

Research Article

Size Controlled CaF₂ Nanocubes and Their Dosimetric Properties Using Photoluminescence Technique

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A new synthetic chemical coprecipitation route for the preparation of well-crystallized size controlled nano- and microcrystalline cubes of CaF₂ is reported. Crystalline cubes in the range of 2 μm–20 nm could be synthesized and their sizes were controlled by varying the solvent:cosolvent ratio. The as-synthesized CaF₂ nanocubes were characterized by different techniques. Photoluminescence (PL) emission spectrum of CaF₂ nanocrystalline powder showed strong emission band at 415 nm. Moreover, the effect of Eu as a dopant on the emission spectrum of CaF₂ was investigated. This dopant was found to get incorporated in its Eu²⁺ and Eu³⁺ forms. The as-produced nanocubes were exposed to UV irradiation and the corresponding PL emission was studied. Excellent results are obtained, where CaF₂:Eu nanocubes were found to be highly sensitive and might be suitable for estimating the doses of UV irradiation using the PL technique.

1. Introduction

Inorganic nanomaterials have a great potential in science and technology applications based on their unique physical properties. Amongst them are fluoride compounds, which have received especial interest [1]. One of these fluoride compounds, calcium fluoride (CaF₂), is an attractive material due to its large band gap (12 eV), high stability with wide transparent spectral range (200–1100 nm), low refractive index, and low phonon energy. The doped and undoped CaF₂ have several applications in the nanotechnology field as spectroscopic windows, color display [2]. It is also a laser material when doped with rare earth materials [3]. Moreover, it is a well-known thermoluminescent (TL) material when doped with different impurities. For example CaF₂:Mn is considered as an extreme dosimeter [4], since it has a high sensitivity for high exposures.

Synthesis of fluoride materials in nanoscale can change their properties and efficiency in optical applications. The change in optical properties is caused by the quantum confinement of electrons within the nanoparticles and strongly depends on controlling the crystal dimensions. Synthesis

of inorganic nano- and micromaterials with well-defined and controllable morphologies has stimulated considerable attention, because it is well known that the properties of the materials closely interrelate with geometrical factors such as morphology, dimensionality, and size [5].

Nanocrystalline structures of CaF₂ with different shapes and size distributions have been prepared by different methods and studied for different application mainly as TL dosimeters. For example, Zahedifar and Sadeghi [3] synthesized CaF₂:Tm nanoparticles as a high sensitive TL dosimeter for the first time by using ethanol in hydrothermal method and the crystallite size was about 40 nm. Europium doped CaF₂ nanoparticles were synthesized by the sol-gel method using the trifluoroacetic acid (TFA) by Hong and Kawano [6]. They reported that the crystalline size increased from 15 to 120 nm depending on the sintering temperature. Salah et al. [7] have evaluated Dy doped CaF₂ nanostructure for its TL response to high exposures of gamma rays. Pandurangappa et al. [8] synthesized Eu doped CaF₂ nanoparticles by coprecipitation method to study the optical absorption and photoluminescence (PL) properties after gamma rays irradiation. They have added nitric acid (HNO₃) in to the

mixture and showed particle size of about 25 nm. Jiang et al. [9] have codoped CaF_2 nano- and microcrystals with Yb and Tm at different sizes using a simple hydrothermal method in order to investigate the influence of sizes on the UV upconversion phenomenon. Stark and coworkers [10] have prepared CaF_2 nanoparticles with diameter of 14 nm using flame synthesis. Nanoparticles of pure CaF_2 and doped with Yb or Er, with an average size of about 20 nm, were synthesized by the Igepal/cyclohexane/water reverse micelles method by Bensalaha et al. [2]. Song et al. [11] have investigated the luminescence properties of oleic acid- (OA-) modified CaF_2 :Eu nanocrystals by a precipitation reaction. Most of these studies have investigated the PL properties in this material; but they have not yet tried to evaluate the PL as a dosimetry technique. They only have focused on producing CaF_2 as a TLD material.

