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## Structural and optical properties of Cerium doped Calcium Fluoride nanoparticles prepared by coprecipitation

### ABSTRACT

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Calcium fluoride nanoparticles with special amount of cerium ion (%1) were synthesized by coprecipitation. Fourier transforms infrared spectroscopy (FTIR), X-ray diffraction (XRD), absorption and photoluminescence (PL) from CaF<sub>2</sub>Ce nanoparticles has been investigated. FTIR spectra reveal that there are some amounts of OH, NO<sub>3</sub> and other organic functional groups on the particle surfaces before the post annealing process. X-ray diffraction results indicate an improvement in crystalline quality with annealing. Intensity of fluorescent bands as well as the absorption edge of the prepared nanoparticles is also very relevant to the annealing temperature.

**Keywords:** Coprecipitation; Nanoparticles; Calcium fluoride; Annealing; Photoluminescence.

### INTRODUCTION

One of the alkali fluoride compounds that were applied in this study is CaF<sub>2</sub>, because of its high stability and non-hygroscopic behavior. Recently CaF<sub>2</sub> gained a renewed interest as a laser material when doped with rare-earth material [1]. CaF<sub>2</sub> nanoparticles were synthesized by different methods such as sol-gel method [2], solvothermal process [3], reverse micelle method, different precipitation methods [4], and flame synthesis [5]. Nanoparticles doped with three valents rare earth (lanthanides), having fluoresce properties, have a good application potential in displays [6], communication [7], lasers and modern electronics equipments [8]. Doping with lanthanides like cerium atoms makes some selected materials suitable for luminescence activities by introducing some extra energy levels in their band gap. Hence, these dopants have a significant effect on optical properties of the materials such as calcium fluoride.

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Nanoparticles of calcium fluoride are quite transparent in optical region due to their low energy phonons and high degree ionizations [9]. These properties make them much more transparent than any other calcium compositions like calcium sulfides or oxides.

Crystalline  $\text{CaF}_2$  with isotropic fluoride structure is a suitable phosphorous host, for having a good transmission in 0.3 to 8  $\mu\text{m}$  region of spectra [10]. Since, the refraction index of  $\text{CaF}_2$  gradually grows up by doping concentration of three valents lanthanides, these doped materials are very good candidate for wave guiding in integrated optical devices. In this research, we have investigated some effects of cerium doping on improving of the optical behavior of  $\text{CaF}_2$  nanoparticles.

## EXPERIMENTAL

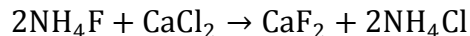
### Materials and instruments

All of the solvents were used without purifications. Calcium chloride (%99.99 from Merck), ammonium fluoride (%99.98 from Sigma-Aldrich), alcohol (%99.9 from Merck) and  $\text{Ce}(\text{NO}_3)_3$  with the purity of %99.99 (from Merck) were provided. IR spectra were recorded by using the KBr disks on a Bruker tensor (model 420) spectrophotometer. Structural characterization of the samples by XRD measurements was carried by an equipment with Cu target of  $\lambda_{k\alpha}=1.540\text{\AA}$ . Absorbance and also photoluminescence from the prepared samples was taken by a V-570 UV and Cary 4000 systems, respectively. SEM images were achieved by FESEM: S-4160: HITACHI.

### Synthesis of $\text{CaF}_2$ nanoparticles

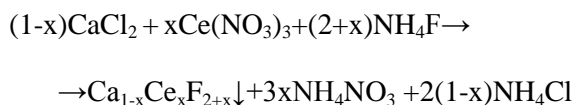
0.01 moles of  $\text{CaCl}_2$  was solved in 100 milliliters of distilled water in an Erlenmeyer. Then 0.02 moles of  $\text{NH}_4\text{F}$  was added and the solution was stirred by a magnetic stirrer with high speed for two hours. Final result was a dark white suspension. This mixture was centrifuged with 5000 rpm for 10 minutes, followed by three times washing up by pure alcohol to remove any extra residual ions of chloride and ammonium. The purified solution was centrifuged again, and the white precipitated solution was dried in ceramic vessel on a sand bath. To obtain powdered material

the sample were crushed by hand with a pestle and mortar. The formula of reaction is:



