Morphology and optical properties of Mg and Sr doped CaF_2 nanocrystals

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ABSTRACT

Magnesium (Mg) and Strontium (Sr) doped Calcium fluoride nanocrystals were synthesized by co-precipitation method. The cubic structure of the samples was confirmed by Powder X-ray diffraction. The average crystallite size of Mg doped samples was found to be ~25 nm whereas in Sr doped one it was ~35 nm. The morphological features revealed that the nanocrystals were agglomerated, crispy and porous. The as-prepared samples showed the presence of hydroxyl groups. The optical absorption spectrum of as-prepared Mg doped samples showed a strong absorption band peaked at ~233 nm whereas the Sr doped one showed a prominent absorption peak at 248 nm. A strong PL emission was observed at ~300 nm in Mg doped samples. However, the Sr doped samples showed two prominent emissions at ~345 and 615 nm.

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1. Introduction

Nanoparticles are of great scientific interest because they act as a bridge between bulk materials and atomic or molecular structures. A bulk material should have constant physical properties regardless of its size. But at the nanoscale this is often not the case due to size-dependent properties such as quantum confinement and high surface to volume ratio. The properties of materials change as their size approaches the nanoscale. High surface to volume ratio provides a tremendous driving force for diffusion of atoms at elevated temperatures. Large surface to volume ratio reduces the melting temperature of nanoparticles [1]. The properties of nanoparticles can be modified by engineering the size, morphology and composition of particles. It has been shown that various material properties such as electrical, mechanical, optical, magnetic are highly influenced by the fine-grained structure and there is an improvement in the concerned properties. Quantum confinement of electrical carriers within nanoparticles, plays a vital role in transfer of energy and charge over nanoscale distances [2]. Nanocrystalline materials are exceptionally strong, hard and ductile at high temperature and chemically very active. They are also much more formable than their conventional and commercially available micron counterparts. Using a variety of synthesis methods, it is possible to produce nanostructured materials in various forms like: thin films, powder, quantum wires, quantum wells, quantum dots, etc. [3].

Fluoride nanoparticles are strategic materials in optical and photonic technologies. They find applications in lighting, optical amplification and lasing. Fluorides also have high band gap wherein allowed electronic transitions of the dopants occur and self-absorption is avoided [4]. One such fluoride with a wide transparent spectral window (190–1100 nm) and large band gap (~12 eV) is Calcium fluoride (CaF_2). CaF_2 single crystal is widely used as host material of luminescent ions, due to its high transparency in a broad wavelength range, low refractive index and low phonon energy. Recently, high power diode-pumped femtosecond laser as well as self-Q-switched laser based on Yb doped and Na-Yb codoped CaF_2 crystals were developed [5]. Light emitting structures based on nanocrystalline Si/ CaF_2 system were developed featuring a great dependence of the photoluminescence properties from the nanoparticles size [6]. Rare earth doped CaF_2 is well studied from the basic research as well application point of view. However, reports on Mg and Sr doped CaF_2 are very rare. The authors have recently studied optical properties of gamma rayed Mg doped CaF_2 single crystals [7]. In the present work Mg and Sr doped (2 mol% each) CaF_2 nanocrystals are synthesized by co-precipitation method and characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM), Infra red spectroscopy (FTIR), Optical absorption and Photoluminescence (PL) techniques.

2. Experimental

The Mg and Sr doped (2 mol% each) CaF_2 nanoparticles were synthesized by taking the nitrates of Mg and Sr, calcium chloride (CaCl_2) and ammonium fluoride (NH_4F). Stoichiometric quantities of magnesium nitrate ($\text{Mg}(\text{NO}_3)_2$) and strontium nitrate ($\text{Sr}(\text{NO}_3)_2$) were taken in separate conical flasks. CaCl_2 and NH_4F were added in to