Several studies were focused on producing nanoparticles of CaF_2 , but the particle size is not yet controlled. Synthesizing the nanoparticles of this important material in controllable manner is expected to be of great importance mainly for modifying its optical properties. This work is mainly focused on developing a new synthetic chemical coprecipitation route for the preparation of well-crystallized size controlled nano- and microcrystalline cubes of CaF_2 . Crystalline cubes in the range of $2\ \mu\text{m}$ –15 nm could be synthesized and their sizes were controlled by using two solvents. Microsized cubes could be grown in the presence of water as a solvent, while using both water and acetone at equal ratio is found to be effective in reducing the particle size to the nanoscale. The as-synthesized CaF_2 were characterized by different techniques like X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron microscopy (XPS), and UV-visible spectroscopy. The effect of particle size on the optical properties of this material was studied. These properties involve photoluminescence and absorption spectra. Moreover, the effect of dopants on the photoluminescence emission spectrum was investigated. The as-produced nanocubes were exposed to UV irradiation for different times and the corresponding photoluminescence was studied. Excellent results are obtained, where CaF_2 :Eu nanocubes are found to be suitable for esteeming the doses of UV irradiation using the PL technique.

2. Experimental Procedure

Nanocrystalline particles of CaF_2 were synthesized by the chemical coprecipitation method. Initially, CaCl_2 (of 99.95% purity) is dissolved in triply distilled deionized water. The normality of the solution is 0.1N. The solution is then mixed with ammonium fluoride (NH_4F) (of 99.95% purity) solution (0.1N) stoichiometrically in the presence of acetone. The solution of NH_4F was added to the solution of CaCl_2 dropwise with continuous stirring. Five different ratios of water:acetone were used to control the particle size. These ratios are 1:0, 0.75:0.25, 1:1, 0.25:0.75, and 0:1. The precipitate collected by centrifuging the solution for 15 min at 3500 rpm and was washed three times with deionized water via centrifugation to eliminate the residual chloride and the

ammonium ions. A white residue, thus, was obtained and was dried at 363 K in an oven for 2 h. The final product was in the form of ultrafine powder.

Doped sample with europium (Eu) was also prepared by the same method using water and acetone as solvents at equal ratio. Eu was used in chloride form at a concentration of 0.1 mole%. The obtained powder sample was dried at 80°C in an oven for 2 h and after that annealed at 300°C for 1 h. Then six samples were exposed to different exposures from a UV source (at a power of 400 watt and distance of 15 cm). They were exposed for different times in the range of 1–24 min. The wavelength of the UV light is 280 nm.

The as-synthesized CaF_2 powder samples were characterized by XRD, using an Ultima-IV (Rigaku, Japan) diffractometer with $\text{Cu K}\alpha$ radiation, while the morphology of these samples was analyzed with a field emission scanning electron microscopy (FESEM), JSM-7500 F (JEOL, Japan) operated at 15–20 kV. The sample synthesized at a solvent:cosolvent ratio of 50:50 was analyzed for its microstructure by a transmission electron microscope (TEM). The obtained micrographs were recorded at 200 kV using ARM-200F, JEOL, Japan.

The absorption spectra for the samples were measured using a UV-visible computerized spectrophotometer (model “UV-1650PC”, Shimadzu, Japan) in the wavelength region 200–1100 nm. PL emission spectra were recorded at an excitation wavelength of 325 nm using a fluorescence spectrofluorophotometer, model RF-5301 PC, Shimadzu, Japan. The measurement was performed at room temperature. X-ray photoelectron spectroscopy (XPS) measurement on Eu doped sample was performed by utilizing PHI 5000 Versa Probe, Japan. The sample irradiation was carried out using monochromatic $\text{Al K}\alpha$ radiation. The obtained curve was fitted using Multipack v8.2c data analysis software provided with the PHI-5000 versa probe ESCA instrument that made use of a combination of Gaussian-Lorentzian peaks.

3. Results and Discussion

Figures 1(a)–1(c) show SEM images of the as-synthesized CaF_2 powders by the coprecipitation method using different solvent ratios. These images show semicubic structures in polycrystalline forms. When water was used as a solvent, micro- and submicrosize particles were formed with sizes in the range of $2\ \mu\text{m}$ –100 nm (Figure 1(a)). Acetone as a solvent was found to provide similar structure but with smaller sizes in the range of 80–200 nm (Figure 1(e)). However, when both solvents were used together the particle size was significantly reduced (Figures 1(b), 1(c), and 1(d)). The minimum size is obtained when both solvents are used at equal concentrations, which is in the range of 20–40 nm (Figure 1(c)). This result is remarkable by means of the use of both solvents, that is, water and acetone; the size of the obtained particle can be controlled, reaching to the nanoscale. To confirm the particle size of CaF_2 nanocubes TEM measurement was performed. A typical TEM image of pure CaF_2 powder produced at equal concentrations of solvents is presented in Figure 2(a). Fine nanoparticles with sizes in the range of 20–50 nm can be seen, which are close to those observed by SEM. Figure 2(b) shows a high-resolution TEM image for these nanoparticles

