OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 1, No. 12, December 2007, p. 677 - 682

Luminescent nanoparticles of doped ZnSe passivated by PVP

SUNIL KUMAR, NIDHI SHARMA, N. K.VERMA, S. K. CHAKARVARTI[a]
School of Physics and Materials Science, Thapar University, Patiala – 147004, India
[a]*Department of Applied Physics, National Institute of Technology (Deemed University), Kurukshetra – 136119, India*

As one of the most important II-VI compound semiconductors with a direct wide band gap, zinc selenide (ZnSe, bulk crystal Eg = 2.7 eV at 300K) exhibits a great potential for various applications. ZnSe doped nanoparticles has been fabricated using chemical precipitation method and steric hindrance is given by polyvinylpyrrolidone. The size and morphology of the nanostructures is determined by the XRD, TEM and SAED. Laser induced photoluminescence studies were also conducted to study various optical parameters like excited state lifetime, emission wavelength and trap-depths of these chalcogenide nanostructures. ZnSe nanostructures show weak electric dipole visible transitions due to the perturbations of added dopants. These type of nanomaterials exhibit fundamentally unique properties with great potential of bringing plethora of next generation technologies in electronics, computing, optics, biotechnology, medical imaging, medicine, drug delivery, structural materials, aerospace, energy etc.

(Received November 12; 2007; accepted November 27, 2007)

Keywords: Nanostructures, Photoluminescence, Electric dipole, Excited State lifetime, Zn Se, PVP

1. Introduction

In nanoparticles the properties (physical, chemical, biological etc.) can be selectively controlled by engineering the size, morphology, and composition of the particles. Nano materials are known to exhibit markedly different properties compared to micron sized ones. These new substances will have enhanced or entirely different properties from their bulk counterparts. It has been shown that various material properties such as electrical, mechanical, optical, magnetic etc are highly influenced by the fine-grained structure and their is generally improvement in the concerned properties. Using a variety of synthesis methods, it is possible to produce nanostructured materials in various forms like: thin films, powder, quantum wires, quantum wells, quantum dots, etc. During synthesis of nanoparticles initial products are known as seeds and over certain time they grow to form nano-crystallites. Further growth in size of these crystallites results in agglomeration to form primary particles. If this growth is not controlled, then due to Ostwald ripening and Van der Waals interactions between particles, they agglomerate and settle down. This agglomeration is controlled by either stabilizing electrostatically or by inducing steric hindrances in the precipitation reaction. Steric hindrance can be achieved by the adsorption of large molecules such as polymers on the surface of the particles. Two effects describe this type of stabilization. First, the fact that the adsorbed molecules are restricted in motion causes a decrease in the configurational entropic contribution to the free energy. Secondly the local increase in concentration of polymer chains between approaching particles results in an osmotic repulsion, since the solvent reestablishes equilibrium by diluting the polymer molecules and this results in the separation of particles.

Light emission from nanocrystalline phosphors is possible through a radiative recombination process of charge carriers generated by higher energy photon absorption. The colour of the emission can be tailored by changing the crystalline size and appropriate doping. Recently, doped semiconducting nanocrystals (NC) have attracted considerable interest due to their interesting properties such as high luminescence quantum efficiency, short radiative lifetime, size dependent color emission tunability etc. These materials are considered to be the luminophors for next generation displays, bio-labels, lasers, etc.

A wide variety of spectroscopic techniques have been employed by scientists to probe the static and dynamic processes occurring in complex molecular systems. The generations of extremely short and intense laser pulses have opened the new way for the study of fast transient phenomena such as energy transfer, energy storage, excitation and de-excitation processes in optical materials. A new field of laser spectroscopy is the time-resolved spectroscopic technique in which the detection of these transient phenomena is being done by using short and intense laser pulses. Time-resolved spectroscopy employing laser excitation is a very convenient method for analyzing optical materials in the ultra short time domain. It provides an insight into various atomic and molecular processes, which occur in the materials in the nanosecond and sub-nanosecond time regime. The relaxation parameters associated with various optical transitions reflect the atomic and molecular processes going on in these materials and their environment. Many physical and chemical properties influencing the optical transitions can

