International seminar on Nanoscience and Technology- conference proceedings. Oct- 2016
Volume 3, Special Issue - Available Online: http://ijrset.in/Volume3,Special-Issue-III.php Pages: 35-41

IJRSET
ISSN 2394-739X
International Journal for Research in Science Engineering and Technology

PREPARATION AND CHARACTERIZATION OF PB$_{1-X}$ZN$_X$S NANOPARTICLES

[1] L. Kungumadevi, [1] R. Priya, [1] P. Visali
Department of Physics, Mother Teresa Women's University, Kodaikanal,
Tamil nadu-624 101, India.

ABSTRACT- In our present work Pb$_{1-x}$Zn$_x$S (x = 0, 0.02%, 0.05%, 0.1%, 0.15%) nanocrystals were synthesized successfully using wet chemical method. The effect of Zinc on the structural and optical properties of Lead Sulphide were studied using powder XRD, FE-SEM, EDAX, FTIR and UV-Visible spectroscopy. The XRD patterns confirmed the face centered cubic structure of the undoped and doped PbS nanocrystals and the particle size are comparable with the exciton Bohr radius of PbS. FE-SEM results confirmed that the nanocrystals are spherically shaped and are agglomerated. EDAX spectrum confirmed the formation of Pb$_{1-x}$Zn$_x$S (x = 0, 0.02%, 0.05%, 0.1%, 0.15%) nanocrystals. The functional groups present in the material are studied with the help of FTIR spectrum. UV-Visible spectroscopy of the prepared samples were examined and the optical bandgap of the material were blue shifted as the doping concentration increases.

1. INTRODUCTION

Lead sulfide is a good IV–VI group semiconductor, which has attracted considerable attention due to its special small direct band gap (0.41eV) and large excitonic Bohr radius of 18nm[1]. Lead sulfide (PbS) is an important p–p semiconductor material. The band gap of PbS can be easily adjusted up to a few electron volts when the size of the particles is reduced. Such a significant widening of the band gap is associated with small effective masses of electrons and holes ($m_e = m_h = 0.09m_0$) as well as with a large exciton Bohr radius of PbS. Nanomaterials of PbS have been discovered to have exceptional third-order nonlinear optical property with potential applications in optical devices such as optical switches[2]. Due to its large Bohr exciton radius one can easily shift the band gap toward lower wavelength (blue shifted) to the spectral region of 700–1500nm on decreasing the PbS QD size[3].

In recent times, the synthesis of metal doped nano PbS has been paid great attention. It was reported that the properties such as bandgap, electrical conductivity and thermoelectric power can be significantly modulated and fine tuned by employing dopants through pertinent material processing approaches[13]. Y.Gulen et al. reported that Ba incorporated PbS thin films increases the optical band gap and optical transmission values[5]. R.Sakthi Sudar Saravanan et al. reported that the conductivity and the band gap values of lead sulphide is increased with the addition of cadmium and manganese as dopant[13]. To enhance the electrical and optical properties of lead sulphide zinc is chose as dopant in our study.

2. EXPERIMENTAL DETAILS

To prepare undoped PbS nanocrystals, 0.1M Lead(III) Acetate trihydrate was dissolved in deionised water and stirred at room temperature. 0.3M Sodium Sulphide was dissolved in deionised water. Then the Sodium Sulphide solution was added drop wise to Lead Acetate solution under constant magnetic stirring. Colour of the solution changed to black. The above mixed solution was stirred at 50ºC for 2 hours. The solution was cooled in open atmosphere and washed with deionised water, Acetone and Ethanol to remove the impurities. After washing the precipitate was dried in hot air oven at 100ºC for 5 hours and collected as the yield. In order to prepare $Pb_{1-x}Zn_xS$ (x=0.02, 0.05, 0.1, 0.15), x mol% of the lead(III) acetate reactant was replaced by the Zinc Sulphate precursor.

Structural characterization was performed using powder diffractometer of the model Bruker advance with monochromated Cu kα radiation ($\lambda=1.541\ \mathring{A}$). The particle morphology was studied using Field Emission Scanning Electron Microscope of the model ZEISS. The proportion of the various materials in the prepared nanocrystals were measured using EDAX of model Bruker. The optical properties of the synthesized nanoparticles were studied using the UV- Vis spectrophotometer of the model ESEC DB-20S.

