

Structural and Optical Properties of Samarium Doped Calcium Fluoride Nanoparticles Synthesized By Co-Precipitation Technique

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Abstract: CaF₂ nanoparticles doped with 0, 1, 2, 3, 4 and 5 mol% Sm³⁺ were prepared by co-precipitation method. These nanoparticles were studied by X-ray diffraction (XRD), transmission electron microscopy (TEM), photoluminescence (PL), photoluminescence excitation (PLE) spectra, energy-dispersive X-ray spectroscopy (EDS) and diffuse reflective spectra. The XRD patterns indicate cubic structure of CaF₂ and no other impurities. TEM images show that CaF₂ nanoparticles have size varying from 15 to 20 nm. The photoluminescence spectra show 4 peaks at 566 nm, 604 nm, 645 nm and 704 nm, which are assigned to different transitions from the ⁴G(4)_{5/2} excited state to the ⁶H_J with J = 5/2; 7/2; 9/2 and 11/2 ground states of Sm³⁺ ions. The PLE spectra show 8 lines, which are attributed to the absorption transitions from the ⁶H_{5/2} ground state to the ⁴H(1)_{9/2}, ⁴D(2)_{3/2}, ⁶P_{7/2}, ⁴F(3)_{7/2}, ⁶P_{5/2}, ⁴M_{17/2}, ⁴I(3)_{13/2} and ⁴M_{15/2} excited states. Six lines among eight excitation lines were observed in the diffuse reflection spectra.

Keywords: CaF₂ nanoparticles, samarium, co-precipitation technique.

1. Introduction

Fluoride materials are attractive materials with potential applications such as dental [1-3], photonics, image display, light amplification and precursors for ceramic processing. Among the alkali fluorides, calcium fluoride (CaF₂) is an attractive material for high stability and non-hygroscopic properties. CaF₂ is an ideal host material for emitting ions in a wide wavelength range, with low refractive index and low phonon energy.

With the development of nanotechnology, many techniques have been developed to synthesize CaF₂ nanostructures such as precipitation [4-8], hydrothermal [9,5,6], spraying [2,3], plasma synthesis in vacuum [1], micro-emulsions [10].

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It is well-known that rare-earth (RE) ions have sharp absorption and emission bands from the UV to infrared range. For that reason, RE doped materials possess potential applications in many different fields such as optoelectronics, photonics and biomedicine . However, to the best of our knowledge, most of previous works have been focused on CaF₂ doped with Dy³⁺ [11], Tm³⁺[11], Sm³⁺ [12], Er³⁺ [10], Eu³⁺ [13], Eu²⁺[9,14], etc... CaF₂ was also co-doped with Mn²⁺ and Eu²⁺ [13], Yb³⁺ and Er³⁺ [15], etc ... Ca²⁺ in the lattice can be replaced by rare earth (RE) ions. According to our knowledge, only a few works were devoted to CaF₂ doped with Sm³⁺ ions [16]. Ion radius of Sm³⁺ is 0.958 Å which is nearly equal to the radius of Ca²⁺ ion (1.000 Å). Therefore, it is expected that the Sm³⁺ ion can easily substitute for Ca²⁺ ion in the host crystal.

In this report, we fabricated CaF₂:Sm³⁺ nanoparticles by co-precipitation method. The structure, absorption, PL and PLE properties of the samples were investigated in detail.

2. Experimental

Undoped and Sm³⁺-doped CaF₂ nanoparticles were prepared by coprecipitation method from solutions of calcium chloride CaCl₂, samarium nitrate Sm(NO₃)₃ and NH₄F. An appropriate amount of NH₄F was dissolved in double distilled water under constant stirring for 10 min to form NH₄F solution. To prepare Sm³⁺-doped samples, stoichiometric amounts of CaCl₂ and Sm(NO₃)₃ aqueous solutions were mixed together. The molar ratio of Sm:Ca was equal to 0; 1; 2; 3; 4 and 5 mol%.

In the next step, appropriate amounts of NH₄F solution were added into the mixed nitrate solution under stirring for 3h at room temperature. After that, the resulting precipitate was filtered off and washed several times in water and ethanol to remove the chemicals remaining in the final products. The products were dried in air at 65 °C for 5 h.