be investigated by nanosecond time-resolved spectroscopy techniques [1-15]. In 1996, R. M. Park et al. had studied time-resolved luminescence data from heavily nitrogen doped ZnSe. The luminescence exhibited a decay time and a rise time, which increased with decreasing energy of observation. Furthermore, both the decay times and rise times decreased with increasing temperature. These observations are consistent with the following model: (i) a band of states was created due to fluctuations in the ionized impurity concentrations; (ii) a portion of the carriers captured by the shallower impurity states were transferred to deeper states prior to recombination. In 2000, J.F. Suyver et al[21]. had studied the luminescence properties of nanocrystalline ZnSe: Mn^{2+} prepared via an inorganic chemical synthesis. Photoluminescence spectra showed distinct ZnSe and Mn^{2+}` related emissions, both of which were excited via the ZnSe host lattice. The Mn^{2+} emission wavelength and the associated luminescence decay time depend on the concentration of Mn^{2+} incorporated in the ZnSe lattice. Temperature-dependent photoluminescence spectra and photoluminescence lifetime measurements were also presented and the results were compared with those of Mn^{2+} in bulk ZnSe. Better results are expected for ZnSe which has a valence band-edge at higher energy with respect to ZnS. In 2005, Changlong Jiang et.al[23]; had studied ZnSe hollow spheres synthesized hydrothermally at 140 °C, by using reducing agent. Both the transverse optic (TO) and longitudinal optics (LO) phonon peaks in the Raman Spectra of the ZnSe showed the obvious shift to lower frequency compared to bulk values, a blue shift has been observed in PL spectra. In 2006, C.X. Shan et. al[24]; had prepared Wurtzite ZnSe nanowires on GaAs substrates by a metal-organic chemical vapour deposition system. Electron microscopy showed that they were smooth and uniform in size. Both transmission electron microscopy and x-ray diffraction reveal the wurtzite structure of the nanowires, which grows along the (0001) direction. Raman scattering studies on individual nanowires were performed in the back-scattering geometry at room temperature. Besides the commonly observed longitudinal and transverse optical phonon modes, a possible surface mode located at 233 cm^{-1} is also observed in the Raman spectrum. A peak located at 2.841 eV was clearly observed in the photoluminescence spectra of the nanowires, which can be assigned to near band edge emissions of wurtzite ZnSe. In 2006, S Venkatachalam et al[25]. deposited Zinc selenide (ZnSe) thin films onto well cleaned silicon (100) and glass substrates at different substrate temperatures (483–589 K) using vacuum evaporation method under a vacuum of 4×10^{-3} Pa. The compositions of the deposited films were determined by Rutherford backscattering spectrometry and the percentage of iodine concentration is calculated as (ZnSe) I 0.001. The x-ray diffractograms reveal the cubic structure of the film oriented along the (111) direction. In optical studies, the transition of the deposited film is found to be a direct allowed transition. The optical energy gaps of the deposited films are found to be in the range 2.72 - 2.60 eV. ZnSe/silicon Schottky diodes were fabricated. From the current–voltage measurement, the ideality factor was found to be in the range 2.01–3.51. From the capacitance–voltage studies, the built in potential was found to be 1.51 V. The values of effective carrier concentration (*N*A) and the barrier height are calculated as 4.37×10^{11} cm^{-3} and 1.95 eV, respectively. Thaddeus J. Norman Jr. et al.[22] had synthesized Cu(II) doped ZnSe nanoparticles using molecular cluster precursors. The Cu(II) dopant had the effect of quenching the ZnSe band edge emission, yet only weak emission from Cu(II) centers was observed. An X-ray Absorption Fine Structure (XAFS) experiment was performed on the Cu(II) doped ZnSe nanoparticles.

