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Effect of Ag doping on structural and optical properties of ZnSe nanophosphors

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ABSTRACT

In the present study undoped ZnSe and silver doped ZnSe viz. $Zn_{1-x}Ag_xSe$ ($x=1\%$, 3%, 5%) nanophosphors are synthesized via a simple hydrothermal route. The prepared nanophosphors were characterized by X-ray diffraction (XRD), UV–vis spectroscopy, Photoluminescence (PL) spectroscopy, Raman spectroscopy and field emission scanning electron microscopy (FE-SEM). XRD patterns of samples reveal the formation of cubic phase for the undoped ZnSe, 1% and 3% Ag doped ZnSe, and 5% silver doped sample indicates the formation of another phase of Ag_2Se along with the original one. The crystallite size is found to increase from 4.2 nm to 13.5 nm for Ag doped ZnSe nanostructures. Some nanorods structures are formed in $Zn_{0.95}Ag_{0.05}Se$ as confirmed by the FE-SEM images. The UV–vis analysis shows a blue-shift of the absorption edge of the undoped ZnSe and Ag doped ZnSe nanophosphors as compared to its value for bulk ZnSe. The gradual decrease in PL intensity with increased amount of Ag doping in the host ZnSe nanophosphors is explained on the basis of concentration quenching mechanism.

1. Introduction

Nanostructured materials have fascinated an important significance in the modern world. Over the past decade, semiconductor nanostructured materials have been developed into a field of research, mainly because of their shape and size effects on the optical and electronic properties [1]. Due to their unique properties, these find a number of applications in solar cells, optoelectronics, light-emitting diodes (LEDs) and bio-labels [2–7]. Among II–VI semiconductors materials, Zinc selenide (ZnSe) is chemically more stable and scientifically better than other semiconductor materials (such as ZnS, ZnO, CdS, CdSe, etc.) and considered to be a promising host material for doping with metals. The fabrication approach of ZnSe nanomaterials tends to be environment and user affable; above and beyond involving small power utilization and low power dissipation [8–13]. ZnSe is an important II–VI semiconductor material, which has intrinsic direct energy band gap ($E_g=2.7$ eV) and a small Bohr exciton diameter of 9 nm. It emits in the violet–blue window when the size is reduced below the Bohr excitonic radius. Zinc selenide is generally known to be an n-type semiconducting material. It is a chemically inert, non-hygroscopic and highly pure product that is very effective in many optical applications due to its extremely low bulk losses, high resistance to thermal shock and stability [14–17]. It is also a promising candidate for the replacement of the toxic CdS or CdSe in the buffer layer due to its wider band gap compared to that of CdS or CdSe and useful in high resolution thermal imaging systems for correcting color distortion, which is often inherent in other lenses used in the system [18]. ZnSe nanoparticles have been synthesized by different techniques: sol gel, aqueous chemical, chemical deposition, microemulsion, chemical precipitation and hydrothermal [19]. The surface alteration

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of the grown nanocrystals has been done to avoid self-agglomeration of particles leading to size control and uniform size distribution of particles. The hydrothermal approach utilized in the present study is a simple and economical method, which is effective to control the particle size and uniform production of ZnSe nanoparticles. The purity of sample synthesized by hydrothermal route is much better than the purity of the starting raw materials due to self-purifying property of the hydrothermal crystallization, as impurities present in the medium are eliminated by the growing crystallites [20,21].

The doping of transition metal ions into the group II–VI semiconductor nanomaterials such as ZnSe, CdSe, CdS, ZnS, etc. is quite interesting because the doping efficiency depends upon the chemical properties of the host and dopant [22]. Transition metal ions doped semiconductor nanoparticles are a new category of materials which have broad range of applications in sensors, displays, electronic devices, laser devices, nonlinear devices, etc. [23]. In the present work we focused on the synthesis and characterization of undoped ZnSe and silver doped ZnSe with different doping concentrations resulting in stoichiometric composition as $Zn_{1-x}Ag_xSe$ ($x=1\%$, 3%, 5%) nanophosphors and correlation of structural and optical properties of the undoped and Ag doped ZnSe nanophosphors using different techniques.

2. Experimental

2.1. Chemicals

For the preparation of undoped ZnSe and $Zn_{1-x}Ag_xSe$ ($x=1\%$, 3%, 5%) nanophosphors, the chemicals used were Zinc nitrate [$Zn(NO_3)_2$] of purity $\geq 99\%$, elemental selenium (Se) of purity 99%, Silver nitrate [$Ag(NO_3)_2$] of purity 99%, Ethylene glycol ($C_2H_6O_2$) of purity 99% and Hydrazine hydrate [$(N_2H_4)\cdot H_2O$] of purity 80%. These chemicals were purchased from Merck and Loba Chemie and used without further purification.