Crystal structure of the obtained powders was analyzed by X-ray diffraction (XRD) using an X-ray diffractometer SIEMENS D5005, Bruker with Cu Kα₁ (λ = 1.54056 Å) irradiation. Surface morphology of the samples was observed by using a Nova nano SEM 450. Composition of the samples was determined by an energy-dispersive X- ray spectrometer (EDS) OXFORD ISIS 300. Room temperature PL and PLE spectra were collected on a spectrofluorometer Fluorolog FL 3-22 Jobin-Yvon-Spex with a 450 W Xenon lamp as excitation source. Diffuse reflection measurements were carried out on a UV-VIS-NIR Cary-5000 spectrophotometer. The spectra were recorded in the wavelength region of 300-600 nm. Absorption spectra of the samples were obtained from the diffuse reflectance data by using the Kubelka-Munk function [2]:

$$F(R) = \frac{(1-R)^2}{2R} = \frac{K}{S}$$

where R , K and S are the reflection, the absorption and the scattering coefficients, respectively.

3. Results and Discussions

3.1 Structure characterization and morphology

Typical XRD patterns of CaF₂ nanoparticles doped with 0; 1; 2; 3; 4 and 5 mol% Sm³⁺ are presented in Fig.1. In all case, the powder XRD analysis evidenced that the obtained CaF₂ samples have simple cubic crystal structure. No diffraction peak of other substances are detected. It is noted

that the introduction of different RE ion concentration does not change the crystal structure of the products.

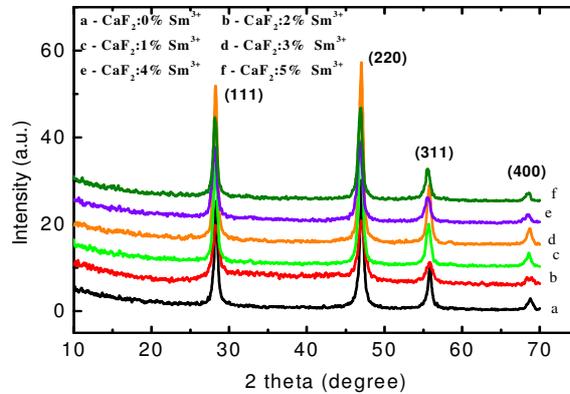


Fig.1. Typical XRD patterns of the undoped and Sm^{3+} -doped CaF_2 nanopowders with different concentration.

The lattice constants of the CaF_2 nanocrystals determined from the XRD patterns are $a = 5.459 \pm 0.001 \text{ \AA}$, which are in good agreement with the standard values $a = 5.463 \text{ \AA}$ (JCPDS 4-864). The average size of the nanocrystals was estimated by using Debye-Scherrer's formula [13]: $D = \frac{0.9\lambda}{\beta \cos \theta}$

where β is the full width at half maximum (FWHM) in radians of the diffraction peaks, θ is the Bragg's diffraction angle and $\lambda = 0.154056 \text{ nm}$. The estimated size of the CaF_2 nanocrystals was $D = 13 \pm 1 \text{ nm}$.

TEM images of the undoped samples are illustrated in Fig. 2. As can be seen from the image, the CaF_2 samples are composed of nanoparticles. The particle diameter ranges from 15 to 20 nm, which are slightly bigger than that calculated by Debye-Scherrer's formula. It is also noted that the nanoparticles agglomerated into big clusters.

