

Photo-Physical and Chemical Properties of $\text{Ca}_{1-x}\text{Fe}_x\text{S}$ and $\text{Ca}_{1-x}\text{Cd}_x\text{S}$ Nanocrystals

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ABSTRACT

Semiconductor nanophosphors are currently considered to have smart technological applications in opto-electronic devices due to their size tunable properties. Intrinsic and extrinsic (doped with transition metal elements) Pure and doped CaS nanocrystals have been synthesized by facile solid state reaction method. Synthesized nanocrystals are further etched with mild acid solutions to reduce the particle size, which augments the surface to volume ratio and confinement of carriers. Powder X-ray diffraction (XRD) has been used to investigate crystallography of synthesized nanomaterials. Optical characterization of synthesized nanomaterials has been done by UV-vis. absorption spectroscopic studies. The photo-catalytic activity of synthesized nanomaterials under UV irradiation has been tested using methylene blue (MB) dye as a test contaminant in aqueous media. Photo-catalytic behavior dependence on dopant concentration and etching has been thoroughly studied to explore the potential of these synthesized nanomaterials for next era optoelectronic industrial applications as well as polluted water purification.

1. Introduction

Doping impurities into nanocrystals enables the introduction and tuning of optical electrical and magnetic properties [1-3]. Successful nanocrystal doping requires an understanding of doping process and the development of new doping strategies.

In 1976, Vij et al [4] made a study of the cathodoluminescence of CaS:Ce phosphor. They studied the emission spectra of CaS: Ce phosphors using ultraviolet and 20 kV electron beam excitation. In 1980, Marwaha et al [5] studied the uv dosimetry by thermoluminescence of bismuth doped CaS. In 1982, Bhatti et al [6] made a study on the relaxation processes in optical and photoconducting materials using pulsed nitrogen laser. In 1984, Bhushan and Chandra [7] investigated the electroluminescence and photoluminescence of CaS: Cu, Er and CaS: Cu and explained the emission spectra on the basis of the Williams-Prenner model. In the same year, Pillai and Vallabhan [8] made a study of the electroluminescence spectrum of CaS: Er phosphor and the energy level splitting in Er^{3+} ions. In 1988, Bhatti [9] studied N_2 -laser excited time resolved spectroscopy of (Fe, Co, Ni) doped CaS and ZnS phosphors. In 1998, Gong et al [10] compared the photoluminescence and upconversion optical properties of the CaS: Sm^{3+} nanocrystallites with that of macrocrystallites. In 2000, Jia et al [11] examined the trapping processes in CaS: Eu^{2+} , Tm^{3+} . Thermoluminescence was measured under different excitation and thermal treatment conditions. In 2001, Xiaolin et al [12] excited the CaS: Eu^{2+} materials prepared by using sulfur-flux method. In the same year, Zhi-yi et al [13] examined the optical absorption spectra of CaS: Eu, Sm at several concentrations of Eu (from 0 to 0.05 mol %) to clarify the electron trapping mechanism for its photo-stimulated luminescence. In 2002, Sun et al [14] synthesized and characterized the strongly fluorescent europium doped calcium sulfide nanoparticles. Nanometer-sized europium-doped calcium sulfide (CaS-Eu) particles were synthesized for the first time for potential use in bioassays, in particular, in biochip-based analysis through a wet chemical process in ethanol. In the same year, Wu et al [15] investigated the delayed photoluminescence (DPL) and infrared-stimulated luminescence (ISL) spectra of Eu^{2+} and Sm^{3+} in CaS: Eu, Sm and found that Eu^{2+} and Sm^{3+} show different characteristic luminescence in DPL and ISL. In 2003, Chen et al [16] measured the hydrostatic pressure dependence of the emission of CaS doped with Eu^{2+} . In 2004, Bhatti et al [17] investigated

the effect of of killer impurities (Fe, Co and Ni) on excited state life-times in CaS phosphors, doped with copper and having variable concentrations of iron, cobalt and nickel. In 2005, Chen et al [18] determined the temperature dependence of PL and ISL in CaS: Eu, Sm between 100 and 700 K.

