

Contents list available at **IJND**
International Journal of Nano Dimension

Journal homepage: www.IJND.ir

Preparation and characterization of $\text{CaF}_2:\text{Ce}^{3+}$ nanoparticles with spectroscopic studies

ABSTRACT

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Received: 19 September 2012

Accepted: 28 February 2013

In this research Calcium fluoride nanoparticles and its different amount of cerium ion dopant (5% and 10%) were prepared. The mentioned nanoparticle were studied by fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), absorption and photoluminescence spectra (PL) and Scanning electron microscopy (SEM). The XRD patterns indicate a typical cubic fluorite structure and no other impurities. SEM results show the synthesized particles having uniform grain size. Many absorption peaks and bands are present in the absorption spectra, corresponding to the rich energy levels of cerium ion.

Keywords: *Organic functional; Groups; Coprecipitation; NanoCaF₂; XRD (X-Ray Diffraction).*

INTRODUCTION

Nanoparticles (NPs) are defined as particles of less than 100nm in diameter. They exist widely in the natural world, for example as the products of photochemical and volcanic activity, and created by plants and algae. The nanomaterials level is the most advanced at present, both in scientific knowledge and in commercial applications. A decade ago, NPs were studied widely because of their size-dependent physical and chemical properties [1] and now they have entered a commercial exploration period. In order to produce small particle size, often a high-speed homogenization or ultrasonication may be employed [2]. Many nanoparticles of different chemical compositions, shapes, and size distributions have been prepared by different kinds of methods such as gas evaporation [3], laser vaporization [4], ionized beam deposition, sol-gel process [5], hydrothermal [6] and solvothermal process [7], etc. Change in physical and chemical properties of materials on nanoscale have resulted important applications and have received considerable attention in various fields.

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One of the alkali fluoride compounds that were applied in this study is CaF_2 , because of its high stability and non-hygroscopic behavior. Recently CaF_2 gained a renewed interest as a laser material when doped with rare-earth material [8]. CaF_2 nanoparticles were synthesized by different methods such as sol-gel method [9], solvothermal process [10], reverse micelle method, different precipitation methods [11], and flame synthesis [12].

Nanoparticles doped with three valents rare earth (lanthanides), having fluoresce properties, have a good application potential in displays, communication, lasers and modern electronics equipment's [13]. 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. Nanoparticles of calcium fluoride are quite transparent in optical region due to their low energy phonons and high degree ionizations [14]. These properties make them much more transparent than any other calcium compositions like calcium sulfides or oxides.

Crystalline CaF_2 with isotropic fluoride structure is a suitable phosphorous host, for having a good transmission in 0.3 to 8 μm region of spectra [15]. Since, the refraction index of 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 CaF_2 nanoparticles.

EXPERIMENTAL

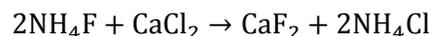
Materials and instruments

All of the solvents were purified by standard methods. 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 $\lambda_{\text{Cu}}=1.540\text{\AA}$. 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 CaF_2 nanoparticles

0.01 moles of CaCl_2 was solved in 100 milliliters of distilled water in an erlenmeyer. Then 0.02 moles of NH_4F 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 CaF_2 : Ce^{3+} nanoparticles (5% and 10%)

A mixture of calcium chloride (0.75 gr) and a mass of 0.15 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 0.43 gr NH_4F was added and stirring was continued for 12 hours. (Those amounts belong to the 5% solution, then for preparation 10% solution of our product another quantities were apply: 0.6 gr CaF_2 , 0.3 gr $\text{Ce}(\text{NO}_3)_3$ and 0.43 gr NH_4F). The above process was done again for powdering CaF_2 : Ce^{3+} . Annealing effects on the prepared samples was examined by calcinations of CaF_2 : Ce^{3+} powder for 4 hours in 400 and 600°C.

RESULTS AND DISCUSSION

FTIR absorption was used in order to check the characteristic bands of the nano CaF_2 . Similar spectra were observed for other nanoparticles. (Figure 1) The spectrum shows two

strong IR absorption bands at 3154.39 and 1409.33 cm^{-1} which are characteristic of H–O–H bending of the H_2O molecules revealing the presence hydroxyl groups in the as prepared sample.

