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Synthesis and Characterization of Water Soluble ZnS: Ce, Cu co-Doped Nanoparticles: Effect of Polyvinyl Alcohol Concentration

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Abstract

ZnS nanoparticles co-doped with Ce^{3+} and Cu^{2+} ions were synthesized through a low cost chemical co- precipitation method using polyvinyl alcohol (PVA) as the capping agent. The prepared nanoparticles were characterized by X- ray diffraction (XRD), energy dispersive X – ray spectroscopy (EDS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), UV –visible and photoluminescence (PL) techniques. From X-ray diffraction studies it was observed that the synthesized nanoparticles have cubic Zinc blende structure with average sizes of about 2-4 nm and particle size decreases with increasing the capping agent concentration. EDS spectra confirmed the presence of corresponding elemental peaks and effective doping of the elements. Morphology and particle size distribution was analyzed by SEM and TEM. Optical absorption studies showed a blue shift in the absorption edge with increasing capping agent concentration and hence the effective band gap energy increases with decreasing the particle size. It was evident from photoluminescence studies that the emission becomes more intensive as the size of the particles is reduced with increasing capping agent concentration.

Keywords: Capping agent, particle size, band gap, Photo luminescence

Introduction

Zinc sulfide (ZnS) is one of the first discovered II-VI compound semiconductor materials with versatile fundamental properties[1]. Rare earth (RE) ion doped nanomaterials play a significant role in modern technology. ZnS is more stable than CaS or SrS as host of Rare earth ion doped luminescent II-VI materials. Semiconductor nanoparticles are themselves highly unstable, and in the absence of capping agent, they agglomerate very rapidly[2]. For this reason bonding of capping agents to nanoparticles is necessary to provide chemical passivation and also to improve the surface state which has substantial influence on the optical and electronic properties of nanoparticles[3]. Zinc sulfide (ZnS) is a promising material for various applications, including light-emitting diodes (LEDs), sensors, lasers, electroluminescence, flat panel displays, infrared windows, and bio devices. The atomic structure and chemical properties of ZnS are comparable to more popular and extensively known ZnO. However, certain properties pertaining to ZnS are unique and advantageous compared to ZnO. ZnS has a direct transition type band structure. The cubic form has a band gap of 3.54-3.6 eV, whereas the band gap of hexagonal form is higher being 3.74-3.87 eV[4-11]. Compared to ZnO (3.4 eV), ZnS has a larger band gap and therefore it is more suitable for ultraviolet (UV)-light based devices such as sensors or photo detectors. On the other hand, ZnS is traditionally the most suitable candidate for electroluminescence devices. In this present study, nanoparticles of ZnS: Ce, Cu capped with PVA is prepared by chemical co-precipitation technique. In this article we report the synthesis and characterization of transition metal and rare earth metal co-doped ZnS nanomaterials capped with polyvinyl alcohol (PVA). The unique luminescence property such as strong and enhanced visible light emission due to transition metal and rare earth ions co-doped ZnS nanoparticles and the effect of capping agent namely Polyvinyl alcohol are discussed.

Material and Methods

All the chemicals used were of analytical reagent grade and used without further purification. The samples were prepared by chemical co-precipitation method using zinc acetate, cerium (IV) sulfate, copper (II) acetate and sodium sulfide. Polyvinyl alcohol (PVA) is used as the capping agent. Appropriate amounts of $Zn(ac)_2$, $Ce(SO_4)_2(H_2O)_x$ and $Cu(OAc)_2$ were dissolved in distilled water. In a typical synthesis, desired molar proportions of $Zn(CH_3COO)_2$. $2H_2O$, $CeCl_3.7H_2O$, $Cu(CH_3COO)_2.H_2O$ and PVA each were dissolved in 50 ml Ultrapure de-ionized water and stirred for 60 minutes. Later Na_2S solution was drop wisely added to the solution at room temperature under constant stirring and stirring continued for 2 hours. The obtained precipitate was washed with de-ionized water for several times and filtered. Finally, the filtered powders were dried for 3 hours at 80^OC and grinded to obtain PVA capped ZnS: Ce, Cu nanoparticles. The same procedure was used to prepare the uncapped ZnS nanoparticles.

