



IMPACT OF Pr AND Ni DOPING ON STRUCTURAL AND PHOTOLUMINESCENCE CHARACTERISTICS OF ZnS NANOPARTICLES

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Abstract: Doping of materials attracted a greater attention as it affects the characteristics of the pristine counter parts. In the present work praseodymium and nickel co-doped zinc sulfide nanoparticles were prepared by a low-cost chemical co-precipitation method at room temperature. Impact of Pr and Ni dopants concentration on structural, morphological, compositional and photoluminescence properties of ZnS were studied. Cubic zinblende structure of Pr, Ni co-doped ZnS nanoparticles was revealed by the broadened X-ray diffraction (XRD) peaks. The surface morphology and composition of Pr, Ni co-doped ZnS nanoparticles were studied by scanning electron microscopy (SEM) equipped with energy dispersive X-ray analysis (EDAX). The photoluminescence intensity of the co-doped nano samples enhanced effectively by the integration of Ni and Pr ions into the ZnS host lattice.

Key words: ZnS, doping, photoluminescence, Surface morphology.

1. Introduction

ZnS is an effective and noble material among II-VI group semiconductors for multi-applications of photocatalysts [1-3], supercapacitor [4], UV-light, gas sensors, bio-sensors and nano-generators [5]. Zinc Sulfide has peculiar and special properties at nano-level due to quantum captivity and increases in surface to volume ratio. Doping of the materials is a highly useful practice in which the dopant impurities are spatially divided from the transport layer, it has become possible to circumvent the limitation of charge carrier mobility in highly doped semiconductors. Efforts have been made to achieve the enhancing the the electrical properties of the chemically unmodified materials but no significant success. It will be highly advantageous to enhance the properties with slight modification by doping. Doping is a classical approach for increasing the conductivity of inorganic systems. Doping also supplies high quantity of charge carriers from the dopants to the target material. A doped ZnS nanoparticle exhibit interesting optical, magnetic and photoluminescence properties and hence finds many applications in luminescence and spintronics [6, 9].

Elevated emissivity resources have fascinated prevalent consideration in the field of thermal protection due to their excellent infrared radiation capabilities. Photoluminescence of doped ZnS can be enhanced by the doping of rare-earth ions and transition metal ions. Agglomeration of the particles is reduced with the help of capping agents and also particle size is reduced remarkably.

In this paper, ZnS nanoparticles co-doped with Pr and Ni ions have been synthesized by chemical co-precipitation at room temperature. The influence of Praseodymium and Nickel dopant concentration on structural, surface morphology, elemental and photoluminescence properties of Pr doped ZnS nanoparticles were studied. Pristine ZnS is denoted as ZnS-0, doped with 2% of Pr as ZnS-1, with 2% Pr and 2% Ni as ZnS-2, 2% Pr and 4% Ni as ZnS-3, 2% Pr and 6% Ni as ZnS-4, respectively.

2. Experimental and characterization techniques

Pr and Ni co-doped ZnS nano samples were prepared by the chemical co-precipitation method using pure zinc acetate, nickel chloride, praseodymium (III) nitrate hexahydrate, and sodium sulfide. Appropriate amounts of $Zn(ac)_2$, $NiCl_2 \cdot 6H_2O$ and $PrH_{12}N_3O_{15}$ were dissolved in 50 ml distilled water. Polyvinylpyrrolidone was used as a capping agent. To this solution, 50 ml of sodium sulfide solution is dropped wisely added under constant stirring to get a fine precipitate of Pr, Ni co-doped ZnS nanoparticles. Then the samples are thoroughly washed several times with distilled water and ethanol.

The chemicals utilized in the preparation of Pr and Ni co-doped ZnS nanoparticles were analytical reagent grade and were used without any further purification. Pr, Ni co-doped ZnS nanoparticles were then subjected to various characterizations. The X-ray diffraction patterns of the samples were collected on a Seifert 3003 TT X-ray diffractometer with the CuK_{α} radiation ($\lambda=1.5405\text{\AA}$). Surface morphology and elemental composition of the prepared nano samples were studied by EDAX using Oxford Inca Penta FeTX3 EDS instrument attached to Carl Zeiss EVO MA 15 Scanning Electron Microscope. Photoluminescence studies of the prepared Pr, Ni co-doped ZnS nano samples have been recorded using a Horiba-Fluorolog-3 (Model FL3-22) spectrofluorometer at room temperature (300 K).

