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Synthesis and Characterization of Co^{2+} Ions Doped ZnS-CdS Composite Nanopowder

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Abstract: ZnS-CdS composite nano-powder doped with (0.01 mol %) Cobalt has been collected by a co-precipitation process at 300 K. The sample is characterized by structural, combined spectroscopic methods and magnetic studies. The prepared samples were belonging to cubic structure no impurity phases were observed. Doping of cobalt increase the neighborhood strain assessment and a decreases lattice constants decides from x-ray diffraction data. The crystallite size is 10.42nm. From UV-absorption and EPR studies revealed that the energy band gap of Co^{2+} doped ZnS-CdS composite nanopowder and extension of sp-d exchange interactions and common d-d transitions. The variation in the energy bandgap varies as a function of cobalt concentration is due to structural modification. Photoluminescence spectrum reveals the defect-related emissions and shows the formation of luminescence. FT-IR spectrum confirmed the feature vibrational manner of Zn, Cd, O–H and sulfide ions are in the host lattice. The doping-induced magnetic properties are studied by vibrating sample magnetometer which matches with the theoretical values besides ferromagnetic nature. Magnetic studies confirm the ferromagnetic nature of the material. Surface morphology and chemical homogeneity studies were carried out by using SEM with EDAX. Transmission electron microscope recommends the crystalline nature of nanoparticles, with average particle size is of the order of 20-100nm.

Keywords: Semiconductors, X-ray diffraction, Composite nanopowder, SEM, Optical properties, VSM.

1. Introduction

Nanomaterials possess tremendous approach and indication in distinctive areas, together with chemistry, physics, optics, electronics, biomedical sciences, and materials science. A set of II-VI compounds have been deliberate widely because of their greater probable in the field of optoelectronics. One of the important properties of the semiconductors which distinguish them from the metals and insulators is their energy bandgap. The wavelength of light absorbed or emitted by the semiconductor can be constructed using display devices and laser materials. Also, the electronic and optical properties of this compound can be superintended by the concentration of impurities in the materials as well as growth and operating conditions. Amongst all these Zinc (Zn) and Cadmium (Cd) chalcogenides are the most important members of this family and the semiconductors having wide band gaps from1.5 eV (Cd-Te) to 3.6eV (ZnS), which are all direct bandgap in nature. In recent times, the combination of at least one chalcogen anion and at least one more electropositive element of the dissimilar category have involved considerable awareness due to their important nonlinear, luminescent properties, quantum size effects and other important physical and chemical properties. Moreover, Semiconductors such as ZnS, CdS, ZnO, CdTe are the foremost promising materials and much in demand for optical and optoelectronic applications [1-3]. Among these Zinc sulfide (ZnS) is a binary compound semiconductor and it has traditionally shown exceptional physical and chemical properties and a promise for novel miscellaneous applications, such as electroluminescence, sensors, and lasers and so on, recent research mainly focused on the various physical and chemical methods to synthesize and mixed with ZnS nanoparticles. However, physical and chemical approaches often utilize toxic chemicals to limit clinical applications and cause environmental concerns applications and it has wide band-gap energy of 3.68 eV for bulk cubic phase. Due to the large bandgap, ZnS is an essential semiconductor host lattice material for electroluminescent devices and it has high transmittance in the visible region and a high refractive index material to test several theoretical models in condensed matter physics. Cadmium Sulphide (CdS) is a semiconductor material as it finds applications in photovoltaic cells (or) solar cells, Cadmium Telluride (CdTe), Copper Indium Gallium Sulphide (CIGS) and Copper Indium Sulphide (CIS). It has additionally approached in diverse electro-optic devices and infra-red devices [4]. The advantages of chemical routes over other assortment strategies are: (a) Easier control of the oxidation states, (b) Ability to make nanostructures of altered sizes and shapes, (c) Relatively inexpensive. Wang et al., [5] suggested the 1-D nanomaterial of CdS/ZnS. previously explored with the ZnS Synthesized nanoparticles through facile CTAB aqueous micellar solution route [6]. It has been observed that nanocomposite with a dopant in their crystal lattice can demonstrate dissimilar from those with ones on their surface. The process of adding impurities to host material is one of the most important goals for attainting novel physical properties in Transition metal (TM) doped nano-sized semiconductors. From last ten decades, many experimental investigations have been carried out to synthesis and characterized different kinds of composite structure such as ZnO/ZnS [7], ZnO/CdS [8], GaN/GaP, ZnO/TiO2 [9,10], PbSe/CdSe [11, 12], ZnS/CdS [13- 18], CdS/ZnS [19-21] and Ge/Si[22].The better activity of the ZnS/CdS compound is due to the response of pictures in the visible region and electron separation. In recent years, TM doped II-VI semiconductors have been investigated comprehensively because of their wide range appliances in electroluminescence devices such as LEDs, optical sensors, etc., In this paper, ZnS and CdS are of particular interest because these wide-band-gap semiconducting substance they have a capable choice of applications, such as sensors, photodetectors, solar cell, and electronic devices. The prepared Co^{2+} doped ZnS-CdS compound by co-precipitation method is to precipitate the chemical from scrap substances in the wastewater by adding together a reagent, which forms a mysterious composite with the to- be-removed matter. Positive ions such as (heavy) metals, but also negative ions like phosphates and sulfates, can be removed via precipitation in air pressure with 300K of a substrate at source temperature. The synthesized and Co^{2+} doped ZnS-CdS composite nanopowder was prepared by using an aqueous solution of sodium sulfide, Zinc acetate dehydrates, Cadmium acetate and ethanol, respectively. The mixture was stirred magnetically at 80^0C. In the presence of TM-doping, it is found that the stabilities of cubic structures. In this article, we are going to present the research work in the area, in which, to the high quality of our information nobody has suggested earlier. The research work consists of a synthesis of Co^{2+} doped ZnS-CdS composite nano-powder effect of co^{2+}concentration on their investigations. However, all the deposition process has a major effect on structural, electrical, energy band gaps, optical and magnetic properties of Co^{2+} doped ZnS-CdS composite nanopowder