Characterization: The X-ray diffraction studies of the samples were carried out on a Rigaku D X-ray diffractometer with the Cu-Kα radiation (λ=1.5406A°). Morphology and compositional analysis of the prepared samples were analyzed through EDAX using Oxford Inca Penta FETx3 EDS instrument attached to a Carl Zeiss EVO MA15 scanning electron microscope.

Morphology and particle size were analyzed using a TECHNAI-TEM FEI transmission electron microscope (TEM), operated at an accelerating voltage of 100–200 kV. The optical absorption measurements were done using a Jasco-V-670 Spectrophotometer. Photoluminescence spectra were recorded in the wavelength range of 400–700 nm using a PTI (Photon Technology International) Fluorimeter with a Xe-arc lamp of power 60 W.

Results and Discussion

Structural analysis: Figure-1 represents the XRD patterns of uncapped and PVA capped ZnS: Ce, Cu nanoparticles. It is clear from the XRD pattern that all the samples are well-crystallized and the diffraction peaks with orientations (111), (220) and (311) can be assigned to cubic (fcc) ZnS (JCPDS card no. 80-0020).

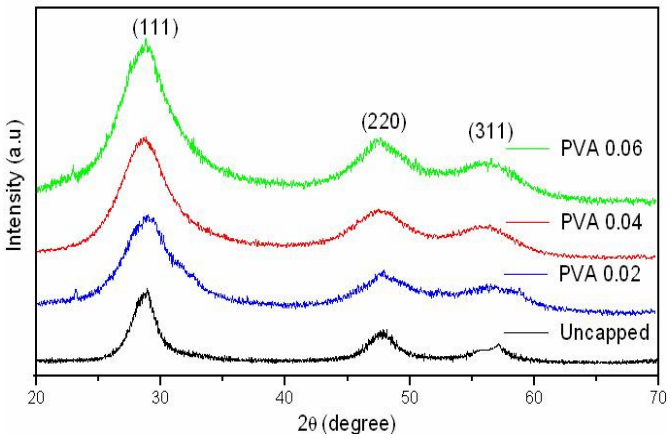

Figure-1
XRD profiles of PVA capped Ce, Cu co-doped ZnS nanoparticles at different PVA concentrations

Dopant incorporation was confirmed by lattice contraction and nanocrystalline nature with broadened XRD pattern. The average particle size of the samples calculated by Debye Scherrer's equation (a)is around 2-4 nm and is tabulated in Table-1.

$$D = \frac{0.9\lambda}{\beta\cos\theta} \quad \text{(a)}$$

Where D is the average particle size, β is full width at half maximum of XRD peak expressed in radians and θ is the position of the diffraction peak.

Table-1
Average Particle size of PVA capped Ce, Cu co-doped ZnS nanoparticles

S. No	PVA concentration (M)	Particle size(nm)
1	Uncapped(0.00)	3.68
2	0.02	3.54
3	0.04	3.22
4	0.06	2.96

It is clearly observed that the average particle size of the ZnS: Ce, Cu nanoparticles decreases with increasing capping agent concentration.

Morphological and compositional analysis: Figure- 2(a) and Figure-2(b) show the SEM images of uncapped and PVA capped ZnS: Ce, Cu nanoparticles respectively. It is clearly observed that the uncapped ZnS: Ce, Cu nanoparticles are seen to be agglomerated whereas the PVA capped particles are having fine distribution and decreased particle size. TEM image shown in Figure-3 confirms the fine distribution of the capped ZnS: Ce, Cu nanoparticles and the size of the nanoparticles is less than 5 nm, which is in good agreement with XRD studies.

