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Rapid gel synthesis and optical characterization of the $Y_{2-x}O_3:xTb^{3+}$ nano phosphor

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ABSTRACT

Light emitting $Y_{2-x}O_3:xTb^{3+}$ nano phosphor was synthesized using rapid gel combustion assisted process. The advantages of gel combustion base process have been exploited to produce nano particles in the pure homogeneous mixture formation. Synthesis conditions such as calcinations temperature and dopant concentration are varied in order to determine the exact optimum conditions for synthesizing $Y_{2-x}O_3:xTb^{3+}$ nano particles with enhanced optical properties and smaller particle size. The prepared phosphor had predominant green colour due to magnetic dipole transition $^5D_4 \rightarrow ^7F_5$ of Tb^{3+} located at 543 nm. The nano crystals obtained through gel combustion method was characterized by using scanning electron microscopy (SEM), X-ray diffraction (XRD) technique and photoluminescence (PL) spectra.

Keywords: Nano phosphor; luminescence; gel combustion; optical properties.

INTRODUCTION

Rare earth ions-activated nanostructure materials have been attracting much interest in the past few years, due to the excellent luminescence and potential applications in luminescent devices and display equipment, such as lighting, field emission display (FED), cathode ray tubes (CRT), and plasma display panels (PDP) resolution [1-6]. But a now a days, FEDs and PDPs are attracting deal of attention as new display technology. Numerous methods such as solid state reactions, sol-gel techniques [7], hydroxide precipitation [8], hydrothermal synthesis [9], spray pyrolysis [10], laser evaporation [11] and combustion synthesis [12, 13, 14] has been investigated for the preparation of oxide phosphors. These methods have their advantages as well as limitations. In multi step processes like heating at high temperatures and long processing time are required. The combustion is a novel technique through which a voluminous, foamy nano

crystalline powder can be prepared within a few minutes. This technique is ideal for producing the fine, pure and single-phase powders. In the present work, preparation and optical characterization of the $(Y_{1-x}Tb_x)_2O_3$ nano phosphor are described. The prepared phosphor had nano size particles, showing high luminescence.

MATERIALS AND METHODS

2.1 Preparation of the nano phosphors

All the chemicals used were of high purity (Aldrich 99.99%). Stoichiometric amounts of yttrium nitrate and terbium nitrate were mixed in minimum doubly distilled water. Proportionate amount the fuel (carbohydrazide) was also calculated as reported by Ekambaram and Patil [15] and was added to the concentrated solution. This mixture was heated in a crucible on a hot plate to form a viscous gel. After evaporating most of the water contents, crucible was placed into a microwave oven for 5 minutes to propagate for the combustion reaction. The reaction initiated immediately in oven with flame appearing on the surface that spread over the entire volume of the crucible, leaving a white powder of an extreme porosity. The materials obtained were powdered using a ball mill having zirconia balls.

Thus a series of phosphor materials with general formula $(Y_{1-x}Tb_x)_2O_3$ ($0.005 < x < 0.1$) was prepared by dissolving the mixtures in proportionate amounts as stated above.

2.2 Characterization of the phosphor

X-ray diffraction (XRD) spectrum of the materials was taken using a Rigaku Spectrophotometer model D/max2000 (Japan) with $CuK\alpha$ radiation. Photoluminescence spectrum was recorded with a Minolta CS 1000 series spectrophotometer (USA). Morphology of the phosphor was determined by the scanning electron microscope using a Philips XL series. Elemental analyses were made by the Philips EDAX PV 9900 series.

RESULTS AND DISCUSSION

Homogenous samples of the green phosphor of terbium doped yttrium oxide could be prepared by gel combustion method within a few minutes with nitrogen based fuel i.e. carbohydrazide. In general a good fuel should react non-violently and produces nontoxic gases. Reaction of carbohydrazide with metal nitrates at $\sim 400^\circ C$ produces combustible gases, finally producing non-toxic gases like N_2 , CO_2 in situ that make the product fluffy [15]. The flame temperature increases with increase of fuel/oxidizer ratio [16]. According to the basics of the propellant chemistry, the oxidizing and reducing valencies of the element are: C = 4, H = 1, O = -2, N = 0, M = 2, 3, or 4 depending on the valency of the metal. Therefore the oxidizing valency of the trivalent metal nitrate $M(NO_3)_3$ is -15 and the reducing valency of the carbohydrazide (mol. formula $N_2H_3CON_2H_3$), the fuel in the present case is +8. The ratio of the trivalent metal nitrates to the carbohydrazide therefore comes out to be 15/8 i.e 1: 1.875. Carbohydrazide used for the combustion of the metal nitrates to convert finally to a complex metal oxide lattices. During the combustion in microwave the metal nitrates were impregnated into polymeric product in the gel form, the reaction initiated somewhere in the interior, flame appeared on the surface and proceeded rapidly throughout the whole volume, leaving a voluminous product with a high porous structure. The gases liberated during the reaction were responsible to make the materials

