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Structural Characterization of CaF_2: Dy Nanoparticles Synthesized by Simple Chemical Co-Precipitation Method

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Abstract: In this work, nanoparticles of dysprosium doped calcium fluoride (CaF_2:Dy) has been prepared by Simple Chemical Co-Precipitation Method in which 0.05 mol of $CaCL_2$ is used as the calcium ion source and 0.05 mol of NH_4F as the fluoride ion source. 1 mol% of $Dy_2O_3$was used as the dopant. The synthesized nanoparticle samples was characterized by X- ray diffraction (XRD) and the crystallite size using the dominant (111) peak was found to be 56.09 nm. SEM image shows the presence of spherical shaped nanoparticles. The PL emissions bands are observed at 479 nm (blue emission peak) and 573 nm (yellow emission peak).

***Index terms*: Calcium Flouride, Co- Precipitation, Dopant, EDAX, Nanoparticles, Photoluminescence, X-ray diffraction**

I. Introduction

As alkaline-earth fluorides exhibit single properties, it finds a number of applications in optics and electronics [1]. Fluorides are transparent in a wide wavelength region from Vacuum Ultraviolet (VUV) to Infrared (IR) due to its large band gap [2,3]. The fluoride materials normally possess low refraction index and phonon energies, usually in the range of 400–500 cm^{-1} as compared to oxides [4], which in turn can decrease the nonradioactive transition probability of the active ions [5]. These materials also finds their applications in laser and frequency conversion when their features are combined with the spectroscopic characteristics of rare earths used as doping ions [6]. Therefore, they can act as the window materials for both ultraviolet and infrared wavelength regions [7]. As calcium fluoride (CaF_2) possesses good stability, non-hygroscopic behavior and applications as optical device, especially in ultraviolet and vacuum ultraviolet (VUV), it had considerable interest among the various fluorides. CaF_2 being one of the alkaline-earth fluorides, it has a well-known fluorite-type structure. Each Ca^{2+} ions lie at the nodes in a face-centered lattice whereas F-ions lie at the centers of the octants [1,8]. CaF_2 nanoparticles exhibit high laser induced damage threshold and high transparency up to vacuum ultraviolet. Therefore, they can be considered as the most promising candidate to replace the fused silica for deep ultraviolet laser lithography techniques and ultraviolet transparent optical lenses [9]. Further

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more, CaF_2 can act as optical waveguide for optoelectronic devices [10,11]. RE-doped CaF_2 is also becoming an attractive material for up-conversion (UC) luminescence and can be compared with RE-doped $NaYF_4$, which is broadly acknowledged as the most efficient UC host [12–15].

In the last 5 years, fluoride compounds are more attracted due to the possibility of preparing nanopowders of fluorides which can produce ultimate effects on their physical properties [16]. Therefore, a number of synthesis methods had been employed to produce CaF_2 nanoparticles such as co-precipitation method [17], hydrothermal method [18–20], reverse micelle method [3], etc. Since the fluoride compounds are very sensitive to water and oxygen which are always present in the environment, the production of fluoride compounds is a challenge for researches. The possibility of contamination with impurities like O^{2-} and OH^- is very high due to similarity of the ionic radius [21,22]. Such impurities can affect the luminescence properties [23] acting as luminescence quenching centers, degradation of the transparency, lights scattering defects and others. However, the chance to incorporate these impurities can be reduced by following the process of annealing. Further, the liquid-phase methods have the advantages of simple operation, controllable granularity and the nanoscale powders materials thus prepared have high surface activity. So, in this work, we synthesized CaF_2:Dy nanoparticles by Co-Precipitation method.

II. Literature Survey

K. Tahvildari et al. [24] prepared thenano-sized calcium fluoride (CaF2) using $CaCl_2.6H_2O$ and ammonium fluorideby co-precipitation method. The characterizations of the as synthesized nanocrystals were done by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM). Further, the crystallite size was estimated using Scherer's formula and found to vary in the range of 20 to 30nm. The SEM imagesrevealed that the nanoparticles were agglomerated, crispy with porous.

