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RESEARCH ARTICLE

Lead (Pb) doped fluoride nanocrystals: Structural and Optical Properties

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Abstract

The aim of the present study is to investigate the structural and optical properties of Lead (Pb) doped fluoride nanocrystals (CaF_2). Pb (3, 5, 7 and 10 mol %) doped nanocrystals were synthesized by precipitation method and characterized by Powder X-Ray Diffraction (PXRD), Fourier Transform Infrared Spectroscopy (FTIR) and Energy Dispersive X-ray Spectroscopy EDAX. Optical studies (UV-Visible Spectroscopy) were carried out. The PXRD pattern shows the cubic structure of the synthesized material. It is observed that crystallite size and lattice constants were increased by increasing the doping concentration. EDAX spectra shows the presence of Pb. FTIR studies show the presence of hydroxyl groups in the as synthesized samples with two strong IR absorption bands at 3370 cm^{-1} and 1631 cm^{-1}. The optical absorption spectrum of pure and doped samples show a prominent common peak at 264 nm and peaks at 211, 214, 241 and 256 nm for other samples respectively. The optical absorption was found to increase with increase in doping concentration. It is also observed from optical studies of prepared samples that with increase in doping concentration, energy band gap decreases and refractive index increases.

Introduction

Nanotechnology is rapidly emerging field of science. The synthesis and control of materials in nanometer dimensions can lead to new material properties and device characteristics in unprecedented ways. It shows great promise for providing us in the near future with many breakthroughs that will change the direction of technological advances in a wide range of applications [1]. Fluoride nanomaterials are of great interest due to their wide range of applications based on their low energy phonons and high transparency (170-780 nm), which extend to a lower fundamental absorption compared with sulfides and metal oxides [2]. Fluoride compounds are very attractive materials for many potential applications such as advanced phosphors, photonics, display monitors, imaging, light amplification and precursors for transparent ceramic processing [3]. Among the alkali fluoride compounds, CaF_2 is an attractive material because of its high stability and non-hygroscopic behavior. Calcium fluoride (CaF_2) is a well known host for luminescent ions due to its high transparency in a broad wavelength range, low refractive index and low phonon energy. It has a wide band gap and large scale transparency [4]. However, reports on synthesis of Pb-doped CaF_2 nanocrystals and studies of structural and optical properties are very few. In this study, 3, 5, 7 and 10 mol% Pb-doped CaF_2 nanocrystals were synthesized by precipitation method and characterized by PXRD, EDAX, FTIR and UV-Visible spectroscopy.

Material and Methods

Synthesis

For the synthesis of Lead (Pb) doped CaF_2 nanocrystals, the starting ingredients are Calcium Chloride ($CaCl_2$), Ammonium fluoride (NH_4F), Lead Nitrate ($Pb(NO_3)_2$), distilled water and absolute ethanol. Stoichiometric quantities of $CaCl_2$, NH_4F and $Pb(NO_3)_2$ (3, 5, 7 and 10 mol%) were taken in a 250 mL conical flask and dissolved in 100 mL of distilled water. The mixture was stirred for 3 h constantly to achieve homogeneity. During stirring, the transparent reaction mixture transforms into opaque white suspension gradually. After stirring, the solution was centrifuged for 20 min at 3000 rpm and a white residue was obtained. The residue was washed thoroughly with ethanol to remove the residual chloride and ammonium ions. The product was extracted on to a Petri dish and dried slowly in an oven maintained at 100 °C.

Characterization

The XRD measurements of synthesized samples was carried out using a X'Pert Pro PANalytical powder diffractometer with Cu-Kα radiation (λ = 1.54056 Å) in the scan range 20 – 80°. The FTIR spectrum was recorded using SHIMADZU FTIR – 8400S spectrometer with KBr pellets in the range 400 – 4000 cm^{-1}. The quantitative elemental composition analysis was carried out by energy dispersive X-ray spectroscopy (EDAX) system attached with SEM machine of JEOL make MODEL JSM 5810 LV. For the optical study, a small amount of dry powder of synthesized nanocrystals was dispersed in dilute HCl. The UV – Visible absorption spectra of the samples were recorded using SHIMADZU 2450 UV – Visible Spectrophotometer to measure the absorption and to determine the band gap of the prepared samples.