2. Synthesis of ZnSe nanophosphors

Nanophosphors[20-31] are prepared by aqueous colloidal precipitation method at room temperature. The colloidal precipitation technique has been found to have a number of advantages including easy processability at ambient conditions passibility of doping of different kinds of impurities with high doping concentration even at room temperature , good control over the chemistry of co-doping particularly when different impurities are in corporated simultaneously in the host lattice , easiness of surface capping with a variety of different steps involved in the synthesis process of nanophosphors. Different synthesis methods viz. reverse micelles, homogeneous precipitation and colloidal precipitation, etc. have been carried out by various researchers to prepare the doped nanocrystalline ZnSe phosphors. By comparing properties of the materials obtained from different routes, colloidal precipitation was found better for producing efficiently luminescent nanophosphors in terms of process simplicity, effectiveness of doping and higher yield etc. Different analytical grade chemicals have been purchased from sd-fine Chemicals, India. The synthesis employed co-precipitaton reaction of inorganic precursors of Zn^{2+} and Se^{2-} with dopant ions (Mn^{2+}, $Cu^{2+}$and Co^{2+}) in aqueous medium containing the capping molecules of 1% PVP prepared by dissolving 1gm of PVP in 100ml of distilled water. The different concentrations of impurities in solution were maintained at (10%, 5%, 1% & 0.1%) with Zn^{2+}, for ZnSe:Mn, ZnSe:Cu, ZnSe:Co samples. 2.195 g of $Zn(ac)_2$ has been dissolved in 50 ml of distilled water to obtain 0.2 M solution. 1.7294 g of Na_2SeO_3 has been dissolved in 50 ml of distilled water to get 0.2 M of solution. In the synthesis of ZnSe, 25ml of $Zn(ac)_2$ solution was mixed with solution of polyvinylpyrrolidone(PVP), the capping agent was added to avoid agglomeration of grown nanoparticles. Nanoparticles with polymer capping were precipitated by slowly adding 25 ml of 0.2 M Na_2SeO_3 solution to the above mixture. A white colloidal suspension was obtained immediately after adding Na_2SeO_3 solution. The precipitates were separated by 2000 rpm centrifugal machine and washed several times with distilled water. Then the sample was dried in a vacuum oven at a temperature of about 80 ^oC.

3. Morphological characterization

3.1 *X-ray diffraction studies*

X-ray diffraction (XRD) is an efficient tool for the structural analyses and morphological characterization of crystalline materials. In the present studies, XRD patterns have been recorded using D/max-2000 Rigaku (Tokyo) powder X-ray diffractometer using copper characteristic wavelength of 1.5418 Å operated at 40 kV and 40 mA keeping step size $(0.02)^0$ s^{-1}. Peak broadening has been observed in recorded diffraction patterns, which shows the formation of nanocrystallites. Fig. 1 shows the XRD pattern recorded for pure ZnSe. Comparison of the recorded XRD pattern with standard JCPDS data file 10979 confirms the wurtzite structure.

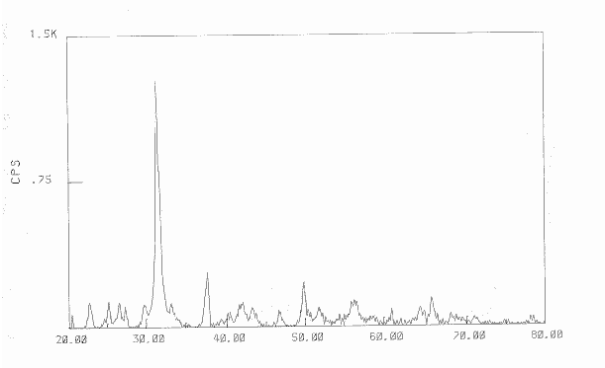


Fig. 1. X-ray diffractogram of the as-synthesized ZnSe nanoparticles.