3. Results and Discussion

3.1. Structural analysis

The X-ray diffraction peaks of pure ZnS and Pr, Ni co-doped ZnS nanoparticles are shown in Fig. 1. All the nano samples exhibit three diffraction peaks correspond to the lattice planes of (111), (220) and (311) with the cubic zinc blended structure (JCPDS card no. 80-0020). The broadening of peaks observed in the XRD spectra shows the nanocrystalline nature of the prepared samples. Diffraction peaks corresponding to the impurity phases were observed.

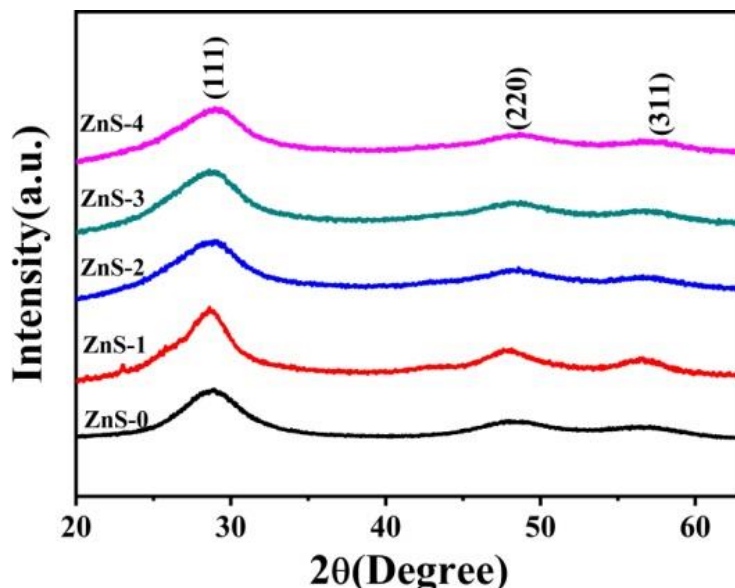


Fig. 1. XRD patterns of pure and Pr, Ni co-doped ZnS nano samples.

The average particle size of the prepared nano samples calculated by Debye Scherrer's equation below in the range of 3 to 5 nm as shown in Table 1.

$$D = \frac{0.94\lambda}{\beta_{hkl} \cos \theta}$$

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

Table1. The average particle size of Pr, Ni co-doped ZnS nanoparticles

SI No	Prestine Material	Dopant (%)		Code	Particle size (nm)
		Pr	Ni		
1	ZnS	-	-	ZnS-0	4.8
2	ZnS	2	-	ZnS-1	4.1
3	ZnS	2	2	ZnS-2	3.8
4	ZnS	2	4	ZnS-3	3.5
5	ZnS	2	6	ZnS-4	3.6

3.2. Raman spectral studies

The Raman spectra of ZnS polytypes have been described by Schneider and Kirby [10]. Nilsen et al. [11]. The Raman Spectra for pure and Ni-doped ZnS is shown in Fig. 2. The Raman spectra of pristine ZnS displayed peaks at 272 and 352 cm^{-1} . The transverse optical (TO) and longitudinal optical (LO) zone center phonons near 267 cm^{-1} , 342 cm^{-1} , 273 cm^{-1} and 351 cm^{-1} were obtained for Ni-doped ZnS Nanoparticles The TO and LO positions are different for Ni-doped ZnS.

