IMPACT: International Journal of Research in Applied, Natural and Social Sciences (IMPACT: IJRANSS)
ISSN (P): 2347–4580; ISSN (E): 2321–8851
Vol. 9, Issue 10, Oct 2021, 37–42

PREPARATION, CHARACTERIZATION, OPTICAL AND PHOTOLUMINESCENCE STUDIES OF GAMMA RAYED ERBIUM DOPED NANOCRYSTALLINE CAF_2

***G N Venkata Reddy*[1] *& C. Pandurangappa*[2]**

[1]*Research Scholar, Department of Physics, HPPC Government First Grade College, Challakere, Chitradurga -577522, India*

[2]*Research Scholar, Department of Physics, RNS Institute of Technology, Channasandra, Bangalore-560098, India*

Received: 27 Oct 2021 **Accepted:** 27 Oct 2021 **Published:** 29 Oct 2021

ABSTRACT

Nanoparticles of calcium fluoride (CaF_2) doped with Erbium doped are prepared using co-precipitation technique. Preliminary characterization of the samples is carried out using PXRD, SEM and FTIR. The nanoparticles are irradiated with γ-rays. Optical studies on the irradiated samples are made through absorption and luminescence measurements. The results of optical absorption (OA) spectra showed generation of various color centers. All the centers responsible for the absorption are identified and attributed to defects generated due to gamma radiation. Photoluminescence (PL) spectrum exhibited emission peaks at ~387, 442, 460 and 517 nm. The mechanisms of OA and PL of the observed samples are discussed in detail.

KEYWORDS: *Nanocrystals; Optical Absorption; Photoluminescence; Lattice Defects; Color Centers*

INTRODUCTION

Development in the preparation, characterization and applications of nanomaterials have drawn more attention in the recent past. Rare earth doped luminescent nanomaterials have potential technological applications in display systems. Nano fluorides have wide range of applications compared to sulfides and oxides of metals. The high stability and non-hygroscopic character of CaF_2 have made it special among other fluoride compounds. CaF_2 has wide transparency range apart from large optical band gap (12eV) [1]. This leads to formation of color center even for low dose irradiation by gamma rays. There are different novel methods to prepare nanoparticles of CaF_2 [2-6]. In the present work nanoparticles of CaF_2 doped with Erbium (Er) are synthesized using co-precipitation method. The prepared samples are characterized by XRD, FTIR, SEM, OA and PL techniques.

EXPERIMENTAL

The synthesis chart of 2mol% Er doped CaF_2 nanoparticles is represented in figure 1. To begin with Stoichiometric quantity of Erbium oxide (Er_2O_3) was transferred in to 250 ml conical flask and nitric acid (HNO_3) was added in to it in small quantity. The mixture was stirred well and was evaporated by slow heating on a sand bath. This process converts Er_2O_3 to erbium nitrate [$Er(NO_3)_2$]. stoichiometric quantities of Ammonium fluoride (NH_4F) and Calcium chloride ($CaCl_2$) were added in to the conical flask. The chemical mixture was dissolved in 100 ml distilled water and kept for stirring for 2 hours. Then solution mixture was centrifuged and the precipitate is extracted. The precipitate was washed thoroughly with ethanol and extracted on to a ceramic dish. The final product (Er doped CaF_2) was obtained by slow drying of the precipitate on a sand bath at 100^{o} C.

The structure of the prepared samples was confirmed by XRD measurements using a Philips X-pert PRO powder diffractometer with Cu-K_α radiation (λ=1.54056Å) with a scan range 10-90^o. The morphological studies of the samples were carried using scanning electron microscopy (JEOL JSM-840A) by sputtering technique with gold as covering contrast material. Then the samples were subjected to FTIR studies using Nicolet Magna 550 spectrometer with KBr pellets. The wavelength range used for the FTIR studies was 400 - 4000 cm^{-1}. Afterwards the Er doped CaF_2 nanoparticles were exposed to Gamma radiations (γ-rays) of dose 5 KGy. The UV-Visible spectrum of the samples was recorded in the wavelength range 200 to 900 nm using V-570 UV/VIS/NIR double beam spectrophotometer. The PL studies of Er doped CaF_2 were carried out using a spectrofluorometer (Jobin Yvon Fluorolog 3) equipped with a 450W Xenon lamp as the excitation source.