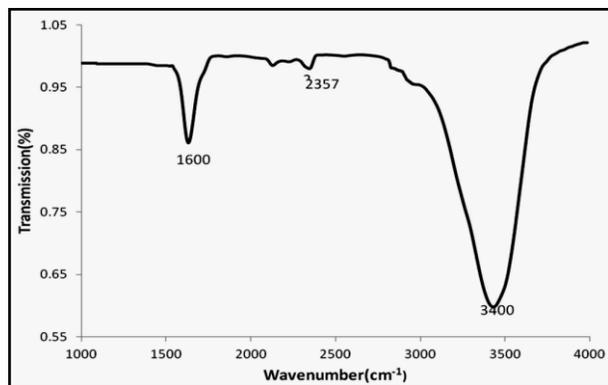


Fig. 1. FT-IR spectrum of nano- CaF_2

Figure 2 shows XRD plot of an undoped sample of CaF_2 nanoparticles prepared by coprecipitation method. Features of this plot indicate the presence of a cubic phase for CaF_2 films which is a typical structure for fluorites with $\text{fm}3\text{m}$ spatial groups. Average lattice constant was 5.46Å which is in agreement with the recorded data of 5.44Å from JCPDF 772096 [12]. Particle's size calculated from Debye-Scherer formula is estimated to be 30-35nm.

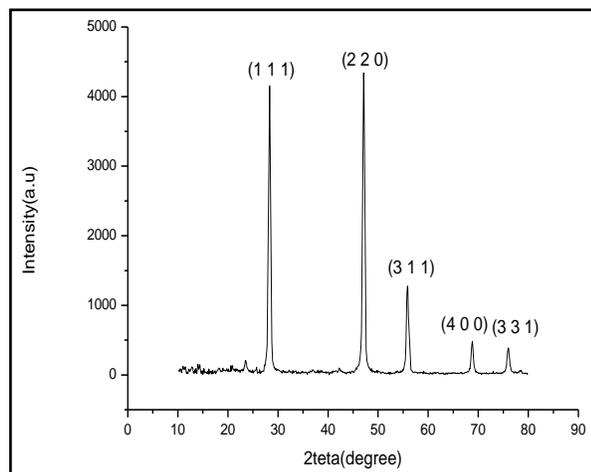


Fig. 2. XRD plot of an undoped sample of nano CaF_2

Figure 3 shows the difference between XRD plot of $\text{CaF}_2:\text{Ce}^{3+}$ (5% and 10%). Full width

half maximum (FWHM) of prepared sample is relatively smaller than for the undoped CaF_2 . However, this factor and subsequently particle's size is very dependent to annealing temperature of doped CaF_2 and becomes the biggest (size of 90nm) for the highest temperature that we examined (600°C). It seems that this is happened since the small holes are pyrolysed followed by a re crystallization in due course of extra heating process.

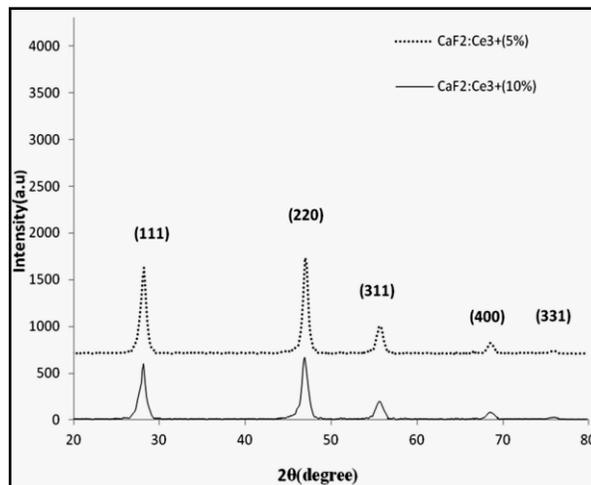


Fig. 3. Comparison between XRD plot of $\text{CaF}_2:\text{Ce}^{3+}$ nanoparticles with different doping percent

Optical absorption spectrum of nano CaF_2 and two $\text{CaF}_2:\text{Ce}^{3+}$ nanoparticles are given in Figures 4 and 5 respectively. As it is clear from this figure there are a strong absorption band in 204nm for grown $\text{CaF}_2:\text{Ce}^{3+}$. By annealing in 400°C and 600°C, absorption band is shifted to 215 and 231nm, respectively. Absorption edge shifts to longer wavelength as annealing temperature increases. This can be due to increase in the surface to volume ratio which occurs in higher temperature and causes more vacancy sites, imperfections and some other point defects. Defects such as Frenkel and Schottky may cause virtual states in band gap of the materials and they have a significant role in optical absorption in UV region of spectra. It seems the particle size grows up by heating, and then some optical absorbent concentration decreases, one may expect a shift to higher wavelength of absorption edge of $\text{CaF}_2:\text{Ce}^{3+}$ nanoparticles.