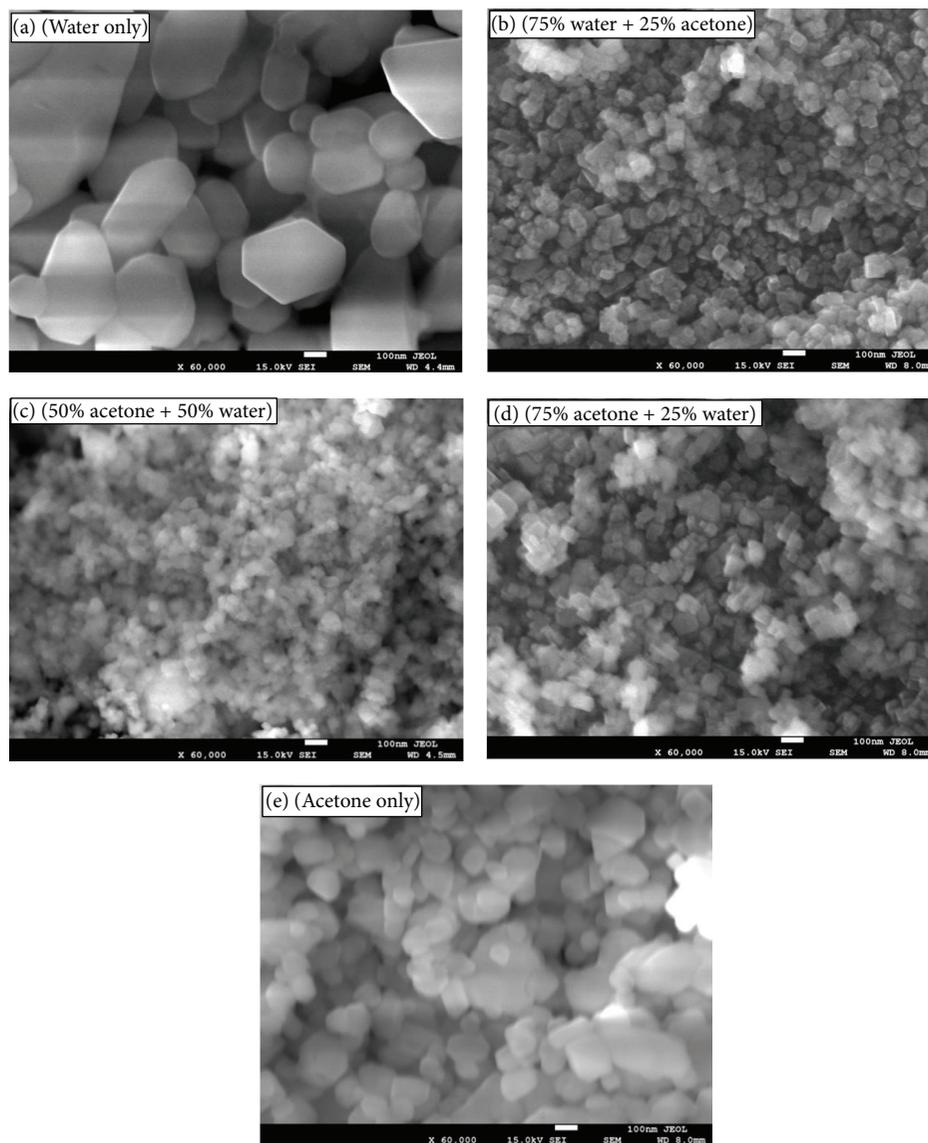


FIGURE 1: SEM images of the as-synthesized CaF_2 nanocubes prepared by using different solvent ratios.

where polycrystalline structure can be seen. Lattice spacing in this crystalline structure is obtained and found to be 0.25 nm (Figure 2(c)). This value is close to that reported in the literature for CaF_2 nanocrystals [12].