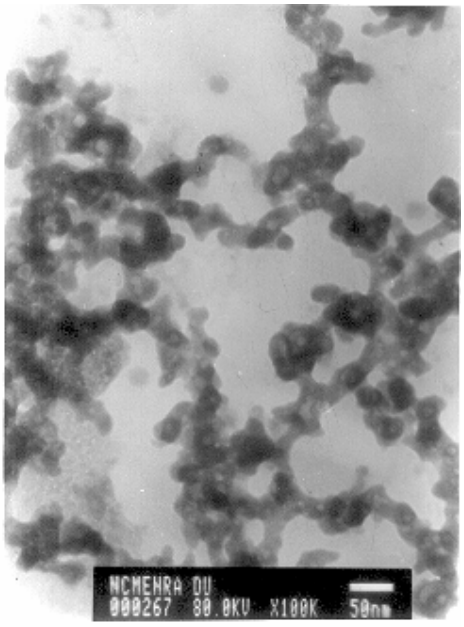
Average crystallite size has been calculated from the recorded XRD patterns using well known Scherrer equation:

$$D = 0.89\lambda/\beta \cos\theta$$

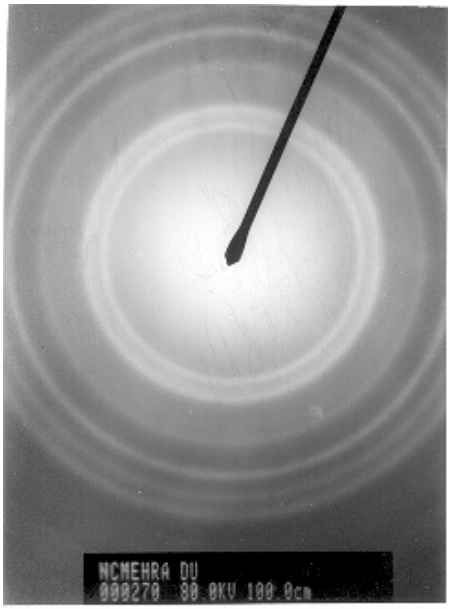
where D is the average crystallite size, λ is the wavelength of incident X-ray, β is the full width at half maximum (FWHM) of X-ray diffraction expressed in radians and θ is the position of the diffraction peak in the diffractograms. The mean calculated crystallite size of doped ZnSe nanoparticles is ~14 nm.

3.2 *Transmission electron microscope (TEM) studies*

Electron microscopy is a good tool for the morphological studies of nanomaterials. In the present studies JEOL JEM 2000 Ex. Type TEM was used for recording the electron micrographs. All the micrograph patters were recorded at 80 kV and the selected area electron diffraction (SAED) patterns were recorded by keeping camera constant 100 cm. Figs. 2 (a) and (b) show the TEM image and SAED pattern for pure ZnSe. It is clear from Fig. 2(a) that all the particles are in nano regime, but the distribution of particles is heterogeneous. Fig. 3 shows the histogram for size distribution of nanoparticles, it is evident from histogram that average particle size is ~14 nm. SAED pattern shown in the fig. 2(b) represents the well defined ring pattern, which confirms the crystalline nature of ZnSe nanoparticles.



a



b

Fig. 2. (a) TEM image of ZnSe (b) SAED pattern for ZnSe nanopartcles.

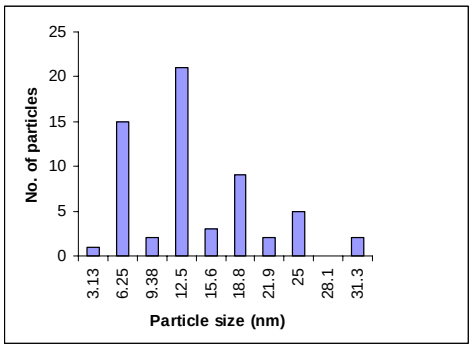


Fig. 3. Histogram for size distribution of ZnSe nanopartricles.