Result and Discussion

Structural and phase analysis (PXRD)

Figure 1 shows XRD pattern of pure CaF_2 nanocrystals prepared by precipitation method. Features of this pattern indicate the presence of a cubic phase for CaF_2 nanocrystals which is a typical structure for fluorides with fm3m spatial groups. Average lattice constant was 5.47222 Å calculated from 2θ values, which is in agreement with the recorded data of 5.4629 Å from JCPDS Card no. 75 – 0363. The sharp diffraction peaks confirm the high crystallinity of the synthesized CaF_2 nanocrystals. The average crystallite size was calculated from Debye – Scherer formula and found to be 53 nm. Figure 2 shows XRD patterns of Pb (3, 5, 7 and 10 mol %) doped CaF_2 nanocrystals. The diffraction peaks correspond to different hkl values of Pb doped CaF_2 nanocrystals and was compared with the JCPDS card no. 75 – 0363, 36 – 1462, 84 – 0323 and 12 – 0067. It is clear from Table 1 that with increase of Pb concentration in CaF_2 nanocrystals, the average crystallite size and lattice constant increases. This may be due to the fact that when Ca^{+2} is substituted by a Pb^{+2} ion, charge compensating F^- ions enter the Fluoride (CaF_2) structure in interstitial cubic sites and the electronic repulsion between F^- ions leads to a net increase of the lattice parameter.

Pb doping Concentration (mol %)	Crystallite Size (nm)	Lattice Constant from 2θ values
0 (Pure CaF_2)	53.03464	5.47222
3	57.48069	5.69405
5	63.96423	6.12241
7	94.97849	6.13438
10	97.62945	6.14360

Table 1: Doping concentration, Crystallite size and Lattice constant of Pb doped CaF_2 nanocrystals.

EDAX analysis

The chemical composition analysis of the Pb doped CaF_2 nanocrystals have been carried out using EDAX. Figure 3 shows the EDAX spectra of 3 %, 5 %, 7 % and 10 mol % Pb doped CaF_2 nanocrystals. Peak at about 0.7 keV and 3.67 keV indicates the presence of F^- ions and Ca^{+2} ions respectively. Peaks at about 1.8, 2.4 and 9.2 keV show the doping of Pb^{+2} ions in the CaF_2 nanocrystals.

FTIR analysis

FTIR absorption spectrum was measured to analyze the structural properties and bonds of CaF_2 nanocrystals. Figure 4 shows the FTIR spectrum of as synthesized pure and Pb doped CaF_2 nanocrystals. The spectrum shows two strong IR absorption bands at 3370 cm^{-1} and 1631 cm^{-1}. Both are the characteristics of H – O – H bonding of the H_2O molecules which shows the presence of hydroxyl groups. The band shows peak at 2347 cm^{-1} due to KBr pallets used during record of FTIR spectrum. Peaks at about 1403 cm^{-1} and 3142 cm^{-1} belong to N – O and O – H bonds respectively [5, 6, 7].

Optical studies (UV – Visible analysis)

Figure 5 shows the optical absorption spectrum of (a) pure and (b) Pb doped CaF_2 nanocrystals. The absorption spectrum shows that characteristic absorption peaks are present in the UV region. Figure 5 (a) shows a prominent absorption band with a peak at 264 nm and a weak one at 205 nm. Figure 5 (b) shows the absorption peaks at 211, 214, 241 and 256 nm.

