© 2014 IJSRSET | Volume 1 | Issue 1 | Print ISSN: 2395-1990 | Online ISSN : 2394-4099
Themed Section : Engineering and Technology

Characterization of Eu^{3+} - Doped Yttrium Aluminum Garnet Nanocrystals - A Review

Anil R. Saradva
The.H.N.S.B.Ltd Science College, Himatnagar, Gujarat, India

ABSTRACT

In the present work, we synthesize Yttrium aluminum garnet:Eu by nitrate–citrate sol–gel process and the structure of the materials was analyzed by means of X-ray diffraction,showing the cubic garnet phase of Yttrium aluminum garnet. We studied the effect of thermal treatment on crystalline size and we distinguished the Eu3+ ion presence by means of optical spectroscopic measurements

Key words: Nanocrystals, Sol- Gel Method , XRD

I. INTRODUCTION

Small crystalline materials with particle diameters of 100 nm or less exhibit many physical properties (like as optical, magnetic, thermal) not found in their bulk. These nanocrystals are of considerable interest for both technological applications and fundamental studies. The doped dielectric nanocrystals present a particular interest.

Yttrium aluminum garnet ($Y_3Al_5O_{12}$ yttrium aluminum garnet) based materials adopt the cubic garnet structure and are widely used in advanced optical technologies since yttrium aluminum garnet doped with a transition metal or lanthanide element exhibits outstanding luminescence properties [1]. Namely, yttrium aluminum garnet can withstand harsh conditions implied by high energy excitations due to an important damage threshold and show emissions of wavelength lying near infrared range to the UV range of the electromagnetic spectrum. These features have made yttrium aluminum garnet a relevant material as window for a variety of lamps, for fiber-optic telecommunication systems, for cathode-ray tubes, field emission displays.

Yttrium aluminum garnet:Tb is a characteristic narrow-band phosphor suitable for contrast enhanced display application in high ambient illumination conditions. Hence, yttrium aluminum garnet:Tb is one of the potential phosphors which may be used in projection CRT's [3]. Eu3+ -doped yttrium aluminum garnet phosphors also have the processing conditions, which are very much responsible for the crystallinity, crystal shape, crystal size, crystal size distribution and phase purity of the resulting powders and the potential for application in field emission devices. Phosphors for field emission and vacuum fluorescent display of these materials increases as the size of the crystals decreases. Optimum performance in these devices can be achieved by employing ultra-fine phosphor particles.

Yttrium aluminum garnet phosphors doped with activators are mainly synthesized by solid-state reaction techniques which require high sintering temperatures (above 1500ºC),long reaction times (10 - 15h) and extensive ball milling, which generally introduces additional impurities and defects. It is reported that two detrimental phases, yttrium aluminum monoclinic- $Y_4Al_2O_9$ and yttrium aluminum perovskite - $YAlO_3$), often coexist with

yttrium aluminum garnet [4]. In order to obtain sharp powders, several chemical synthesis techniques, such as sol–gel [5-6],co precipitation [9,10], precipitation of hydroxides,spray pyrolisis and combustion methods , hydrothermal syntheses have received great attention recently. In this paper we employed a sol-gel method using nitrates and citric acid. This method has the advantages of both wet-chemical and solid-state synthesis methods, such as low temperature synthesis (~1000ºC), well-dispersed nanoparticles, inexpensive precursors, ease of preparation.

II. SOL-GEL TECHNIQUE

Sol-gel technology is a well-established colloidal chemistry technology, which offers possibility to produce various materials with novel, predefined properties in a simple process and at relatively low process cost. The sol is a name of a colloidal solution made of solid particles few hundred nm in diameter, suspended in a liquid phase. The gel can be considered as a solid macromolecule immersed in a solvent. + Sol-gel process consists in the chemical transformation of a liquid (the sol) into a gel state and with subsequent post-treatment and transition into solid oxide material. The main benefits of sol–gel processing are the high purity and uniform nanostructure achievable at low temperatures.