4. Photoluminescence studies

For room temperature (300 K) studies, the sample is taken in the form of a powder in a groove specially prepared in a perspex sheet or in the form of a thin film pasted with xylene on a glass plate. Nitrogen laser is the most suitable excitation source (337.1 nm) to irradiate the doped phosphors as laser energy excites the luminescent centers introduced by the dopants in the phosphors very effectively. High photon flux density (10^{19} photons per pulse) of the laser is very useful to excite the short-lived shallow trapping states which otherwise were impossible to excite using conventional light sources like mercury vapor lamp or xenon flash lamp. Short pulse-width of Nitrogen laser (5-7 ns) is helpful to determine the lifetime values accurately in the milli- and micro-seconds time domain without introducing its own effect. The short lived phosphorescence from the sample at an angle of 90° to the incident beam was collected by a fast photomultiplier tube through an assembly of monochromator as a wavelength selective element and glass slab to filter out the UV radiation. The decay signals from the phosphors are recorded by a fast digital type storage oscilloscope, which is interfaced with a computer. Computer simulations are done to calculate lifetime values accurately of the different excited states contributing to the phosphorescence hyperbolic decay.

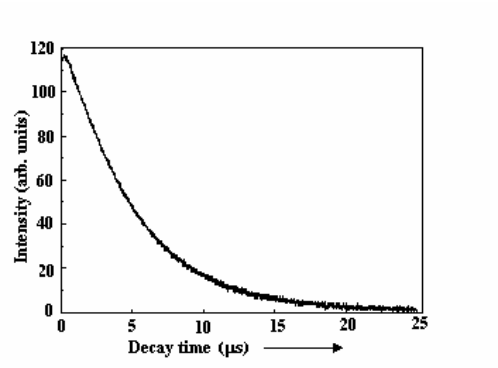


Fig. 4. Hyperbolic type of phosphorescence decay curve for ZnSe:Mn (10%)

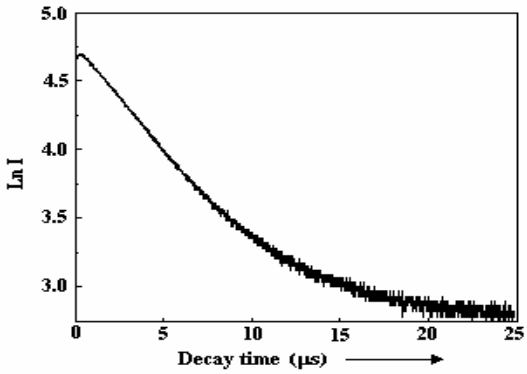


Fig. 5. Ln I vs decay time graph for ZnSe:Mn (10%).

Table 1. Excited state lifetime values of pure and doped ZnSe nanophosphors.

Sample No	Phosphor: impurity(wt%)	Wavelength (nm)	Lifetime values(μs)at 300K		
			τ`	τ``	τ```
1	ZnSe	450(feeble)	6.22	12.9	50.25
2	ZnSe:Mn(10%) ZnSe:Mn(5.0%) ZnSe:Mn(1.0%) ZnSe:Mn(0.1%)	422nm 422nm 407nm 443nm	6.82 7.00 6.54 6.72	13.0 17.3 11.1 16.1	45.0 243.3 28.8 297.0
3	ZnSe:Cu(10%) ZnSe:Cu(5.0%) ZnSe:Cu(1.0%) ZnSe:Cu(0.1%)	440 475 440 420	12.4 4.9 7.48 7.36	28.7 5.9 17.4 14.6	145.0 10.4 67.8 59.2
4	ZnSe:Co(10%) ZnSe:Co(5.0%) ZnSe:Co(1.0%) ZnSe:Co(0.1%)	449 427 475 456	6.99 7.01 6.98 6.44	11.9 13.5 13.6 10.2	46.7 51.7 53.1 38.3

Table 2. Trap-depth values of pure and doped ZnSe nanophosphors recorded at room temperature.