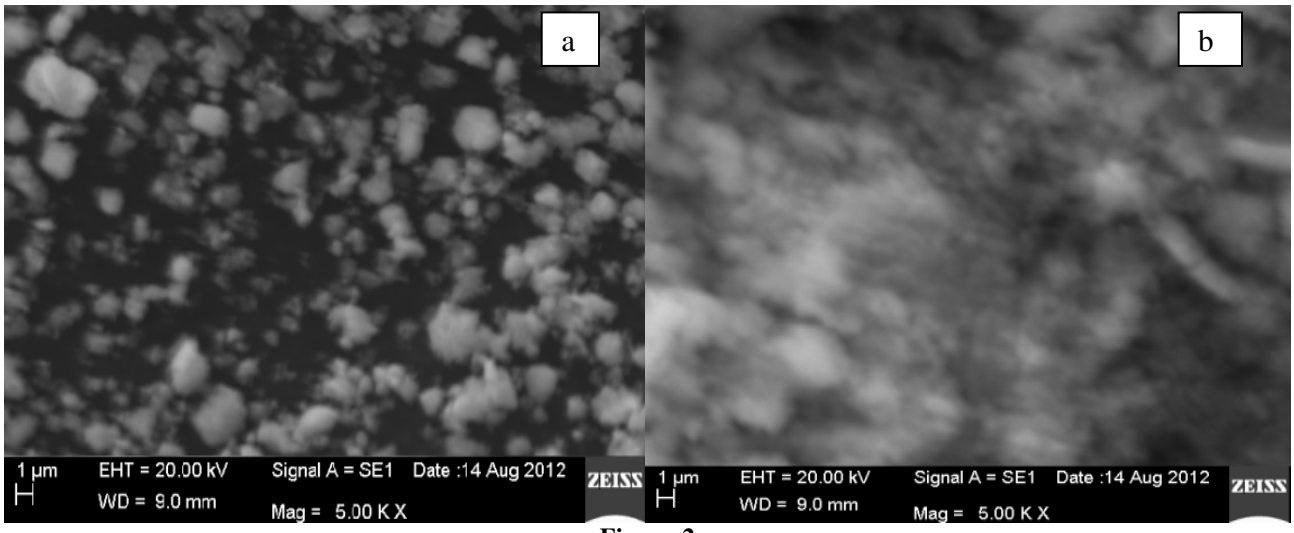

Figure-2
(a)SEM image of Uncapped ZnS: Ce, Cu nanoparticles Figure-2 (b) SEM image of PVA capped ZnS: Ce, Cu nanoparticles

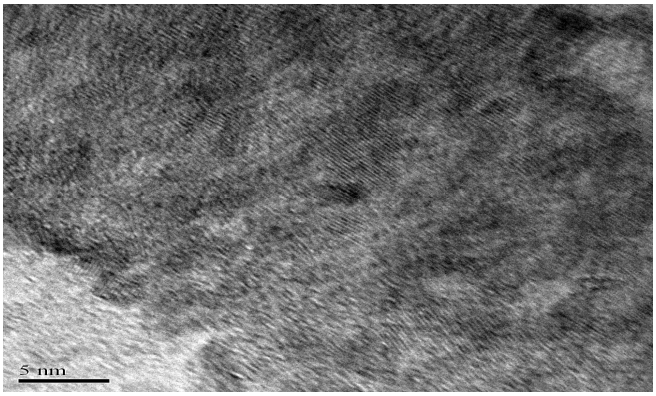

Figure-3
TEM image of PVA capped ZnS: Ce, Cu nanoparticles

The compositions of the samples were examined using an energy-dispersive X-ray (EDS) spectroscopy analysis. The EDS analysis (figure-4) demonstrated that Zn, Ce, Cu and S elements are present in the sample which further confirmed the successful doping of Ce and Cu ions in the ZnS host structure.

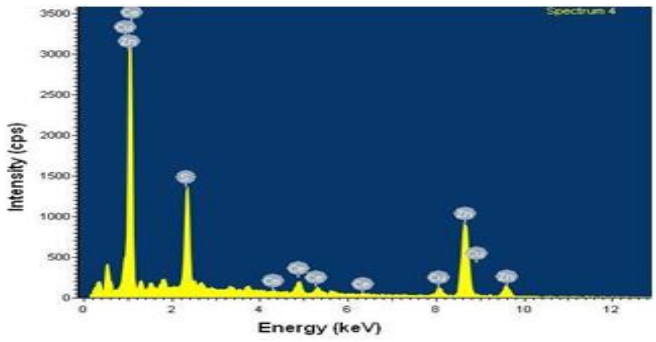

Figure-4
EDS spectrum of Ce, Cu co-doped ZnS nanoparticles

Optical absorption studies: UV-Vis absorption analysis (figure-5) reveals that chemical modification was achieved by reaction of Zn, Ce, Cu, PVA precursor with Sodium Sulfide in aqueous medium. The optical band gap values of the samples with varying PVA concentration are presented in table-2.