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each conical flask in stoichiometric quantities. The mixture was dissolved in 100 ml of distilled water and stirred for 2h constantly. The resulting solution mixture was centrifuged for 10min at 3000 rpm. The residue was washed thoroughly with ethanol and extracted onto a ceramic dish. The products ($\text{CaF}_2\text{:Mg}$, $\text{CaF}_2\text{:Sr}$ nanoparticles) were dried slowly on a sand bath maintained at about 100°C and collected into separate containers. The XRD measurements of synthesized samples was carried out using Philips X-pert PRO powder diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) in the scan range of 10° – 90° . The morphology of synthesized samples was studied using scanning electron microscopy (JEOL JSM-840A) by sputtering technique with gold as covering contrast material. The FTIR spectrum was recorded using Nicolet Magna 550 spectrometer with KBr pellets in the range from 400 to 4000 cm^{-1} . The optical absorption measurements of the samples were carried out in the wavelength range of 200 to 900 nm using V-570 UV/VIS/NIR double beam spectrophotometer. The PL emission spectra of the samples were recorded at room temperature using spectrofluorometer (Jobin Yvon Fluorolog 3) equipped with a 450 W Xenon lamp as the excitation source.

3. Results and discussion

3.1. Morphological features

The powder X-ray diffraction patterns (XRD) of as prepared Mg and Sr doped CaF_2 nanoparticles are shown in Fig. 1. The patterns were compared with JCPDS Card no. 87-0971. The XRD patterns confirm the cubic phase of synthesized nanoparticles. Using the $\langle h k l \rangle$ values of different peaks, the lattice constant (a) of the samples was calculated. The average value of lattice constant in Mg doped samples was found to be $\sim 5.443 \text{ \AA}$ whereas in Sr doped samples it was found to be $\sim 5.452 \text{ \AA}$. The values were in good agreement with literature [8]. The XRD patterns present broad peaks revealing the small crystallite size of the synthesized samples. The crystalline size was calculated from the full width at half maximum (FWHM) technique using Scherrer formula $D = K\lambda / (\beta \cos\theta)$ where K is a constant (0.99), λ is the wavelength of $\text{Cu-K}\alpha$ ($1.54 \text{ \AA}$) line, β is the FWHM and θ is the diffraction angle. The crystalline size of Mg doped nanoparticles was found to be $\sim 25 \text{ nm}$ whereas in case of Sr doped one it was $\sim 30 \text{ nm}$. The XRD patterns of Mg and Sr doped CaF_2 nanoparticles revealed their iso-structural nature.

Fig. 2(a) and (b) shows the SEM pictures of as prepared Mg and Sr doped CaF_2 nanoparticles respectively. The SEM results reveal that the powder was porous and agglomerated with polycrystalline nanoparticles. The larger particles exhibited numerous spherical perturbances

Fig. 2. SEM of a) $\text{CaF}_2\text{:Mg}$ and b) $\text{CaF}_2\text{:Sr}$ nanoparticles.

on the surface, indicating their formation due to precipitation of smaller particles. The as-prepared products were agglomerated from few microns to few tens of microns, fluffy and porous. By comparing the SEM pictures of the Mg and Sr doped samples it was found that, Mg doped CaF_2 nanoparticles were smaller in size and less agglomerated. FTIR absorption spectrum was measured to check the purity of the synthesized powder. Similar spectra were observed for Mg and Sr doped samples as shown in Fig. 3. The spectrum showed two strong

Fig. 1. X-ray diffraction spectrum of a) $\text{CaF}_2\text{:Mg}$ and b) $\text{CaF}_2\text{:Sr}$ nanoparticles.

Fig. 3. FTIR spectrum of a) $\text{CaF}_2\text{:Mg}$ and b) $\text{CaF}_2\text{:Sr}$ nanoparticles.

IR absorption bands at ~ 3400 and 1550 cm^{-1} which are characteristic of H–O–H bending of the H_2O molecules. Thus FTIR spectra reveal the presence of hydroxyl groups in the as-prepared samples. The fundamental frequency at $\sim 364\text{ cm}^{-1}$ arises due to hindered rotations of the hydroxyl ions [9,10].