Sample No	Phosphor: impurity(wt%)	Wavelength(nm)	Trap depths(eV)		
			E`	E``	E```
1	ZnSe	450(feeble)	0.226	0.245	0.280
2	ZnSe:Mn(10%)	422	0.228	0.245	0.271
	ZnSe:Mn(5.0%)	422	0.229	0.253	0.321
	ZnSe:Mn(1.0%)	407	0.227	0.241	0.266
	ZnSe:Mn(0.1%)	443	0.228	0.251	0.326
3	ZnSe:Cu(10%)	440	0.244	0.266	0.308
	ZnSe:Cu(5.0%)	475	0.220	0.225	0.239
	ZnSe:Cu(1.0%)	440	0.231	0.253	0.288
	ZnSe:Cu(0.1%)	420	0.230	0.248	0.284
4	ZnSe:Co(10%)	449	0.225	0.243	0.278
	ZnSe:Co(5.0%)	427	0.229	0.246	0.281
	ZnSe:Co(1.0%)	475	0.229	0.246	0.282
	ZnSe:Co(0.1%)	456	0.222	0.239	0.273

5. Results and discussion

The optical properties of nanocrystalline semiconductors had been studied extensively in recent years due to their interesting applications suitable for making advanced opto-electronic systems [16-19]. These nanomaterials behave differently from bulk semiconductors due to quantum confinement effect and large surface- to- volume ratio. It was reported that doped nanocrystals of semiconductors can yield high luminescence efficiency. In the present investigation, excited state lifetime measurements of doped ZnSe nanocrystals have been carried out using a pulse excitation method. High peak power, UV pulsed N_2-laser has been used as the excitation source. Hyperbolic decay curves have been observed in case of pure and doped ZnSe nanophosphors with variable concentration of Mn, Cu and Co impurities. Pure exponential components of decay curves were extracted from the hyperbolic decays (Fig. 4 & 5) with the help of computer software as shown in Fig (6-8). The excited state life-times in case of pure and doped ZnSe nanophosphors are in microseconds time domain and varies from 6.22 to 50.25 μs for pure ZnSe (Table 1) and the excited state lifetimes in case of doped ZnSe nanophosphors vary from 4.4 [ZnSe:Cu(5%)] to 297.00μs [ZnSe:Mn(0.1%)] at room temperature. The lifetime values don't show any appreciable trend with variation of impurity concentration and the emission wavelength also don't show much change with impurity concentration as blue emission is observed for all the samples. The trapping states which contribute significantly to the luminescence, range from 0.226 to 0.280 eV in case of pure ZnSe nanophosphors (Table 2.). When Mn, Cu, and Co impurities are added to ZnSe nanophosphor, the trap depth values lie between 0.220[ZnSe:Cu(5%)] to 0.326eV [ZnSe:Mn(0.1%)]. However, the decay curves remain hyperbolic in nature and do not change with the addition of the impurities.

In the present investigation the lifetime values are in microsecond time regime. This suggests that emission is due to the weak electric dipole transitions. But the excited state lifetimes and trap-depth values don't show appreciable trend with variation in impurity concentration, these decrease and increase randomly. Moreover blue emission is observed for all the sample with slight change in emission wavelength with impurity concentration. So it is clear from the above observations that Mn, Cu and Co dopants in ZnSe nanoparticles don't give their characteristic emissions, these impurities are just perturbing the levels of the host. Although dopant characteristic emission is not observed, but the decay time and emission wavelength can be monitored from 4.9-297.0 μs and 407-475 nm by selecting appropriate impurity concentration.

6. Conclusions

ZnSe nanoparticles are fabricated by using chemical precipitation technique and confirmation of size is done by XRD and TEM studies. Passivation is done by PVP. Laser induced photoluminescence behaviour shows weak electric dipole visible transitions in these nanostructures. Dopants have only a perturbation effect on the already existing crystal defects in the host ZnSe nanostructures.

Acknowlegement

This research work has been supported by Department of Science and Technology(DST), New Delhi through major Research Project No. SR/S2/CMP/02/2005 dated May, 2006. The financial support by DST is gratefully acknowledged.