2. Experimental techniques

The fabrication of complex nanopowder is characterized by a powder X-ray diffraction pattern of the produced sample is recorded on SHIMADZU XRD-6100 diffract meter. A material band is that the tiny fraction of occurrence emission fascinated by the matter more than a collection of frequencies. Optical Absorption (UV-VIS) band be taken from the JASCO-67 Spectrophotometer in the wavelength region of 200-1400 nm. Light radiation from any composition of material after the incorporation of photons acquired from (PL) spectrum consideration result grasp out from Horiba Jobin-Yvon Fluorolog-3 Spectra of fluorimeter with (450 W) Xe stable and pulsed (35 W) lamps as excitation. Fourier Transformed Infrared (FT-IR) spectrum was recorded by using KBr pellet on SHIMADZU IR Affinity-IS in the wavenumber order from 4000-400 cm^{-1}. The EPR spectrum was preference attentive from JEOL JES-TE 100 EPR spectrometer functioning at X-band frequencies and possesses a100Hz frequency inflection. The magnetic interconnections were carrying out with the vibrating sample magnetometer (Lakeshore7404). The microstructural descriptions are recorded by using SEM: CARL ZEISS EVO18. To regulate the morphological view of the sample is shaped from EDX interfaced with SEM analysis. The TEM images are approved out by using the TEM HITACHI H-7600 device and CCD CAMERA arrangement AMTV-600 by spreading samples in ethanol 100-kHz field modulation. The magnetic hysteresis loop was obtained from a Lake Shore 7407 vibrating sample magnetometer (VSM).

3. Experimental Results and discussion

3.1. Materials & description

All chemical reagents exit scientific grade and were purchased from Merck Chemicals, India. The new synthesized route of a Co^{2+} doped ZnS-CdS composite nanopowder has the following reagents had been considerably Zinc acetate Zn $(CH_3COO)_2$, Cadmium acetate Cd $(CH_3COO)_2$, Vanadium(V_2O_5), Sodium sulfide (Na_2S), Ethanol and De-ionised water

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3.2. Preparation of ZnS-CdS composite nanopowder

The formation of ZnS and CdS nanoparticles can be noted by variation in color of the solution from colorless to milky white to pale yellow respectively which confirmed by a two-step chemical method.