### Synthesis of $\text{CaF}_2$ : $\text{Ce}^{3+}$ nanoparticles (%1)

A mixture of calcium chloride (0.79 gr. weight) and a mass of 0.03 grams of  $\text{Ce}(\text{NO}_3)_3$  was solved in 180ml of pure alcohol in such a way that controlled concentration of metallic cations was 0.04mol/L. Stirring by a magnetic stirrer for 10 minutes made the colorless solution. Then 0.55 gr  $\text{NH}_4\text{F}$  was added and stirring was continued for 12 hours. The above process was done again for powdering  $\text{CaF}_2$ :  $\text{Ce}^{3+}$ . Annealing effects on the prepared samples was examined by calcinations of  $\text{CaF}_2$ : $\text{Ce}^{3+}$  powder for 4 hours in 400 and 600°C. Therefore we have the below reaction:



## RESULTS AND DISCUSSION

FTIR absorption was used in order to check the characteristic bands of the synthesized powders. Similar spectra were observed for other nanoparticles. (Figure1, 2) The spectrum shows two strong IR absorption bands at 3154.39 and 1409.33  $\text{cm}^{-1}$  which are characteristic of H–O–H bending of the  $\text{H}_2\text{O}$  molecules revealing the presence hydroxyl groups in the as prepared sample. Figure 3 shows XRD plot of an undoped sample of  $\text{CaF}_2$  nanoparticles prepared by co precipitation method. Features of this plot indicate the presence of a cubic phase for  $\text{CaF}_2$  films which is a typical structure for fluorites with fm3m spatial groups. Average lattice constant;  $a$ , was  $5.46\text{\AA}$  which is in agreement with the recorded data of  $5.44\text{\AA}$  from JCPDF 772096 [11]. Particle's size calculated from Debye-Scherrer formula is found to be in between 30nm-35nm. Figure 4 shows the XRD plot of a) as prepared, b) and c) annealed  $\text{CaF}_2$ : $\text{Ce}^{3+}$  at 400 and 600°C, respectively. Full width half maximum (FWHM) of as prepared sample is relatively smaller than for the undoped  $\text{CaF}_2$  (see Figure 3). However, this factor and

subsequently particle's size is very dependent to annealing temperature of doped  $\text{CaF}_2$  and becomes the biggest (size of 90nm) for the highest temperature that we examined ( $600^\circ$ ). It seems that this is happened since the small holes are pyrolysis followed by a re crystallization in due course of extra heating process. The study of optical absorption is important to understand the behavior of insulator nanoparticles. Figure 5 shows the optical absorption spectra of  $\text{CaF}_2:\text{Ce}^{3+}$  before and after annealing stage. As it is clear from this figure there are a strong absorption band in 202nm for as grown  $\text{CaF}_2:\text{Ce}^{3+}$ . By annealing in  $400^\circ\text{C}$  and  $600^\circ\text{C}$ , absorption band is shifted to 215 and

231nm, respectively. Absorption edge shifts to longer wavelength as annealing temperature increases indicating the red-shift in the absorption spectra is found with increasing size of the nanoparticles. This can be a reflection of the band gap increase owing to quantum confinement effect. Alternatively, defects such as Frenkel and Schottky may cause virtual states in the band gap of the nanoparticles and make a significant role in optical absorption in UV region of spectra. It seems that as the particle size grows up by heating, then some optical absorbent concentration decreases and one may expect a shift to higher wavelength of absorption edge of  $\text{CaF}_2:\text{Ce}^{3+}$  nanoparticles.