Energy band gap

Figure 5 (c) and (d) shows the energy band gap curve of pure and Pb doped CaF_2 nanocrystals respectively. The energy band gap E_g was obtained from the optical absorption spectra by extrapolating the straight line plot of $(\alpha h\nu)^2$ versus $(h\nu)$ to the energy axis by the method proposed by Wood and Tauc [8]. The energy band gap was found to be E_g = 4.4175 eV for pure CaF_2 nanocrystals (Figure 5 (c)). The refractive index of the synthesized samples was calculated using the following relation between Refractive index (η) and Energy band gap (E_g) [9].

$$\eta = K (E_g)^C$$

Where, K = 3.3668 and C = − 0.32234 are constant. The refractive index of pure CaF_2 nanocrystals was found to be 2.1285. Table 2 shows the calculated energy band gap and refractive index of pure and Pb doped CaF_2 nanocrystals with different doping concentration.

Pb doping Concentration (mol %)	Energy band gap E_g (eV)	Refractive index η
Pure CaF_2	4.4175	2.1285
3	4.4140	2.0862
5	4.4031	2.0878
7	4.3864	2.0904
10	4.3788	2.0916

Table 2: Energy band gap and refractive index of pure and Pb doped CaF_2 nanocrystals with different doping concentration.

It is clear from the Table 2 that with the increasing concentration of Pb, energy band gap decreases and refractive index increases. It is observed that doping of the Lead (Pb) ions in the CaF_2 nanocrystals tends to change the energy band gap of Pb doped CaF_2 nanocrystals, as compared to energy band gap of pure CaF_2 nanocrystals.