The effect of acetone on controlling the particle size, particle morphology, and crystalline phases was studied by several workers [13–15] on different materials. For example, Kwak et al. [13] have used acetone as a solvent. This solvent could produce spherical NiO nanoparticles with sizes in the range of 3–15 nm and could provide a good dispersion by using a solvothermal treatment. Yu et al. [14] found that the solubility of l-glutamine in mixed solvents (water + acetone) increases with an increase in temperature. Wu et al. [15] prepared TiO_2 nanospheres with an average diameter of 70 nm and highly porous structure by using water-acetone mixed solvent in the solvothermal process. Similarly, in the present study the use of both solvents, that is, water and

acetone, is found to be effective in controlling the particle size of CaF_2 . When the amount of acetone is equal to that of water, the particle size is significantly reduced. The solubility of the initial precursors in these solvents is different, which results in controlling the growth of CaF_2 cubes and limiting their sizes at particular values. It has been reported that the reaction and solubility of some materials are faster in water than organic solvents (pure water has higher dissolving power) [14, 16]. Therefore, in the present case when water is only used as a solvent the formed CaF_2 cubes are relatively big, which are in the microsize range (Figure 1(a)); however, when acetone was added as a cosolvent the solubility of the initial compounds was reduced. This ultimately results in slow crystal growth and formation of smaller particles in the nanoscale range. In other words, addition of organic cosolvent, that is, acetone, could suppress nucleation of the formed CaF_2 cubes. The optimal ratio of the used solvents for

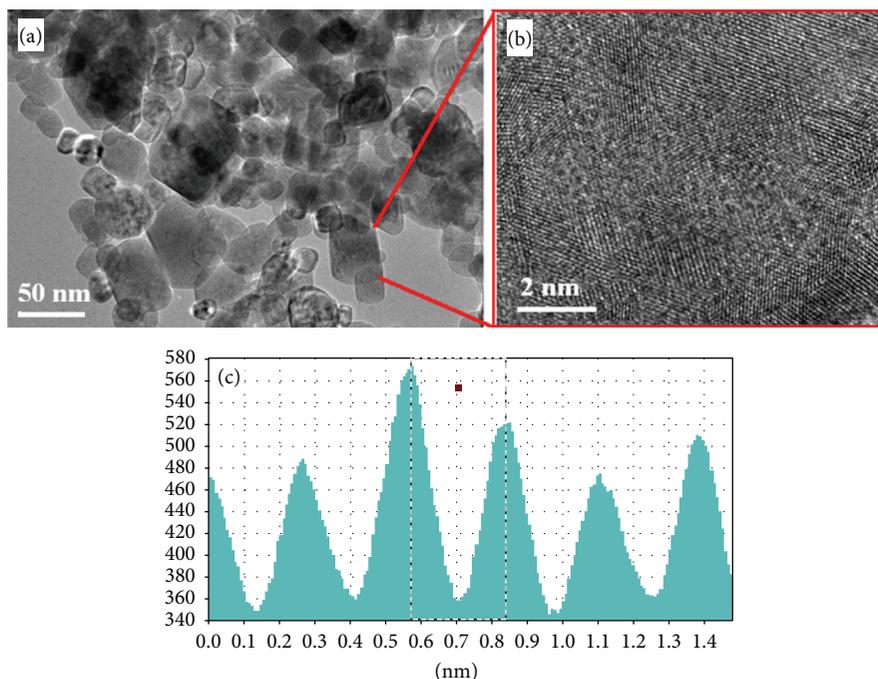


FIGURE 2: (a) TEM image of the as-synthesized CaF_2 nanocubes prepared using water and acetone as solvents at the ratio 50 : 50, (b) HRTEM image, and (c) line scan of the HRTEM image showing a d -spacing of around 2.7 Å.

producing smallest sizes is found to be 1 : 1 (Figure 1(c)). These results showed that the used low cost solvents are effective in tuning and controlling the CaF_2 crystal size.

