sol. (c)* **5**(9), 3135 (2008).
- [15] O. Akinwummi, M. A. Elereja, J. O. Olowalafe, G. A. Adgboyega, E. O. B. Ajayi, *Opt. Mat.* **13**(2), 255 (1999).
- [16] O. S. Kumar, E. Watana, R. Nakai, N. Nishimoto, Y. Fujita, *J. Cryst. Grow.* **298**, 491 (2007).
- [17] S. Bhushan, T. Chandra, *Turk. J. Phys.* **32**, 21 (2008).
- [18] S. Bhushan, S. Shrivastava, A. Shrivastava, *J. Mater. Sci.* **41**, 7483 (2006).
- [19] R. S. Singh, S. Bhushan, *Chal. Lett.* **5**(12), 377

- (2008).
- [20] S. Bhushan, S. Pillai, *Cryst. Res. Technol.* **43**(7), 762 (2008).
- [21] S. Bhushan, A. Oudhia, *Ind. J. Pure Appl. Phys.* **47**, 60 (2009).
- [22] S. Bhushan, A. Oudhia, *Opto-elect. Rev.* **17** (1), 30 (2009).
- [23] T. Chandra, S. Bhushan, *J. Mater. Sci.* **39**, 1 (2004).
- [24] T. Chandra, S. Bhushan, *J. Phys. D: Appl. Phys.* **37**, 2945 (2004).
- [25] S. Agrawal, A. Khare, *Arab. J. Chem.* (2012, in press).
- [26] A. Khare, R. B. Sahu, S. K. Sharma, *Optik-Int. J. Light Elect. Opt.* **123**, 1133 (2012).
- [27] A. Khare, *J. Lumin.*, **130**(7), 1268 (2010).
- [28] A. Khare, *J. Phy. Chem. Sol.* **73**(7), 839 (2012).
- [29] K. U. Isah, N. Hariharan, A. Oberafo, *Leonardo J. Sci.* **7**(12), 111 (2008).
- [30] E. C. Subba Rao, D. Chakravorty, M. F. Merriem, V. Raghavan, L. K. Singhal, *Experiments in Materials Science*, Mc-Graw Hill Book Company, (1972) Newyork.
- [31] A. Khare, S. Bhushan, *Cryst. Res. Technol.* **41**(7), 689 (2006).
- [32] S. Bhushan, S. Shrivastava, *Cry. Res. Technol.* **1**, 8 (2007).
- [33] S. Bhushan, S. Agrawal, A. Oudhia, *Chalgen. Lett.* **7**(3), 165 (2010).
- [34] J. Y. Choe, D. Ravichandran, S. M. Blomquist, K. W. Kirchner, E. W. Forsythe, D. C. Morton, *J. Lumin.* **93**, 119 (2001).
- [35] A. V. Feitosa, M. A. R. Miranda, J. M. Sasaki, M. A. Arujo-Silva, *Braz. J. Phys.*, **34**(2B), 656 (2004).
- [36] A. U. Ubale, V. S. Sangawar, D. K. Kulkarni, *Bull. Mater. Sci.* **30**(2), 147 (2007).
- [37] S. Sadhu, A. Patra, *J. Chem. Sci.* **120**(6), 557 (2008).
- [38] V. A. Arutyunyan, K. S. Aramyan, G. S. Petrosyan, *Semiconductors* **38**, 335 (2004).
- [39] L. Wenyia, C. Xuna, C. Quilonga, Z. Zhibin, *Mater. Lett.* **59**, 1 (2005).
- [40] H. Tang, H. Berger, P. E. Schmid, F. Levy, *Sol. Stat. Commun.* **92**, 267 (1994).
- [41] M. K. Karanjai, D. Dasgupta, *J. Phys. D.: Appl. Phys.*, **21**, 1769 (1988).
- [42] R. H. Bube, *Photoconductivity of Solids* (New York: Wiley) 1960.

---

\*Corresponding author: akhare.phy@nitrr.ac.in