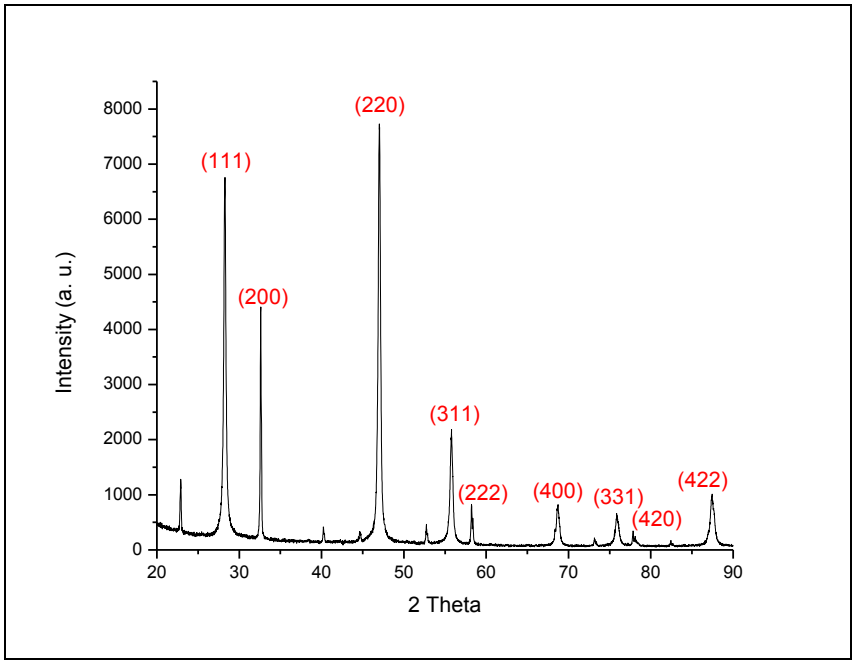

Figure 1: XRD pattern of undoped CaF_2 nanocrystals

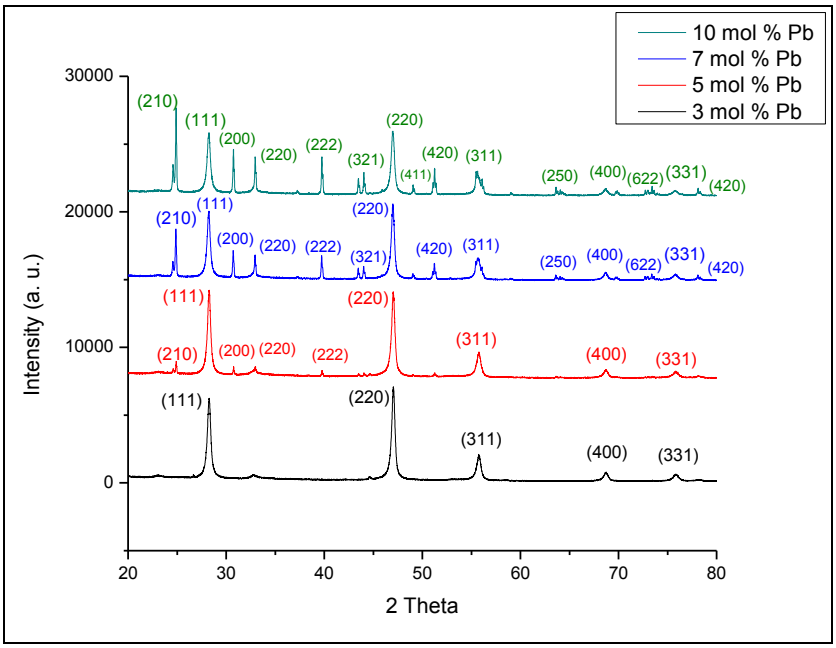

Figure 2: XRD patterns of Lead (Pb) doped CaF_2 nanocrystals with different doping percent.

