www.amlett.com, www.amlett.org, DOI: 10.5185/amlett.2012.6374 Published online by the VBRI press in 2013

Fabrication of ZnS:Cu/PVA nanocomposite electroluminescence devices for flat panel displays

Sakshi Sahare[1], S. J. Dhoble[2*], Pranav Singh[1], Meera Ramrakhiani[1]

[1]*Department of Post Graduate Studies and Research in Physics and Electronics, Rani Durgawati University, Jabalpur, India*
[2]*Department of Physics, R. T. M. Nagpur University, Nagpur 440033, India*

[*]Corresponding author. E-mail: sjdhoble@rediffmail.com

Received: 18 June 2012, Revised: 21 August 2012 and Accepted: 26 August 2012

ABSTRACT

The powder of ZnS nanoparticles were prepared by using chemical deposition technique and characterized by electroluminescence techniques are reported in this paper. The estimated size of ZnS:Cu nanocrystals with change in capping agent concentration and ZnS:Cu/PVA nanocomposites and no effect of doping has been observed on the absorption spectra. Electroluminescence (EL) investigations of nanocrystalline powder as well as nanocomposites, it is seen that Log B vs. 1/√V curve is a straight line with negative slope. This indicates that EL is produced by acceleration-collision mechanism. The detail EL characterization and application in display devices of these materials are reported in this paper. Copyright © 2013 VBRI press.

Keywords: Nanoparticles; electroluminescence; lamp phosphor; ZnS:Cu; display devices.

Sakshi Sahare is assistant professor in Govt. College Bichhua, Chhindwara (M.P.), India. She is working on optical properties of copper doped zinc sulphide nanocrystals. Her research interest is in synthesis and characterization of inorganic materials for lighting applications.

S.J. Dhoble obtained M.Sc. degree in Physics from Rani Durgavati University, Jabalpur, India in 1988. He obtained his Ph.D. degree in 1992 on Solid State Physics from Nagpur University, Nagpur. He is presently working as an Associate Professor in Department of Physics, R.T.M. Nagpur University, Nagpur, India. He is involved in the synthesis and characterization of solid state lighting nanomaterials as well as development of radiation dosimetry phosphors using thermoluminescence, mechanoluminescence and lyoluminescence techniques. He published several research papers in International reviewed journals on solid-state lighting, LEDs, radiation dosimetry and laser materials. He is an executive member of Luminescence Society of India.

Pranav Singh is presently working as computer programmer in Department of Postgraduate studies and Research in Physics and Electronics, R.D. University, Jabalpur, India. His field of research is Condensed Matter Physics: Luminescence & Optical properties, Nanomaterials and nanotechnology, Photovoltaic effects, Electronic & optical properties of semiconductor (OLED's), Advances in Artificial Intelligence, Expert Systems. He has published sixteen research papers in International Journals, National Conferences and Seminars.

Meera Ramrakhiani is presently Professor and Head, Departemnt of Physics and Electronics, Rani Durgavati University Jabalpur. She has done her graduation, M.Sc.and Ph.D from the University of Jabalpur (now Rani Durgavati University) and has 35 years of teaching experience at under graduate and post graduate level. Fifteen students have completed their Ph.D. under her supervision and many more are working in the field of nanomaterials, luminescence and photovoltaic solar cells. She has participated in about 50 seminars/symposia etc. and presented has work at national/ International level. She has visited Italy, Hungary, Singapore, USA and China for the research work. About 300 published papers are there to her credit. She has successfully carried out two research project funded by MPCST. Dr. M.Ramrakhiani has received Vijaya Shree Award by India International Friendship Society in 1997, The 20th Century Award of Achievement by International biographical Center, Cambridge, England in 1998, Women of the Year 2005 Jeweler Issued by American Biographical Institute, Inc.