porous, henceforth particles size smaller. The product obtained had good phase purity and homogeneity over the entire volume of the phosphor material.

3.1 Effect of the activator concentration

The effect of concentration of activator i.e. terbium varied from 0.005 to 0.1 moles in the Y_2O_3 matrix on luminescence property was studied. The photoluminescence intensity of the phosphor increased up to 0.07 moles of Tb_2O_3 per mole of the Y_2O_3 and then decreased above this level due to the concentration quenching [17]. The best results for luminescence were obtained if terbium concentration was taken between 0.02 to 0.07 moles for the yttrium oxide lattice. Hence we have taken 0.04 moles concentration of the terbium for the further analysis of the phosphor.

3.2 Crystal size and Morphology

Scanning electron micrographs of the material showed the particle size to be smaller than 25nm (Fig 1). The average size of the crystallite was ~30 nm as estimated from the full width at half maximum of the peaks using the Scherrer's equation. This confirmed that the material made by the present method was highly fragile and fluffy and produced nano crystalline material on grinding. Fig. 2 is the XRD patterns obtained for nano phosphor composition (a) $(Y_{0.96}Tb_{0.04})_2O_3$ (b) $(Y_{0.96}Tb_{0.04})_2O_3$ with additional heat treatment. XRD patterns as shown in Fig. 2 conclude that the peaks of material synthesized by gel combustion method further sharpened with the additional heating of the phosphor material on the higher temperature showed the crystalline nature of the phosphor material. The morphology of the crystalline powder confirmed a cubic structure that resembled with the pattern card of JCPDS-No 43-1036 [18].

3.3 Spectral properties

The prepared material showed the uniform bright green color emitting maximum at 543 nm when exposed to a 254 nm UV source. The emission spectra of green $Y_{2-x}O_3:xTb^{3+}$ nano phosphor in fig 3. shows several emission lines. In case of Tb^{3+} ion there are eight 4f –electrons (which is a half filled $4f^7$ and plus one electron) and the 4f shell readily releases an electron and the intra ionic transition $4f^8 \rightarrow 4f^7 5d^1$ absorption takes place at a relatively low energy. The 5d orbit, being the outer orbit of the ion, is strongly influenced by the electric field of the surrounding ions creating intense absorption band [19]. The emission spectra of $Y_{2-x}O_3:xTb^{3+}$ nano phosphor obtained after firing $700^\circ C$ for 1 hr are shown in Fig. 3 peaking at 403, 435, 545 and 585 nm, the emission line correspond to transition $^5D_3 \rightarrow ^7F_5$, $^5D_3 \rightarrow ^7F_4$, $^5D_4 \rightarrow ^7F_5$ and $^5D_4 \rightarrow ^7F_4$.

The CIE chromaticity coordinates of the above prepared nano phosphor fall in the green region of the colour triangle with $x = -0.214$, $y = -0.515$ as shown in the Fig. 4.

The predominant green colour from magnetic dipole transition $^5D_4 \rightarrow ^7F_5$ of Tb^{3+} was located at 543 nm. The spectral energy distribution is also strongly dependent on the terbium concentration. The emission wavelength does not vary with the terbium concentration but emission intensity changes a lot with the terbium concentration. As the terbium concentration is 5mol % the optimum luminescence intensities of the phosphor nanoparticles can be achieved.