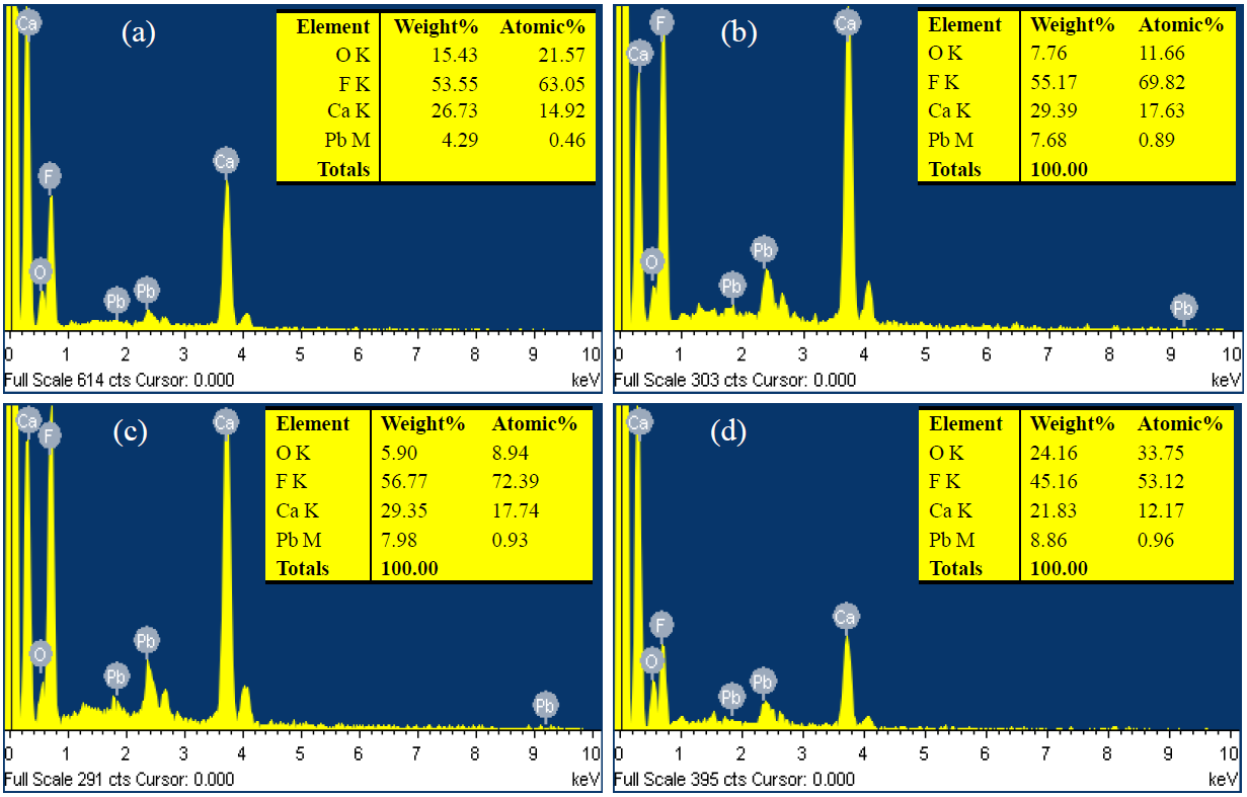

Figure 3: EDAX spectra of (a) 3 mol %, (b) 5 mol %, (c) 7 mol % and (d) 10 mol % Pb doped CaF_2 nanocrystals.

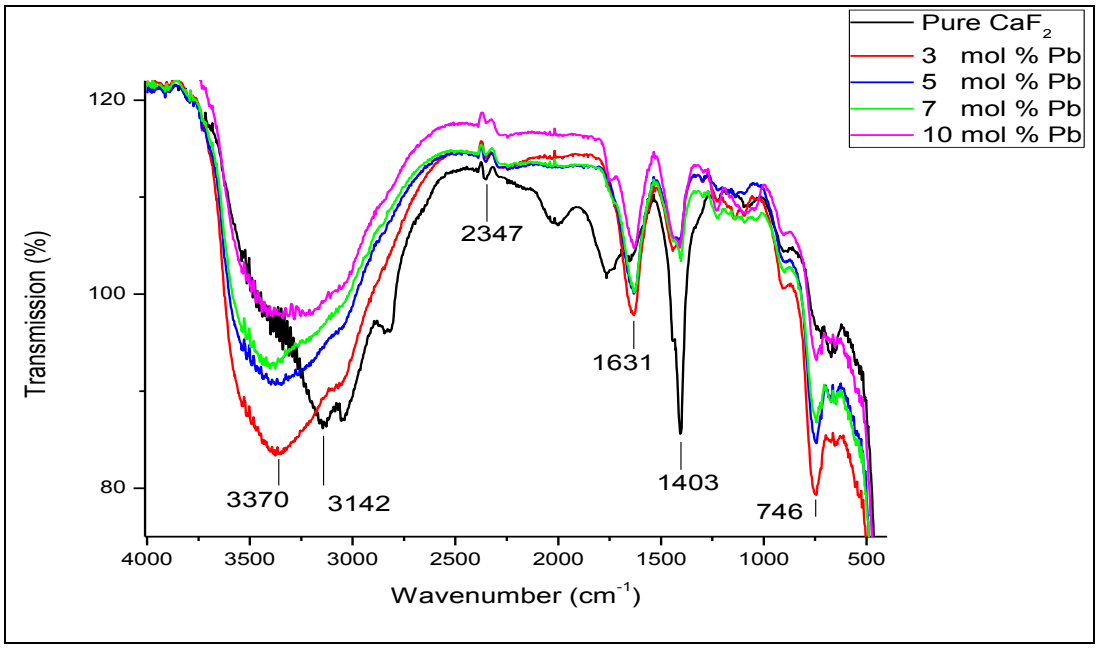

Figure 4: FTIR spectra of pure and Pb doped CaF_2 nanocrystals showing the presence of modes of vibrations.