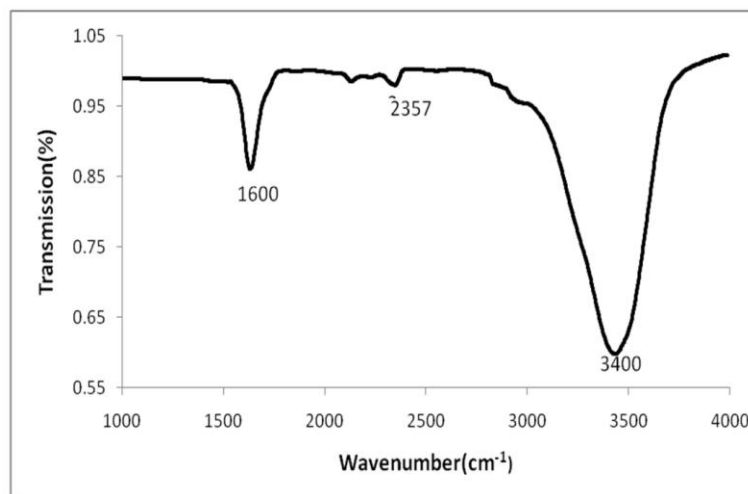


Fig. 1. FTIR spectrum of nano- $\text{CaF}_2$ .

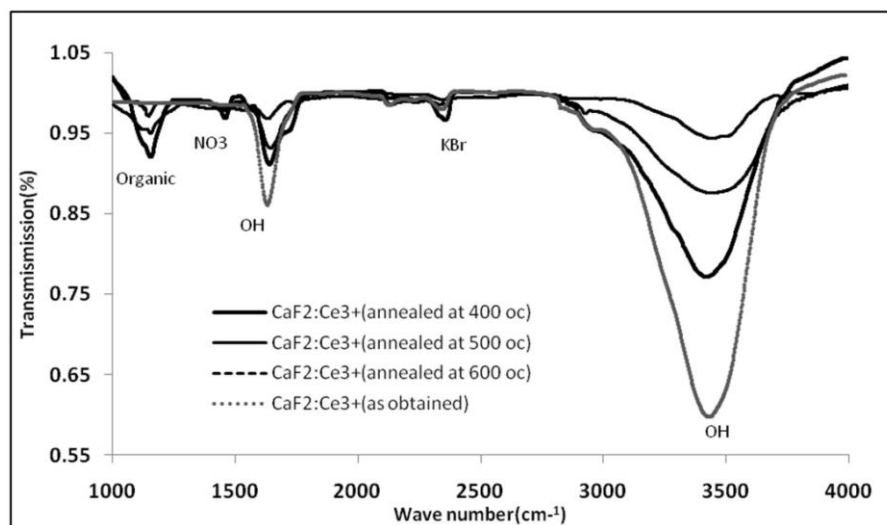


Fig. 2. FTIR spectrum of  $\text{CaF}_2:\text{Ce}_3+$  nanoparticles in different annealing temperature.