Introduction

Semiconductor nanocrystals are described as a state of matter that is intermediate between individual molecule and bulk [**1**]. Transition from bulk to nanoparticles lead to the display of quantum mechanical properties and an increased dominance of surface atoms which increases the chemical reactivity of a material. Notable examples include tunable bandgap [**2**] and catalytic behavior [**3**]. The small size and high optical activity of certain semiconductors make them interesting for applications in disciplines ranging from optoelectronics [**4**], catalysis [**5**] to fluorescence microscopy [6]. Recently, Dhoble and co-workers reported the some of organic and inorganic phosphors for lamp industry are prepared by power saving techniques and important characteristics are considered for lamp application [**7-10**]. Nanometer sized semiconductor clusters are representative of a state of matter intermediate between molecules and bulk matter. These have attracted growing interest of material scientists, physicists, chemists as well as biologist during last two decades due to their novel characteristics and size dependent properties. It has been demonstrated by several groups that nanocrystalline materials of II-VI semiconductors can be used as light emitting material for preparation of electroluminescence devices. Semiconductor nanocrystals exhibit many unique properties, which are promising for the improvement of electroluminescence (EL) devices. The effect of reducing the size of nanocrystals /nancmpositesis expected to improve the performance of these devices and also their characteristics can be tailored. Combination of polymer and semiconductor nanocrystals allows the fabrication of flexible and lightweight EL devices. The incorporation of nanocrystals in polymer is expected to increase the life of the device and enhance the brightness of emission. In present work ZnS:Cu nanpartices/nanocomposites of different sizes by varying capping agent cncentratin or loading percentage of ZnS:Cu in PVA matrix have been synthesized.

Experimental

Preparation of samples

The most important step in the studies of nanoparticles is their synthesis. There are various methods supported for synthesis of nanoparticles. Chemical route is used in the present investigation. The powder of ZnS nanoparticles were prepared by using chemical deposition technique. For synthesis, the 1M aqueous solution of $ZnCl_2$ and 1M aqueous solution of Na_2S were mixed in the presence of various concentration of mercaptoethenol (C_2H_5OSH) solution. $CuCl_2$ was also mixed in the solution in ratio 99:1, while stirring the solution continuously. The obtained precipitate was washed thoroughly three to four times in double distilled water and then separated by centrifuge at 3500 rpm, and finally air dried. Special care has to be taken to maintain the same physical condition during the synthesis of the sample.

Nanocrystal-polymer samples of ZnS have been prepared with different loading (5%, 10%, 20%, 30% and 40%) of nanocrystals. For preparation of composites, the polymer granules were dissolved in suitable solvent. Then proper amount of zinc acetate was added to it and H_2S was passed to obtained nanocomposites. The solution was cast on glass substrates; upon solvent evaporation, nanocomposite films were obtained. For characterization, films were deposited on plane glass plates and for EL studies; these were deposited on SnO_2 coated conducting glass plates.

Characterization

All the samples were characterized at Inter University Consortium (IUC) Indore. The morphologies and sizes of the mercaptoethanol capped ZnS:Cu and PVA/ZnS:Cu composites were determined by X-ray diffraction studies with Cu Kα radiation (λ=1.5418 Å). XRD data were collected over the range 20^0-70^0 at room temperature. X-ray diffraction patterns have been obtained by Rigaku Rotating Anode (H-3R) diffractometer. The particle size was calculated using the Debye-Scherrer formula. The samples have been characterized for their X-ray diffraction (XRD). An X-ray differaction spectrometer usually consists of a generator, water-cooled primary radiation source units, a diffractometer and a measuring electronic unit. X-ray diffraction instruments may vary slightly, depending upon the manufacture. Size of nanocrystals is determined from broadening of XRD peaks. The absorption spectra of the sample have been studied by Perkin Elemer λ-12 spectrometer. UV/VIS spectroscopy is the measurement of the attentuatin of a beam of light after it passes through a sample. Ultraviolet /Visibe light are energetic enough to promote outer electrons to higher energy levels. This more qualitative application usually requires recording at least a portion of the UV-VIS spectrum for characterization of the optical properties of materials. The increase in the effective band gap has been estimated from blue shift in the absorption edge or peak and the particle size is computed using effective mass approximation model.