3. RESULTS AND DISCUSSION

3.1 Structural analysis:

The XRD patterns of $Pb_{1-x}Zn_xS$ (x=0, 0.02, 0.05, 0.1, 0.15) nanoparticles are shown in Fig.1a. All the diffraction peaks in the spectra are analogous to the literature pattern of face-centered cubic phase PbS powder (JCPDS file no. 00-006-0632). This confirms the formation of PbS nanoparticles. The strong and sharp diffraction peaks suggest that the particles are well crystallized. The intensity of the diffraction peaks decreases and broadens as the proportion of Zinc in PbS is increased. This implies that the particle size is reduced as PbS is doped with Zn. The diffracted peaks corresponding to 0.02%, 0.05%, 0.10% and 0.15% Zn doped PbS nanoparticles are left shifted with respect to that of undoped PbS and this shift is shown in fig 1b.

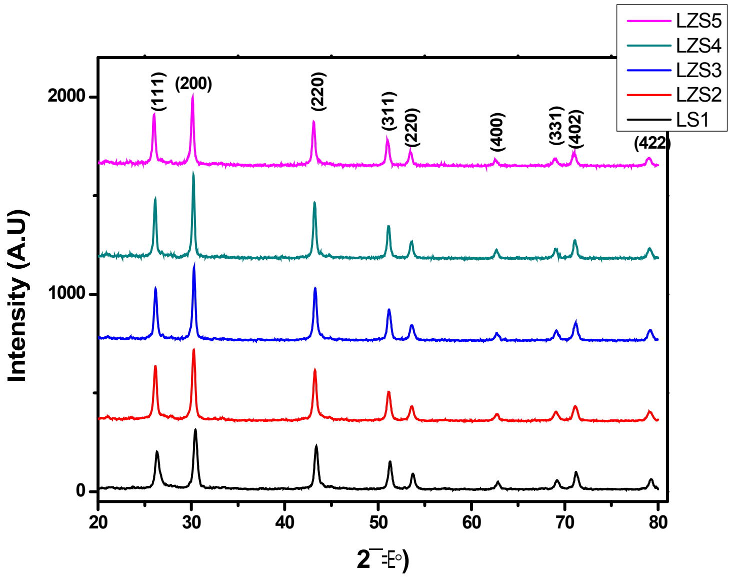

Figure 1a- XRD $Pb_{1-x}Zn_xS$ nanoparticles

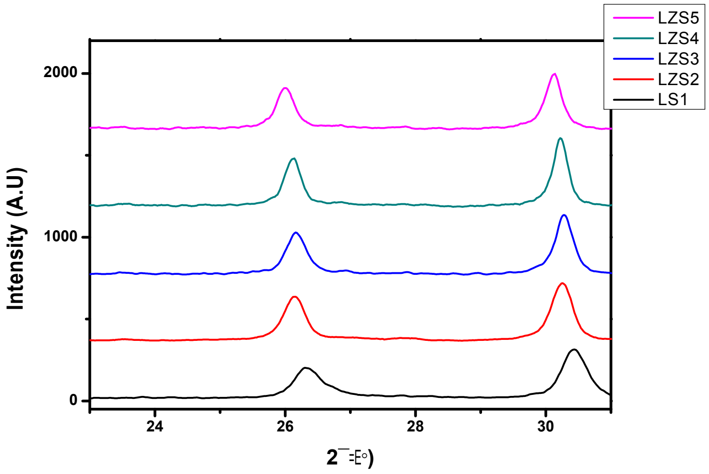

Figure1b- Shift towards left as the doping concentration increases

The crystallite size was calculated using Debye Scherrer formula. The formula is,

$$D = \frac{k^{a}}{\cos^{-}}$$

Here D is the crystallite size, k is the shape factor (0.9), λ is the wavelength of X-ray used (1.541Å̌) and β is the full width at half maximum.