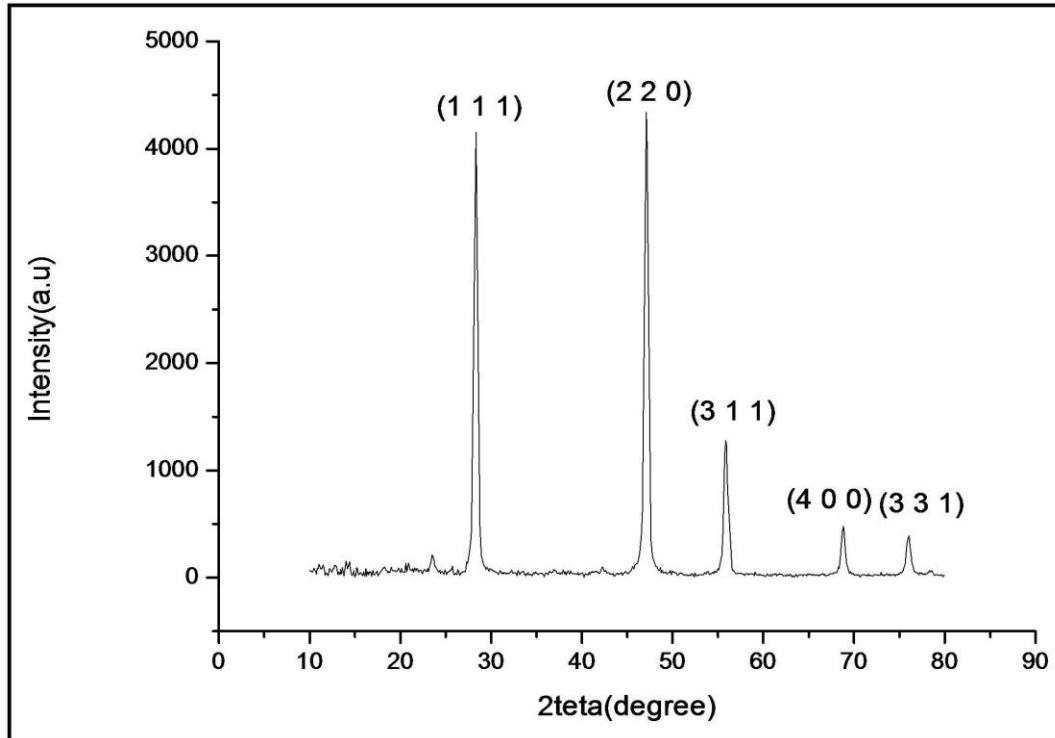


Fig. 3. XRD plot of an undoped sample of  $\text{CaF}_2$  nanoparticles.

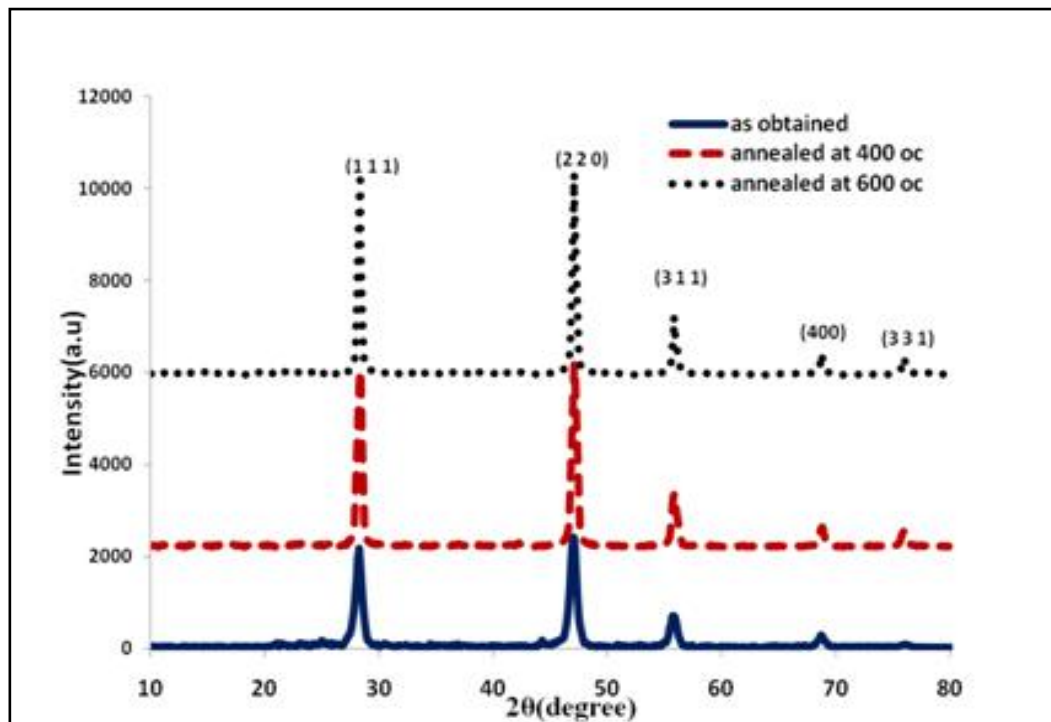


Fig. 4. XRD plot of a) as prepared, b) and c) annealed  $\text{CaF}_2:\text{Ce}^{3+}$  at 400 and 600 $^\circ\text{C}$ , respectively.