Electroluminescence measurements

For EL investigations, the emission material layer is placed between conducting glass and aluminum electrodes. In case of nanocrystalline powder samples, a piece of mica sheet having a window of 2×2 mm is placed over the conducting glass and the sample powder is placed within this window and fixed with adhesive. In case of films, mica sheet with window was placed over the film layer deposited on the conducting glass plate. An aluminum strip is fixed over the sample along with conducting gel in order to obtain good contact. For luminescence studies, the prepared EL cell is connected to AC EL power supply. The EL cell is placed at the slit of PMT (Photo Multiplier Tube) which is connected with the high voltage power supply and the picoammeter is connected for corresponding current, which record the output of the PMT. The EL excitation source was a low distortion audio generator coupled with an electroluminescence power supply (Wide Band Amplifier), AC Voltage at different frequencies was applied and EL brightness at different voltages was measured at each frequency, with the help of

photomultiplier tube connected to a picoameter. The corresponding current was recorded by a multimeter, which is connected in series with the EL cell. A particular frequency is set in the audio generator and gradually voltage applied to the EL cell was increased and corresponding current and EL brightness were recorded.

Table 1. Comparative XRD parameters of various ZnS nanocomposites.

Sample name	Capping agent concentration	Angle 2θ (Å)	Hkl	d (Å)	Standerd 'd' (in Å) (JCPDS-80-0020)	Crystal size D (in nm)	Crystal size D (in nm) EMA
ZnS:Cu I	0M	28.88	111	3.08	3.08	9.136	10.22
		48.43	220	1.88	1.88		
		56.7	311	1.61	1.61		
ZnS:CuII	0.005M	29.17	111	3.08	3.08	5.601	4.3
		48.72	220	1.88	1.88		
		56.09	311	1.61	1.61		
ZnS:CuIII	0.01M	29.32	111	3.08	3.08	4.03	3.96
		48.38	220	1.88	1.88		
		57.04	311	1.61	1.61		
ZnS:CuIV	0.015M	29.47	111	3.08	3.08	3.8	2.60
		48.48	220	1.88	1.88		
		57.28	311	1.61	1.61		
ZnS:Cu/PVA	10%	28.63	111	3.11	3.08	5.0	4.3
	loading	41.24	220	1.88	1.88		
		49.63	311	1.61	1.61		
ZnS:Cu/PVA	20%	28.7	111	3.18	3.08	4.59	3.96
	loading	41.43	220	2.18	1.88		
		49.67	311	1.83	1.61		
ZnS:Cu/PVA	30%	28.79	111	3.10	3.08	3.35	3.54
	loading	41.49	220	2.17	1.88		
		49.69	311	1.83	1.61		

Results and discussion

X-ray diffraction studies

The XRD studies indicate that most of the samples are cubic in nature. The broadening of peaks is indicative of small particle size. The sizes have been computed busing Dubey-Scherrer formula [**11**] and obtained in the range of 2 to 20 nm.

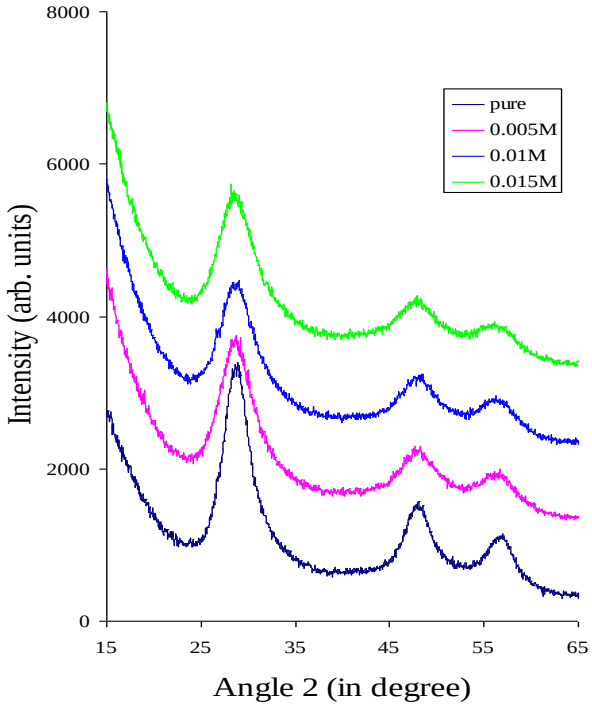

Fig. 1. XRD Patterns of ZnS:Cu nanocrystals.