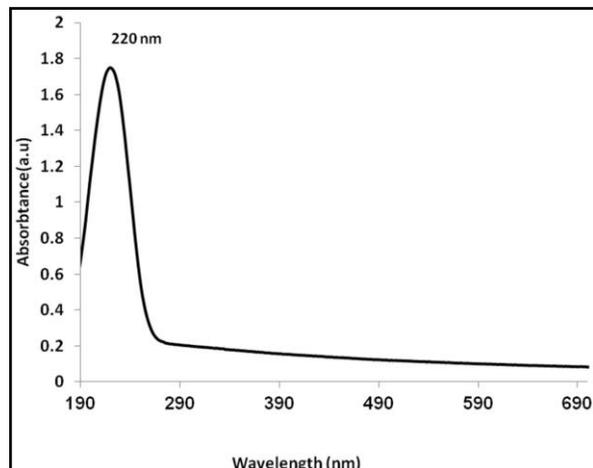


Fig. 4. Optical absorption spectrum of nano CaF_2

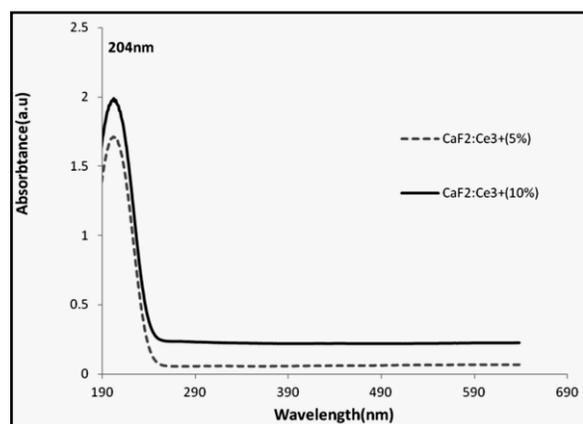


Fig. 5. Optical absorption spectrum of $\text{CaF}_2:\text{Ce}^{3+}$ nanoparticles with different doping percent

Photoluminescence (PL) Results

Emission spectra of the prepared CaF_2 nanoparticles (Figure 6) were taken by a fluorescent spectrophotometer of Cary 4000 at excitation wavelength of 254nm. PL spectra from $\text{CaF}_2:\text{Ce}^{3+}$ nanoparticles shows (Figure 7) two UV bands at 316 and 337nm, in agreement with the literature [16].

However, No features was detected from undoped CaF_2 spectra, indicating that the above features are related to the 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 Ce^{3+} ions. The double structure of the peaks is a characteristic of ground state splitting which occurs in $F_{5/2}$ and $F_{7/2}$.

Cerium is a three valent mineral material and can loss, in a chemical reaction, two electrons from 6S and one from 4f orbital. Ground state of Ce^{3+} split in two sub bands of $2F_{5/2}$ and $2F_{7/2}$ by obtaining energy related to $2000\text{-}3000\text{Cm}^{-1}$. In a Cubic crystal field, 5d excited state of Ce^{3+} becomes also splitted to T_{2g} and E_g , by getting energy of 25000Cm^{-1} . Energy levels of Ce^{3+} are schematically drowned in Figure 8. Electron transitions cause emission and absorption bands in 200-305nm region. Emission from 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 give both aide and also sharp emission bands in PL spectra's. Ce^{3+} ions and Ca^{2+} are not covalent, so Ce^{3+} ions can cooperate in CaF_2 lattice with a different symmetry. As a Ca^{2+} ion is replaced by a three valents Ce^{3+} an extra F^- ion will enter in this region and make electric charge neutrality in the CaF_2 lattice. These replacements cause the major structural defects in $\text{CaF}_2:\text{Ce}^{3+}$. If the dopant concentration is low enough (less than 0.1% cerium ions), F^- ions fill the holes present in next nearest neighbor of Ce^{3+} and makes isolated trigonal (C_{3v}), tetragonal (C_{4v}) or rhombohedra (C_{2v}) defects.

Intensity of flourcent 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 [17].

