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EFFECT OF DOPING CONCENTRATION OF Eu^{3+} ION ON CaF_2 NANOPARTICLES

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The $Ca_{1-x}F_{2+x}$: Eux particles were synthesized by simple chemical co-precipitation method in an ethanol solution. The Prepared CaF_2: Eu nanoparticles were characterized using X ray diffractometer (XRD) and transmission electron microscopy (TEM). The intensity of XRD peaks decreased and full width at half maximum (FWHM) increased gradually with increasing the doping concentration of Eu^{3+} ions. The XRD analysis reveals the cubic structure of Eu^{3+} doped CaF2 Crystals. The particle size calculated from XRD data was decreased with increasing concentration of dopent ion and the average particle size was in the range of 63 to 26 nm. The transmission electron microscopy (TEM) shows nearly spherical morphology of CaF2: Eu nanoparticles.

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1. Introduction

The investigation of nanoscale materials opened up new dimension in material science; materials can be produced and modified at atomic scale. The different chemical and physical properties are significantly changed when parent material s are transformed from bulk to their nano phase [1,2] nanomaterals fascinate the materials world promising applications in science and technology. Metal fluorides are strategic materials in optical and photonic technologies, funding application in lighting, optical application, and lasing industries. Luminescent materials also find application in the field of radiation detections scintillators for medical, scientific, industrial, and security application. Some of well known luminescent fluorides like CaF_2Eu, BaF_2, and $CeF_3$are used in high energy physics experiments [3]. The CaF_2 crystal with an optically isotropic fluorite structure is suitable as a phosphor host because it exhibits outstanding transmission properties in wide range of wavelength [4]. Besides the rare earth ions substituted in the CaF_2 host will cause an increase in the refractive index with respect to the pure CaF_2 [5]. Because of lower refractive index, low phonon energy, and wide range of solubility for trivalent rare earth ions, CaF_2 crystal is very important host material for application in laser and optoelectronic devices [6,7].

Owing to the outstanding properties of rare earth impurity doped CaF_2 nanoparticles, the present article deals with the study of effect of doping concentration of Eu^{3+} ions on the size of CaF_2 particles. The doped CaF_2 particles were synthesized by simple chemical precipitation method and characterized by X- ray diffraction, transmission electron microscopy.

2. Experimental

The chemicals $CaCl_2$, $EuCl_3$ and NH_4F (sdfine chemi. ltd) were used as reactants. The Eu^{3+} doped CaF_2 nanoparticles were synthesized by simple chemical co-precipitation method. Both $CaCl_2$ and NH_4F can dissolve significantly in water. But the CaF_2 is an insoluble salt in

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water, which will precipitate from an aqueous solution. Thus, the solid CaF_2 precipitation can be obtained easily by the reaction of the $Ca^{2+}$and F^- ions that formed by the dissociation of $CaCl_2$ and NH_4F respectively in an aqueous solution. However, it is difficult to control particle growth of CaF_2 crystalline because high Ca^{2+} and F^- ion concentration in an aqueous solution resulted in significant reaction rates. Therefore, the reactions to synthesize Eu^{3+}doped CaF_2 nanoparticles were carried out in an ethanol solution in sealed flasks under ambient pressure. When mixture of $CaCl_2$ and NH_4F powders was stirred in an ethanol solution, only very low F^- ion concentration can be formed because the solubility of NH_4F in an ethanol solution is much smaller than that in an aqueous solution. Thus, the particle growth of the precipitated CaF_2 solid is very limited due to very small F^- ion concentrations in an ethanol solution. The CaF_2 nanoparticles could be obtained by the combination of the Ca^{2+} and F^- ions in an ethanol solution. With the proceeding of precipitation to form CaF_2 nanoparticles, the F^- ion concentrations in the ethanol solution will decrease gradually. Thus, more F^- ions will be released stepwise by the dissociation of the NH_4F in order to maintain the equilibrium concentrations of the F^- ion in the ethanol solution. Those released F^- ions will continue to combine with the Ca^{2+} ions to form more CaF_2 nanoparticles.

