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STUDY OF OPTICAL PROPERTIES OF CaF_2 : Eu NANOPARTICLES SYNTHESIZED BY SIMPLE CHEMICAL CO-PRECIPITATION METHOD

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Abstract

In this work, nanoparticles of europium doped calcium fluoride (CaF_2:Eu) 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 $Eu(NO_3)_3$ was used as the dopant. The synthesized nanoparticle samples was characterized by X- ray diffraction (XRD) and the average crystallite size was found to be 25.58 nm. The energy band gap is found to be 3.75 eV.

Keywords: Calcium Flouride, Co-Precipitation, Dopant, Nanoparticles, X-ray Diffraction.

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 find 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]. Furthermore, 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 nano powders 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 nanoparticles by Co-Precipitaion method.

Experimental Details

Eu doped 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% of $Eu(NO_3)_3$ 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

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obtain the powder samples and the same was annealed at 300°C, 400°C, 500°C, 600°C and 700°C each for 2 h to obtain CaF_2:Eu nanoparticles.

Results and Discussion

XRD Study

The structural characterization was done by an X-ray diffractometer (Bruker D8 Advance) in the 2θrange (0^o–80^0) using CuKa radiation of wavelength λ= 1.5406A°. The XRD patterns of CaF_2 Nanoparticles is shown in figure 1. The formation of CaF_2 Nanoparticles is confirmed by the standard reference JCPDS Card No. 4-864 and the nanoparticles possess simple cubic crystal structure. The good crystallinity of the material is indicated by narrow and sharp peaks corresponding to corrected crystal planes (111), (220) and (311). Further, the introduction of rare earth ions on concentration does not change the crystal structure of the product, which is confirmed by the absence of other diffraction peak of other substances in the XRD pattern. The inter planar spacing (d spacing) is calculated by using Bragg's equation,

$$n\lambda = 2d\sin\theta \quad \ldots\ldots\ldots\ldots\ldots (1)$$

where λ = 1.5406A° (wavelength of incident X-ray), θ = Peak position (in radian), n = 1(order of diffraction), d = inter planar spacing or d spacing (in A°).

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

$$a = d\,(h^2 + k^2 + l^2)^{1/2} \quad \ldots\ldots\ldots\ldots\ldots (2)$$

The crystallite size of CaF_2:Eu nanoparticles is calculated by using Scherrer's formula,

$$D = \frac{K\lambda}{\beta \cos\theta} \quad \ldots\ldots\ldots\ldots\ldots (3)$$

where K is a constant (= 0.94), β is the full width at half maximum (FWHM) in radian at 2θ [24]. Assuming spherical crystal, the diameter of the sphere (L) can be estimated by

$$< L > = (4/3)D \quad \ldots\ldots\ldots\ldots\ldots (4)$$

where D is the crystallite size [25]. The structural parameters are shown in table 1.

Table 1. Structural parameters of CaF_2:Eu

2θ(degree)	Miller index (hkl)	d value(A^0)	Crystallite size D(nm)	Diameter <L> (nm)	Lattice Constant, a_0(A^0)	Average Crystallite Size (nm)
28.55	111	3.13	31.88	42.50	5.41	25.58
47.09	220	1.97	7.11	9.47	5.57	
56.01	311	1.64	19.73	26.30	5.43	
68.70	400	1.37	29.93	39.90	5.50	
75.97	331	1.25	39.25	52.33	5.44	

From the above table 1, it is clear that the planes giving rise to the smallest Bragg's angle will have the largest d-spacing which is in good agreement with theoretical prediction. The crystallite sizes corresponding to crystal planes are also comparable with earlier workers [26]. The average crystallite size is 25.58 nm. The value of lattice constants are also comparable with the literature value

a = 5.435 A° [27].