2.2. Synthesis

The undoped ZnSe and $Zn_{1-x}Ag_xSe$ ($x=1\%$, 3%, 5%) nanophosphors were synthesized by a simple hydrothermal route. Freshly prepared aqueous solutions of Zinc nitrate, and elemental selenium were used as precursors. Zinc nitrate (10.317 g) was dissolved in 100 ml deionised water and stirred at 70 °C for 30 min. Similarly, selenium (2.735 g) was dissolved in 40 ml Hydrazine hydrate and 20 ml Ethylene glycol and stirred at 70 °C for 30 min, and then these two solutions were mixed. Silver nitrate was dissolved in citric acid solution and added dropwise in the above mixed solution and stirred at 70 °C. In the above prepared solution ascorbic acid and thiourea were added dropwise and stirred at 70 °C for 2 h. After completion of the reaction, the solution was transferred to a stainless steel Teflon lined autoclave and kept at 200 °C for 20 h and then cooled to room temperature. The solution was filtered and precipitate was washed with ethanol and distilled water. The wet precipitate was dried in an oven at 100°C for 5 h.

2.3. Characterization techniques

The crystal structure and phase identity of the synthesized samples were observed by X-ray diffraction pattern on Rigaku mini-desktop diffractometer using graphite filtered Cu-Kα radiation with wavelength (λ) as 1.54 Å, The operating voltage of X-ray tube was 40 kV with current 100 mA and scanning rate was fixed at 3 °/min. UV–visible absorption spectra were recorded on a UV–visible double beam 550 Spectrophotometer (Camspec) in the spectral range 250–900 nm using a spectral bandwidth of 1 nm at room temperature. Photoluminescence spectra of prepared undoped ZnSe and Ag doped ZnSe nanoparticles were carried out on Shimadzu RF-530 Spectrofluorometer in the wavelength range 200–900 nm. The Raman spectra were recorded using 514.5 nm emission line of Ar^+ ion laser as the excitation wavelength on Renishaw micro-Raman setup at room temperature. Field emission Scanning electron microscope (FE-SEM) image was used to investigate the size and morphology, which was carried out with a scanning electron micro-analyzer using JEOL-JSM6700 microscope, operating at 10 A and 15 kV.

3. Results and discussion

3.1. X-ray diffraction analysis

The X-ray diffraction patterns of nanocrystalline undoped ZnSe and $Zn_{1-x}Ag_xSe$ ($x=1\%$, 3%, 5%) powder samples are shown in Fig. 1. Undoped ZnSe and $Zn_{1-x}Ag_xSe$ ($x=1\%$, 3%) are found to be of cubical symmetry with major Bragg-reflection peaks at (111), (220), (311), (400) and (331) planes. These peaks are well consistent with those mentioned in the standard JCPDS No. 37-1463. $Zn_{0.95}Ag_{0.05}Se$ sample has all the major peaks of pure ZnSe in addition to small extra peaks. The small extra peaks indexed with ⁎ are of Ag_2Se and matched well with the JCPDS No. 24-1041 corresponding to reflection planes (020), (112), (121), (122) and (220). The peaks corresponding to 2 theta values at 28.30°, 33.48°, and 34.77° are assigned to silver as confirmed from its standard JCPDS No. 01-1167.

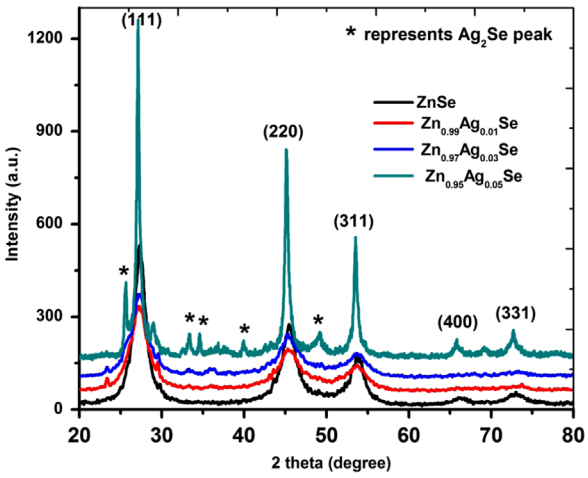

Fig. 1. XRD patterns of undoped ZnSe and Ag doped ZnSe.