3.2. Optical characterization

The optical absorption spectra of Mg and Sr doped CaF_2 nanocrystals are shown in Fig. 4. A strong absorption peak was observed in Mg doped samples at $\sim 233\text{ nm}$ whereas the Sr doped ones showed strong absorption at $\sim 250\text{ nm}$. The optical absorption is more intense in Sr doped samples. The absorption peaks are found to be characteristic of doped CaF_2 . The origin of these absorption peaks can be explained in the following way. Morphological studies have shown that both Mg and Sr doped samples have voids. The voids can cause fundamental absorption in the UV wavelength range. Also, several defects such as dangling bonds, regions of disorder and impurity species are reported to result in optical absorption in nanocrystalline materials [11]. Surface defects like Schottky and Frenkel which exist in the lattice structure at all temperatures do cause absorption at different wavelengths. It is also possible that, during synthesis of nanoparticles oxygen may enter into the crystalline lattice and replace the fluorine molecule resulting in oxygen impurity and a fluorine ion vacancy (impurity–vacancy). Oxygen ions with a neighboring fluorine vacancy incorporated during the preparation of nanoparticles form the oxygen defects [12]. In the as-prepared nanocrystalline sample surface defects, oxygen defects and impurities present in the lattice cause absorption of light. Thus the absorption peaks at 233 and 250 nm in the present study could be attributed to one or the other of the above defects.

The photoluminescence emission spectra of the Mg and Sr doped CaF_2 nanoparticles are shown in Fig. 5a and b respectively. Mg doped samples showed a strong PL emission at $\sim 300\text{ nm}$ when excited at the absorption maxima i.e. 233 nm. However, when the Sr doped samples were excited at their absorption maximum i.e. 250 nm they showed two prominent emissions at ~ 345 and 615 nm . The PL intensity is found to be more in case of Sr doped samples. It is reported that substitution of Mg^{2+} ($R = 0.86\text{ \AA}$) for Ca^{2+} ($R = 1.14\text{ \AA}$) at cation sites in CaF_2 does not cause any significant distortions of the surrounding lattice [13]. CaF_2 is a material with strong electron–phonon coupling in which excitons localize by means of a lattice deformation to form self-trapped excitons (STE). STE play an important role in defect production. In Mg doped CaF_2 , STEs are typically formed when a free electron is localized at a self-trapped hole. Exciton is trapped around the doping-induced anion vacancy. The resulting excitons can decay radiatively yielding a distinctive luminescence [14]. The PL emission peak at

Fig. 5. Photoluminescence spectrum of a) $\text{CaF}_2\text{:Mg}$ and b) $\text{CaF}_2\text{:Sr}$ nanoparticles.

300 nm in the present study is attributed to surface defects like self-trapped excitons (STE) [15].

It is reported that doping the CaF_2 crystal with Sr results in an emission in the wavelength range of $300\text{--}350\text{ nm}$ and its intensity increases with the impurity concentration. This emission band was attributed to radiative decay of excitons trapped by Sr^{2+} ions [16]. Hence, the emission at 345 nm in the present studies is attributed to Sr^{2+} ions. When CaF_2 is doped with Sr, the doped Sr^{2+} ions substitute some of the Ca^{2+} ions in the CaF_2 lattice and result in the local elastic deformation of the CaF_2 lattice. The distance between F^- ions in CaF_2 lattice is $2.77\text{ \AA}$ whereas in F_2^- molecule it is $1.902\text{ \AA}$ [17]. In the process of diffusion of self-trapped excitons, the breaking of the chemical bond of a F_2^- molecule and the bonding transfer to the next lattice site takeplace [18]. Consequently the diffusion of such a mobile particle into a region where interionic distances are already reduced by the influence of an impurity ion may result in the localization of the center on a trap. Thus the 615 nm emission in the present study is attributed to self-trapped excitons.

4. Conclusions

Co-precipitation synthesized Mg and Sr doped CaF_2 nanoparticles were found to be porous and agglomerated. The Mg doped nanocrystals were found to have crystallites smaller than that ones doped with Sr. Optical absorption peaks indicate the presence of surface defects in the as prepared nanocrystalline materials. The incorporation of Mg produces less lattice distortion compared to that of Sr doped one. STE play an important role in defect production in both Mg and Sr doped samples. The optical absorption and PL intensity are relatively more in Sr doped samples.

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Fig. 4. Optical absorption spectrum of a) $\text{CaF}_2\text{:Mg}$ and b) $\text{CaF}_2\text{:Sr}$ nanoparticles.

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