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Estimation of particle size and micro strain in Europium doped Yttrium oxide nanoparticle synthesized by homogenous coprecipitation method

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Abstract:

Europium (Eu) doped Yttrium Oxide (Y_2O_3) nanoparticles were successfully synthesized by homogenous coprecipitation method (HCP) with Yttrium nitrate hexahydrate as inorganic precursor and Europium nitrate hexahydrate as dopant. Particle size was estimated by XRD analysis while microstrain by Williamson-Hall plotting method. The effect of doping on structural properties of Y_2O_3 was reported in this study.

Key words: Particle size, Micro strain, Homogenous Coprecipitation method.

Introduction:

Nanotechnology is an excellent example of an emerging and newly developed technology, offering nanostructured fabricated materials with the great potential for producing various products with substantially improved performances.[1,2] Nanomaterials, an exciting class of materials have emerged in recent years which are in high demand due to variety of practical applications.[3,4,5,6] Currently, nanomaterials find employable roles in scratch-free and dust-free paints, cosmetics, surface coatings, sports equipment, electronics, sensors, energy-storage devices, environmental remediation and food industry.[7,8]

The fabrication of new nanomaterial with acceptable size, shape and surface morphology has been achieved by various physical, chemical and biological methods.[9,10,11,12,13] Among all these reported methods, the homogenous co-precipitation method (HCP) was well documented better approach for high yield production of spherical particles with controllable sizes. [14,]

Out of different sesquioxides, the Y_2O_3 has been attracted widely as the host material for rare earth ion doping because of its thermomechanical stability, wide-ranging optical transparency (0.2 to 8 µm), having a band gap of 5.6 eV, less annealing temperature (800^{o}C), low maximum photon energy (380 cm^{-1}), high refractive index (~1.87) and thermodynamically stable crystal structures. The similarities in the physico-chemical properties,

crystalline structure, ionic radius and lattice constant of inner transition metal ions and Y_2O_3 make it a promising candidate for host material. In recent years, the studies on incorporation of RE in a single host material has fascinated and being extensively investigated. Due to similarities in ionic radius of RE (Eu^{3+}= 0.947 Å,) the cell parameter (A) of synthesized nanoparticle is found to be much similar to that of pure Y_2O_3 (Y_2O_3: Eu = 10.659 Å, Y_2O_3 = 10.616 Å). Therefore, it can be considered as a new generation long-lasting luminescent nanomaterial.

In this study, the estimation on particle size and microstrain in crystal structure of pure and Eu doped Y_2O_3 by XRD analysis and Williamson-Hall plotting method was reported. Also the effect of doping on cell parameter of Y_2O_3 was discussed.

Experimental method:

Pure and Eu doped Y_2O_3 crystallites were synthesized by homogenous coprecipitation method (HCP). The details about material used, experimental procedure was briefly discussed in our earlier report.[15] After calcinations at ~800°C, the obtained white powder was analyzed for its crystalline size and microstrain in the lattice by XRD and Williamson-Hall plotting method. The effect of doping on crystalline size of Y_2O_3 nanoparticle was estimated.

Result and discussion:

The XRD patterns for 1% to 4% Eu doped Y_2O_3 nanoparticle were presented in figure 1 to 4.