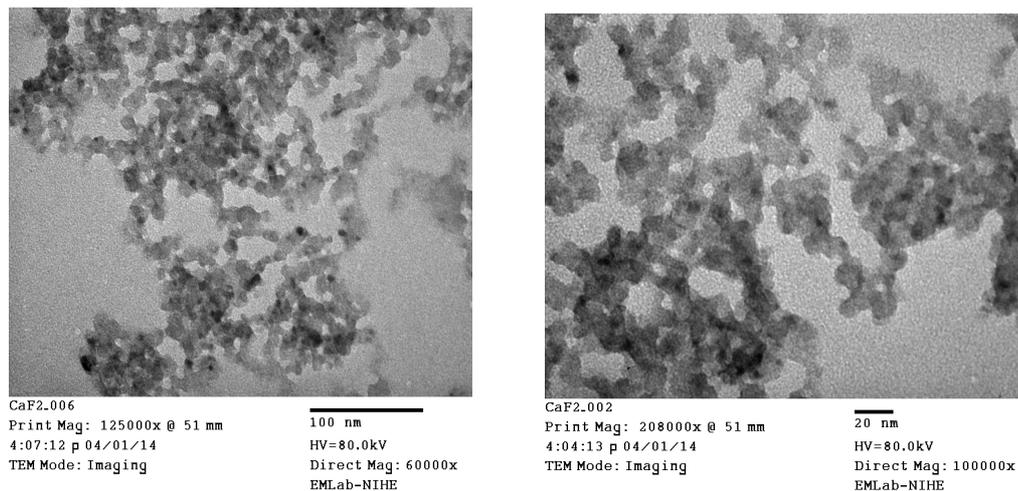


Fig. 2. TEM image of the undoped CaF_2 nanoparticles.

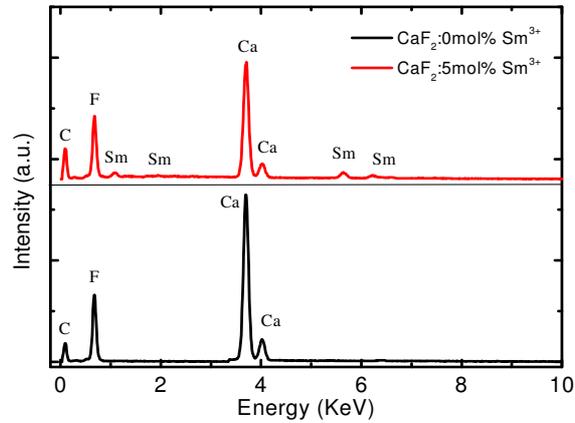


Figure 3. EDS spectra of undoped CaF_2 nanoparticles and CaF_2 nanoparticles doped with 5 mol% Sm^{3+} .

The EDS spectra of the undoped (a) and 5 mol% Sm^{3+} -doped (b) CaF_2 nanoparticles are shown in Fig. 3. The undoped sample mainly consisted of canxi (Ca), fluor (F) elements, whereas in the $\text{CaF}_2:5\%\text{Sm}^{3+}$ sample Sm element appeared, indicating the incorporation of Sm^{3+} ions into the host lattice. It is noted that peak related to carbon (C) comes from the carbon tapes used for EDS measurement.

3.2. Photoluminescence and absorption properties

Fig.4 shows the room temperature PLE spectrum monitored at 604 nm emission line and the PL spectrum under excitation wavelength of 400 nm of the CaF_2 nanoparticles doped with 2 mol% Sm^{3+} . As will be seen in Fig.4, the lines in the spectra are interpreted as the absorptive and radiative intra-configurational f-f transitions within the Sm^{3+} ions.

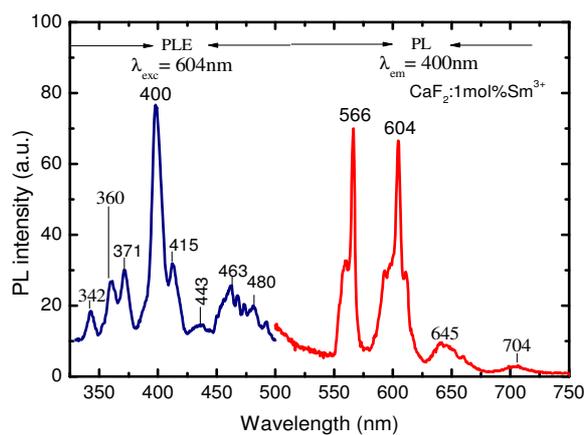


Fig. 4. PL (with $\lambda_{\text{exc}} = 400$ nm) and PLE (at $\lambda_{\text{em}} = 604$ nm) spectra of the $\text{CaF}_2:1$ mol% Sm^{3+} sample.

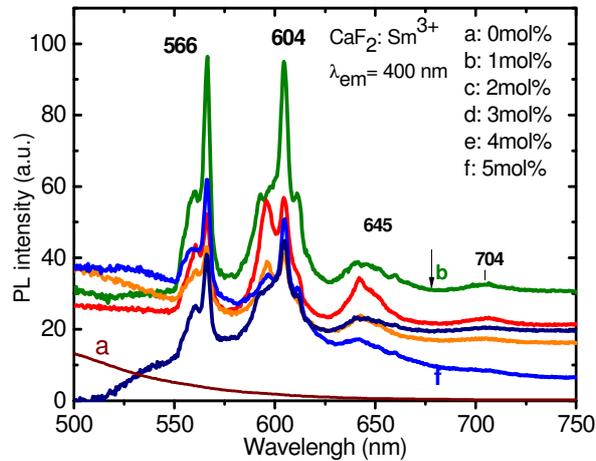


Fig.5. The PL spectra of the $\text{CaF}_2:\text{Sm}^{3+}$ nanopowders doped with different dopant concentrations under 400 nm excitation wavelength.