Step-1

The composite nanopowder ZnS-CdS has been successfully prepared via a co-precipitation procedure. In the classical approach, 0.2 mol% of Zn $(CH_3COO)_2$ in 50mL identical mass of the water-ethanol mixture and equivalent molar quantity of Na2S aqueous solution were mixed drop by drop. The obtained solution was stirred magnetically for a homogeneous solution for 80°C. Finally, a milky white precipitate appears under the room temperature condition which designates the assembly of ZnS nanoparticles.

Step-2

Cadmium acetate (0.09mol %) is added to 50mL equivalent volumes of the water-ethanol matrix with steady stirring. Subsequently, ten min (0.1mol %) 50 mL Na_2S of the mixture was added to the above-prepared product dropwise. After 4h constant stirring, the colorless solution changed into yellow-colored precipitate formed which specifies the construction of ZnS-CdS composite nanopowder. Lastly (0.01) mol% of Co^{2+}melted in 50 ml identical volumes of a water-ethanol matrix. This is added to the above colloidal suspension and stirred for 3h. The nanocomposite emulsion was purified with deionized water repeatedly to take apart surplus contaminants. The acquired compound was kept in an ultracentrifuge at 10000 rpm for half an hour. The fine precipitate was dried in a hot furnace at for 2h at120°C and granulates with agate motor by hand milling. The synthesized Co^{2+} doped ZnS-CdS composite nano powder was characterized by various techniques.

3.3. Results & discussion

3.4. X-ray diffraction (XRD) study:

X-ray diffraction present in the formation of concerning the arrangement about crystalline materials and synthesized Co^{2+} doped ZnS-CdS composite nanopowder was determined by X-ray diffractometer from 10° - 70° as shown in Fig.1.There is a strong and intense peak that occurs at $2\theta=27.40^{o}$. The diffraction peaks of ZnS-CdS composite nanopowder match with standard (JCPDS card, No's. 05-0566 for ZnS & 80-0019 for CdS). Upon doping, no secondary reflections were noticed to designate the cubic phase of ZnS and CdS structures and are not disturbed by cobalt substitution which shows that there are no impurities present in the sample. This is an indication of Co^{2+} ion occupying the lattice site rather than interstitial ones.

ZnS consists of five important peaks of and the discrepancy of d-spacing with corresponding (h k l) planes for cobalt substitution are (1 1 1) 3.1269Å, (2 0 0) 2.7079 Å, (2 2 0) 1.9147 Å, (3 1 1) 1.6329 Å, and (2 2 2) 1.5634 Å. Similarly for CdS showed three broad peaks are assignable to the digression of d-spacing with corresponding (h k l) planes (1 1 1) 3.3348 Å, (2 0 0) 2.8880 Å, and (2 2 0) 2.0421

Å, respectively. The nature of the nanopowder particles confirmed by broad X-ray peaks, the mean grain size was obtained using Debye Scherer's formula.

$$\mathbf{D = (K\lambda / \beta\, Cos\theta)} \qquad \mathbf{(1)}$$

From the above equation, the constant λ is the wavelength x-ray Cu-Kα irradiation (λ = 1.5405A0), K = (0.9) is a shape factor and 'θ' is the angle of diffraction and β is the full width of the diffraction peak at half maximum (FWHM). From the surface scattering of nanoparticles, the Co^{2+} doped ZnS-CdS composite nano-powder particles are of small size. Due to the initiation of Co^{2+} atoms in the present lattice decrease in intensity, high FWHM may be expected and the X-ray peaks shifted slightly towards higher angle '2θ' which leads to a reduction of lattice constant it may be attributed to a lowering in grain size. The lattice parameter of 'a' the unit cell for the cubic structure was evaluated by

$$\frac{1}{d_{hkl}^2} = \frac{h^2+k^2+l^2}{a^2} \qquad \mathbf{(2)}$$

The constitutional parameters such as microstrain (**ε**) and dislocation density (*δ*) values were considered from the following interrelation. The dislocation density (**δ**) was deliberated using formula $\boldsymbol{\varepsilon = \beta \cos\theta / 4}$ and $\boldsymbol{\delta = 1/D^2}$ respectively. From Scherer's formula, the evaluated value of crystallite size and dislocation density were found to be D = 10.42nm, 0.056, and 9.20 X 10^{15} lines/m^2 respectively. Williamson and Hall (W–H) indicate a formula to study both the crystallite size and microstrain of the prepared sample.

