

Optical study of Yttrium oxide doped with zinc prepared by simple methods

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Yttrium oxide nanophosphors doped with zinc were prepared using simple methods like sol-gel and solvothermal with solvents like Ammonium Hydroxide, and Sodium Hydroxide as precipitating reagents. Calcining and grinding are necessary to obtain phosphors in the range of 20-30 nm. The Photoluminescence properties investigation reveals that Yttrium oxide samples doped with zinc show a strong blue-green emission with the strongest peak centered at 500nm under the excitation of 250nm UV light.

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1. Introduction

The selection of host lattices and active centers for an nanophosphor is important. Yttrium oxide shows high refractory property, chemical stability etc., for example, Yttrium oxide doped with Europium is the prominent red emitting phosphor with high luminescence quantum efficiency and widely used in lamps and display. Yttrium oxide can be used as a advanced ceramics [1, 2], superconductor [3], insulator [4] and sensor [5]. Recently the synthesis of yttrium oxide based nanophosphors received increasing attention. Yttrium oxide microprisms [6] and microspheres [7] have been prepared by Lin et.al through a facile hydrothermal method.

On the other hand, nanophosphor materials such as ZnO have potential applications in high brightness light emitting diode applications [8]. Effect of size induced emission in visible region, radiative life time shortenings [9] and blinking effects [10] are prominent at nanoscale range. ZnO nanomaterial, having a wide band gap, is one of the promising candidates for general illumination applications due to its high optical transparency and color tenability [11].

In this paper, we demonstrated that yttrium oxide nanostructures were prepared by various simple methods like sol-gel, and solvothermal method which was doped with Zinc nano particles by using Zinc acetate dihydrate and Ammonium hydroxide and Sodium hydroxide solutions as precipitating reagents. This bottom-up approach was motivated due to the considerable interest in the fabrication of optoelectronic devices [12, 13] as the luminescent efficiency drastically changes with the particle size [8, 9].

The oxide lattice has proved to be an excellent host material for some of the most powerful laser built. Among them, yttrium oxide is characterized by low phonon frequencies which make inefficient nonradiation relaxation

of the excited states. The yttrium oxide host has chosen due to its high refractory properties with a melting point of about 2450°C, a very high thermal conductivity of 33W/mK and a density of 5.03gcm³. Y₂O₃ is a suitable photonic waveguide due to its high energy bandgap of 5.8eV, a high refractive index about 2, and a wide transmission region from 280nm to 8μm [14]. Since europium doped yttria is being widely applied in display panels, screen techniques etc., improvement in its luminescence efficiency are very important. For this purpose, in the present work we investigated the optical properties of samples with zinc as the dopant.

2. Experimental

2.1 Sol- gel method

In this method, the nanocrystalline yttrium oxide doped zinc powders were prepared by taking the precursors, Yttrium Nitrate hexahydrate (Y(NO₃)₃·6H₂O), zinc acetate dihydrate in three different compositions along with the ammonium hydroxide solution to get samples A1, A2 and A3. Three samples each of 1g of Yttrium nitrate hexahydrate was dissolved in 10 ml of distilled water. Solutions were stirred for the salt to dissolve completely, till clear solution was obtained. 0.25g, 0.5g and 1g of zinc acetate dihydrate were added to samples A1, A2 and A3 and the precipitate was obtained. To these solutions 50ml of ammonium hydroxide was added in drops. The precipitate was left for 15 hours to settle. Then the obtained precipitate was washed with water and dried in an oven at 373K for 3 hours. After drying, the powder was obtained as agglomeration, which was finely ground. The yttrium hydroxide doped zinc powder thus obtained were converted into yttrium

oxidized zinc through calcination by heating the sample at 623K for 15 hours and cooled to room temperature [15].

2.2 Solvothermal method

In this method, Yttrium oxide doped zinc samples B1, B2 and B3 were prepared by dissolving 0.6g of $Y(NO_3)_3 \cdot 6H_2O$ in 160ml of absolute ethanol under stirring. When the Yttrium nitrate hexahydrate was dissolved completely, 6.4g of sodium hydroxide solid was dropped into those solutions. To get B1, B2 and B3 samples, 0.15g, 0.3g and 0.6g of zinc acetate dihydrate were added to the resulting solutions. Then further 30 minutes vigorous stirring was continued. After that the samples were heated at 433K for 3 hours and cooled to room temperature. The white powder formed at the bottom was washed with ethanol and distilled water several times to remove any possible remnants. Finally the product was dried at 353K for 2 hours [15].