Standard		Observed										hkl
		PbS		$Pb_{99.98}Zn_{0.02}S$		$Pb_{99.95}Zn_{0.05}S$		$Pb_{99.9}Zn_{0.1}S$		$Pb_{99.85}Zn_{0.15}S$		
2θ	**d(Å)**	**2θ**	**d(Å)**	**2θ**	**d(Å)**	**2θ**	**d(Å)**	**2θ**	**d(Å)**	**2θ**	**d(Å)**	
25.96	3.429	26.33	3.3187	26.144	3.405	26.174	3.401	26.114	3.409	26.000	3.424	(111)
30.06	2.970	30.44	2.9340	30.255	2.951	30.282	2.949	30.225	2.954	30.120	2.964	(200)
43.03	2.100	43.37	2.0843	43.236	2.090	43.263	2.089	43.206	2.092	43.108	2.096	(220)
50.94	1.790	51.28	1.7800	51.139	1.784	51.139	1.783	51.130	1.785	51.024	1.788	(311)
53.38	1.714	53.73	1.7045	53.614	1.4788	53.603	1.708	53.587	1.708	53.481	1.711	(222)
62.49	1.485	62.83	1.4777	62.781	1.358	62.707	1.480	62.692	1.480	62.577	1.483	(400)
68.83	1.362	69.16	1.3572	69.073	1.324	69.089	1.358	69.026	1.359	68.983	1.361	(331)
70.89	1.328	71.21	1.3230	71.124	1.209	71.172	1.323	71.077	1.325	71.041	1.326	(420)
78.88	1.212	79.26	1.207	79.108	1.208	79.147	1.209	79.077	1.210	79.002	1.325	(422)

Table 1- The 2θ and d values of standard, pure and Zn doped PbS nanoparticles

The calculated crystallite sizes of the synthesized nanoparticles are comparable with the exciton Bohr radius of PbS (~18) bulk material. This indicates that the quantum confinement effects of the synthesized nanoparticles can become more operative.

The lattice parameter of the crystal structure is calculated from the lattice constant d value using the formula,

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

Where hkl is the miller indices, a is the lattice parameter and d is the interplanar spacing. The calculated lattice parameter a values and crystallite sizes of undoped and Zn doped PbS nanoparticles are given in Table 2. The observed values of lattice constant are lesser than the standard which may be attributed to that the ionic radii of Zn2+(0.088nm) is lesser than the ionic radii of Pb2+ (0.133nm). Hence there may lattice distortion.

Index	Crystallite size D (nm)	Lattice parameter a (Å)	
		Standard	Observed
PbS	18.52	5.940	5.887
$Pb_{99.98}Zn_{0.02}S$	18.83	5.940	5.903
$Pb_{99.95}Zn_{0.05}S$	20.44	5.940	5.898
$Pb_{99.90}Zn_{0.10}S$	22.91	5.940	5.909
$Pb_{99.85}Zn_{0.15}S$	23.14	5.940	5.929

Table 2- Structural parameters of zn doped PbS nanoparticles

3.2 Morphology and Compositional analysis:

Figure 2 and figure 3 show the FESEM image of Zn doped lead sulfide nanoparticles .This FESEM image reveals that the particles are in aggregation state due to their extremely small dimensions and high surface energy. It can be seen that the particles adopt irregular morphology with different sized particle.