The room temperature PL spectra of CaF_2 nanoparticles undoped and doped with 1;2;3; 4 and 5 mol% Sm^{3+} excited by 400 nm wavelength are illustrated in Fig. 5. The undoped CaF_2 nanoparticles do not exhibit the groups of emission lines in the wavelength range from 550 to 750 nm, whereas the Sm^{3+} -doped CaF_2 nanoparticles show a group of four emission lines at 566, 590, 604, and 640 nm. Fig. 5 indicates that the PL intensity related to Sm^{3+} ion reaches maximum value when the dopant content is 1 mol%.

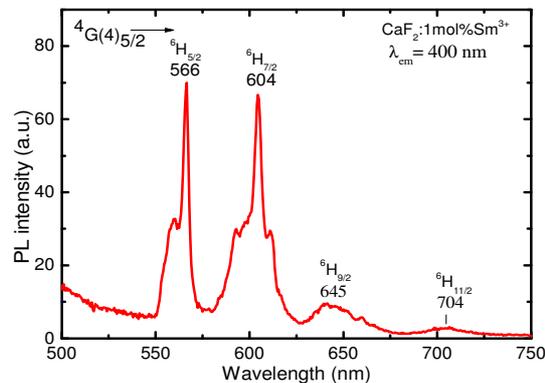


Fig.6. The room temperature PL spectrum of $\text{CaF}_2:1\%\text{Sm}^{3+}$ sample excited by 400 nm wavelength and corresponding transitions.

Fig. 6 depicted typical PL spectrum excited by 400 nm wavelength of 1 mol% Sm^{3+} -doped CaF_2 nanoparticles. The group of emission lines at 566, 590, 604, and 640 nm are assigned to the transitions

from the excited state ${}^4G(4)_{5/2}$ to the ground states 6H_J with $J = 5/2; 7/2;$ and $9/2$ of Sm^{3+} ion, respectively.

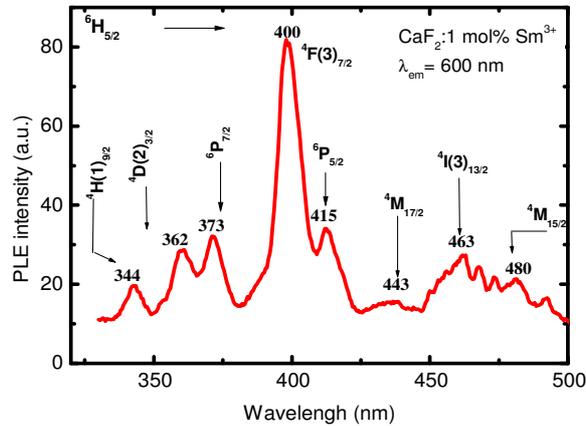


Fig. 7. The PLE spectrum of $\text{CaF}_2:1\text{mol}\%\text{Sm}^{3+}$ sample monitored at emission wavelength of 604 nm and corresponding transitions.

It is worth noting that all the mentioned above emission lines have the same excitation spectra, which demonstrates that all these lines possess the same origin. Typical PLE spectrum monitored at 604 nm emission line of 1mol% Sm^{3+} -doped CaF_2 nanoparticles is illustrated in figure 7. The excitation lines located at 345, 361, 372, 400, 413, 443, and 468 nm are attributed to the absorption transitions from the ${}^6H_{5/2}$ ground state to the ${}^4H(1)_{9/2}$, ${}^4D(2)_{3/2}$, ${}^6P_{7/2}$, ${}^4F(3)_{7/2}$, ${}^6P_{5/2}$, ${}^4M_{17/2}$, and ${}^4I(3)_{13/2}$ excited states, respectively. Fig. 8 depicts diffuse reflection spectra measured at room temperature of the undoped CaF_2 and the 1, 2, 3, 4, 5 mol% Sm^{3+} -doped CaF_2 nanoparticles. It can be seen that there is no absorption line in the diffuse reflection spectrum of the undoped CaF_2 nanoparticles, while eight weak absorption lines at 361, 373, 400, 415, 440, 462, 477 and 560 nm are clearly observed in the spectra of Sm^{3+} -doped CaF_2 nanoparticles.