Table-2
Optical bandgap for PVA capped ZnS: Ce, Cu nanoparticles

S.No	PVA Concentration(M)	Optical Bandgap(eV)
1	Uncapped (0.00)	3.82
2	0.02	3.88
3	0.04	3.92
4	0.06	3.96

This blue-shift also confirms the nanocrystalline nature of the samples and is caused by the strong quantum size effect in nanoparticles. The absorption edge shifts towards lower wavelength side or blue region as the capping agent concentration is increased indicating that effective band gap energy increases with decreasing the particle size.

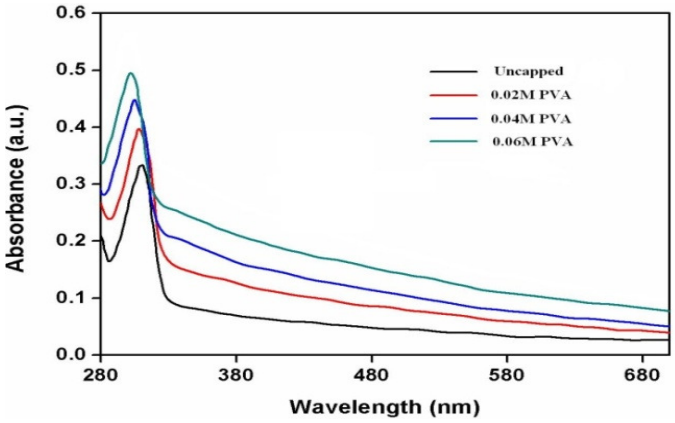

Figure-5
Absorption spectra of Ce, Cu co-doped ZnS nanoparticles capped with PVA

Photoluminescence studies: The Photo luminescence spectra for PVA capped ZnS: Ce, Cu nanoparticles consists of sharp peaks centered at 510 nm in the green region. This is close to the value reported by Klausch et al.[12] and Song et al.[13] and may be ascribed to the transition from the shallow defect state to T_2 state of Cu. From PL spectra (figure-6), it is evident that with the increasing of PVA amount, the luminescence intensity improved.Figure-6 shows PL emission spectra obtained for the Ce, Cu co-doped ZnS nanoparticles capped with PVA and the excitation wavelength used in this study is 320 nm.

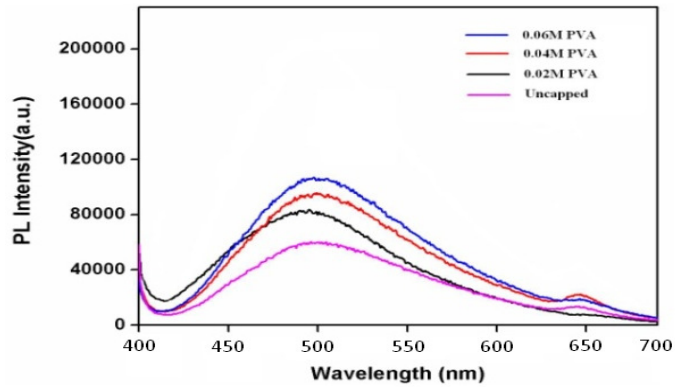

Figure-6
PL spectra of Ce, Cu co-doped ZnS nanoparticles capped with PVA

Conclusion

In summary, PVA capped ZnS: Ce, Cu nanoparticles have been successfully synthesized by a chemical co-precipitation method at different PVA concentrations. X-ray diffraction (XRD) measurements showed that the PVA capped ZnS: Ce, Cu nanoparticles have fcc zinc blende structure and well crystalline

nature. The morphology and particle distribution was studied by scanning electron microscopy and transmission electron microscopy and the size of the particles was found to be less than 5nm. Compositional analysis of the prepared samples was successfully carried out by energy dispersive X-ray spectroscopy. With the increasing of PVA concentration particle size of the Ce, Cu co-doped ZnS nanoparticles decreased, band gap increased and PL intensity enhanced.

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