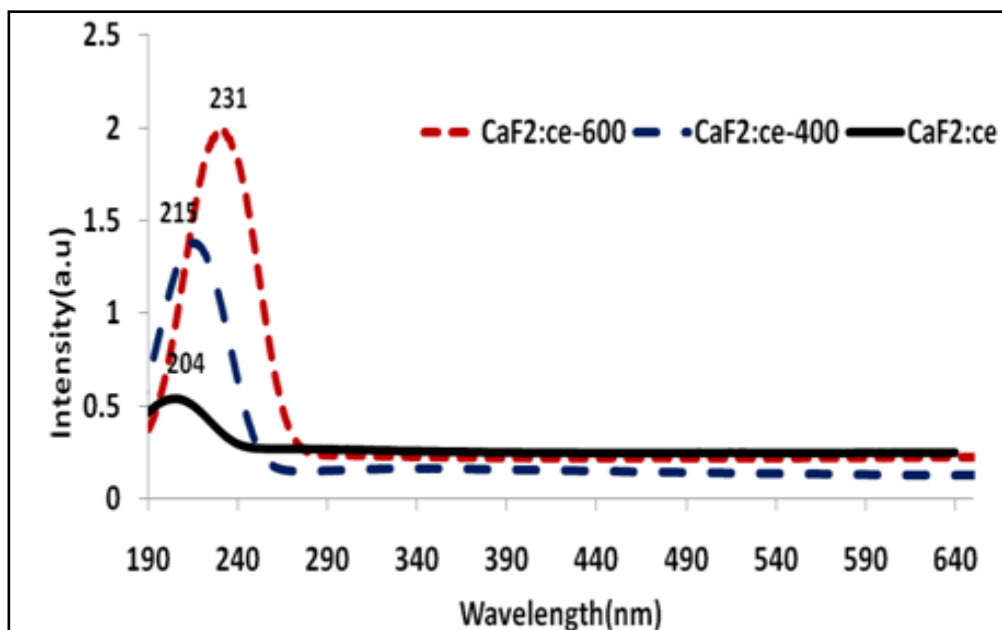


Fig. 5. Optical absorption spectra of  $\text{CaF}_2:\text{Ce}^{3+}$  before and after annealing stage.

### Photoluminescence (PL) Results

Emission spectra of the prepared  $\text{CaF}_2$  nanoparticles were taken by a fluorescent spectrophotometer of Cary 4000 at excitation wavelength of 254nm. PL spectra from  $\text{CaF}_2:\text{Ce}^{3+}$  nanoparticles show (Figure 6) two UV bands at 316 and 337nm, in agreement with the literature [12].

However, No features was detected from undoped  $\text{CaF}_2$  spectra, indicating that the above features are related to the  $\text{Ce}^{3+}$  luminescence centers present in the doped material. It is believed that here, there are some transitions from the 5d excited state to 4f of  $\text{Ce}^{3+}$  ions. The double structure of the peaks is a characteristic of ground state splitting which occurs in  $F_{5/2}$  and  $F_{7/2}$  (Figure 7).

Cerium is a three valent mineral and can lose, in a chemical reaction, two electrons from 6s and one from 4f orbital. Ground state of  $\text{Ce}^{3+}$  split in two sub bands of  $2F_{5/2}$  and  $2F_{7/2}$  by obtaining energy related to 2000-3000 $\text{cm}^{-1}$ . In a Cubic crystal field, 5d excited state of  $\text{Ce}^{3+}$  becomes also splitted to  $T_{2g}$  and  $E_g$ , by getting energy of 25000 $\text{cm}^{-1}$ . Energy levels of  $\text{Ce}^{3+}$  is schematically drawn in Figure 7. Electron transitions cause emission and absorption bands in 200-305nm region. Emission from  $\text{Ce}^{3+}$  is due to dipole transition of 4f-5d, which has a permitted parity and spin with a fairly strong vibration force. These

transitions gives both wide and also sharp emission bands in PL spectra.  $\text{Ce}^{3+}$  ions and  $\text{Ca}^{2+}$  are not covalent, so  $\text{Ce}^{3+}$  ions can cooperate in  $\text{CaF}_2$  lattice with a different symmetry. As a  $\text{Ca}^{2+}$  ion is replaced by a three valents  $\text{Ce}^{3+}$  an extra  $\text{F}^-$  ion will enter in this region and make electric charge neutrality in the  $\text{CaF}_2$  lattice. These replacements cause the major structural defects in  $\text{Ce}^{3+}\text{CaF}_2$ . If the dopant concentration is low enough (less than 0.1% cerium ions),  $\text{F}^-$  ions fill the holes present in next nearest neighbor of  $\text{Ce}^{3+}$  and makes isolated trigonal ( $C_{3v}$ ), tetragonal ( $C_{4v}$ ) or rhombohedral ( $C_{2v}$ ) defects.