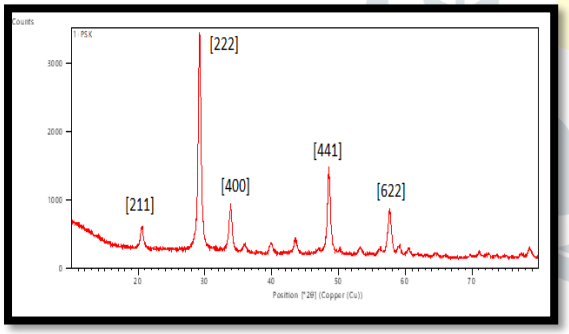

Fig. 1 XRD for 1 % Eu^{3+} doped Y_2O_3 NPs

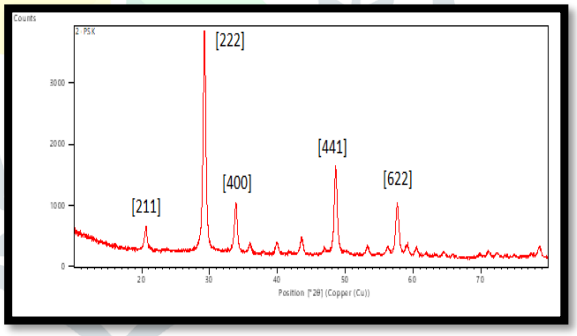

Fig. 2 XRD for 2 % Eu^{3+} doped Y_2O_3 NPs

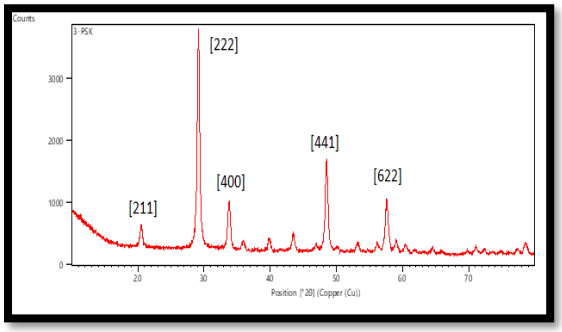

Fig. 3 XRD for 3 % Eu^{3+} doped Y_2O_3 NPs

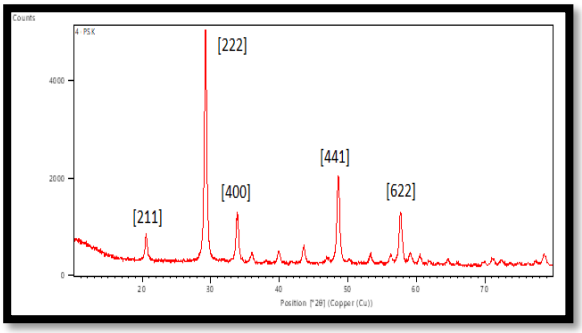

Fig. 4 XRD for 4 % Eu^{3+} doped Y_2O_3 NPs

The XRD patterns show that the intensities of five basic peaks of the (211), (222), (400), (441), and (622) planes are more than that of other peaks. The observed intense peaks refer the excellent growth of crystal size

and assembly of larger clusters. The crystallite size (D) was calculated from the full width at half maximum (FWHM) of the strongest diffraction peak by using the Debye-Scherer formula[16,]

$$D = \frac{K\lambda}{\beta \cos\theta}$$

The following Table 1 shows the XRD parameters and crystalline size of pure and 1% to 4% Eu doped Y_2O_3 NPs (222) plane orientation.

Table 1: The XRD parameters and crystalline size of pure and 1% to 4% Eu doped Y_2O_3 NPs

Sample	2 θ (deg)	FWHM	d (obs) Å	D (nm)
Pure Y_2O_3	29.2615	0.4225	3.04962	32.42
1% Eu:Y_2O_3	29.1828	0.4499	3.05755	33.25
2% Eu:Y_2O_3	29.2148	0.4299	3.05438	34.81
3% Eu:Y_2O_3	29.1238	0.4065	3.06372	36.80
4% Eu:Y_2O_3	29.2107	0.3699	3.05481	40.45

The crystalline size of pure and 1 % to 5 % Eu^{3+} doped Y_2O_3 NPs is almost similar within the range of 32 to 40 nm. It indicates that there is no any major structural change or alteration in the crystal of Y_2O_3 NPs due to incorporation of Eu^{3+} ions. (as Eu_2O_3). The significance of broadening of peaks evidences grain refinement along with the large strain associated with the powder. The presence of impurities in crystal, changes the lattice energy and responsible to cause the excess strain in the lattice structure. The micro strain induced in powder due to crystal imperfection and distortion was calculated using Williamson-Hall equation [17],

$$\beta \cos\theta = \frac{k\lambda}{D} + 4\varepsilon \sin\theta$$

Where ε is the strain and D is the mean size of the crystallite. The W-H plots for 1 % to 5 % Eu^{3+} doped Y_2O_3 NPs were represented in figure 5 to 8. From the linear fit to the data, the crystalline size was calculated from the y-intercepts, and the micro strain, from the slope of the W-H plot for all samples.