In the same year, Singh et al [19] prepared CaS phosphor activated with Dy ions by the solid-state diffusion method. In 2006, Bhatti et al [20] made a study of fast luminescence decay processes of doped CaS phosphors. Singly and doubly doped CaS phosphors have been synthesized using the flux method. In the same year Bhatti et al [21] studied the enhanced photoluminescence decay processes of doped CaS phosphors at low temperature. CaS phosphor samples singly doped with Mn impurity and doubly doped with Mn and X (X=Fe, Co and Ni) have been synthesized using a flux method. In 2006, Kumar et al [22] studied the irradiation effect on bismuth doped CaS nanocrystalline phosphors and their possible applications to solid state dosimetry. They used the wet chemical co-precipitation method for the preparation of nanocrystallites and concluded from the results that the TL glow curve shifts to higher temperature in nanocrystalline phosphors. During the same time, Kumar et al [23] used the wet chemical co-precipitation method to synthesize CaS:Bi nanoparticles and obtained the nanoparticles having an average diameter of 30–35 nm. At the same time Kumar et al [24] discussed the thermoluminescence (TL) studies of CaS: Bi nanocrystalline phosphors prepared by the wet chemical co-precipitation method and exposed to γ -rays. In 2007, Kumar et al [25] prepared the CaS:Bi nanocrystalline powder of average grain size 35 nm by wet chemical co-precipitation method and irradiated with 100 MeV oxygen ions at fluences between 1×10^{12} and 1×10^{13} ion/ cm^2 .

CaS host material doped with rare earth ions, transition ions and even closed shell ions has attracted much attention as a good phosphor that has been studied since 1971 with potential use in cathode ray tubes, TV screens, fluorescentscreens, fluorescence lamps and thermo luminescence dosimetry. By controlling crystalline size or doping with luminescent ionic centres, one can tailor the optical properties of the nanocrystallites. Calcium sulphide has long been investigated for its interesting photoluminescent and thermo-luminescent properties. AESs doped with rare earth ions and transition metal ions are used for alternating current thin film electroluminescent devices and for optical data storage applications. Iron-doped and cadmium doped calcium sulphide nanoparticles have been newly developed and studied for the purpose of hyperthermia due to their promising magnetic properties. The stability, tenability and higher efficiency of the luminescent nano crystallites may

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replace all existing bulk phosphor in the future. For instance, it has been shown that smaller the particle size, higher the screen resolution and lower the screen loading.

In the present investigations emphasis has been given to explore the photo-catalytic activity potential of $\text{Ca}_{1-x}\text{Fe}_x\text{S}$ and $\text{Ca}_{1-x}\text{Cd}_x\text{S}$ ($0 \leq x \leq 0.1$) nanocrystals synthesized via facile solid state reaction method. The photo-catalytic behavior of synthesized nano photo-catalysts have been studied by recording MB dye degradation in aqueous media under UV radiation exposure. Photo-catalytic activity dependence on the nanocrystals morphology and dopant concentration has been thoroughly studied.

2. Experimental Methods

$\text{Ca}_{1-x}\text{Fe}_x\text{S}$ ($0 \leq x \leq 0.1$) nanocrystals have been synthesized by the solid state diffusion method. Analytical reagent (AR) grade chemicals; calcium sulphate, ferric nitrate, sodium thioisulphate, carbon powder and ethanol were used as the starting materials without further purification. Carbon acts as a reducing agent for the reduction of sulphate to sulphide at high temperature, and iron acts as an activator. Sodium thioisulphate acts as flux for the reaction. The calculated quantities of calcium sulphate, carbon powder, ferrous sulphate and flux were mixed thoroughly with the help of agate pestle and mortar. For the uniform distribution of dopant, initially dopant precursor was dissolved in small volume of ethanol, and then this solution was mixed with the entire charge. Then, the resulting mixture was transferred to a clean graphite crucible (which was already baked at the firing temperature) and a thin layer of carbon powder spread over it. The charge in the crucible was covered with another similar crucible. The thin layer of the carbon over the charge created a reducing environment at high temperature. This whole arrangement was placed in the muffle furnace, and the charge was fired at 950°C for two hour. Firing at high temperature causes the incorporation of iron in the host lattice. After two hour, the red hot charge was taken out and rapidly crushed. Finally, the prepared powder sample was collected in dry sample tubes for further studies. For the further reduction of the particle size, the synthesized samples were etched with dilute hydrochloric acid. The particles were dispersed in etching solution (HCl aqueous solution) using mechanical stirring. The solution was allowed to settle for a couple of minutes. Then, the etched nanoparticles were collected by centrifugation and redispersed in ethanol. Then these particles were dried in vacuum oven at ambient temperature for further studies. For $\text{Ca}_{1-x}\text{Cd}_x\text{S}$ ($0 \leq x \leq 0.1$) nanocrystals all experimental steps are same as for Fe doped CaS except different dopant precursor.