To synthesize Eu^{3+}-doped CaF_2 nanoparticles, an appropriate amount of $CaCl_2$ and $EuCl_3$ salt was added to a beaker containing 180 ml of ethanol, the total concentration of metal cation was controlled to be 0.04 mol/L. After being stirred magnetically for about 10 min, the mixture became a colorless transparent solution. A slight excess ammonium fluoride, NH_4F, was added to the beaker and a white suspension formed upon stirring. After the mixture was stirred for 12 h, the precipitation was separated by centrifugation and it was washed with ethanol and de ionized water in sequence several times to remove possible impurities such as $CaCl_2$. Then the precipitate was dried at 60^{o}C for 12 h. The prepared samples are subjected to different characterizations. Fang Wang et. al.(2005) was employed similar method for synthesizing CaF2:Eu nanoparticles [8]

3. Results and discussions

The XRD data is recorded on Rigaku- Minflx II X-ray diffractometer. Fig. 1 shows the XRD patterns of the CaF_2 nanoparticals doped with Eu^{3+} ions. The resultant compound is of the form $Ca_{1-x}F_{2+x}$:Eu_x (doping concentration x= 0.00, 0.01, 0.05, 0.1, 0.15). The XRD patterns exhibits significant peaks which indicates the cubic CaF_2 crystals.

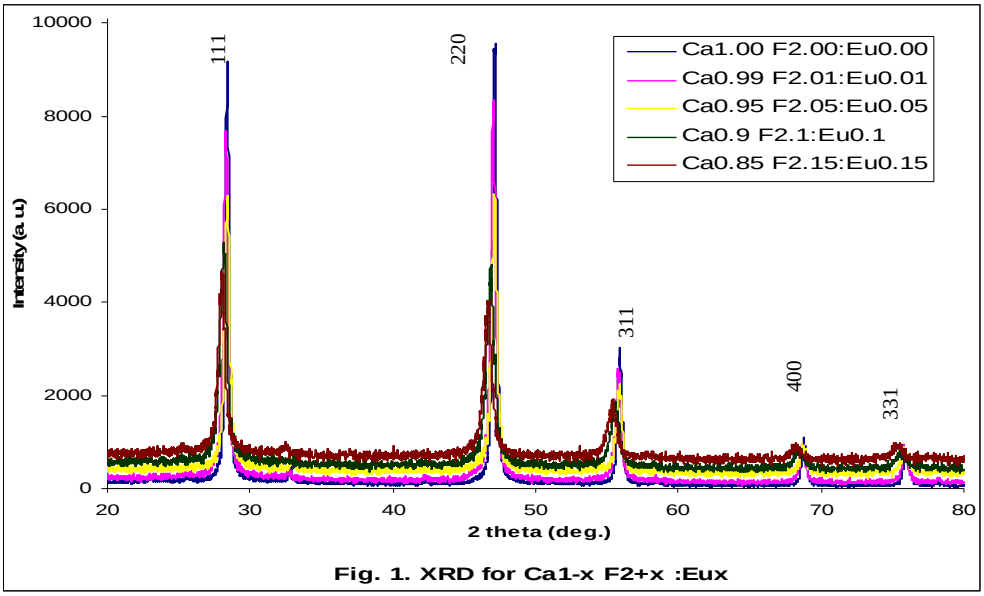

Fig. 1. XRD for Ca1-x F2+x :Eux

The peak positions of XRD Pattern for Pure Caf_2 (x = 0.00) and CaF_2 doped with Eu3+ (x =0.01, 0.05, .0.1, 0.15) closely coincide which indicates that Eu^{3+} ions isostructured with CaF_2 crystal. C. Pandurangappa, et.al.(2010) was investigated the similar XRD structure for CaF_2 crystals [9]. XRD data shows with increase the doping concentration of Eu^{3+} ion, however, the intensity of the diffraction peaks decreased and full width at half maximum (FWHM) is gradually increased, similar findings are made in the work of Fang Wang et. al.(2005) [8]. The increase of doping concentration results the decrease of crystallity and increase of disorder effect which resulted in the broadening and decrease of intensity of the XRD peaks. From the XRD data the size of CaF_2 particles is calculated using scherrer relation

$$g = k\lambda/\beta_{2\theta}\cos(\theta)$$

Where,

K= 0.94

λ =1.54 Å(wavelength of K_α line)

β=FWHM at 2θ.

The variation of particle size with doping concentration is displayed in table 1 and presented in figure 2. With increase of doping concentration of Eu^{3+} ion, the size of CaF_2 particles is decreased significantly. For x =0.1 and 0.15, the average range is 29 nm and 26 nm respectively.