Benjamin Ritter et al. [25] synthesized nanoscopic rare earth doped calcium fluoride sols. Through a fluorolytic sol–gel process, spherical monodisperse ,5 nm sized nanoparticles were achieved using a simple and reproducible one-pot-wet chemical route at room temperature. Under UV excitation at room temperature, the as-synthesized clear sols exhibit an intense red and green luminescence. A spectroscopic study of the sols revealed the characteristic transitions .

Numan Salah et al. [26]synthesized nanostructures of calcium fluoride (CaF2) doped with Eu, Tb, Dy, Cu, and Ag were synthesized by the coprecipitation method and studied for their thermoluminescence (TL) and photoluminescence (PL) properties. The PL emission spectrum of pure CaF_2 nanostructure was observed with broad band in the 370–550nm range. Similar spectra were also observed in case of doped samples. It was also observed that with increase in Dy concentration, the particle size of CaF_2 nanostructure was significantly reduced indicating that Dy is a proper activator in the host of CaF_2 nanostructure.

Mahesh S. et al. [27]prepared, nanoparticles (NPs) of dysprosium doped calcium fluoride (CaF_2:Dy) using simple chemical co-precipitation method and their thermoluminescence (TL) dosimetric properties were studied. The particle size calculated from XRD pattern was found around 30 nm. The surface morphology and shape were also observed by scanningelectron microscopy (SEM). It was also observed that the total areas of all the TL glow peak intensities are dramatically changed with increase in annealing temperature. Further, TL glow curve of the CaF_2:Dy annealed at 400 ° C, indicated very sharp linear response in the dose range from 1 Gy to 750 Gy.

Alexander Rehmer et al.[28]synthesized nanoscopic calcium fluoride by the fluorolytic sol–gel process. They prepared the antireflective coatings of CaF_2 from sols obtained by the reaction of $CaCl_2$ with HF and subsequent dip coating. The solid state NMR spectroscopy, dynamic light scattering (DLS) and X-ray powder diffraction (XRD) were used to study the formation and crystallisation of CaF2 nanoparticles and the morphology of a CaF_2-film was analysed by high resolution scanning electron microscopy (HR-SEM). The Crockmeter test was also employed for evaluation of the mechanical stability of a CaF_2-film.

Duong Thi Mai Huong et al. [29]prepared CaF_2 nanoparticles doped with 0, 1, 2, 3, 4 and 5 mol% Sm^{3+} by coprecipitationmethod. The XRD patterns confirmed the cubic structure of CaF_2 and absence of other impurities. The size of CaF_2 Nanoparticles was found to vary from 15 to 20 nm. The photoluminescence spectra were also observed peaking around at 566 nm, 604 nm, 645 nm and 704 nm.

Xiaohong Yang et al. [30]synthesized CaF_2 and CaF_2:Ln^{3+} (Ln = Eu, Tb, Ce/Tb) with tunable particle size (about 2.5 mm) by one-step facile and effective hydrothermal method. The particles showed highly uniform spherical structure andwell-dispersed. Under UV excitation, strong green photo-luminescence was observed.

III. Experimental Details

Dydoped Calcium Fluoride nanoparticles was prepared by the chemical co-precipitation method. Calcium chloride and ammonium fluoride of AR grade were taken as the calcium ion source and fluoride ion source respectively. 0.05 mol of $CaCl_2$ was dissolved separately in 20 ml double distilled water to form a clear solution. 0.05 mol of NH_4F was also dissolved in 20 ml of distilled water to form a clear solution. Then 1 mol% $Dy_2O_3$was added to the $CaCl_2$ solution and the mixture was stirred continuously for 20 minute and subsequently 50 ml ethanol was added to the solution. The same is further stirred for 10 min. The NH_4F solution was added drop wise in the solution until the precipitation was complete. The precipitates so formed were filtered out and washed four times with double distilled water. The precipitate was finally dried at 120^oC for 5 h. to obtain the sample. The sample is crushed to obtain the powder samples and the same was annealed at $400^oC$for 2 h to obtain CaF_2:Dy nanoparticles.