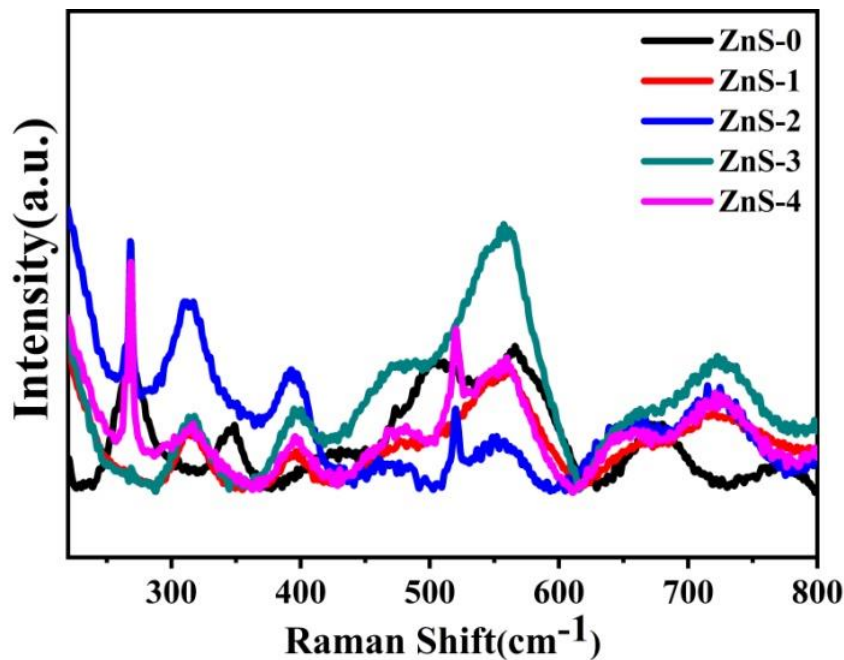


Fig. 2: Raman spectral analysis of Pr and Ni co-doped with ZnS Nanoparticles in different concentrations.

The phonon frequency at 440 cm^{-1} is observed for pristine as well as for doped samples is the E2 high mode which involves the motion of oxygen atoms in the wurtzite lattice and is a characteristic peak of ZnS [12]. The mode at around 407 cm^{-1} is characterized as the E1(TO) optical phonon mode [13]. The additional vibrational modes that observed at 564 cm^{-1} and 671 cm^{-1} after doping is due to the Ni^{2+} occupation at Zn^{2+} sites or defects in the nanoparticles [14]. The multi - phonon scattering process arising from the zone boundary phonons is appeared at 724 and 292 cm^{-1} [15].

3.3. Scanning electron microscope analysis

The morphology of pristine, Pr doped and Pr -Ni co-doped ZnS nano samples were studied by scanning electron microscope as shown in Fig.3(a-f) and EDAX pattern of ZnS-3 is depicted in Fig. 3(g). EDAX pattern for other samples is also confirmed and shown in supporting information. The presence of Zn, S, Ni and Pr is confirmed by EDAX analysis.