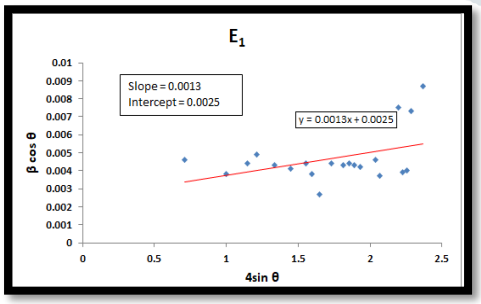

Fig. 5 The W-H plot for 1 % Eu: Y_2O_3

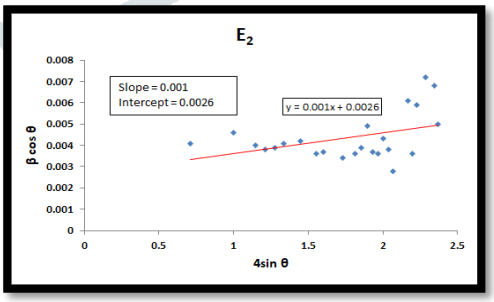

Fig. 6 The W-H plot for 2 % Eu: Y_2O_3

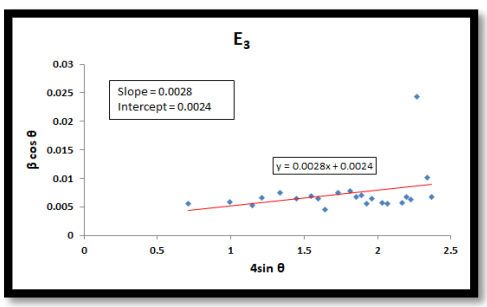

Fig. 7 The W-H plot for 3 % Eu: Y_2O_3

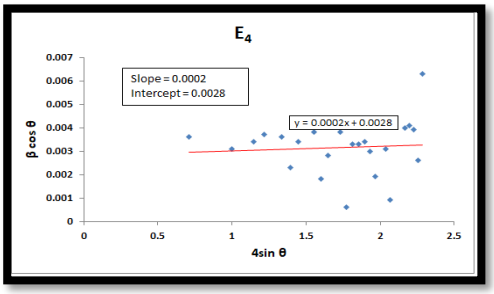

Fig. 8 The W-H plot for 4 % Eu: Y_2O_3

The crystallite size (D) determined from W-H plot, for pure and 1% to 5% Eu^{3+} doped Y_2O_3 NPs is represented in following Table 2. It was observed that the crystallite size (D) determined from W-H plot is more than that of obtained from Scherrer formula, indicating the micro strain has significant effect on the particle size of these samples.[18]

Table 2: The crystalline size (D) and microstrain for Eu^{3+} doped Y_2O_3 from W-H analysis.

Sample	Slope = Microstrain	Y- Intercept	D
Pure Y_2O_3	0.0008	0.0028	51.12
1% Eu:Y_2O_3	0.0013	0.0025	57.92
2% Eu:Y_2O_3	0.0010	0.0026	55.70
3% Eu:Y_2O_3	0.0028	0.0024	60.34
4% Eu:Y_2O_3	0.0002	0.0028	51.71

During doping, the d-spacing for a given (hkl) plane will change (i.e. peak shift) and induced lattice strain can be calculated. The peak broadening is either due to random microstrain induced by dislocation (strain broadening) or due to shrinkage of coherent scattering volume (size broadening). The observed broadening of peak is likely the combined results of both effects.[19] The low value of microstrain, shows almost absence of other impurity in the crystal lattice. The crystallite size calculated by using Scherrer's formula varies with the peak used. In comparison, the crystallite size determined from W-H plot, does not changes according to peak positions.

Conclusion:

The Eu doped Y_2O_3 NPs were succesfully synthesized by homogenous coprecipitation method. The XRD pattern confirms the cubic structure of Europium doped Y_2O_3 and the crystalline size is found to be 32 to 40 nm while the crystalline size estimated by W-H analysis is within the range of 51 to 60 nm, indicating presence of microstrain due to incorporation of Eu^{3+} ion substituted in place of Y^{3+} ion at C_2 symmetry site of Y_2O_3 NPs. Also the increase in crystalline size was observed due to incorporation of dopant Eu^{3+} ion in Y_2O_3 NPs. Scherrer's method gives avarage particle size of all crystallites present in the sample in a direction perpendicular to a perticular (hkl) plane, but W-H method gives avarage particle size in all directions of all individual particles. As the crystalline size obtained is within the nanometer range, Eu doped Y_2O_3 NPs can be considered as a best candidate luminescent nanomaterial for its emplobility in display devices and biomedical field.

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Conflict of interest: The authors declare no conflict of interest.

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