IV. Results and Discussion

XRD Analysis :

X-ray diffraction pattern of CaF_2:Dy nanoparticles is shown in Figure 1. The sharp peaks were assigned to diffractions on (111) plane and the low intensity peaks were attributed to diffractions on (200), (220), (311), (222) and (420) planes. These findings reveal that the sample is $CaF_2$with cubic lattice structure and corresponds to ICSD collection code No. 060368. From XRD pattern, the crystallite size was estimated using the Scherrer'sformula:

$$D = \frac{k\lambda}{\beta \cos\theta} \ldots\ldots\ldots\ldots(1)$$

Where D is crystallite size, k is a constant which is equal to 0.9, λ is the wavelength of CuKα(1.5406 A^0) line, β is the full width at half-maximum (FWHM) and θ is the diffraction angle. The crystallite sizes, D of CaF_2:Dyusing the dominant (111) peak was calculated and found to be 56.09 nmapproximately.Further, the introduction or doping of dysprosium ions on concentration is confirmed by the presence of very low intensity peaks in the XRD pattern. The inter planar spacing (d spacing) is calculated by using Bragg's equation,

$$n\lambda = 2d\sin\theta \ldots\ldots\ldots\ldots(2)$$

where λ = 1.5406A^o (wavelength of incident X-ray), θ = Peak position (in radian), n = 1(order of diffraction), d = inter planar spacing or d spacing (in A^o).Th value of **d**- spacing for dominant peak was found to be 3.44 A^0 .

The lattice constants for cubic phase is determined by using the relation

$$a = d\sqrt{h^2 + k^2 + l^2} \ldots\ldots\ldots..(3)$$

The corresponding value of lattice constant, **a** was found to be 5.95 A^0 which is comparable with the literature value, a = 5.435 A^o [31].

Assuming spherical crystal, the diameter of the sphere (L) can be estimated by

$$< L > = \left(\frac{4}{3}\right) D \ldots\ldots\ldots..(4)$$

Where D is crystallite suze. The value of $< L >$corresponding to the dominant (111) peak was found to be 74.78 nm.

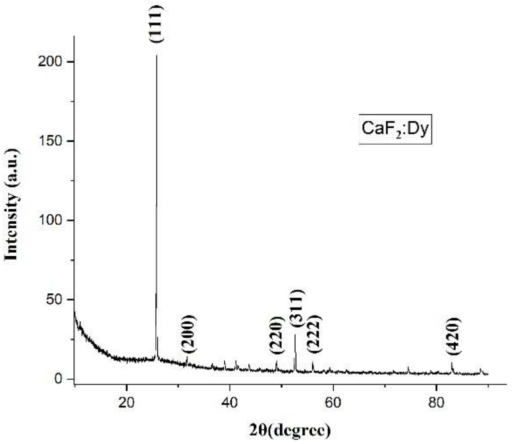

Fig. 1. XRD Pattern of CaF$_2$:Dynanoparticles

Photoluminescence Study :

Surface morphology :

The surface morphology of CaF$_2$:Dy nanoparticles was examined by scanning electron microscopy (SEM). Figure 2 shows the SEM image of CaF$_2$:Dy nanoparticles. It isobserved that the as-prepared nanoparticles are nearly spherical in shape and they have pores on their surface. The agglomeration of nanoparticles is also observed.