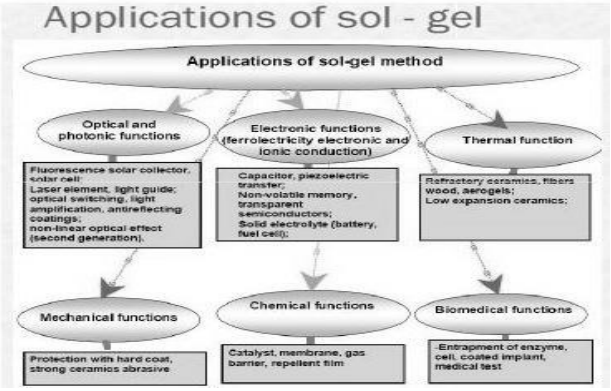

Figure 1

III. EXPERIMENTAL

3.1. Materials and sample preparation

In the sol–gel process for preparing yttrium aluminium garnet: Eu3+ phosphors, yttrium nitrate,europium nitrate and aluminum nitrate were dissolved in distilled water. The prepared solutions were mixed according to the chemical formula of $Y_{2.97}Eu_{0.03}\ Al_5O_{12}$ with 3 at. % europium ions doped with respect to yttrium ions In order to obtain Eu^{3+} : yttrium aluminium garnet nanocrystals, aqueous solutions of $Y(NO_3)_3 \times 5H_2O$ 1.93M, $Al(NO_3)_3$ Al$\times 9H_2O$ 2.12M, and $Eu(NO_3)_3 \times 5H_2O$ 1.93M are mixed in a molar ratio Y:Eu:Al of 2.97:0.03:5 ($Y_{2.97}Eu_{0.03}\ Al_5O_{12}$). The mixture was added to a citric acid solution ($C_6H_8O_7 \times H_2O$) 2M, in molar ratio citric acid: nitrates of 3:1. The mixture was evaporated at 90°C until a transparent viscous gel was obtained. The gel was decomposed at 500°C for 5h obtaining a black powder, which then was calcinated at ~800°C for 5h in air, achieving this way a white powder implying that organic compounds were burned away during calcination.

3.2. XRD measurements

The structure of the precursor powder of yttrium aluminum garnet:Eu prepared by the sol-gel process is determined using x-ray diffraction measurements were performed at room temperature on a TUR M 62 diffractometer operating with Co –Kα radiation using an filter.

3.3. Optical spectroscopy

The luminescence spectrum of Eu3+ substituted for Y 3+ in yttrium aluminum garnet has been measured on samples calcinated at various temperatures. The fluorescence was excited with a Xenon lamp with suitable filters. The luminescence spectra were recorded with a double monochromator GDM 1000 equipped with an S-20 photomultiplier in photon counting configuration.

IV. RESULTS AND DISCUSSION

The gel was annealed at various temperatures. Since no obvious diffraction peaks are observed for the samples heat-treated up to 800°C, it can be concluded that the powders are still amorphous. The yttrium aluminum garnet crystallization occurs at ~ 830°C.The

XRD pattern shows yttrium aluminum garnet to be the only crystalline component (Fig. 1).

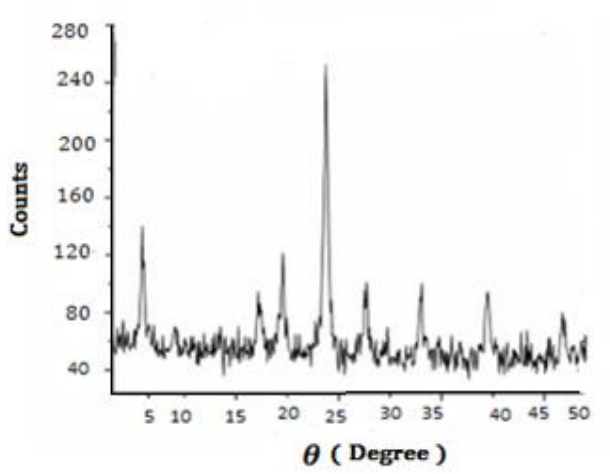

Figure 1. X-Ray Diffraction patterns of the sample heated at 800°C.

Increasing the annealing temperature, the diffraction pattern shows higher intensity and narrower diffraction lines. It denotes that the yttrium aluminum garnet crystallites grow as the annealing temperature increases. Thus, in Fig. 2 we show the XRD patern of an yttrium aluminum garnet:Eu powder annealed at 1200ºC.