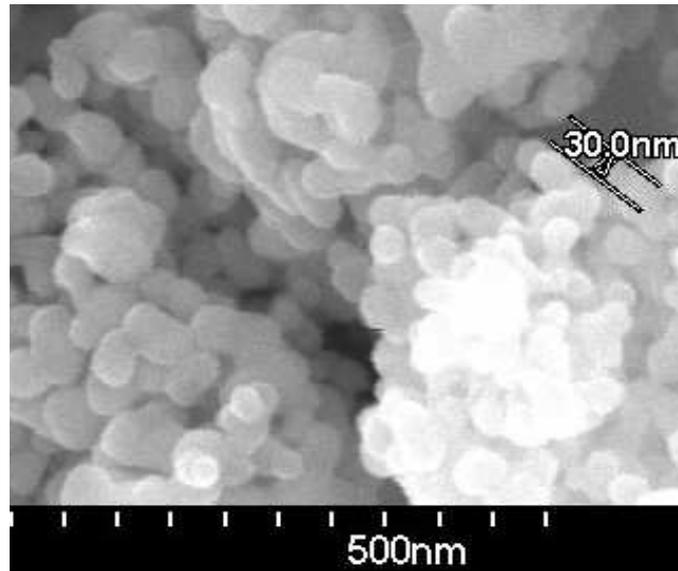


Fig. 1: Scanning electron micrograph of $(Y_{0.96}Tb_{0.04})_2O_3$ phosphor

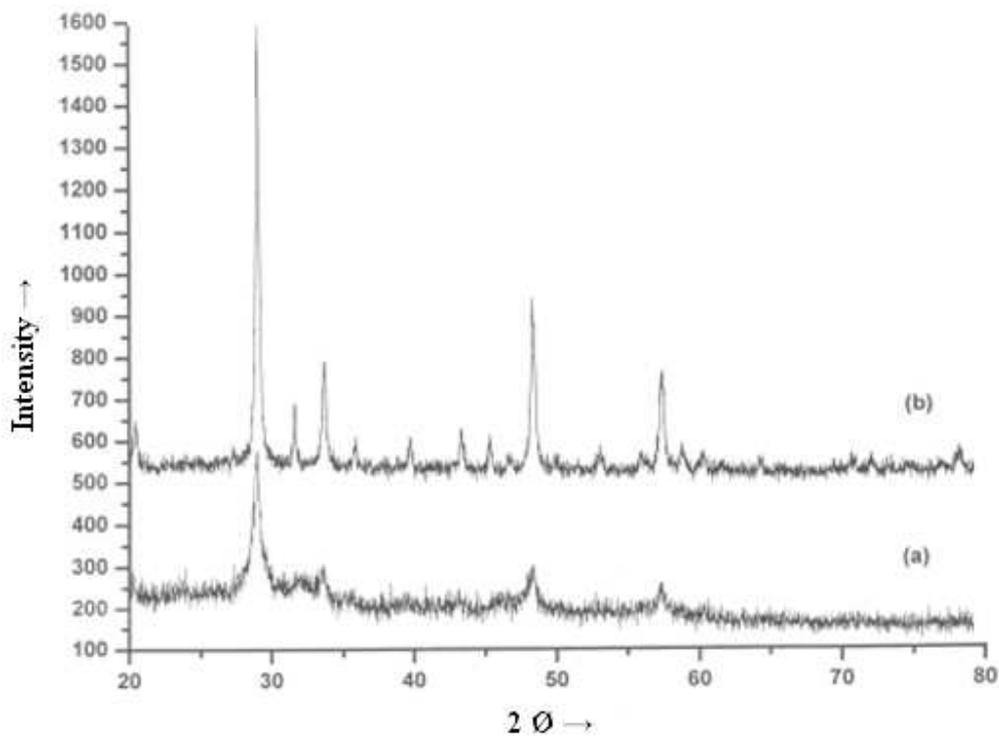


Fig. 2: XRD patterns of (a) $(Y_{0.96}Tb_{0.04})_2O_3$ phosphor (b) $(Y_{0.96}Tb_{0.04})_2O_3$ Phosphor with additional heat treatment for 1 hr at $700^\circ C$