$$\boldsymbol{\beta\ Cos\theta = (0.9\lambda/D)\ + 4\varepsilon Sin\theta} \qquad \mathbf{(3)}$$

W-H plot of 4sinθ against βcosθ as shown in Fig. 2. The slope of the line provides the microstrain (**ε**) and the intercept (kλ/D) of the line represents crystallite size (D). From the W–H method crystallite size, microstrain, and dislocation density were found to be D = 10.66nm, 0.078 and 8.80 X 10^{15} are lines/m^2 respectively. These values are well coordinated with that acquired from Debye-Scherer's equality.

4. SEM with EDX study:

SEM shows the typical morphology of the grains is distinguished to be nearspherical and is more consistent throughout the analyzed region in the sample. The present sample can be observed that a spherical-like nanostructure with uniform size and also reveal the striking difference in the surface roughness of the present sample as shown in Fig.3. The molecule size of the specimen produced via co-precipitation method was in synchronization with that of the x-ray diffraction and is in the order of nanosize. Compositional analysis of the Co^{2+} ions doped ZnS-CdS composite nanopowder done by EDX and are displayed in Fig. 4 brings out the presence of the atomic weights percentages of sulfur (45.51%), cobalt (0.23%), zinc (27.37%) and cadmium (27.89%) peaks, with no other relevant elemental composition are present in the sample. This shows that the augmentation in the concentration of EDX. The co-precipitation method undergoes a beneficial conclusion in command of the stoichiometry of the Co^{2+} doped ZnS-CdS composite nanopowder.

5. TEM study:

The microstructures of the arranged sample were further studied using TEM. TEM images were obtained by dispersing the powder in ethanol by ultrasonic vibration. The powder sample in ethanol with the assistance of ultrasonic vibration it may be seen that the cobalt doped composite nanopowder became formed from extremely nice spherical grains that were loosely gathered. The TEM images of Co^{2+}doped ZnS–CdS composite nanopowder were shown in Fig. 5. The uniform Co, Zn, Cd, S particles have spherical-like shapes with weak accumulation. The average particle size is around 20nm. It is in the order of nanoscale. These results conclude that the average calculated particle size from the XRD studies coincides with that of TEM micrographs.

6. FT-IR study:

Fig.6 shows the spectral bands of Co^{2+} doped ZnS-CdS composite nano-powder 400-4000 cm^{-1}. It exhibited several bands of stretching and bending mode of assignments followed by Zn-S, Cd-S, C-H, O-H, C=O, H-O-H, and O-H band. The vibrational modes notice at 445cm^{-1} are assigning to the Cd-S [23] and a feeble at 606cm^{-1} of Zn-S due to a smaller amount of ZnS in the prepared material [24]. The band detected at 1113 cm^{-1} is allocated to the O-H stretching approach of the H_2O molecule [25]. The loop at 1362 cm^{-1} matches up with C-H bending vibrations.[26] The observed band at 1531cm^{-1} has been given to the extended mode of the C=O family [27]. The band at 1634 cm^{-1}is ascribed to the H-O-H flexible mode of vibration. The band observed at 3454, 3740, 3865 cm^{-1}is imputed to the resonance bands of O-H Stretching [28].

7. UV-Vis absorption study:

Free ion Co^{2+} (d^7) has an electronic configuration [Ar]$3d^7$, Which offers the high spin records approximately the unbound ion terms ^4F, ^4P, ^2G, and several other doublet terms. In a weak octahedral (o_h) crystal field, the terms ^4F and ^2G split in to $^4T_{1g}(F)$ + $^4T_{2g}(F)$ + $^4A_{2g}(F)$ and $^2A_{1g}(G)$ + $^2T_{1g}(G)$ + $^2T_{2g}(G)$ + $2_{Eg}(G)$ respectively, whereas 4P converted as $4T_{1g}(p)$ among all these states and the ground state is $^4T_{1g}$ (F). In the octahedral crystal field, the term $4T_{1g}$ (F) occupies lowest-energy state and in strong crystal field (Dq =1500 cm^{-1}) ^2Eg (G) is the ground state. For the existing case, the crystal field parameter Dq =950 cm^{-1}. However, the ground state continues to be $4T_{1g}$ (g). Theoretically, the energy transitions are $^4T_{1g}$ (F) $\rightarrow$ $^4A_{2g}$ (F):ϑ_2 and 4T1g (F)$\rightarrow$$^4T_{2g}$(F):$\vartheta_1$ is almost constant and varies from 1.9 to 2.2 [29, 30].