As it is clear from Figure 8, intensity of fluorescent bands is very dependent on the annealing temperature. In other words, the bigger the particle sizes the more intense emission. This features which is also reported in other nano materials doped with rare earth elements is attributed to particle size as well as surface defects [13].

As we know, atomic coordinates in surface of the solids are different from in the bulk. Surface atoms are not as quite spherical as they are in the bulk, so they have more potential energy to absorb a different kind of chemical compounds present on the surface. Chloride and also nitride salts in water were used in our synthesis method of  $\text{Ce}^{3+}\text{F}_2$ , so surface of the prepared nanoparticles are

simply covered by organic residual materials like  $\text{Cl}_2$ ,  $\text{NO}_3$  and  $\text{OH}$  groups. These groups have a high photonic frequency and high capability to act as luminescence bleaching centers, so they attenuate the PL intensity in undoped samples. By annealing, these centers are significantly decreased and

particles size also becomes greater. These two factors however are relevant since heating process decomposes the surface species and diminish the surface absorption. Alternatively, since the particles are now bigger concentration of the bleaching centers may become lower.

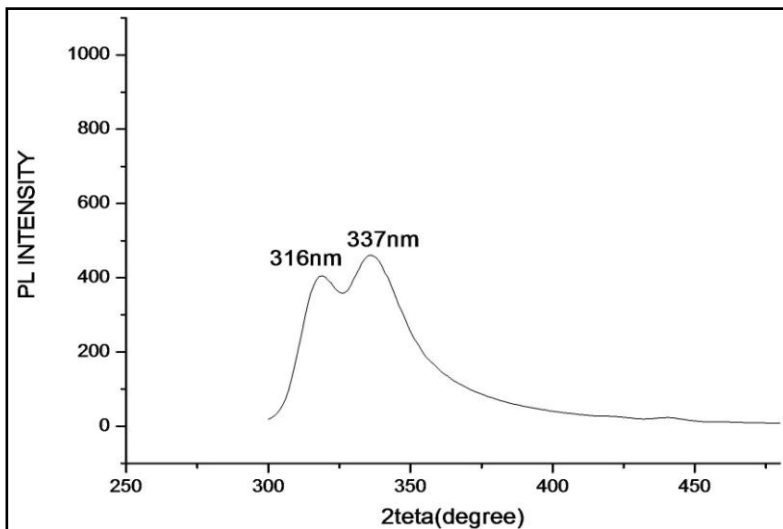


Fig. 6. PL spectra from  $\text{CaF}_2:\text{Ce}^{3+}$  nanoparticles.

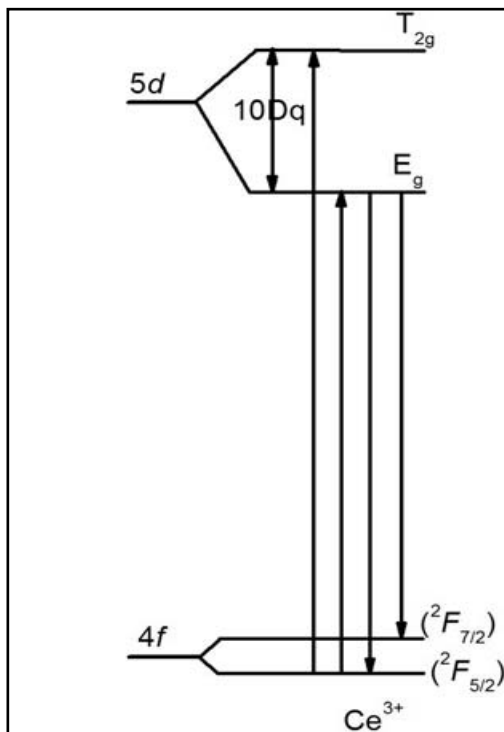


Fig. 7. Schematic levels of  $\text{Ce}^{3+}$  in  $\text{CaF}_2:\text{Ce}^{3+}$  nanoparticles.