RESULTS AND DISCUSSION

PXRD, SEM and FTIR

Figure 2 shows powder X-ray diffraction patterns (PXRD) of Er doped CaF_2 samples. It confirmed the cubic crystallinity of prepared nanocrystals. The XRD peaks are indicate cubic phase of fluorite structure belonging to space group Fm3m. The JCPDS Card no. 87–0971[7] was used to compared XRD pattern with literature. The XRD analysis showed that the average lattice constant of obtained nanocrystals is 0.5464 nm. Scherrer's formula was used to calculate crystalline size and the calculated value was found to be about 30 nm. SEM pictures of Er doped CaF_2 shown in figure 3 revealed that CaF_2 nanoparticles are fluffy, porous and agglomerated. SEM also indicates that the nanocrystals are spherical in shape and are distributed homogeneously. They are found to contain voids [8]. Figure 4 shows FTIR spectrum of the samples with two IR absorption bands located at ~3419 and 1555 cm^{-1}. These are found to be characteristic of H_2O molecules indicating the presence small quantity of hydroxyl groups during preparation of sample. The 364 cm^{-1} peak is attributed to hindered rotations of hydroxyl ions. The band peaked at 3419 cm^{-1} is assigned to $I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} ions [9]. The ~2360 cm^{-1} band is because of KBr pellets utilized for recording FTIR spectrum.

Optical Absorption Studies

Optical absorption (OA) spectrum of γ-irradiated Er doped nanocrystalline CaF_2 samples is shown in figure 5. A series of absorption peaks with a noticeable and solid one at ~333 nm and three feeble ones at 413, 485 and 584 nm are observed. The origin of these absorption bands is accounted based the defects created during γ-radiation. In rare earth doped CaF_2 substitution of host ion by the dopant accomplishes charge compensation along with formation of lattice vacancies and interstitials. Additional positive charge of Erbium ions is compensated through fluoride ions at interstitials. Gamma-irradiation is proved to produce color centers in CaF_2. F-aggregates along with F-center are the significant defects created by γ-rays. Free electrons liberated by γ-rays get trapped at negative ion vacancies and form F-centers. An F-center is a fluoride ion vacancy trapping an electron. In CaF_2 an F-center is formed when an electron transits from 1s state to 2p state. The absorption peak at 333 nm may be attributed to V_k center [10]. The 413 and 485 nm absorption peaks may be assigned to perturbed V_k and M centers respectively. The V_k arises when electron transits to the excited states of ${}^4G_{11/2}$ from the ground state where as M center forms due to spectroscopic transition to ${}^4F_{5/2}$ state from the ground state ${}^4I_{15/2}$ [11,12]. The absorption at ~584 nm is attributed to Calcium colloids.

Photoluminescence Studies

Photoluminescence (PL) is used to identify specific defects and their relative concentration. PL is able to detect the defects which overlap in absorption spectrum. The PL spectrum of γ-rayed CaF_2:Er is as shown in figure 6. The emission peaks lying from UV to infrared region are found to be characteristic transitions of Er. The gamma rayed CaF_2 nanoparticles were excited under 330 nm. The corresponding PL emissions are peaked at ~387, 442, 460 and 517 nm. In irradiated Er doped CaF_2 nanocrystals erbium can be in trivalent (Er^{3+}) state. As mentioned earlier, irradiation of CaF_2 forms centers particularly F and F-aggregate centers. When irradiated CaF_2 nanocrystals are excited with UV light, electronic transitions result in the release of absorbed by the defects gets in the form of photons. This is referred as PL emission. The PL spectra depends on the dopants and their concentration along with the location in the host lattice. Based on these facts the PL emissions could be attributed to different electronic transitions as a result of irradiation [13]. The PL emission at 387 nm is attributed to $^4G_{9/2} \rightarrow {}^4I_{15/2}$ transitions of Er^{3+} ions. Similarly 442 nm, 460 and 517nm emissions are attributed to $^2G_{9/2} \rightarrow {}^4I_{15/2}$, $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^2H_{11/2} \rightarrow {}^4I_{15/2}$ transitions respectively [14, 15].