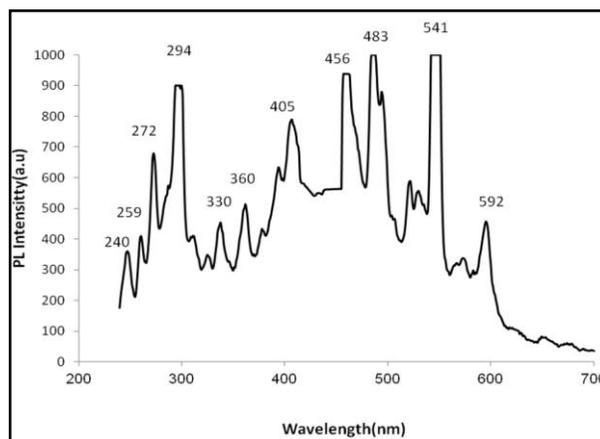


Fig. 6. PL spectrum from nano CaF_2 , $\lambda_{\text{ex}}=218\text{nm}$

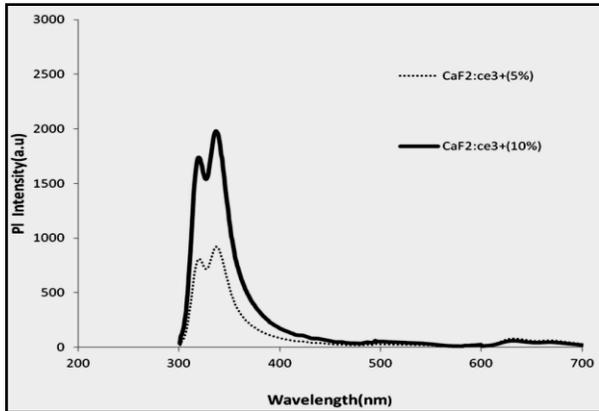


Fig. 7. PL spectrum from $\text{CaF}_2:\text{Ce}^{3+}$ nanoparticles with different doping percent

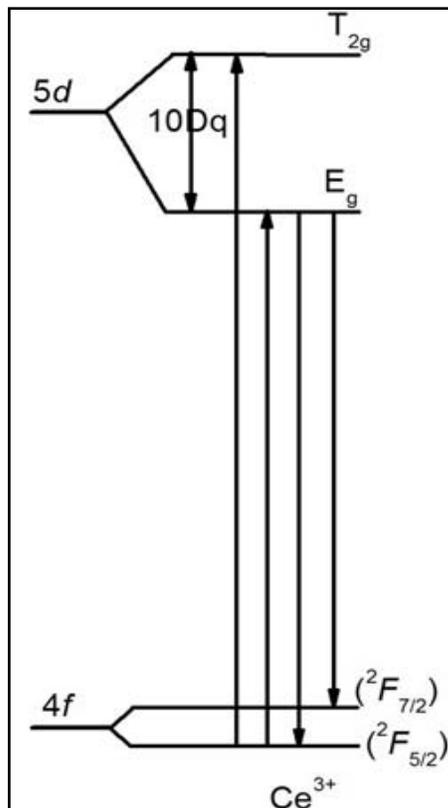


Fig. 8. Schematic levels of Ce^{3+} in $\text{CaF}_2:\text{Ce}^{3+}$ nanoparticles

According to the Figure 9a, 9b and 9c, the SEM pictures demonstrated the spherical morphology of particles that become smaller and agglomerated by increasing dipping percent. The average size of particles is measured by image j software for each sample.

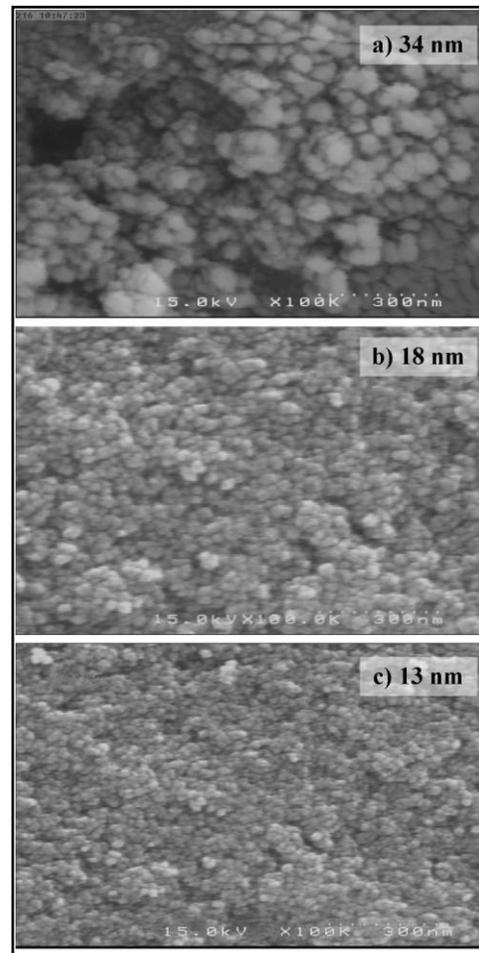


Fig. 9 SEM picture of a) nano CaF_2 b) $\text{CaF}_2:\text{Ce}^{3+}$ nanoparticles 5% c) $\text{CaF}_2:\text{Ce}^{3+}$ nanoparticles 10% (with average size of them)

CONCLUSION

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 $\text{CaF}_2:\text{Ce}^{3+}$, so surface of the prepared nanoparticles are simply covered by organic residual materials like Cl_2 , NO_3 and 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.

ACKNOWLEDGEMENTS

The authors wish to thank Dr. Gh. Rezaei Behbahani for his valuable helps. This work was supported by International Imam Khomeini University.

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Cite this article as: M. Khanlary et al.: Preparation and characterization of CaF₂:Ce³⁺ nanoparticles with spectroscopic studies. *Int. J. Nano Dimens.* 5(2): 163-168, Spring 2014