It is observed that smaller particles are obtained by increasing capping agent concentration and loading percentage. **Fig. 1** shows the XRD pattern of the ZnS:Cu nanoparticles and **Fig. 2** shows the XRD pattern of the ZnS:Cu/PVA nanocomposites. Both are reveals cubic zinc blend structure. The inter planner spacing (d) and lattice constant (a) is computed from the Bragg's formula and obtained the value of a (a=5.34A) which matches with standard 'a' of JCPDS data card (JCPDS-80-0020). The average particle size was calculated from full width at half maxima (FWHM) of the first peak at approximately 2θ=28° corresponding to (111) plane using Scherrer formula. The estimated size of ZnS:Cu nanocrystals with change in capping agent concentration and ZnS:Cu/PVA nanocomposites are shown in **Table 1**.

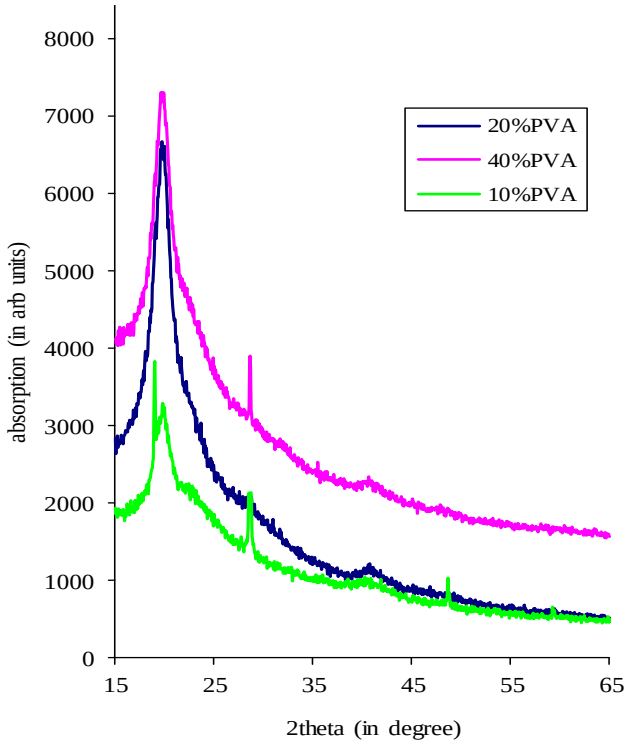

Fig. 2. XRD patterns of ZnS:Cu/PVA nanocomposite film.

Absorption studies

Absorption spectra of nanocrystals have shown blue shift in absorption edge, as compared to their bulk counterpart indicating increased band gap energy. The absorption edge is found to shift towards higher energies for smaller particles. **Fig. 3** shows the absorption spectra of ZnS:Cu nanocrystals prepared with different capping agent concentrations and **Fig. 4** ZnS:Cu/PVA nanocomposites with different loading. No effect of doping has been observed on the absorption spectra. The effective band gap energy has been determined from the absorption spectra and particle size is computed from the effective mass approximation (EMA) model. The particle sizes obtained by this method are in agreement with those from XRD. In our samples absorption edge was obtained at about 335 nm, 331 nm, 296 nm, 290 nm, and 250 nm for the samples 0 gm, 0.5 gm, 1.0 gm, 1.5 gm, 2.0 gm respectively. The absorption edge was found at shorter wavelength with decreasing the particle size. As the

capping agent concentration increases, band gap is found to increase and particle size is decreased.

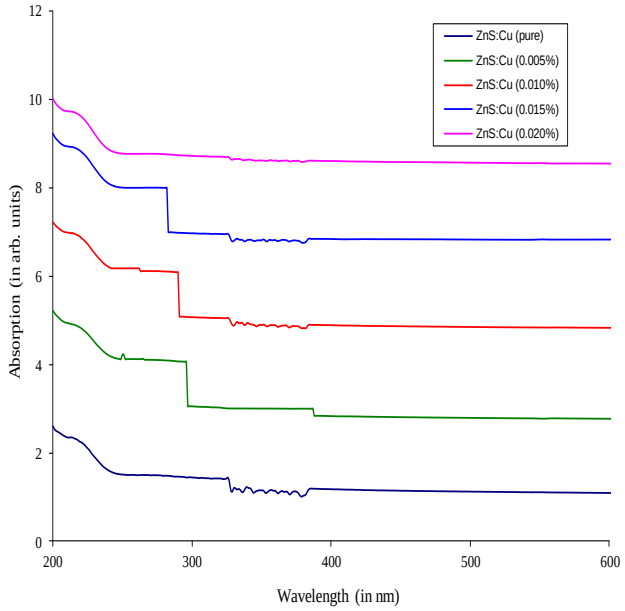

Fig. 3. Absorption spectra of ZnS:Cu nanocrystals.