CONCLUSIONS

Er doping of CaF_2 nanoparticles was successfully prepared by co-precipitation method. The nanocrystalline CaF_2:Er was characterized by XRD, SEM, FTIR, Optical absorption and PL. PXRD showed that the average particle size of CaF_2:Er is about 30 nm. The morphological features studied using SEM showed that the as-prepared samples were agglomerated from few microns to a few tens of microns, fluffy and porous. Optical absorption showed that γ-radiation creates F-aggregate centers in Er doped nanocrystalline CaF_2. PL studies revealed various transitions responsible for emission in γ-rayed nanocrystalline CaF_2:Er.

ACKNOWLEGEMENT

Authors of this article are greateful to the Management and Principal of RNS Institute of Technology, Bengaluru, India for providing the experimental facility and constantly supporting the authors to carry out this research. The authors thank IISc, Bengaluru, India for providing XRD, SEM and FTIR spectra. The authors greatly indebted to IGCAR, Kalpakkam, India for Providing the gamma irradiation, Optical absorption and Photoluminescence studies.

REFERENCES

1. *J. Wang, J. Hao, Q. Wang, Y. Jin, F. Li, B. Liu, Q. Li, B. Liu, Q. Cui, Pressure-induced structural transition in CaF2 nanocrystals, Phys. Status Solidi Basic Res, 2011,248,1115–1118*
2. *C. Pandurangappa, B.N. Lakshminarasappa ,Spectroscopic studies of g-rayed CaF2:Sr, Journal of Luminescence, 2013, 138,61-64*
3. *L. Ma, L. L. Yang, Y. G. Wang, X. P. Zhou, and X. Y. Xu,Microwave-assisted preparation of nearly monodisperse flower-like CaF2 microspheres, Ceram. Int. 2013, 39, 5973.*
4. *A. Safronikhin, H. Ehrlich, and G. Lisichkin,, Double-jet precipitation synthesis of CaF2 nanoparticles: The effect of temperature, solvent, and stabilizer on size and morphology, J. Alloys Compd, 2017 694, 1182.*

5. *P. Dolcet, A. Mambrini, M. Pedroni, A. Speghini, S. Gialanella, M. Casarina, and S. Gross,, Room temperature crystallization of highly luminescent lanthanide-doped CaF2 in nanosized droplets: first example of synthesis of metal halogenide in miniemulsion with effective doping and size control, RSC Adv, 2015,5,16302.*
6. *V. V. Osipov, V. V. Lisenkov, V. V. Platonov, and E. V. Tikhonov, Processes of interaction of laser radiation with porous transparent materials during their ablation, Quantum Electron. 2018 48, 235*
7. *V. G. Il'vesa, S. Yu. Sokovnina, M. G. Zuevb , M. A. Uiminb, M. Rähne , J. Kozlovae and V. Sammelselge, Effect of Annealing on Structural, Textural, Thermal, Magnetic, and Luminescence Properties of Calcium Fluoride Nanoparticles, Physics of the Solid State, 2019, Vol. 61, No. 11, pp. 2200–2217*
8. *Najlaa D. Alharbi, Size Controlled CaF2 Nanocubes and Their Dosimetric Properties Using Photoluminescence Technique, Journal of Nanomaterials Volume 2015, Article ID 136957, 8 pages*
9. *Mohammad S. Al-Ajely, Kareema M. Ziadan and Rafed. M. Al-Bader, Preparation and characterization of calcium fluoride nano particles for dental applications, , International Journal of Research, 2018, Vol. 6 No. 1*
10. *Shatavari Kulshrestha & Shakir Khan & Sadaf Hasan & M. Ehtisham Khan & Lama Misba & Asad U. Khan, Calcium fluoride nanoparticles induced suppression of Streptococcus mutans biofilm: an in vitro and in vivo approach, Applied Microbiology and Biotechnology,2016, 100, pages1901–1914*
11. *Weiwei Ma, Liangbi Su, Xiaodong Xu, Jingya Wang, Dapeng Jiang, Lihe Zheng, Xiuwei Fan, Chun Li, Jie Liu, and Jun Xu, Effect of Erbium concentration on Spectroscopic properties and 2.79 micrometer laser performance of Er:CaF2 crystals, Optical Materials Express, 2016,Vol. 6, Issue 2,pp. 409-415*
12. *Mical Culp, Vernessa M. Edwards, Bommareddi Rami Reddy, Optical absorption Spectroscopy, energy upconversion and white light emission characterstics of erbium doped calcium fluoride, Journal of Photonics for Energy,2017, 7(2) 026001.*
13. *M. Zahedifar a,b,□ , E. Sadeghi a , S. Harooni, Thermoluminescence characteristics of the novel CaF2:Dy nanoparticles prepared by using the hydrothermal method, NIMB, 2012, Volume 291, 15, Pages 65-72.*
14. *Claudiane dos S.BezerraMário E.G.Valerio, Structural and optical study of CaF2 nanoparticles produced by a microwave-assisted hydrothermal method, , Physica B: Condensed Matter, 2016,Volume 501, 15, Pages 106-112*
15. *Duong Thi Mai Huong, Le Van Vu, Nguyen Ngoc Long, Duong Ngoc Thanh,, Structural and Optical Properties of Samarium Doped Calcium Fluoride Nanoparticles Synthesized By Co-Precipitation Technique, VNU Journal of Science: Mathematics – Physics, 2016,Vol. 32, No. 1, 44-51*