The crystallinity and crystal phases of the as-synthesized materials were characterized by X-ray diffraction technique. X-ray diffraction pattern of CaF_2 samples prepared at different ratios of solvents is shown in Figure 3(a–e). The XRD results indicate that the products are of CaF_2 in a complete crystalline structure. All the diffraction peaks can be indexed to a pure CaF_2 cubic phase (space group $225:Fm\bar{3}m$), which are in agreement with the standard values for cubic CaF_2 (JCPDS card number 87-0971) [5]. The displayed peaks in Figure 3 correspond to (h k l) values of (1 1 1), (2 2 0), (3 1 1), (4 0 0), and (3 3 1). This result is similar to those reported in [7, 17, 18]. It is clear that, by mixing both solvents together, there is a significant broadening in the XRD peaks (Figure 3(c)) revealing a small crystallite size of the prepared samples.

The size of CaF_2 nanocrystalline obtained at equal concentrations of solvents was estimated by using the Debye-Scherrer formula and found to be around 15 nm. This result is in agreement with that obtained by TEM (Figure 2(b)). There are few small extra diffracted peaks that can be seen in Figure 3, which are of the sample prepared with water only. The most prominent one is at around 33.4° , which might be due to the formation of small part of $\text{Ca}(\text{OH})_2$ phase [19, 20]. This peak can be identified as the (101) plane of $\text{Ca}(\text{OH})_2$ phase and its intensity is decreased by reducing the amount of water and adding acetone. Moreover, by annealing this sample at different temperatures from 200 to 500°C for 1 h (Figure 4(a–e)), the XRD pattern for the heated sample retained the original peaks for CaF_2 only. This result

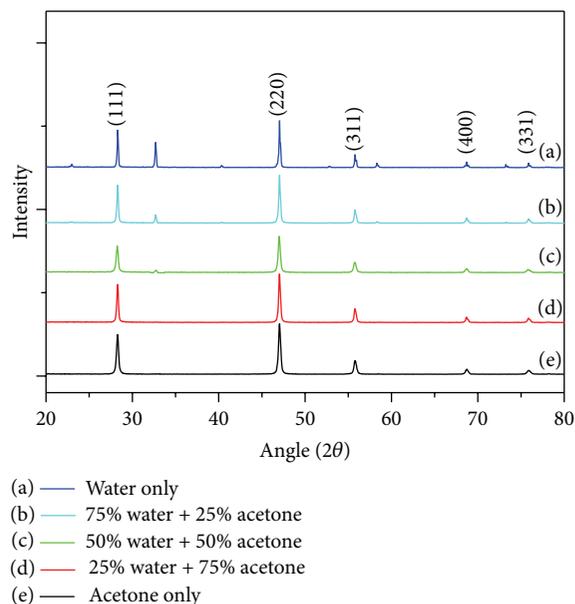


FIGURE 3: XRD pattern of the as-synthesized nanocubes of CaF_2 prepared by using different solvent ratios.

shows that the sample prepared using water only contains a considerable amount of another phase or water content, which could be released by heating at high temperatures.

To investigate the optical properties, the as-synthesized CaF_2 nanoparticles were characterized by UV-visible spectroscopy at room temperature. Figure 5(a–e) shows the optical absorption spectra of the CaF_2 samples prepared at

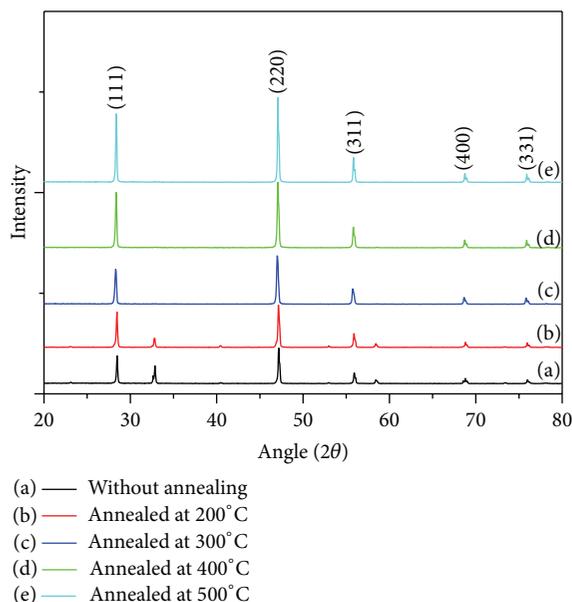


FIGURE 4: XRD pattern of the as-synthesized nanocubes of CaF_2 prepared by using water as a solvent and annealed at different temperature.