Optical absorption luminosity of Co^{2+} ions doped ZnS-CdS composite nanopowder illustrated in Fig.7.The spectrum consists of four intense peaks at 1196, 676, 560, and 512nm (8369, 14784, 17869, and 19538 cm^{-1})respectively. This exists functional bands of Co^{2+} ions in octahedral site consistency. The octahedral symmetry of Co^{2+} ions confirmed by x-ray diffraction studies as the band positions ratio, J_2 toJ_1 is nearly equal to 2.132. The fitted Inter-electronic repulsion (B and C) parameters are given by Dq = 950, B = 820 also C = 3500 cm^{-1}. These band positions provide a significant fit for the experimental positions.

8. EPR study:

EPR Spectroscopy is a very sensitive and enlightening technique has been exploited for the investigation of various paramagnetic species in solid or liquid states. The spectrum of the present sample is characterized at 300K. Moreover, the octahedral coordination of Co^{2+} ions have longitudinal relaxation time is extremely low. However, at high temperatures, the spectrum becomes broader due to low relaxation time [31]. In perfect octahedral symmetry, the lowest of an orbital quantum state of d^7 Configuration is divide by spin-orbit combination to provide a ground state Kramer's doublet with g = 4.33[32]. In the current research, the EPR spectrum of Co^{2+} doped ZnS–CdS composite nanopowder exhibits resonance signal around g = 2.5 at 100K as shown in Fig.8 which suggests that the Co^{2+}ion resonance signal is due to unsystematic allotment of distortions in octahedral symmetry.[33-36]. By estimating EPR and optical amalgamation spectral data, the covalence constraint (k_o) is determined by [37]

$$\mathbf{g = \frac{10}{3} + k_o - \frac{15}{2}(\lambda/\Delta)} \qquad \mathbf{(4)}$$

and pure ionic bonding respectively. The estimated and the calculated value of k_o is 0.92 namely where the spin-orbit pairing stable value λ ($-178cm^{-1}$) and g is the observed g-factor and the energy difference 'Δ' between the transitions is

$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$. Notionally k_o value repose in the middle values of 0.5 and 1.0, the maximum value of pure covalent the indication of the bonding stuck between Co^{2+} ions and its ligands are practically covalent complexion.

9. Photo Luminescence study:

Fig.9 depicts the recorded fluorescence spectrum with a λ_{ext} =310 nm on Co^{2+} doped ZnS- CdS composite nanopowder. The luminescence peak exhibits four intense wavelength emission on 375nm (3.30eV), and 532nm (2.33eV), 680nm (1.87eV) and 735nm (1.68eV). Due to the visible broadband region of 500-800nm transition metal ions were widely used [38]. The emission at 375nm (3.30eV) which may possibly be recognized to a combined charge at the sulfur interstitials and donor level with holes restrained at the Zinc vacancies on acceptor level [39]. A sharp yellow emission at 532 nm (2.33eV) is attributed to the characteristic of cobalt [40]. A red emission at 680nm (1.87eV) confirms the CdS peak [41] and the sharp and most intense peak at 735nm (1.69eV) gives orange-red emission in the NIR region [42, 43-45]. In general, the role of surface quality, surface defects of the composite material is very important in terms of emission characteristics towards the optical application. The stoichiometric defects at electronic levels are influenced by photoluminescence in II-VI semiconductors. The present strong tip at 532nm is due to the energy transition from $^4A_{2g}$ (F) → $^4T_{1g}$ (F) for Co^{2+} ions.

9.1 CIE coordinates

The CIE chromaticity diagram is used to visualize the color Gamut's (i.e. the ranges of producible colors) for various output devices.