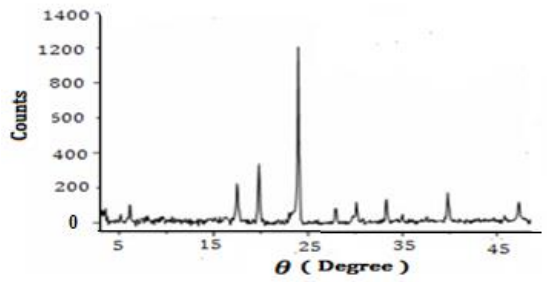

Figure 2. X-Ray Diffraction patterns of the sample heated at 1200°C.

The presence of the Eu3+ ion in the yttrium aluminum garnet nanocrystals was evidenced using optical spectroscopy measurements. The fluorescence spectrum of Eu3+ in samples annealed at 800ºC (Fig. 3) is characteristic for the amorphous state.

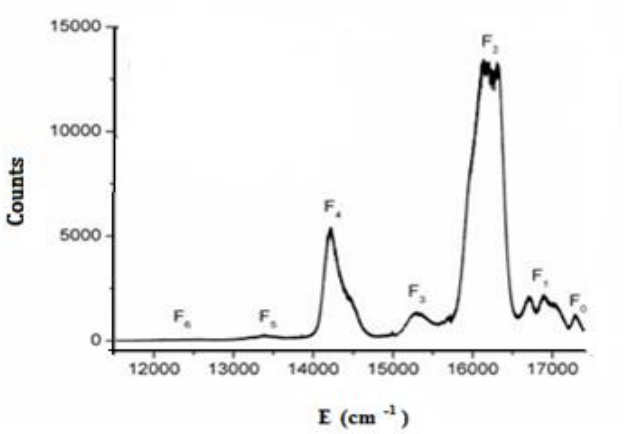

Figure 3. The fluorescence spectrum (5D 0 →7F j) of Eu3+ in samples annealed at 800ºC – amorphous state.

When heated at 930º C the fluorescence spectrum of Eu3+ in yttrium aluminum garnet is obtained (Fig. 4).

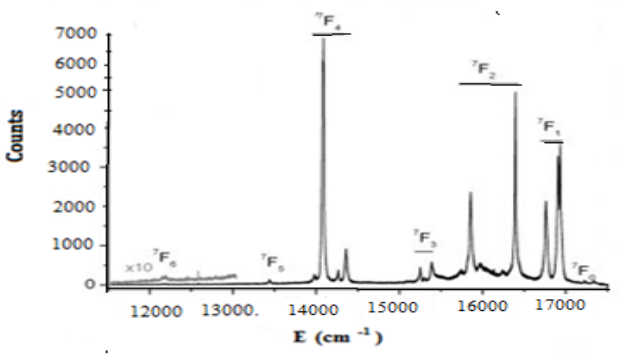

Figure 4. The fluorescence spectrum ($^5D_0 \rightarrow {}^7F_j$) of Eu3+ in samples annealed at 830ºC - the fluorescence spectrum of Eu3+ in YAG

With the increase of the annealing temperature the fluorescence lines become narrower. To illustrate this behavior, we measured the temperature dependence of the linewidth of two isolated fluorescence lines belonging to the transition $^5D_0 \rightarrow {}^7F_j$ (Fig. 5). A monotonous decrease of the linewidth with annealing temperature is observed. We interpret this behavior as a reduction of the disorder produced by the nanocrystals' surface as the crystallites increase.

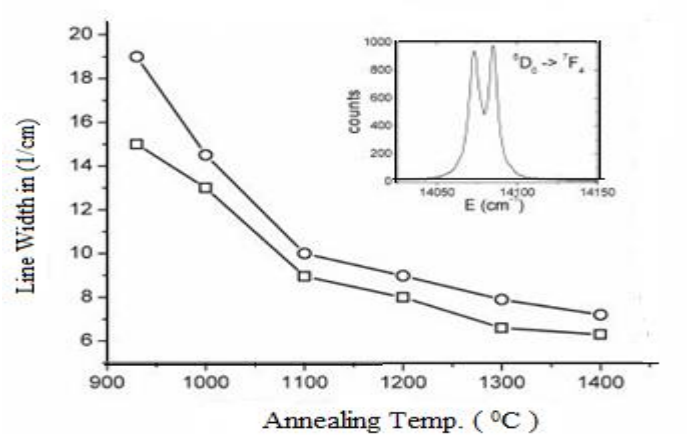

Figure 5. Dependence of line width with annealing temperature of two isolated fluorescence lines belonging to the transition 5D0→7F4. Inset: the two analyzed lines