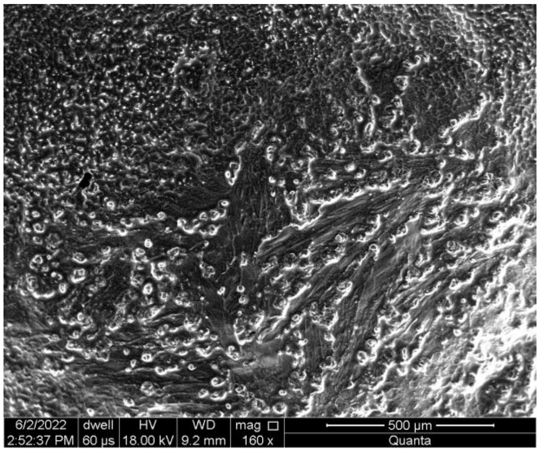

Fig. 2. SEM image of CaF$_2$:Dy nanoparticles

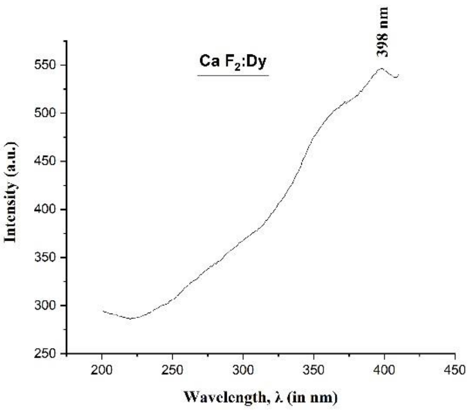

Fig. 3 : PL Excitation Spectrum of CaF2:Dy nanoparticleswith excitation wavelength at 398 nm

The excitation spectrum is obtained by scanning at 1200 nm/min the sample at a pre-defined wavelength range, 200 – 401 nm and is shown in figure 3. The excitation peak is observed at 398 nm.

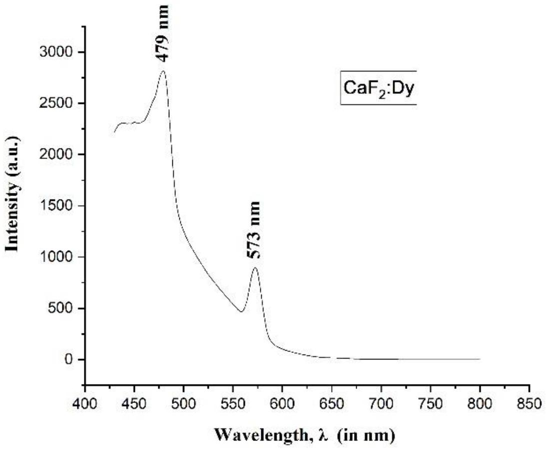

Fig. 4 : PL Emission Spectra of CaF_2:Dy nanoparticles with emission wavelengths at 479 nm and 573 nm.

The PL emission Spectra of CaF_2:Dy nanoparticles is shown in figure 4. The Dy ion acts as a well known activator mostly showing its emission in the visible regions because this ion gets introduced into the host of CaF_2 matrix in its Dy^{3+} form.The PL emissions bands are observed at 479 nm (blue emission peak) and 573 nm (yellow emission peak). These emission bands can be attributed due to transitions from $^4F_{9/2}$ to $^6H1_{5/2}$ and $^6H_{13/2}$ respectively [32].The blue shifting is caused due to decrease in particle size (quantum size effect).This in turns reduces the number of allowed transitions to some extent in the nanoparticles.Dysprosium ions can be considered as good source of blue because of its strong blue luminescence and this property creates the possibility of using CaF_2:Dy nanoparticles in blue lasers. Further, it can be interpreted that the surface defects like Schottky and Frenkel do not exist in the lattice structure of alkali halides at all temperatures. Because, any other emission peaks except at 479 nm and 573 nm can not be observed in the PL emission spectra. This suggests that the non-radiative relaxation of excited electrons does not take place i.e. phonons are not emitted due to the absence of defects and only radiative relaxation of excited electrons takes place. This means that the sample i.e. CaF_2:Dy nanoparticles so synthesized ultimately becomes a direct band gap material and hence, the crystal momentum of electrons and holes is the same in both the conduction and the valence band. So, CaF_2:Dy nanoparticles thus prepared will become a potential candidate for optical devices.

V. Conclusion

We have demonstrated the preparation of dysprosium doped CaF_2 nanoparticles by simple co-precipitation method. The nanoparticles so synthesized are characterized by XRD and PL Spectroscopy. The crystallite size of CaF_2:Dyusing the dominant (111) peak is found to be 56.09 nm. The PL study reveals that CaF_2:Dy nanoparticles thus prepared may find application for optical devices.

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VII. References

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