The CIE Chromaticity diagram

The commission International de'Eclariage (CIE) in 1931is an additional base in terms of major values are X, Y, and Z, which permits to counterpart all observable colors as a linear combination with high-quality coefficients only. The main three primary shades the main colors of a television screen in the visible spectrum are represented on the chromaticity figure by a triangle combination of the coordinates for the main primary three colors. In the current investigation, the proposed values of chromaticity coordinates are ($x = 0.32$, $y = 0.39$) and are indicated by a dark dot (.) and these values determined with the NTSC criterion CIE chromaticity synchronized values. The dark spot on the Chromaticity graph represents the reddish-yellow locations shown in region Fig. 10. The correlated color temperature (CCT) is intended by McCamy relation [46]

$$\mathbf{CCT = -449\ n^3 + 3525\ n^2 - 6823.3n + 5520.33} \qquad \mathbf{(5)}$$

Where $\mathbf{n = (x-x_e)/(y-y_e)}$ is converse slope line with $(x_e, y_e) = (0.3320, 0.1858)$. Mentioned CCT is a sign of a color form of the light emitted utilizing the light source from 5000 to 20,000 K may be executed to circadian lights. Generally, CCT significance greater than 5000 K shows cold white light used for a commercial light purpose and less than 5000 K suggests warm white light used for home applications [47]. In the present investigation, CCT value is 5783K which indicates cold white light emission.

10. VSM

Fig.11. Shows, ferromagnetic hysteresis loops for Co^{2+} doped ZnS-CdS composite nanopowder. The calculated values of coactivity (H_c) = 526.28G, remnant magnetization (M_r) = 94.103× 10^{-6} emu/g and the saturation magnetization (Ms) = 423.07× 10^{-6} emu/g, The accumulation of cobalt ion creates more imperfect sites and the unbalanced spins in Co^{2+}ions which may be responsible for the magnetic behavior of the host lattice. Both transition metals additionally defects are responsible for the magnetic exchange. In a recent study understand the Co–VO (valance) pair imperfection [48] because the maximum possible possibility for the near-RT FM in Co^{2+} doped ZnO and exhibit that such center can surely 'S' stimulate to long-range coupling, but, the desired absorption of such defects are significantly excessive and the estimated T_c is also under 300 K. The exchange interactions between Co^{2+} ions mediated by carriers contribute at room temperature results the ferromagnetism exhibits enough to the existence of defects such as impurity defect, vacancies or hydrogen chemical adsorption, grain boundaries and dislocation have been induced magnetism [49] The sp–d interchange requires the well-built interaction concerning to local d-type electron of transition metal ions and the contained s or p band electron found in Zn or C atom [50].

4. Conclusion

In summary, Co^{2+} doped ZnS-CdS composite nanoparticles were successfully synthesized via chemical precipitation technique. Powder X-ray diffraction pattern revealed the structure was cubic. From diffraction data, the average grain size was estimated from Scherer's method and W–H plots which are in the sequence of nanoscale. Our result is evident that the decrease in structural parameters confirms a slight increase in crystallite size after the deposition of CdS. SEM with EDAX and TEM images appear homogeneously dispersed sphere like composition. FT-IR scale showed the characteristic resonance manner of Zn, Cd, O–H, sulfide ions together within-host lattice. Optical and EPR spectrum established that the doped Co^{2+} ion free at deformed octahedral site equilibrium for which crystal field (Dq) and inter-electronic repulsion (B, C) constants are estimated. The optical absorption spectra (UV–Vis) reveals and established the efficiency of the Co^{2+} doped ZnS-CdS composite nanopowder the analyzed, crystal field and bonding parameters show the bonding nature is moderately covalent. PL spectra of powder sample suggest that the tough yellow light emission with suppressed red color emission is a successful method to improve the optical properties. The obtained CIE color chromaticity values indicated that this sample can be used for a White -LED appliance. The exchange interaction between Co^{2+} ions mediated by carriers contribute to the ferromagnetism at room temperature exhibits due to the existence of defects such as impurity defects, vacancies or hydrogen chemisorption grain boundaries and dislocation have been induced magnetism.

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