Fig. 4 shows the UV/VIS optical absorption spectra 0f ZnS:Cu/PVA I to ZnS:Cu/PVA-V samples in the range 200nm to 800nm prepared with different loading of Zinc accetate starting from 5% to 40%. It can be seen from the spectra that there is slight increase in absorbance starting from 600 to 450nm. For ZnS:Cu/PVA-I sample, edge of absorption is obtained at about 340nm. Similarly the absorption edge for other samples is obtained at 310, 300, 290, 280nm for ZnS:Cu/PVA-II to ZnS:Cu/PVA-V samples, respectively. It is clearly seen from the graph that the absorption spectra of ZnS:Cu/PVA nanocomposits shift towards shorter wavelengths by increasing loading of zinc acetate.

Electroluminescence studies

The EL studies on nanocrystalline powder samples and nanocrystal/polymer composites have shown that the light emission starts at certain threshold voltage, different for different specimens, and then usually increases rapidly with increasing voltage (**Fig. 5**). It is found that for smaller nanocrystals, threshold voltage is lower and EL brightness (B) increases rapidly with voltage. The relationship between applied voltage (V) and current is found to be linear indicating ohmic nature. In general higher brightness is obtained at higher frequencies. Similar results are obtained for nanocrystal/polymer composites. By increasing nanocrystalline loading, EL starts at lower threshold voltages and higher intensity is observed.

Fig. 6 shows the variation of EL brightness by increasing the loading in the nanocomposite (ZnS:Cu/PVA). It can be seen that at higher voltages, saturation of EL intensity occurs for lower concentrations of nanocrystalline loading. This shows that such composites can be easily used for EL devices with advantage of better flexibility and good quality films. It has been speculated that the luminescent is due to recombination emission from electron trapped in the shallow defects and hole trapped in the deep defects, and shallowly trapped electron still posses small effective masses and therefore exhibit the quantum size effect.

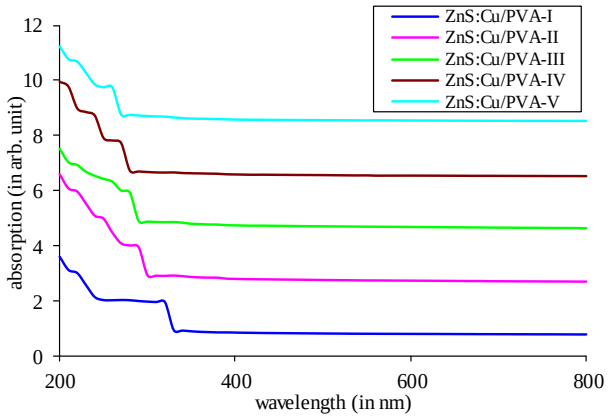

Fig. 4. Absorption spectra of ZnS:Cu/PVA nanocomposites.

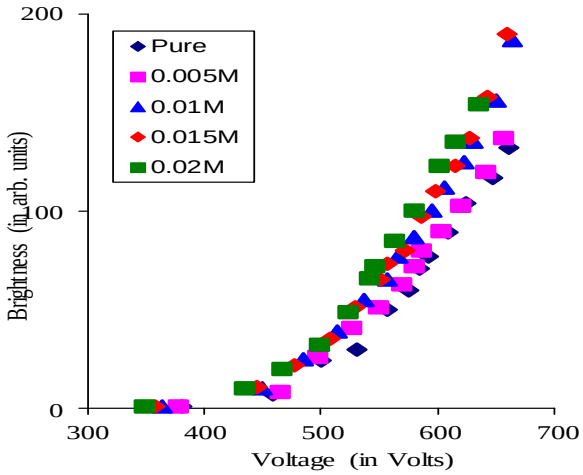

Fig. 5. Electroluminescence brightness for ZnS:Cu nanocrystals.