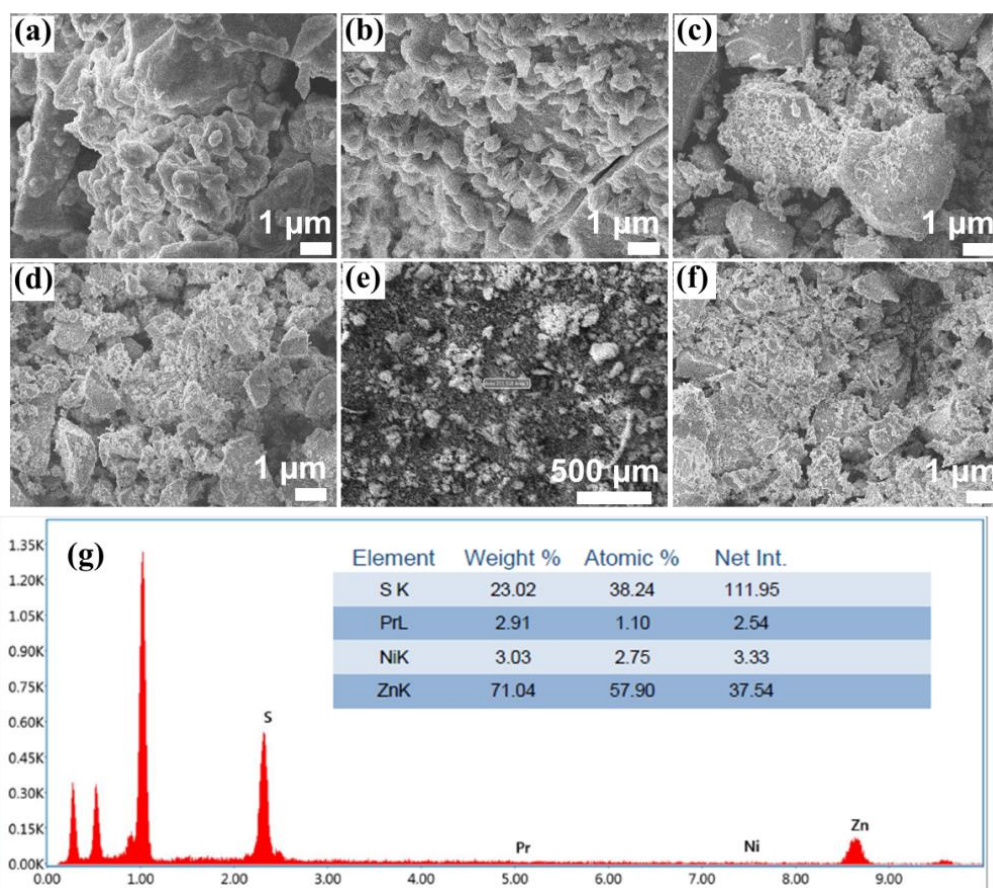


Fig.3. SEM image of (a) ZnS-0, (b) ZnS-1, (c) ZnS-2, (d) ZnS-3 (e) Expanded ZnS-3, (f) ZnS-4, and (g) EDAX pattern of ZnS-3.

3.4. Absorbance and photoluminescence studies

The UV-absorption measurements were studied for the prepared nanoparticles and are illustrated in Fig. 4. The absorption maximum for ZnS-0, ZnS-1, ZnS-2, ZnS-3, ZnS-4, were observed at 296.01 nm, 296.84 nm, 298.50 nm, 299.33 nm and 300.170 nm, respectively. The photoluminescence spectra of prepared nanoparticles are shown in Fig.4.

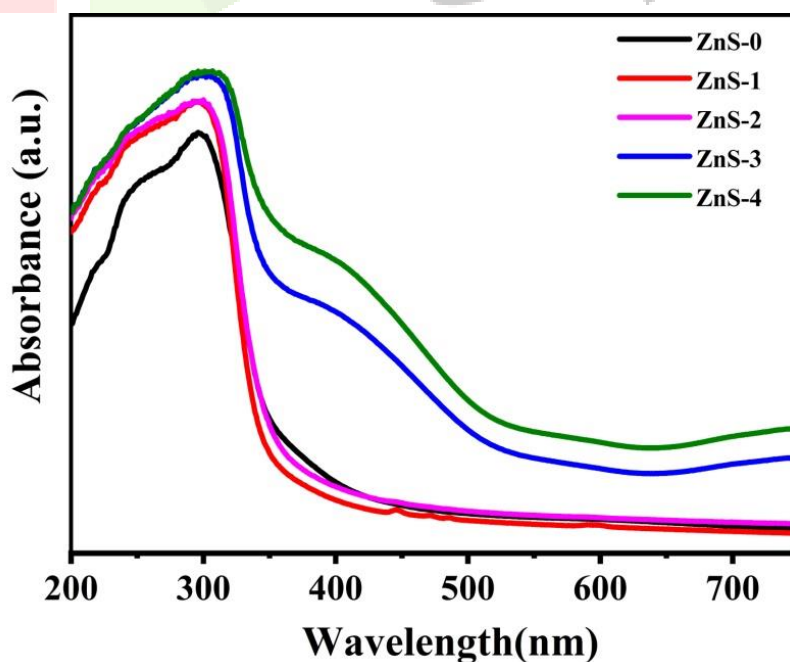


Fig.4. UV Absorption spectra for Prestine and co-doped samples.

All the nano samples were excited at a wavelength of 320 nm. A broad emission peak at around 450 nm was observed for pure ZnS nanoparticles [16]. The broad peak observed around 450 nm may be due to sulfur vacancies created in the ZnS due to radioactive recombination's [17]. Pr doped and Pr, Ni co-doped ZnS nanoparticles showed emission peaks at around 583 nm. As shown in Fig.4, with the increase in Ni dopant concentration, Pr doped Nanosamples showed increased luminescence intensity. This may be due to the increase in crystalline nature with the decrease in particle size and reduction of surface defects [18]. At higher dopant concentrations of nickel, the intensity of the photoluminescence peak decreases as the particle size slightly increases.

4. Conclusion

In summary, pristine ZnS, and Pr, Ni co-doped nanoparticles were successfully prepared by a cost-effective chemical co-precipitation method at room temperature. All the prepared nano samples exhibited cubic zincblende structure and the broadened XRD peaks indicating nanocrystalline nature. The average particle size is in the range of 3-5 nm for the synthesized samples. Morphological and composition of nanoparticles shows agglomerated particles and effective elemental composition of the as-prepared nano samples. Photoluminescence study reveals the enhancement in PL intensity of Pr, Ni co-doped ZnS nanoparticles with an increase in nickel dopant concentration.

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