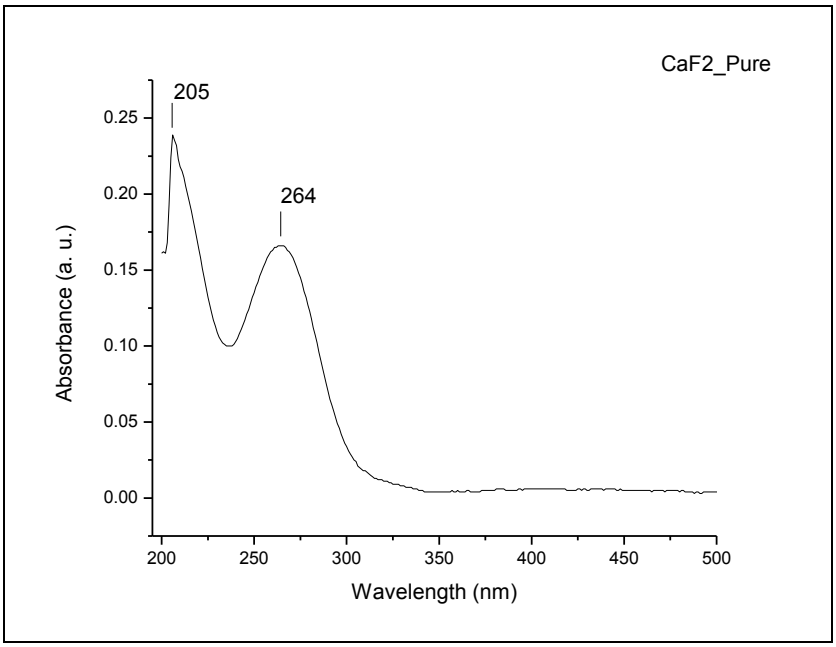

Figure 5 (a): UV – Visible absorption spectra of pure CaF_2 nanocrystals

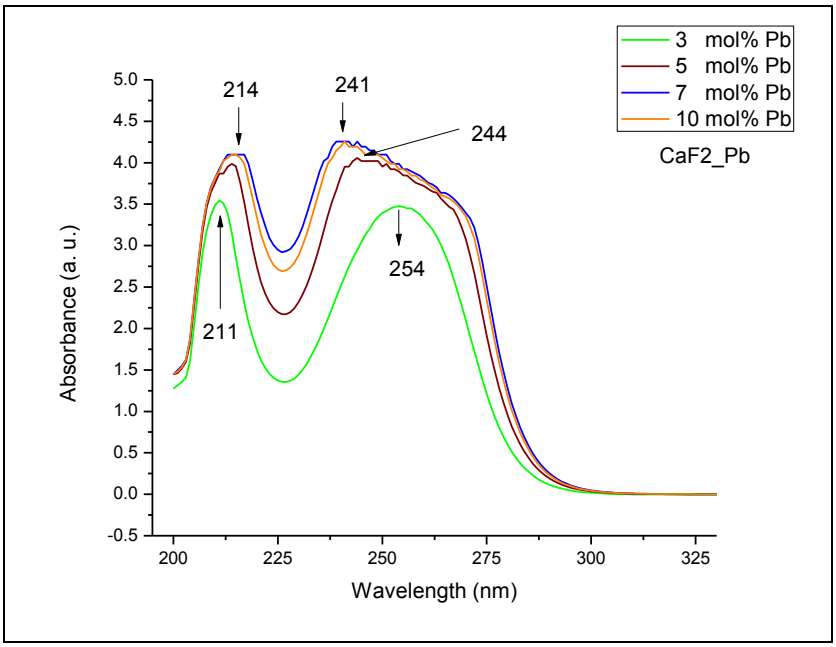

Figure 5 (b): UV – Visible absorption spectra of Pb doped CaF_2 nanocrystals with different concentration.