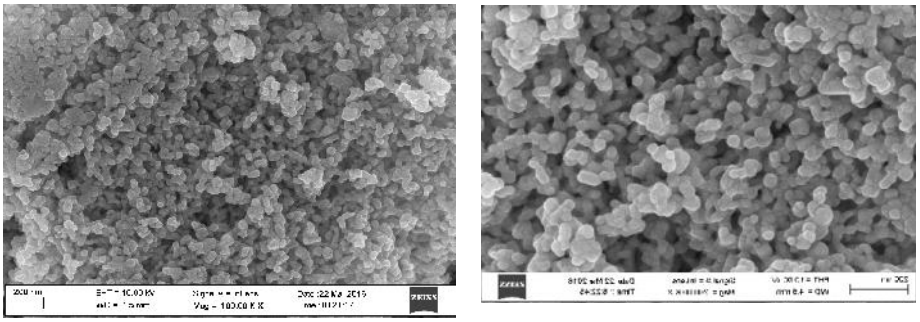

Figure 2- FE-SEM image of $Pb_{1-x}Zn_xS$ (x=0.10) nanoparticles

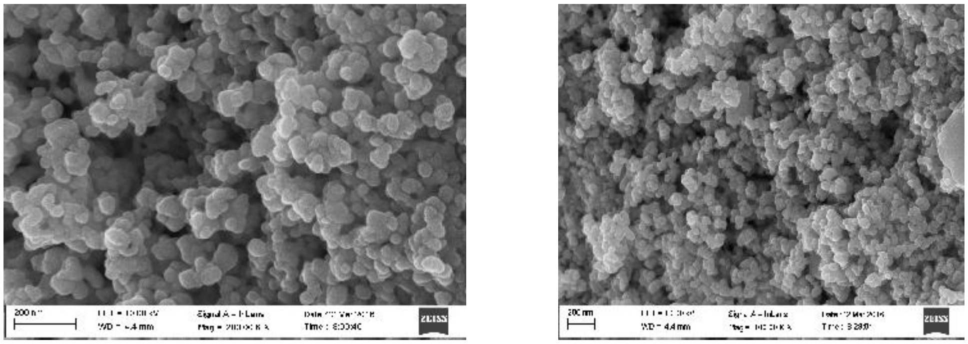

Figure 3- FESEM image of $Pb_{99.90}Zn_{0.10}S$

The formation of Zn doped PbS nanoparticles of $Pb_{99.90}Zn_{0.10}S$, $Pb_{99.85}Zn_{0.15}S$, were confirmed using EDAX analysis . The EDAX spectrum of these nanoparticles is shown in Figure4.

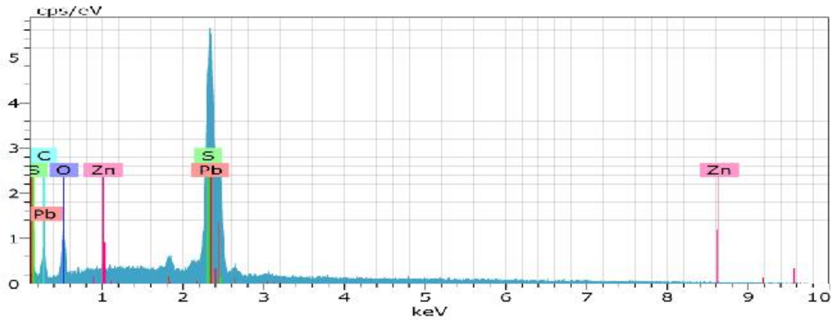

Figure 4a- EDAX spectrum of $Pb_{99.90}Zn_{0.1}S$ nanoparticles

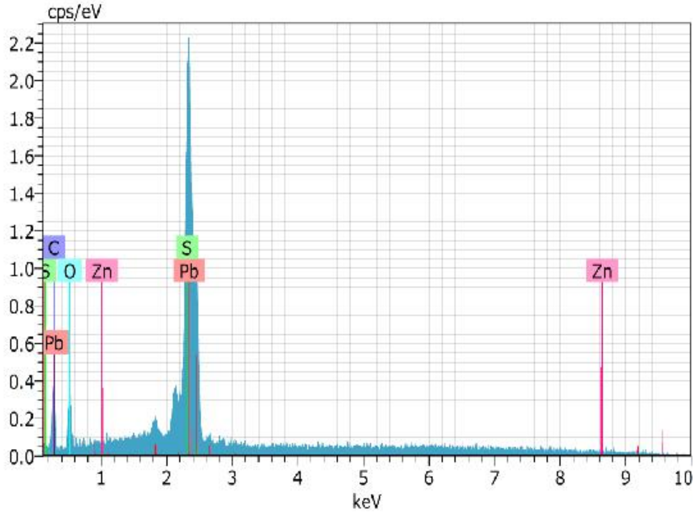

Figure 4b- EDAX spectrum of $Pb_{99.90}Zn_{0.1}S$ nanoparticles

3.3 FTIR ANALYSIS:

The peaks at 994 and 1116 correspond to C-O or S-O bonding of acetone or sulphate. The small peak at 618 cm^{-1} indicated the formation of Pb-S and Zn-S bonds as this region is assigned to Metal-Sulphur bonds. It is a supporting experiment to confirm the successful doping of Zinc in PbS [15].