Crystallographic characterization of synthesized materials has been done by powder X-ray diffraction (XRD) pattern recorded for pure CaS in 2θ range 20° – 70° keeping step size 0.0171 at generator tension 45 kv and generator current 40 mA . The phase identification from the recorded diffraction pattern has been carried out with the help of standard JCPDS database (and also known as ICDD database). Average crystalline size calculated from scherrer formula.

The photo-catalytic activity of synthesized $\text{Ca}_{1-x}\text{Fe}_x\text{S}$ ($0 \leq x \leq 0.1$) nanocrystals was studied by monitoring the degradation of methylene blue (MB) ($\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S} \cdot 2\text{H}_2\text{O}$) dye in an aqueous suspension containing nanocrystals under the UV-radiation exposure with continuous magnetic stirring. A 350 mL of aqueous suspension was prepared by completely dissolving 1.1322 mg of the MB dye and then dispersing 140 mg of the $\text{Ca}_{1-x}\text{Fe}_x\text{S}$ nanocrystals in the deionized water. The resulting suspension was equilibrated by stirring in the dark for 1 h to stabilize the adsorption of MB dye on the surface of nanocrystals. The stable aqueous suspension was then exposed to the UV-radiation with continuous magnetic stirring, using the home made photoreactor containing two 18 W tubes as the UV-source ($\lambda = 200 - 400\text{ nm}$). Following the UV-radiation exposure, 10 mL sample of aqueous suspension was taken out after every 10 min interval for the total 80 min of the UV-radiation exposure. Suspension sample was centrifuged to filter out the nanophoto-catalyst particles, then nanophoto-catalyst free aqueous dye solution was examined using UV-vis absorption spectrophotometer (Hitachi U-2900) to study the photo-degradation of the MB dye.

For band gap analysis, 0.01 g of sample was dissolved into 10 mL distilled water and was kept in sonication machine for 1 hr . Then the solution was examined in Ultraviolet Spectroscopy. The reading was noted and the graph was plotted between absorbance and wavelength. The band gap was calculated with the relation $E = h\nu = hc/\lambda$.

3. Result and Discussion

Nominally broadened XRD patterns have been recorded for the synthesized $\text{Ca}_{1-x}\text{Fe}_x\text{S}$ samples. Fig. 1 shows X-ray diffractograms recorded for pristine CaS nanocrystals. Recorded diffractograms confirm the

formation of nanocrystallites. Average crystalline size of pure CaS nanoparticle calculated from Scherrer formula comes out to be 57.2 nm .