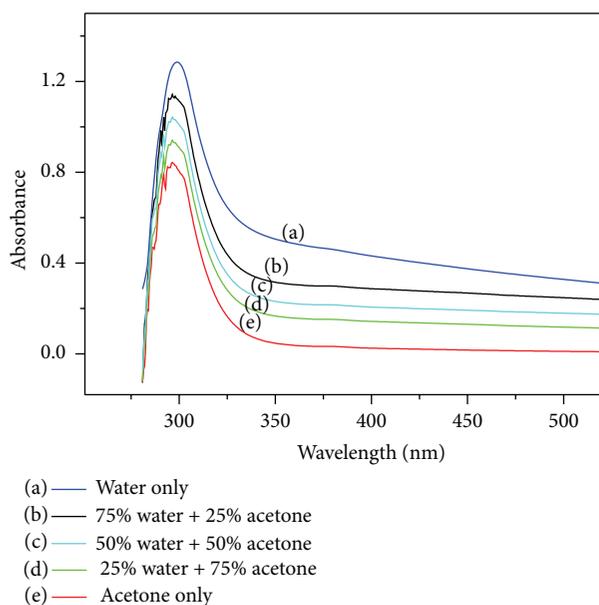


FIGURE 5: UV-Vis absorption spectra of the as-synthesized CaF_2 nanocubes prepared by using different solvent ratios.

different solvents. The spectra show strong absorption bands at around 300 nm in the UV range, which might be due to surface defects in nanocubes of CaF_2 . The maximum absorption is observed in the case of using water as a solvent, and then the intensity value decreases by reducing the amount of water and adding acetone. This is a remarkable result where the absorption intensity of nanomaterials is less than that of micromaterials. The diameters of these materials might have significant role on the absorption process. Water

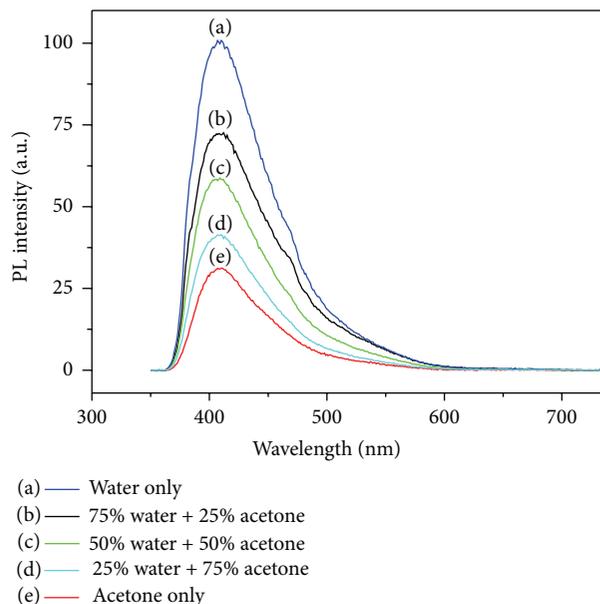


FIGURE 6: PL emission spectra of the as-synthesized CaF_2 nanocubes prepared by using different solvent ratios.

only as a solvent gives higher absorption intensity than other solvents. The possible reason in this case might be due to the formation of higher amount of permanent oxygen defects in the host of CaF_2 , which might be maxima in case of water as a solvent.

Figure 6 shows the PL emission spectra of CaF_2 nanocrystalline powder prepared at different solvents (curves (a)–(e)). When the samples were excited by 325 nm, strong emission bands located at ~ 415 nm are observed. The maximum intensity was observed in case of sample prepared using water as a solvent (Figure 6(a)). This result is similar to that reported by Pandurangappa et al. [18], who found a peak at ~ 407 nm, when the samples were excited at 218 nm. They attributed this peak to surface defects, like Schottky and Frenkel, which exist in the lattice structure of alkali halides at different temperatures. These kinds of vacancies, present on the surface of nanoparticles, were reported to create PL peaks at different wavelengths, in visible range [18, 21]. These emissions can be attributed to the oxygen defects, which might be created during the synthesis process. The formation of oxygen impurity vacancy in the nanocrystalline lattice during the synthesis leads to PL emissions [18].