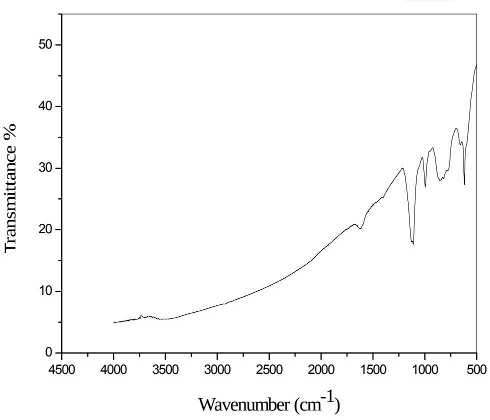

Figure 5a- FTIR spectrum of $Pb_{99.98}Zn_{0.02}S$ nanoparticles

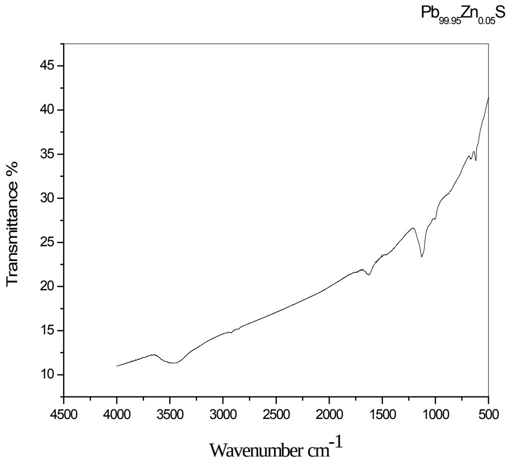

Figure 5b- FTIR spectrum of $Pb_{99.95}Zn_{0.05}S$ nanoparticles

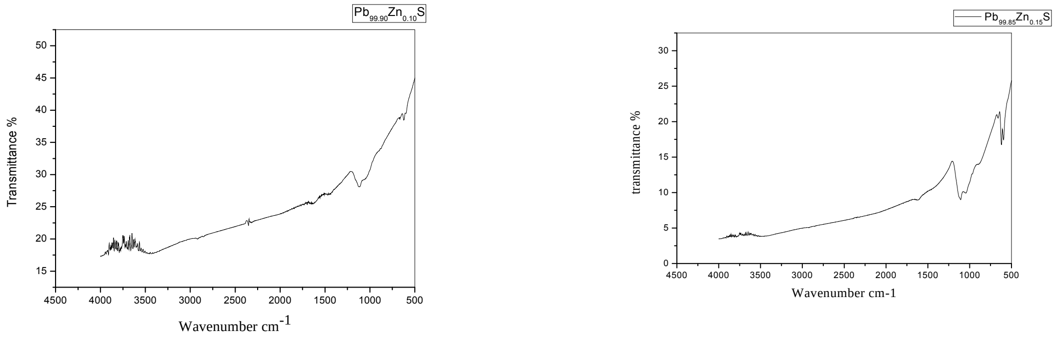

Figure 5a- FTIR spectrum of $Pb_{99.9}Zn_{0.10}S$ nanoparticles, Figure 5b- FTIR spectrum of $Pb_{99.85}Zn_{0.15}S$ nanoparticles

3.4 UV –VISIBLE SPECTROSCOPY

The optical absorption properties of semiconductor are related to the energy band structure,which is a crucial factor in determining the photocatalytic activity. The study of optical absorption is important to understand of semiconductor nanoparticles. A fundamental property of semiconductor is the band gap –the energy separation between the filled valence band and the empty conduction band. The room temperature UV-visible spectrum in the absorption mode is measured for PbS nanopowders. The optical band gap of the nanoparticles is calculated from UV absorption study using the following formula, $E=hc/\lambda$

The samples exhibit a strong absorption peak at 824nm, 821nm, 823 nm, 824nm for capped Zn doped PbS nanoparticles suggesting blue shift. The band gap energy of the samples corresponding to the absorption edge is found to be. The observed value 1.49eV, 1.50eV, 1.50eV,1.496 eV, is higher than the bulk value (E_s=0.41eV). This may be due to the quantum confinement effect.