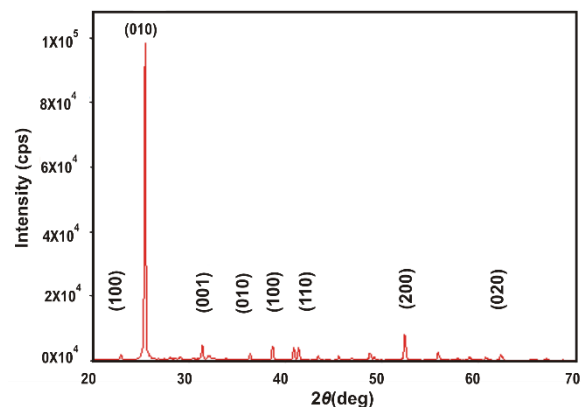


Fig. 1 XRD pattern of pure CaS nanocrystals

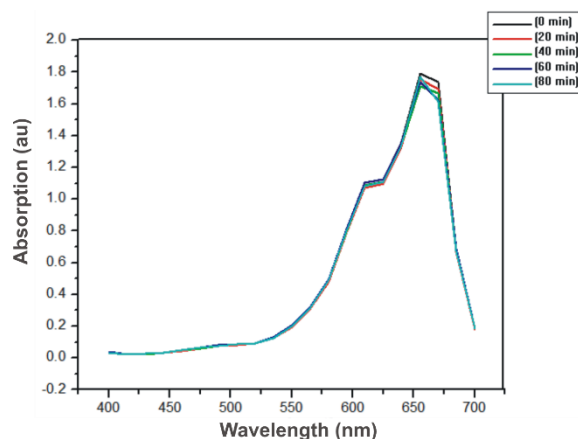


Fig. 2 Absorption spectra of pure CaS

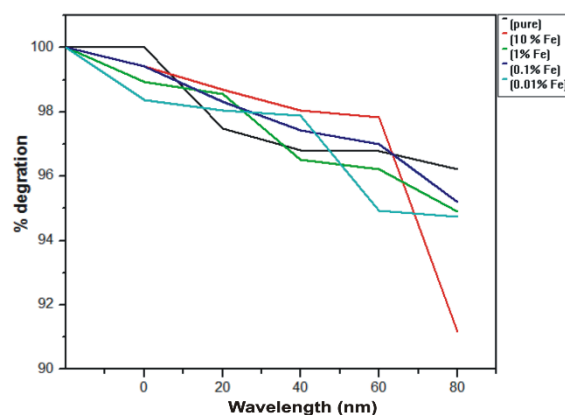


Fig. 3 Percentage of degradation of CaS doped with Fe

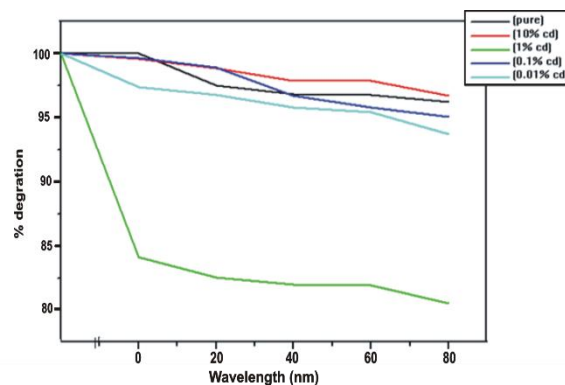


Fig. 4 Percentage of degradation of CaS doped with Cd

3.1 Photo-Catalytic Activity

Fig. 2 shows the absorption spectra of the MB dye solution in the presence of pure CaS nanocrystals for different durations of UV radiation exposure. Fig. 3 and Fig. 4 shows the absorption spectra of dye solution for different durations of UV-radiation exposure in the presence of Fe doped and Cd doped CaS nano-photocatalysts at different doping concentrations. Decrease of absorbance with increasing irradiation time shows the efficient degradation of MB dye; hence the synthesized nanocrystals have excellent photo-catalytic activity potential to purify the dye contaminated water.

3.2 Energy Band Gap Analysis

Fig. 5 and Fig. 6 shows the UV-visible absorption spectra of $\text{Ca}_{1-x}\text{Fe}_x\text{S}$ ($0 \leq x \leq 0.1$) and $\text{Ca}_{1-x}\text{Cd}_x\text{S}$ ($0 \leq x \leq 0.1$) nanocrystals respectively.