The effect of dopant on the PL emission of CaF_2 nanocubes was also studied. Europium (Eu) was selected as an impurity in this study at a concentration of 0.1 mol%. The PL emission spectra of pure and Eu doped CaF_2 nanocubes are shown in Figure 7 (curves (a) and (b)). The doped sample has the same band of pure CaF_2 nanoparticles along with two smaller ones at 590 and 617 nm. But the band of pure sample is significantly increased after doping with Eu beside a slight shift to the higher wavelength region. This indicates that the PL enhancement is caused by the doping of Eu ions. The two bands located at 590 and 617 nm of Eu doped sample are the well-known emissions of Eu^{3+} ion [1, 22, 23]. It is understood

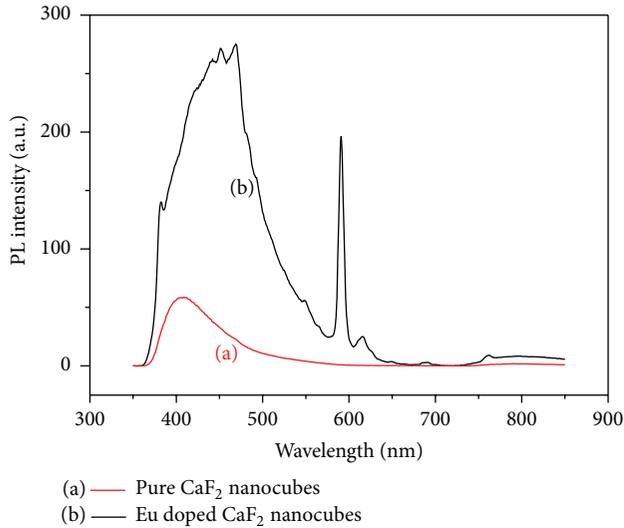


FIGURE 7: PL emission spectra of pure and Eu doped CaF₂ nanocubes.

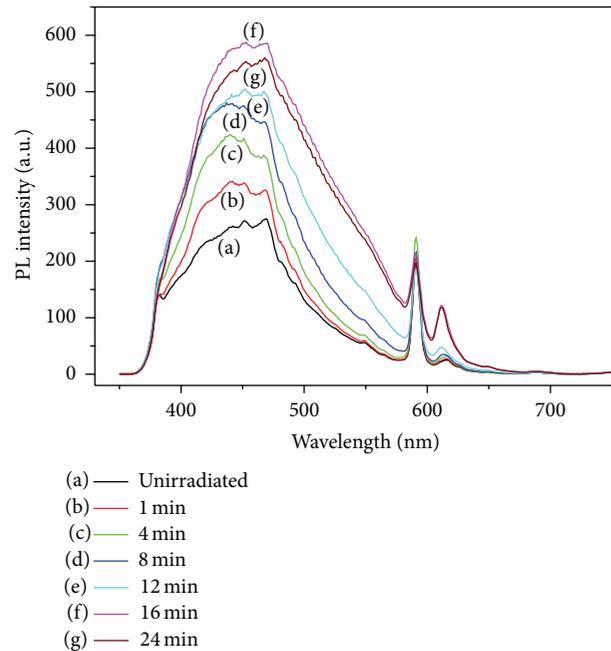


FIGURE 9: PL emission spectra of CaF₂:Eu nanocubes exposed to different exposures of UV irradiation.

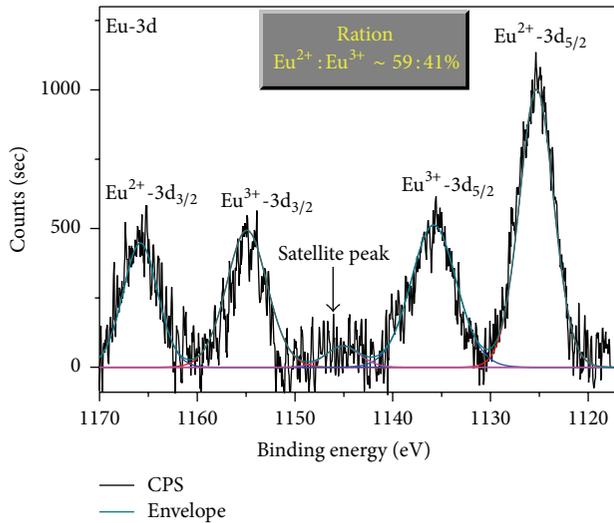


FIGURE 8: XPS spectra of Eu-3d peaks of Eu doped CaF₂ nanocubes.

that Eu²⁺ ion has a very strong broad emission in the blue region in different materials [24–26]. Therefore, it is possible that some part of Eu dopant has been incorporated in its Eu²⁺ form. This could provide a large PL enhancement in CaF₂ nanocubes.