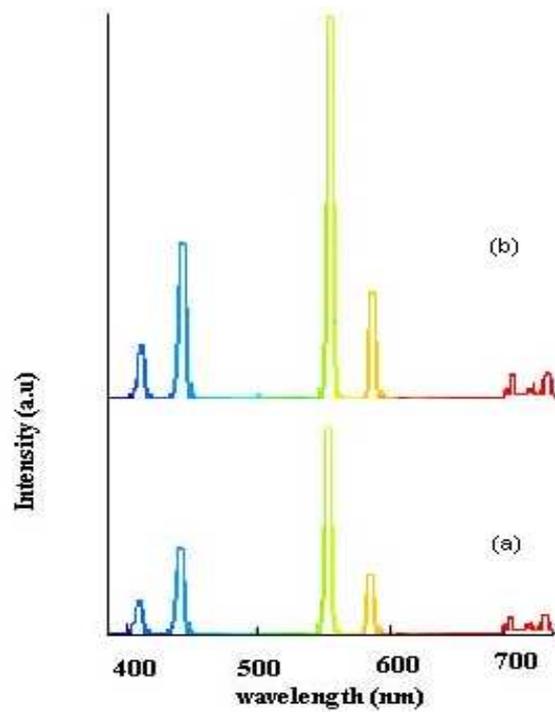


Fig. 3: Comparison of PL spectrum of (a) $(Y_{0.96}Tb_{0.04})_2O_3$ phosphor (b) $(Y_{0.96}Tb_{0.04})_2O_3$ Phosphor with additional heat treatment for 1 hr at $700^\circ C$

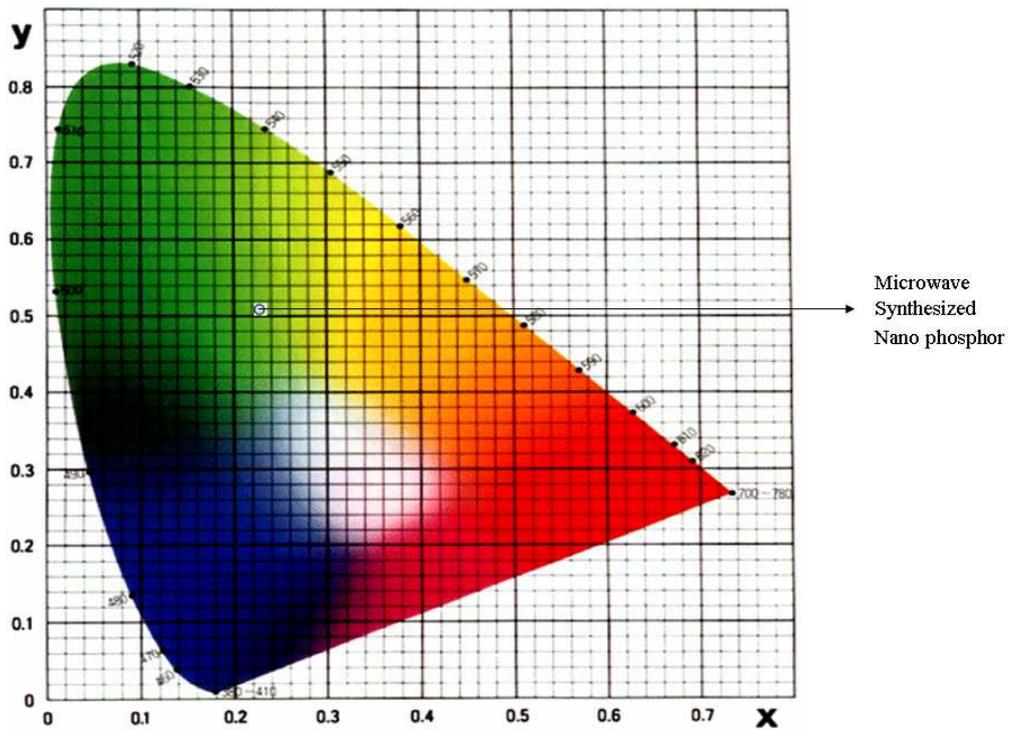


Fig. 4: Colour Triangle showing the different coordinates of the $(Y_{0.96}Tb_{0.04})_2O_3$ nano phosphor

CONCLUSION

Nano crystalline $(Y_{0.96}Tb_{0.04})_2O_3$ phosphor could be prepared using carbonylhydrazide as fuel and utilizing the facile gel combustion synthesis technique. The process involves a low temperature self-propagating ignition route which is safe, simple and rapid for the production of fine and homogeneous powders, displaying bright luminescent green color with high luminous efficiency. The phosphor produced the bright green luminescence at the 543 nm having the average nano crystalline particle size ~ 30 nm. The brilliant luminescence properties make it a possible nano phosphor for display applications.

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