V. CONCLUSIONS

Pure garnet phase yttrium aluminum garnet:Eu phosphor can be synthesized at calcination temperatures ~ 830°C by nitrate–citrate sol–gel process. Single-phase cubic Yttrium aluminum garnet: Eu is formed by direct crystallization from amorphous materials and no intermediate phase (such as YAM or YAP) is observed. Yttrium aluminum garnet:Eu powders of various particle sizes can be synthesized by varying the calcination temperature.

Both XRD and optical spectroscopy measurements illustrated the yttrium aluminum garnet phase.

VI. REFERENCES

[1]. T. WELKER, "Recent development of Phosphors for fluorescent lamps and cathode-raytubes" J. Lumin. 48, 49 (1991).

[2]. A. IKESUE, I. FURUSATO AND K. KAMATA, "Oscillation spectra and dynamic effects in a highlydoped microchip Nd:YAG ceramic laser" J. Am. Ceram. Soc. 78, 225 (1995).

[3]. M. VEITH, S. MATHUR, A. KAREIVA, M. JILAVI, M. ZIMMER, V. HUCH, Low temperature synthesis of nanocrystalline Y_3 ⟦Al⟧_5 O_12 (YAG) and Ce-doped Y 3 Al 5 O 12 via different sol-gel methods", J.Mater.(1999).

[4]. Z. SUN, D. YUAN, X. DUAN, X. WEI, H. SUN, C. LUAN, Z. WANG, X. SHI, D. XU, M. LV,"Preparation and characterization of Co2+-doped Y_3 ⟦Al⟧_5 O_12nano-crystal powders by sol-gel technique", J. Crystal Growth 260, 171 (2004).

[5]. JI GUANG LI, TAKAYASU IKEGAMI, JONG-HEUN LEE, TOSHIYUKI MORI, AND YOSHIYUKI Yajima "Reactive yttrium aluminate garnet powder via coprecipitation using ammonium hydrogen carbonate as the precipitant" J. Mater Res. 15, 1864 (2000).

[6]. G.PANG, X. XU, V. MARKOVICH, S. AVIVI, O. PALCHIK, YU. KOLTYPIN, G. GARODETSKY, Y. YESHURUN, H. P. BUCHKREMER, A. GEDANKEN "Preparation of La 1-x Sr x MnO3 nanoparticles by sonication-assisted precipitation" Mat. Res. Bull. 38, 11 (2003).

[7]. S.M. SIM, K. A. KELLER AND T.-I. MAH "Phase formation in yttrium aluminum garnet powders synthesized by chemical methods," J. Mat. Sci. 35, 3, (2000).

[8]. Y.C. KANG, Y.S. CHUNG, S.B. PARK, "Polycrystalline YAG:structural or functional?" J. Am. Ceram. Soc. 82, 2056 (1999).

[9]. Y.C. KANG, I.W. LENGGORO, S.B. PARK, K. OKUYAMA,"YAG:Ce Phosphor Particles Prepared by Ultrasonic Spray Pyrolysis" Mat. Res. Bull. 35, 789, (2000).

[10]. O. A. LOPEZ, J. MCKITTRICK AND L. E. SHEA, "Fluorescence Properties of Polycrystalline Tm 3+Activated Y_3 ⟦Al⟧_5 O_12 and Tm3+-Li+Co-Activated Y_3 ⟦Al⟧_5 O_12in the Visible and Near IR Ranges",J. Lumin.,(1997).

[11]. T. TAKAMORI AND L. D. DAVID., "Controlled Nucleation for Hydrothermal Growth. of Yttrium Aluminum Garnet Powders," J. Ceram. Soc. Bull (1986).