3. Characterization

X-ray powder diffractograms (XRD) were recorded for all the samples, using PANalytical X'pert Pro MPP, equipped with a Cu anode and RTMS detection technology. The generator was operated at 60kV and 60mA. The powder samples are evenly spread over the glass plate to take studies. UV-Visible analysis was performed with UV-Vis-NIR Varian Cary 500 Spectrophotometer. The sample was dissolved in ethanol and mounted in quartz cuvette. The reference cuvette was filled with ethanol. And the samples were exposed for 10 minutes for study. The photoluminescence spectra were obtained with Horbin FluoroMax4 in the wavelength range of 300-700nm using an excitation of 250nm.

4. Results and discussion

4.1 X-ray diffraction (XRD)

Fig. 1 (a) and (b) shows the XRD patterns of the six Y_2O_3 samples deposited using the different methods. The diffractograms all show a small broad peak at $\sim 29^\circ$ which corresponds to reflections from the $\langle 222 \rangle$ planes of Y_2O_3 [16]. The cubic phase of Y_2O_3 was expressed primarily by reflections from the $\langle 222 \rangle$ planes [17, 18]. The XRD of A1 sample shows more shift which was attributed to the presence of yttrium hydroxide (JCPDS 832042) [15], which may be the reason for less particle size in this particular sample. Table 1 lists the crystallite sizes of synthesized particles estimated from the well defined known Debye-Scherrer's equation.

$$\text{Crystallite size} = \frac{K\lambda}{\beta \cos \theta}$$

Where K is the shape factor, λ is the X-ray wavelength, β is the FWHM and θ is the Bragg angle.

Table 1. Details of composition and calculated crystallite size of samples.

Sample	Precipitating reagent	Crystallite Size(nm)
A1	Ammonium Hydroxide	14.7
A2	Ammonium Hydroxide	29.3
A3	Ammonium Hydroxide	19.3
B1	Sodium Hydroxide	29.6
B2	Sodium Hydroxide	29.93
B3	Sodium Hydroxide	29.66

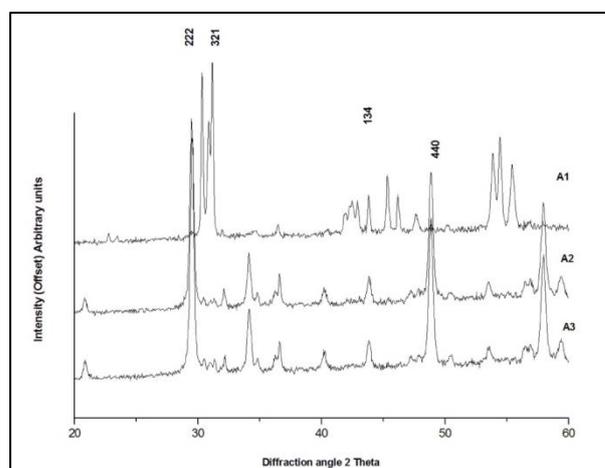


Fig. 1(a) XRD diffraction patterns of samples A1, A2 and A3.

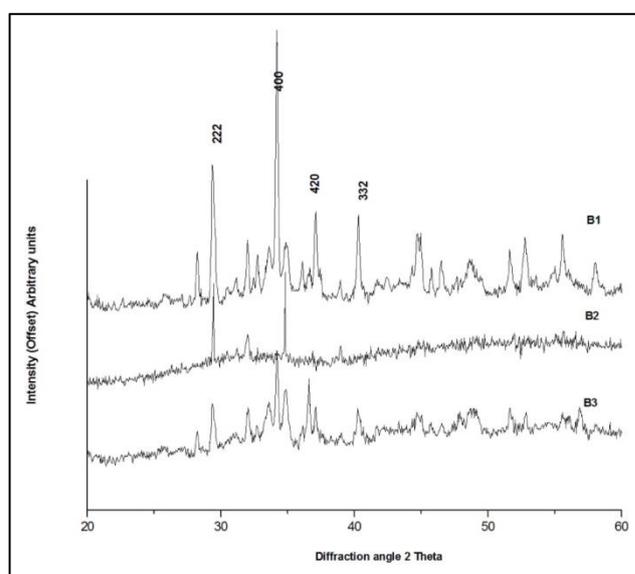


Fig. 1(b) XRD diffraction patterns of samples B1, B2 and B3.