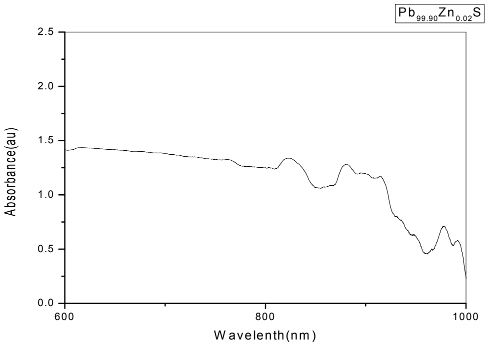

Figure 6a- UV-Vis spectrum of $Pb_{99.98}Zn_{0.02}S$ nanoparticles

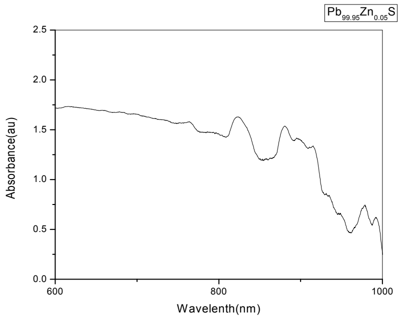

Figure 6a- UV-Vis spectrum of $Pb_{99.95}Zn_{0.05}S$ nanoparticles

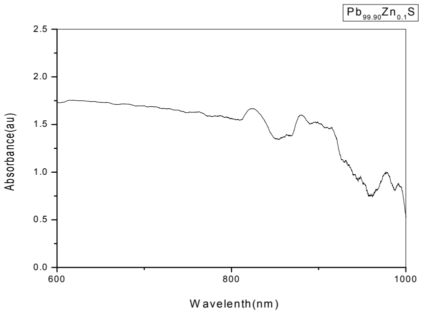

Figure 6a- UV-Vis spectrum of $Pb_{99.9}Zn_{0.10}S$ nanoparticles

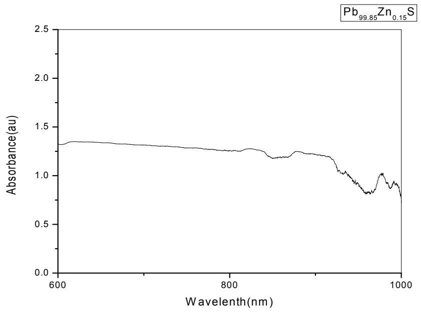

Figure 6a- UV-Vis spectrum of $Pb_{99.85}Zn_{0.15}S$ nanoparticles

CONCLUSION

$Pb_{1-x}Zn_xS$ (x = 0, 0.02%, 0.05%, 0.1%, 0.15%) nanoparticles were synthesized successfully using wet chemical method. Wet chemical method is simple, cost effective and less time consuming. The XRD patterns confirmed the face centered cubic structure of the undoped and doped PbS nanocrystals and the particle size are similar to the exciton Bohr radius of PbS. FE-SEM results showed that the nanocrystals are spherically shaped and are agglomerated. EDAX spectrum confirmed the formation of $Pb_{1-x}Zn_xS$ (x = 0, 0.02%, 0.05%, 0.1%, 0.15%) nanocrystals. The functional groups present in the material were studied with the help of FTIR spectrum. UV-Visible spectroscopy of the prepared samples were examined and the optical bandgap of the material were blue shifted as the doping concentration increases. The optical properties of the obtained small size, spherical nanocrystals find has been improved while doping Zinc in lead sulphide nanoparticles.

REFERENCES

[1]. Talaaat M.Hammad, JamilK.Salem, Journal of luminescence, (2015), 157, 88-92

[2] R. Sathyamoorthy, L. Kungumadevi, Advanced Powder Technology 26(2) (2015) 355-361

[3]. Firoz Alam, Neetash Kumar, Materials Research Bulletin, (2015), 65, 89-93

[5]. Y.Gulen, Acta Physica Polanica A, 2014,126

[6]. Masood Mehrabian, Kavoos Mirabbaszadeh, Hossein Afarideh, Optik, 2015, 126, 570-574

[7]. M.M.Tavakoli, A.Simchi, H.Aashuri, Materials Chemistry and Physics,2015, 156, 163-169

[8]. Gajanan Pandey, Sarika Shrivastav, Harendra K.Sharma, Physica E, 2014, 56, 386-392

[9]. Syamanta K.Goswami, Eunsoon Oh, Materials Letters, 2014, 117, 138-141

[10]. F.Gode, E.Guneri, F.M. Emen, Journal of Luminescence, 2014, 147, 41-48

[11]. Linda Dyorisse Nyamen, Neerish Revaprasadu, Peter Teke Ndifon, Materials Science in Semiconductor Processing, 2014, 191-196

[12]. Mohsen Cheragizade, Ramin Yousefi, Farid Jamali-Sheini, Materials Science in Semiconductor Processing, 2014, 26, 704-709

[13]. R.Sakthi Sudar Saravanan, M.Meena, Journal of alloys and Compounds, (2015), 627, 69-77

[14]. Xingliang He, Iraida N.Demchenko, Journal of Physical Chemistry C, (2012), 116, 22001-22008

[15]. U.Jabeen, S.M.Shah, N.Hussian, J.Photochemistry and Photobiology A: Chemistry 325 (2016) 29 - 38