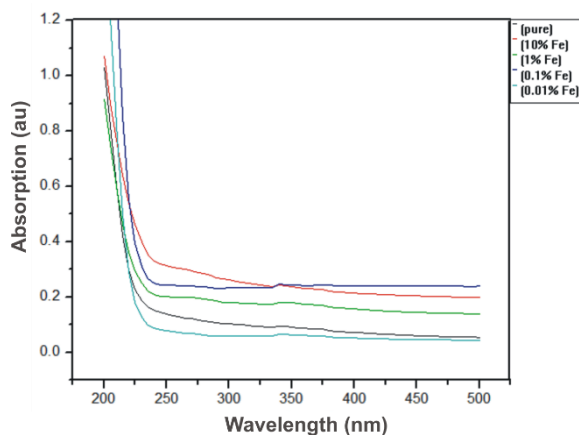


Fig. 5 UV-vis absorption spectra of Pure CaS and doped with Fe

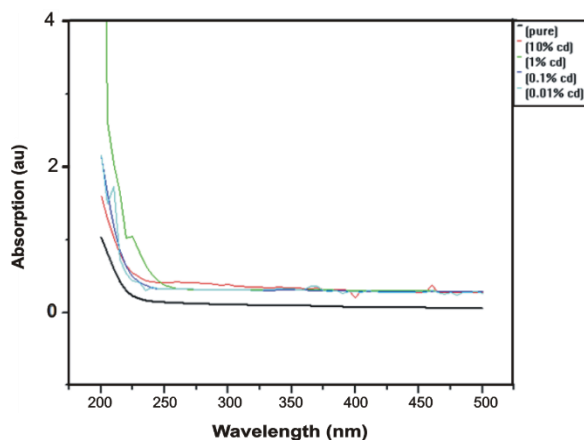


Fig. 6 UV-vis absorption spectra of Pure CaS and doped with Cd

From the calculation from the graph we calculated the band gap. Band gap of Pure CaS is 4.5 eV and with doping it decreases.

3.3 Band Gap with Tauc's Relation

The optical band gap of Nano composite has been determined at different concentration of iron and cadmium (Figs. 7-8) respectively from fundamental absorption edge of UV-visible spectra. The shift of absorption edge in UV-visible spectrum is correlated with optical energy band gap by Tauc's relation (Fig. 5) and the same is revealed by Table 1.

$$\alpha h\nu = B(h\nu - E_g)^n$$

where, α - absorption coefficient
 $h\nu$ - denotes photon energy
 B - Constant
 Index n is connected with distribution of density of states
 For direct allowed transition energy gap $n=2$ and for indirect $n=1/2$

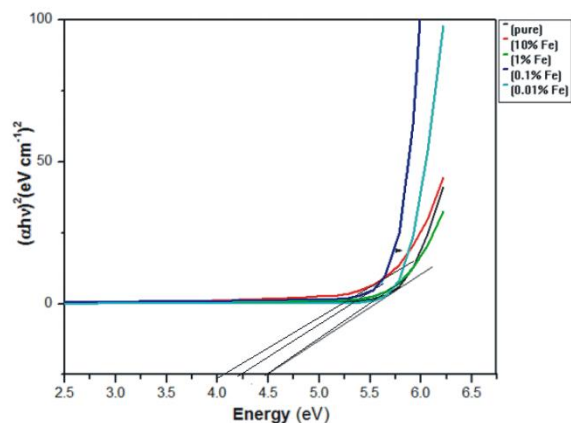


Fig. 7 Tauc's plot of synthesized CaS and Fe doped CaS

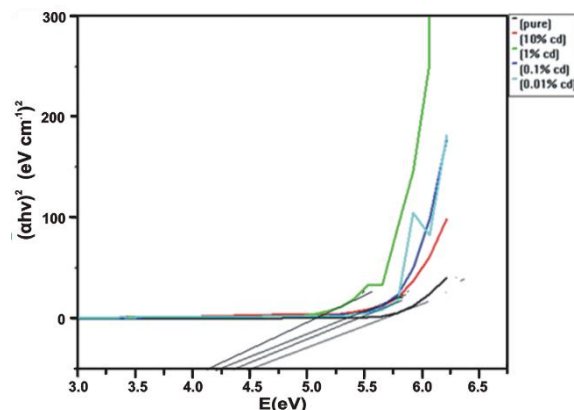


Fig. 8 Tauc's plot of synthesized CaS and Cd doped CaS

Table 1 Band Gap for $\text{Ca}_{1-x}\text{Fe}_x\text{S}$ ($0 \leq x \leq 0.1$) and $\text{Ca}_{1-x}\text{Cd}_x\text{S}$ ($0 \leq x \leq 0.1$) nanocrystals

Nanomaterial	Fe doping (eV)	Cd doping (eV)
Pure	4.5	4.5
10% doping	4.1	4.2
1% doping	4.3	4.3
0.1% doping	4.5	4.4
0.01% doping	4.4	4.4

4. Conclusion

In the present work solid state method have been used for the synthesis of CaS nanoparticle with high yield. From the recorded XRD pattern the crystal structure of pure and doped CaS nanoparticle were found to be wurtzite and average crystalline size of pure CaS 57.2 nm have been found respectively. From the photo catalytic activity it have been proved that the synthesized CaS Nanoparticle act as efficient photocatalyst in UV; therefore used for water purification. From the recorded data of bandgap of pure CaS is 4.5 eV.

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