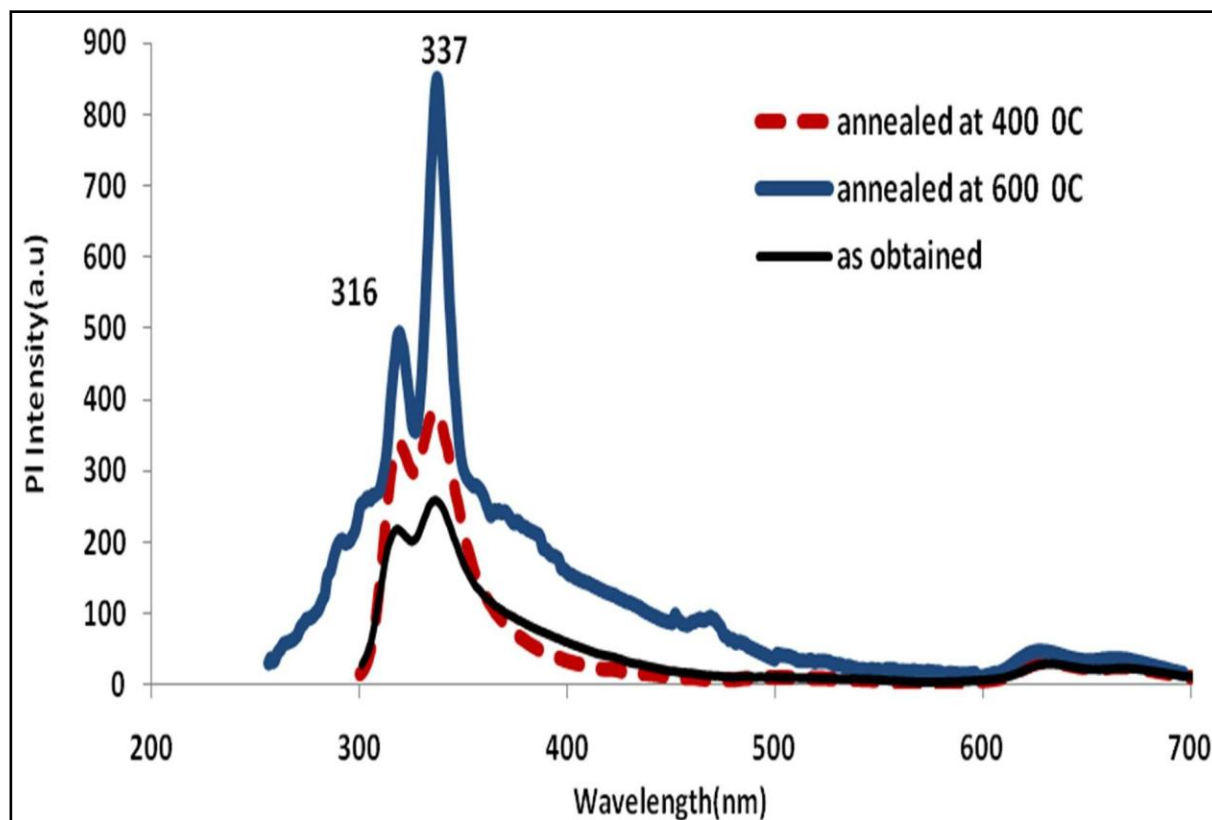


Fig. 8. Emission spectra of CaF<sub>2</sub>: Ce<sup>3+</sup> before and after annealing stage.

## CONCLUSIONS

The nanoparticles of CaF<sub>2</sub>:Ce were grown by coprecipitation technique. The XRD pattern indicated the growth of the nanoparticles. The size of nanoparticles was found to increase with increasing annealing temperature. The measurement of optical absorption spectra indicated red-shift with increasing size of the nanoparticles. Two relatively intense UV peaks were obtained in the photoluminescence spectra of CaF<sub>2</sub>: Ce nanoparticles, where the dominant one lies at 337nm and the other in 316nm.

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