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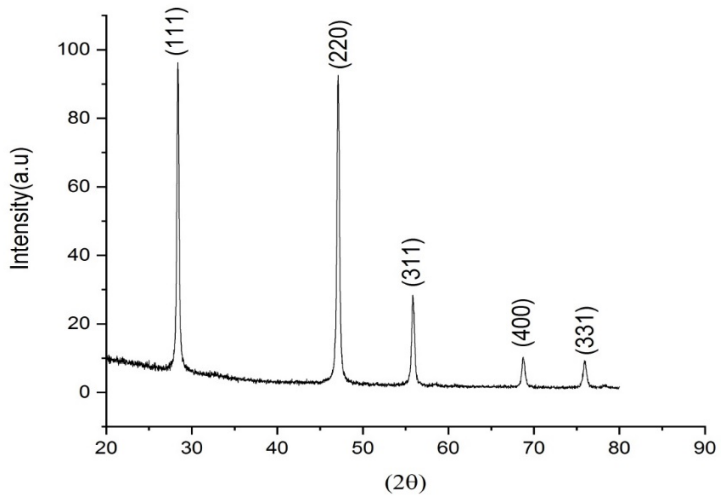

Figure 1. XRD pattern of Eu doped CaF_2 nanoparticlesOptical Study.

The optical property of CaF_2:Eu nanoparticles is studied with the help of UV-Visible Spectroscopy. The UV absorption spectrum of europium doped Calcium fluoride, CaF_2:Eu nanoparticles taken at room temperature are shown in Figure 2. The absorption coefficient α associated with the strong absorption region of the sample, absorbance (A) and the cuvette thickness (t) are related as below [28, 29].

$$\alpha = 2.303\ A / t \qquad \ldots\ldots\ldots\ldots (5)$$

The absorption coefficient of direct band gap semiconductor is given by [30]

$$\alpha = c\ (h\nu - E_g)^{1/2} / h\nu \qquad \ldots\ldots\ldots\ldots\ldots (6)$$

where α is absorption coefficient, c is a constant, hν is incident photon energy and E_g is the band gap. Graph between hν vs $(\alpha h\nu)^2$ is plotted and shown in Figure 3. The intercept of the extrapolated straight line at the $(\alpha h\nu)^2 = 0$ axis gives the value of the E_g of the material. The values of E_g so obtained is found to be 3.75 eV which is very small as compared to value in bulk state, 12.1 eV. [31]

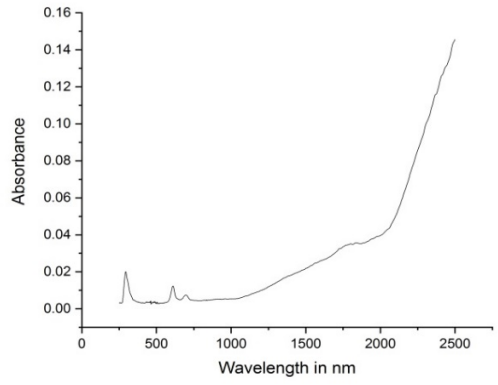

Figure. 2. Absorption spectrum of CaF_2:Eu naoparticles

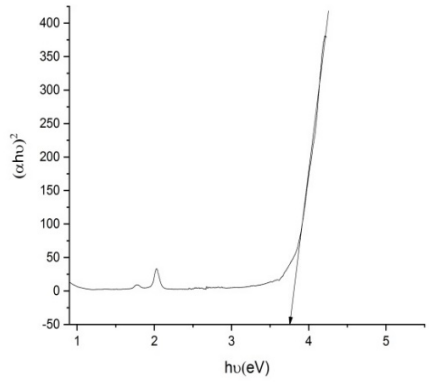

Figure. 3. Plot of hν vs $(.\alpha h\nu)^2$ ofCaF_2:Eu nanoparticles


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Conclusion

We have demonstrated the preparation of europium doped CaF2 nanoparticles by simple co-precipitation method. The nanoparticles so synthesized are characterized by XRD and UV-Visible Spectrometer. The average crystallite size is found to be 25.58 nm. The Energy Band Gap of NPs synthesized by this method is found to decrease at 3.75 eV. The materials having such energy band gap may find many applications in laser and optical devices [32].

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