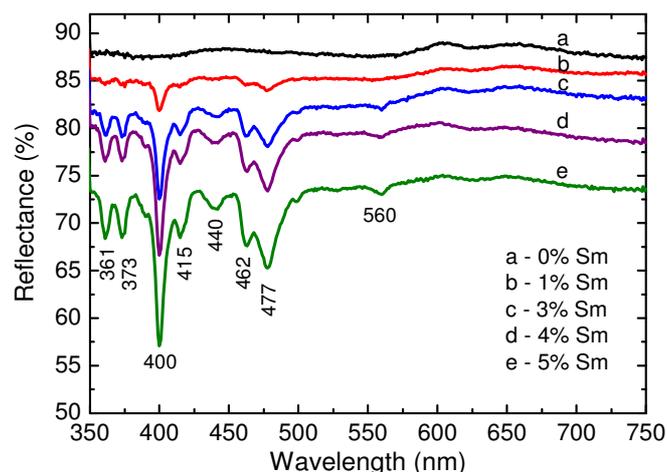


Fig. 8. Diffuse reflectance spectra of the $\text{CaF}_2:\text{Sm}^{3+}$ samples with different dopant concentrations.

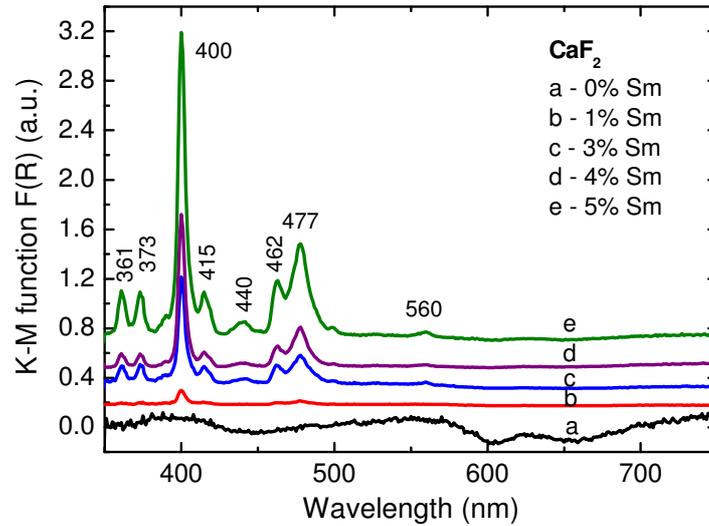


Fig. 9. Kubelka-Munk function graph of Sm^{3+} -doped CaF_2 samples.

Absorption spectra obtained from the diffuse reflectance data by using the Kubelka–Munk function $F(R)$ for the undoped CaF_2 and the 0÷5 mol% Sm^{3+} -doped CaF_2 nanoparticles are shown in figure 9. It is interesting to note that all the mentioned above absorption lines observed in the plot of Kubelka-Munk function have appeared in the excitation spectra as shown in figure 7. The absorption lines located at 361, 373, 400, 415, 440, 462, 477 and 560 nm are assigned to the optical transitions from the $^6\text{H}_{5/2}$ ground state to the $^4\text{D}(2)_{3/2}$, $^6\text{P}_{7/2}$, $^4\text{F}(3)_{7/2}$, $^6\text{P}_{5/2}$, $^4\text{I}(3)_{13/2}$, $^4\text{M}_{15/2}$, and $^4\text{G}_{5/2}$ excited states, respectively.

4. Conclusion

Sm^{3+} -doped CaF_2 nanoparticles were prepared by co-precipitation method. The XRD analysis showed that the nanoparticles have a pure cubic structure. The fluorescent measurements indicate that PL intensity is strongest in the CaF_2 samples doped with 1mol% Sm^{3+} . The PL and PLE spectra of Sm^{3+} ions result from the optical intra-configurational f–f transitions. Some excitation lines were observed as well in diffuse reflection spectra measured at room temperature.

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