Table 1. Variation of doping concentration v/s size of nanoparticles.

Sr. No.	Concentration of Eu^{3+} Dopant	Size of CaF_2 particles in nm
1	0	63
2	0.01	46
3	0.05	43
4	0.1	29
5	0.15	26

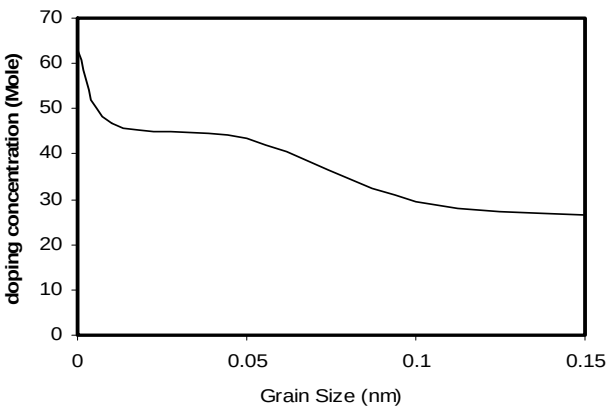

Fig.2 : dopping concentration plotted against the grain size.

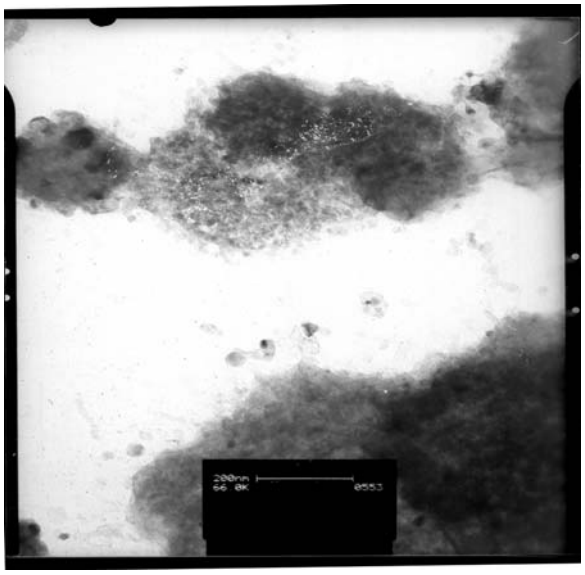

Fig. 3. TEM scan for $Ca_{0.85}F_{2.1}5Eu_{0.15}$

TEM scan for Ca0.85 F2.15:Eu0.15 nanoparticle is presented in figure 3. The TEM image exhibits the spherical morphology of Ca0.85 F2.15:Eu0.15. The approximate particle size obtained from TEM image is 20-26 nm which is consistent with particle size calculated from XRD data using scherrer's formula.

4. Conclusions

From the XRD and TEM data it is concluded that Eu^{3+} doped CaF_2 nanoparticles can be synthesized by chemical co-precipitation method. In the view of the results discussed the size of Eu^{3+} doped CaF_2 nanoparticles can be controlled by doping concentration of rare earth ions.

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References

[1] C. Burda, X. B. Chen, R. Narayanan, M. A. El-Sayad, Chem. Rev. **105**, 1025 (2005).
[2] B. L. Cushing, V. L. Kolesnichenko, C. J. OConnor, Chem. rRev. **104**, 3893 (2004)
[3] P. Lecoq, A. Annenkov, A. gektin, M. Korzhik, Springer Verlag, Berlin, Germany (2006) cha. 2.
[4] M. Y. Sharonov, Z. L. Zhmurova, E. A. Kirvandina, A. A. Bystrova, I. I. Buchinskaya, B. P. Sobolev, Opt. Commum. 124, 558 (1996).
[5] T. Balaji, G. Lifaante, E. Daran, R. Legros, G. Lacoste, Thin Solid Films **339**, 187 (1999).
[6] G. A. Kumar, R. Raiman, S. C. Chen, Y. N. Jang, I. K. Bae, H. S. Moon, J. Appl Phys. **95**, 295 (2004).
[7] R. S. Quimbly, Mater. Sci. **32-33**, 551 (1988).
[8] F. Wang, X. Fan, D. Pi, M. Wang,Solid State Commun. **133**, 775 (2005).
[9] C. Pandurangappa, B. N. Laxminarasappa, B. M. Nagabhushana, J. All, and Compoun. 489 (2010).