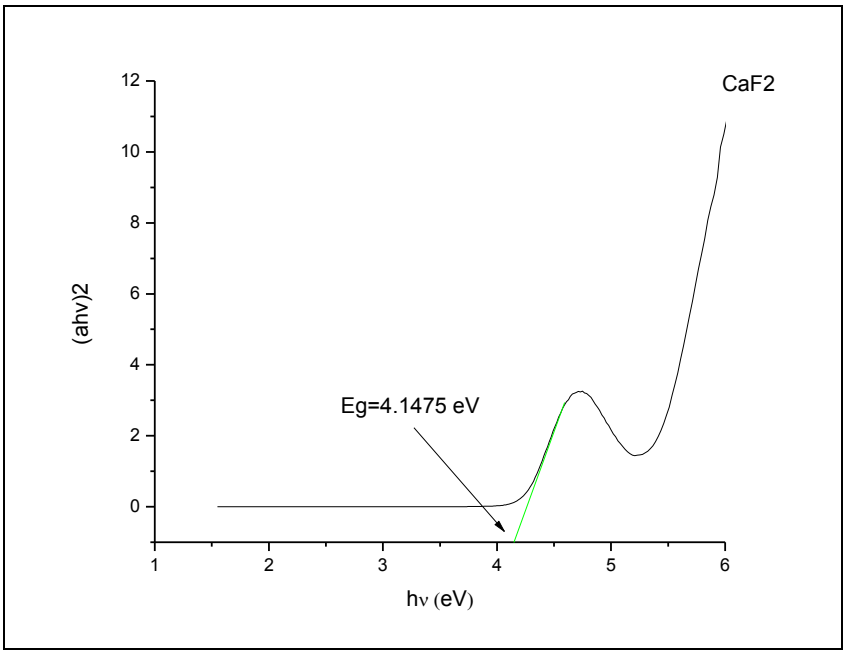

Figure 5 (c): Energy band gap of pure CaF_2 nanocrystals

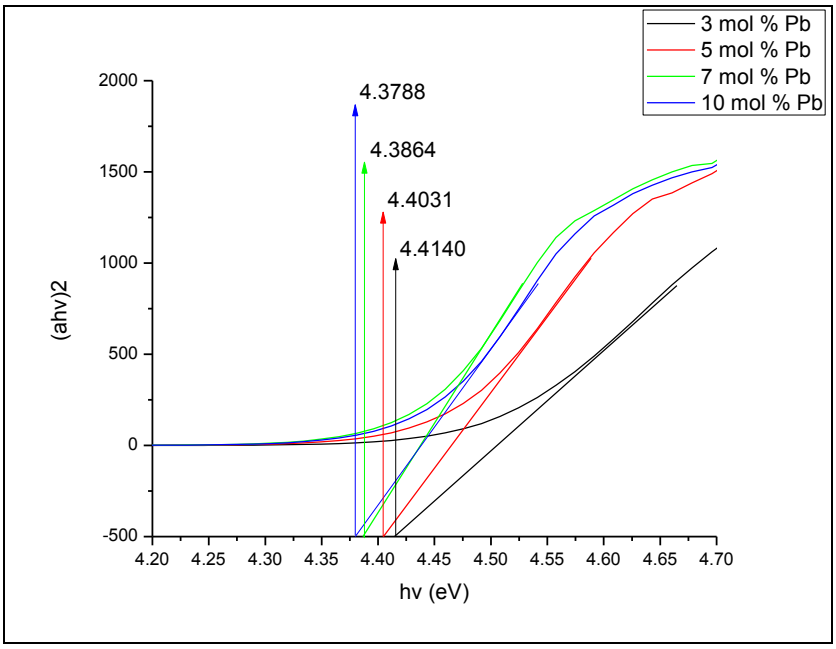

Figure 5 (d): Energy band gap of Pb doped CaF_2 nanocrystals with different doping concentration.

Conclusions

In summary, Structural and Optical properties were studied. Pure and Pb (3, 5, 7 and 10 mol %) doped CaF_2 nanocrystals have been synthesized. It was confirmed from the PXRD patterns that Cubic phase with high crystallinity is observed. It is observed that by increasing the concentration of Pb, crystallite size and lattice constants were also increased. The results of EDAX analysis show the presence of dopant (Pb) in the synthesized samples. FTIR studies show the structural properties and presence of the hydroxyl groups and different bonds in the synthesized samples. The optical absorption spectra of pure CaF_2 nanocrystals show a prominent peak at 264 nm and 211, 214, 241 and 256 nm for Pb doped CaF_2 nanocrystals with different doping concentrations. It is observed that by increasing the Pb concentration absorbance of the prepared samples increases. It is also observed that by increasing the concentration of Pb, energy band gap decreases and refractive index increases.

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