FIGURE CAPTIONS

- Figure 1. Flow chart for the synthesis of Erbiuum doped CaF_2 nanoparticles by co-precipitation method
- Figure 2. Powder XRD spectrum of Er doped nanocrystalline CaF_2
- Figure 3. SEM pictures of Er doped nanocrystalline CaF_2
- Figure 4. FTIR Spectra of Er doped nanocrystalline CaF_2

- Figure 5. Optical absorption spectrum of Er doped nanocrystalline CaF_2
- Figure 6. Photoluminescence spectrum of Er doped nanocrystalline CaF_2

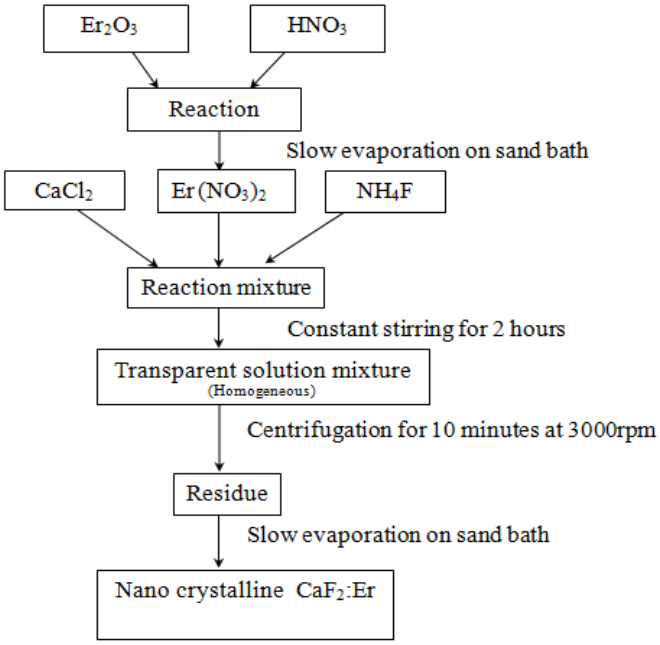

Figure 1

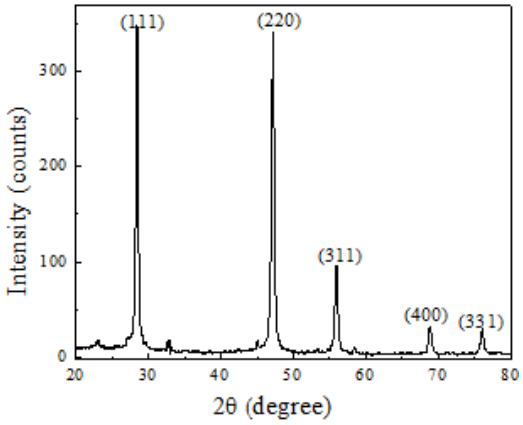

Figure 2

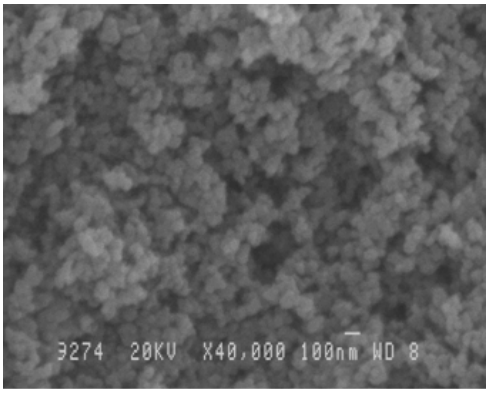

Figure 3

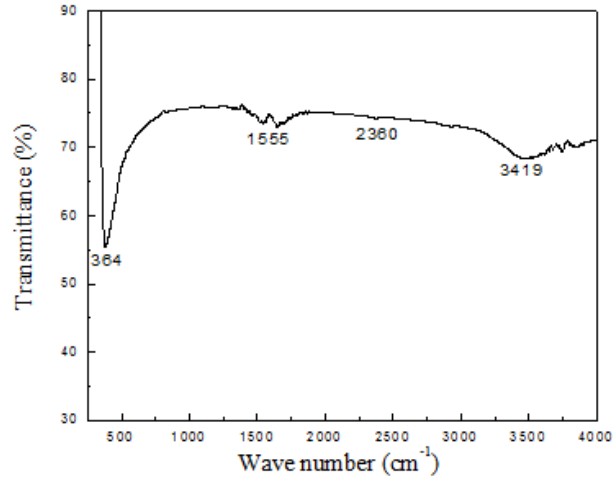

Figure 4

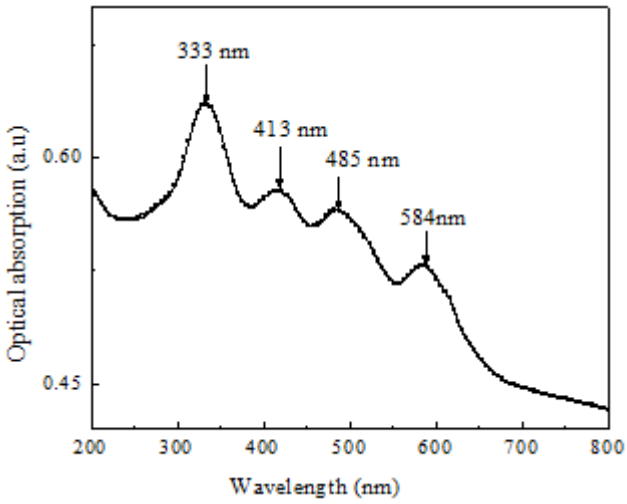

Figure 5

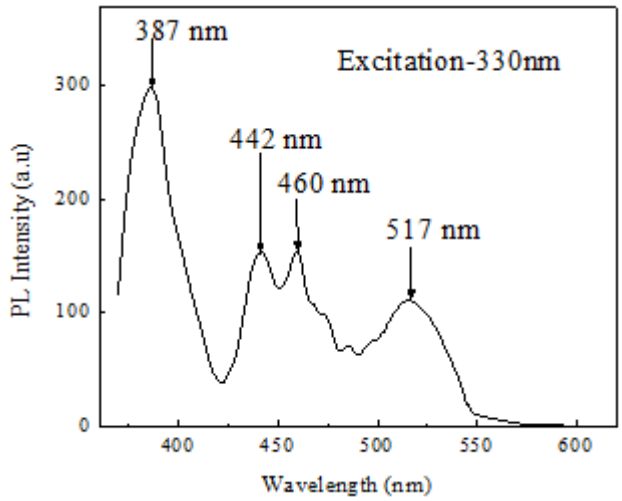

Figure 6