4.2 UV-Visible spectrum

The absorbance spectrum of A1, A2, A3 samples were shown in Fig. 2. From Fig. 2 it was seen that strong absorption occurs in UV wavelength at 270nm and 306 nm. The weak absorption area covers almost the whole of the visible field ranging between 400 and 800 nm. The absorbance spectrum of samples B1, B2 and B3 were shown in Fig. 2. It has similar peak when compared with samples prepared by sol-gel method. This reveals that the samples prepared by both the methods have similar response in the UV-Visible region. The distortion in the lower wavelength region was attributed due to the influence of ethanol in which the sample was dissolved for UV-Vis measurements.

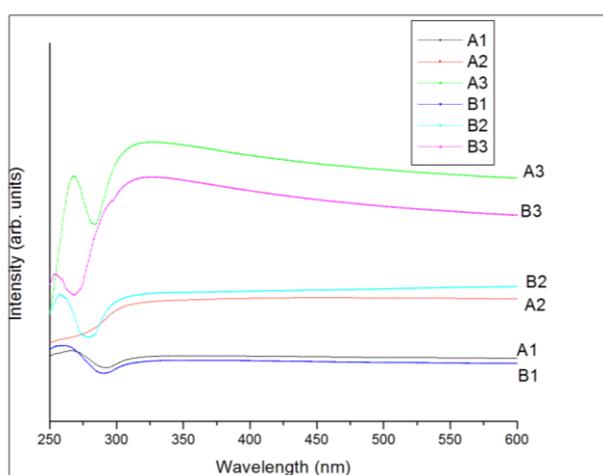


Fig. 2. Absorption spectra of samples A1, A2, A3, B1, B2 and B3.

4.3 Photoluminescence studies

The emission spectra of the yttria nanophosphors doped with zinc prepared by different methods with varying concentration of dopants was in the spectral region 500nm after exciting at a wavelength of 250nm were shown in Fig. 3. All samples PL measurements were done at room temperature. All samples showed characteristic peak at 500 nm which corresponds to the blue-green emission. These emissions were found to be extremely broad and this broadening may be due to phonon assisted by transition [19]. It was concluded that synthesis of $Y_2O_3:Zn$ by sol-gel method has more luminescence intensity as compared to synthesis of $Y_2O_3:Zn$ by solvothermal method.

Analysis of the data considered above suggests that, in yttrium oxide with an excess of zinc ($Y_2O_3:Zn$), oxygen vacancies VO or (in terms of ionic compounds) *F*-centers were responsible for green luminescence. Since the *F*-center in Zn contains two electrons, its states were similar to those of an autolocalized exciton in alkali halide crystals; i.e., we were dealing with exciton-like triplet-

singlet luminescence [20]. In samples with an excess of oxygen, VZn centers were responsible for the blue-green luminescence.

5. Conclusion

In conclusion we report here the implementation of simple approach of the fabrication of $Y_2O_3:Zn$ nanostructure. A high quality $Y_2O_3:Zn$ nanocrystalline samples had been prepared by sol-gel and solvothermal method with various concentrations of the dopant. The structural and optical properties of the samples were studied. Maximum crystalline size was obtained as 30 nm and band gap energy was found to be nearly 4eV. XRD show that the sample exhibited a single-crystalline structure. Room temperature PL spectra of the samples show a strong blue-green emission band located at 500 nm which was ascribed to the *F*-centers. Thus our experimental nanostructure studies would help exploring more potential applications in luminescent, nanophotonic and optoelectronic devices.

Finally properties of the $Y_2O_3:Zn$ samples prepared by sol-gel and solvothermal methods can be very good, out of which samples prepared by sol-gel method has more efficiency which makes this method promising for fabricating the optoelectronic nanodevices, such as LED and LD economically in future.

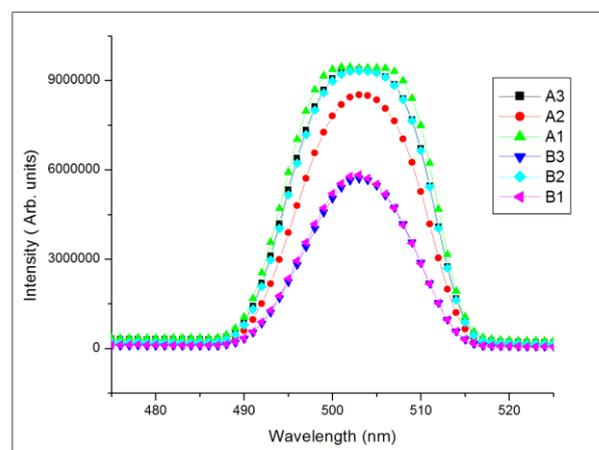


Fig. 3. Room temperature Photoluminescence spectra of samples A1, A2, A3, B1, B2 and B3.

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