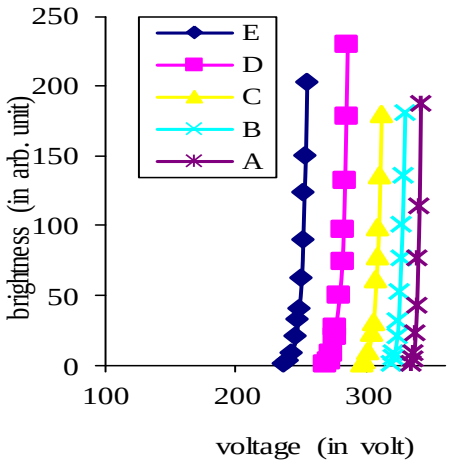

Fig. 6. Electroluminescence brightness for ZnS:Cu/PVA (5%) nanocomposites.

From the EL investigations of nanocrystalline powder as well as nanocomposites, it is seen that Log B vs. $1/\sqrt{V}$ curve is a straight line with negative slope. This indicates that EL is produced by acceleration-collision mechanism. Low energy states are also populated by electrical excitation that can not be populated by optical process. Therefore EL emission is obtained at photon energies much less than the band gap of the material. The investigations have revealed that the EL efficiency can be increased by reducing the size of semiconductor crystals to nanometer range. The device performance is improved if the nanoparticles are embedded in polymer matrix.

Conclusion

Cu^{+} activated ZnS nanoparticles were prepared by chemical deposition technique. The XRD studies indicate that most of the samples are cubic in nature. The broadening of peaks is indicative of small particle size. The sizes have been computed busing Dubey-Scherrer formula and obtained in the range of 2 to 20 nm. Absorption spectra of ZnS:Cu nanocrystals with different capping agent concentrations and ZnS:Cu/PVA nanocomposites with different loading , no effect of doping has been observed on the absorption spectra.The effective band gap energy has been determined from the absorption spectra and particle size is computed from the effective mass approximation (EMA) model. The particle sizes obtained by this method are in agreement with those from XRD. An increasing nanocrystalline loading on the prepared Cu^{+} activated ZnS nanocrystal/polymer composites the EL starts at lower threshold voltages and higher intensity is observed. The variation of EL brightness by increasing the loading in the nanocomposite (ZnS:Cu/PVA). It can be seen that at higher voltages, saturation of EL intensity occurs for lower concentrations of nanocrystalline loading. This shows that such composites can be easily used for EL devices with advantage of better flexibility and good quality films.

Reference

1. Cyr, P. W.; Tzolov, M.; Hines, M.A.; Manners, I.; Sargent, E.H.; Scholes, G.D.; J. Mater. Chem., **2003**, 13, 2213. **DOI:**10.1039/B306583A
2. Fendler, H.; Meldrum, F.C.; Adv. Mater., **1995**, 7, 607–632. **DOI:** 10.1002/adma.19950070703
3. Lopez, N.; Janssens, T.V.W.; Clausen, B.S.; Xu, Y.; Mavrikakis, M.; Bligaard, T.; Norskov, J.K. J. Catal. **2004**, 223, 232–235. **DOI:** Org/10.1016/j.jcat.
4. Alivisatos, A.P.; Science **1996**, 271, 933–937. **DOI:** 10.1126/science.271.5257.933
5. Ahmadi, T.; Wang, Z.L.; Green, T.C.; Henglein, A.; M.A. El-Sayed, Science. **1996**, 272, 1924–1926. **DOI:** 10.1126/science.272.5270.1924.
6. Yelin, D.; Oron, D.; Thiberge, S.; Moses, E.; Silberberg, Y. Opt. Express. **2003**, 11, 1385–1391. **DOI.**org/10.1364/OE.11.001385
7. Thejo Kalyani**,** N.; Dhoble, S. J.; Pode, R.B. Adv. Materials Letters, **2011**, 2(1), 65-70**.** **DOI:** 10.5185/amilett.2010.10169
8. Raut, S.B.; Dhoble, S.J.; Atram, Adv. Mat. Lett. **2011**, 2(5), 373-376. **DOI:** 10.5185/amlett2011.3075am2011
9. Abhay D.; Deshmukh, Dhoble, S. J.; Dhoble, N.S.; Adv. Materials Letters, **2011**, 2(1), 38-42**.** **DOI:** 10.5185/amlett.2010.10171
10. Parag Nimishe; Dhoble, S. J. Adv. Mat. Lett. **2011**, 2(5), 358-361. **DOI:** 10.5185/amlett.2011.3073am2011
11. Guinier, A. *X-ray Diffraction*, *Freeman*, San Francisco **1963**.