The valance/chemical state of the incorporated Eu ions in CaF₂ nanomaterial was determined by the XPS technique. The XPS spectrum of Eu-3d core level of the Eu doped CaF₂ sample is presented in Figure 8. Four peaks are observed in this spectrum located at around 1124, 1134.5, 1154, and 1165.3 eV. The first two peaks are of Eu²⁺ and Eu³⁺ 3d_{5/2} core level, while the other peaks at 1154 and 1165.3 eV are of Eu²⁺ and Eu³⁺ 3d_{3/2} core level, respectively [27]. One satellite peak is observed at 1145 eV, which might be of two components. This peak is perhaps due to the chemical shift between Eu²⁺ and Eu³⁺ states [27, 28]. The ratio of Eu²⁺ : Eu³⁺ is 59 : 41% as

shown in Figure 8. These results have proved that Eu ions are present in both Eu²⁺ and Eu³⁺ chemical states, which are in agreement with the PL result presented in Figure 7.

The above result shows that Eu doped CaF₂ nanoparticles have strong emission in the visible region; therefore, this emission has been tested for its response to UV irradiation. Six samples were exposed to different exposures of UV irradiation. The result is presented in Figure 9. These samples were initially annealed at 300°C for 1 h and then exposed to UV irradiation for different times in the range of 1–24 min. The sample exposed for 1 min shows that the intensity of the band in the blue region at 415 nm significantly increased (curve (b)). Further exposure to UV irradiation has showed additional increases in intensity of this band. The maximum intensity was observed at irradiation of 16 min and beyond that it decreases. The intensities of Eu³⁺ bands show only slight changes. This is a remarkable result, where the broadband of CaF₂ is responding to the amount of radiation exposures.

Figure 10 shows intensity of the broadband at 415 nm of CaF₂:Eu nanocubes as a function of exposure time. The observed curve is linear in the range of 1–16 min and the intensity is decreasing above this range. From the application point of view this band of CaF₂:Eu nanocubes might be suitable for esteeming the doses of UV irradiation using the PL technique. It is understood that UV irradiation and other ionizing radiations have several applications, but their doses need to be precisely determined. Therefore, this nanomaterial might be suitable for other ionizing radiations, but it needs to be tested and exposed to them. Then this nanomaterial can be used as a dosimeter using PL technique.

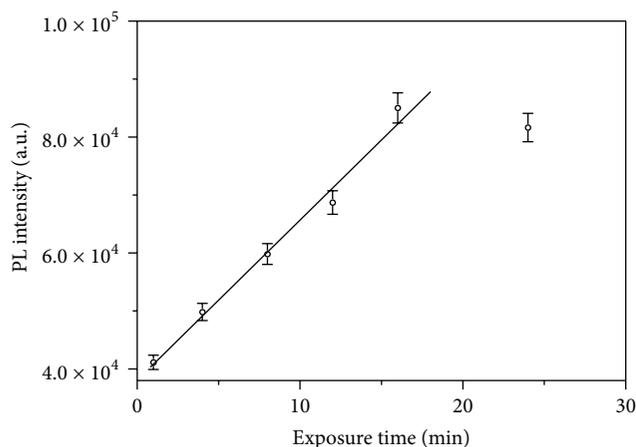


FIGURE 10: PL response curve of $\text{CaF}_2:\text{Eu}$ nanocubes exposed to different exposures of UV irradiation.

4. Conclusions

Well-crystallized size controlled nano- and microcrystalline cubes of CaF_2 were produced by the coprecipitation method using a mixture of water and acetone as solvents. The result of PL emission spectra of CaF_2 nanocrystalline powder showed that there is a possibility of using this nanomaterial as a dosimeter using PL technique. One broad strong emission is observed at 415 nm, which is responding linearly with the absorbed doses of UV irradiation. This nanomaterial might also be tested for estimating the doses of other ionizing radiations using the PL technique.

Conflict of Interests

The author declares that there is no conflict of interests regarding the publication of this paper.

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