References

[1] W. Lehmann, Journal of Luminescence **5,** 87 (1972).
[2] C. R. Ronda, Journal of Alloys & Compounds **225**, 534 (1995).
[3] H. Choi, C. H. Kim, C. H. Pyun, S. J. Kim, Journal of Solid State Chemistry, **138**, 149 (1998).
[4] V. G. Kravets, Journal of Optical Materials **16**, 369 (2001).
[5] R. P. Khare, C. D. BhaskerRaj, T. B. Sebastian, Indian Journal of Pure & Applied Physics **23**, 102 (1995).
[6] Y. Yamura, A. Shibukawa, Japanese Journal of Applied Physics, Part 1 (Regular Papers & Short Notes), **32**(7), 3187 (1993).
[7] P. Yang, M. Lu, D. Xu, D. Yaun, C. Song, G. Zhou, Journal of Physics & Chemistry of Solids **62**, 1181 (2001).
[8] T. D. Harris, F. E. Tytle, Ultrasensitive Laser Spectroscopy, Academic Press Inc., New York, (1983).
[9] A. W. Ali, A. C. Kolb, A. D. Anderson, Journal of Applied Optics **6**, 2115 (1967).
[10] P. W. Smith, M. A. Duguay, E. P. Ippen, Progress in Quantum Electronics, Pergamon Press, Oxford, (1974).
[11] W. Demtroder, Laser Spectroscopy: Basic Concepts and Instrumentation, Springer Verlag, New York, (1988).
[12] P. B. Carlin, W. R. Bennet Jr, Journal of Applied Optics, **15**, 2020 (1976).
[13] Ch. K. Chan, Laser Technical Bulletin, Spectra Physics **8**, 20 (1978).
[14] P. R. Hartig, K. Sauer, G. C. Lo, Laskovar, B, Review of Scientific Instruments **47**, 1122 (1976).
[15] C. Lewis, W. R. Ware, L. J. Doemney, T. L. Nemzek, Review of Scientific Instruments **44**, 107 (1973).
[16] J. T. Randall, M. H. F. Wilkins, Proceedings Regional Society, London, Service A **184**, 390 (1945).
[17] R. H. Bube, Physical Review **80,** 655 (1950).
[18] K. L. Jain, J. D. Ranade, Indian Journal of Physics **48,** 1080 (1974).
[19] H. S. Bhatti, N. U. V. Nair, R. D. Singh, Indian J Pure & Appl Phys, **20**, 5 (1982).
[20] C. Kothandaraman, I. Kuskosky, G. F. Neumark, R. M. Park, Appl. Phys. Lett. **69**(11), 1523 (1996).
[21] J. F. Suyver, S. F. Wuister, J. J. Kelly, A. Meijerink Phys. Chem. Chem. Phys. **2**, 5445 (2000).
[22] Thaddeus J Norman Jr., D. Maganr, F. Bridges, Z. Zhang Jin, Mat. Res. Soc. Symp. Proc. Material Research Society (USA), 776 (2003).
[23] Changlong Jiang, Wangqun Zhang, Guifu Zou, Weicao Yu, Nanotech. **16**, 551 (2005).
[24] C. X. Shan, Z. Liu, X. T. Zhang, C. C. Wong, S. K. Hark, Nanotech. **17**, 5561 (2006).
[25] S. Venkatachalam, D. Mangalaraj, K. Narayandass Sa, J. Phys. D: Appl. Phys. **39**, 4777 (2006).
[26] W. Lehmann, F. M. Rayan, Journal of Electrochemical Society **118**, 477 (1971).
[27] J. Kuhl, H. Klingenberg, P. Vonder Linde, Journal of Applied Physics, **18**, 279 (1979).
[28] C. S. Gupta, Indian Journal of Pure & Applied Physics **37**, 906 (1999).
[29] C. S. Gupta, Indian Journal of Pure & Applied Physics **38**, 821 (2000).
[30] C. S. Gupta, Indian Journal of Physics **75A**(5), 535 (2001).
[31] E. F. Kaeble, Handbook of X-rays, McGraw-Hill, New York, 1967.

*Corresponding author: sunilkumar32@gmail.com