# One Step Combustion Synthesis Of Compounds In Eu<sup>3+</sup> Activated Y<sub>2</sub>0<sub>3</sub>–Al<sub>2</sub>0<sub>3</sub> System Using Mixed Fuel

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### Abstract

In  $Y_2O_3$ -Al<sub>2</sub>O<sub>3</sub> system, compounds  $Y_3Al_5O_{12}$  (yttrium aluminum garnet-YAG), YAP (yttrium aluminum perovskite-YAlO<sub>3</sub>) and  $Y_4Al_2O_9$  (yttrium aluminate monoclinic-YAM,) are well known. YAG and YAP are of considerable technological importance. The conventional solid-state reaction techniques require high sintering temperatures (above  $1800^{\circ}C$ ) to prepare phase pure compounds. Though several soft chemical routes have been explored for synthesis of YAG, YAP and YAM, most of these methods are complex. Moreover, phase pure materials are not obtained in one step, but prolonged annealing at temperatures around 1000 C is necessary. One step combustion synthesis of these compounds is reported in this paper using a modified procedure and employing mixed (glycine + urea) fuel. Phosphors based on  $Eu^{3+}$  activation were also prepared which exhibited characteristic photoluminescence. The emission spectrum of Eu<sup>3+</sup> doped YAG phosphor is dominated by orange emission due to  ${}^{5}D_{0}$ - ${}^{7}F_{1}$  transition with inversion symmetry. However, the emission spectrum of  $Eu^{3+}$  doped YAP phosphor is dominated by red emission due to  ${}^{5}D_{0}$ - ${}^{7}F_{2}$  transition without inversion symmetry. The PL spectrum of  $Eu^{3+}$  doped YAM phosphor consists of similar emission intensities for both  ${}^{5}D_{0}$ - ${}^{7}F_{1}$  (590) nm) and  ${}^{5}D_{0}$ - ${}^{7}F_{2}$  (607 nm) transitions.

Keywords: phosphors; combustion synthesis; luminescence; Eu<sup>3+</sup>; YAG ; YAP ; YAM

#### Introduction

In  $Y_2O_3$ -Al<sub>2</sub>O<sub>3</sub> system, compounds  $Y_3Al_5O_{12}$  (yttrium aluminum garnet-YAG-, m.p. 1970 C) having cubic garnet structure with Al-richer composition, YAP (yttrium aluminum perovskite-YAlO<sub>3</sub>, m.p. 1870 C) and  $Y_4Al_2O_9$  (yttrium aluminate monoclinic-YAM, 1942 C) which is a monoclinic Y-richer phase, are well known. A metastable hexagonal phase (YAH) with the same YAP stoichiometry, normally appearing during the synthesis of YAG and YAP by soft chemistry routes, has also been identified. The crystal structure of YAG is similar to that of the natural gem "garnet"; hence the name. The unit cell of YAG (Fig. 1), crystal structure of YAP (Fig. 2) and YAM (Fig. 3) is shown in respective figures.



Figure 1:- Part of YAG unit cell showing 8 coordination of  $Y^{3+}$  with neighbouring oxygen ions



Figure 2:- YAP crystal structure showing 12 coordination of  $Y^{3+}$  with neighbouring oxygen ions.



Figure 3:- YAM crystal structure showing 7/6 coordination of  $Y^{3+}$  with neighbouring oxygen ions

The dodecahedral (Y<sup>3+</sup>), octahedral (Al<sup>3+</sup>), and tetrahedral (Al<sup>3+</sup>) sites of the garnet structure are suitable substitutional sites for many activators[1]. YAG based phosphors are useful in a variety of display applications including projection TV, field emission display and backlight source[2]. YAG is an important solid state laser host material. Nd-doped YAG has widespread use in commercial, medical, military and industrial applications[3]. Ce<sup>3+</sup>-doped YAG is the most widely applied phosphor in white light LEDs[4,5,6]. Part of the blue light from the (In,Ga)N LED is absorbed by a thin layer of Ce<sup>3+</sup>-doped YAG and then it is converted into yellow light. The combination of blue and yellow gives a bright white light source with an overall energy efficiency that is approaching that of the compact fluorescent lamp. YAP doped with rare earth or transition metals also demonstrate very attractive properties[7] being a promising material as a host matrix for laser, phosphors[8], scintillator[9], thermoluminescent detector[10], holographic recording medium[11] and pigments[12]. Perovskite-Type aluminates and gallates are widely used[13] as substrate materials for the epitaxy of HTSC and CMR materials, and GaN films[14], as materials for solid oxide fuel cells[15], active and passive laser media[16], scintillators[17] and as microwave dielectric materials[18].



On the one hand, the rare-earth ions are characterized by a partially filled 4f shell that is well shielded by  $5s^2$  and  $5p^6$  orbitals. The emission transitions, therefore, yield sharp lines in the optical spectra. The use of rare-earth element-based phosphor, based on "line-type" f–f transitions, can be narrow to the visible, resulting in both high efficiency and a high lumen equivalent [19]. Among the  $Ln^{3+}$  ions, the trivalent europium ion,  $Eu^{3+}$ , is the mostly used choice due to the fact that  $Eu^{3+}$  (4f<sup>6</sup>) ions emit narrow-band, almost monochromatic light and have long life time of the optically active states.  $Eu^{3+}$  doped phosphors are commonly used as red emitting materials, which exhibit higher luminescence efficiency compared with other luminous materials. Further,  $Eu^{3+}$  ions have often been used as probes for estimation of local environment around the  $Ln^{3+}$  ions can be obtained quite easily from its f–f transition spectra. Since the ground  $^7F_0$  state and first excited  $^5D_0$  state of  $Eu^{3+}$  ions are non-degenerate under any symmetry, information regarding the local environment around the  $Eu^{3+}$  ion depends only on the splitting of the  $^5D_0-^7F_J$  emission spectra [20–24].

YAG phosphors doped with activators are mainly synthesized by solid-state reaction techniques that require high sintering temperatures (above 1800°C) to eliminate YAM and YAP phases[25]. Fluxes such as BaF<sub>2</sub>, YF<sub>3</sub>[26] or NH<sub>4</sub>Cl[27] can lower the sintering temperature down to 1500 C. Several novel methods have been used to obtain phase pure YAG at lower temperature[28]. These include various combustion procedures like nitrate–citrate combustion[29], combustion synthesis[30,31], gel-combustion using ammonium triacetic acid[32], sol-gel combustion[33] etc. Combustion synthesis has also been described for synthesis of YAP[34,35]. However, in most of the methods described in the literature, the desired compounds are not produced in one step. Additional heating at temperatures, often exceeding 1000 C, is invariably needed. This takes away several advantages of the combustion synthesis, such as fast, low cost, moderate temperature (500 C) method. The necessity of the additional heating may be due to the fact that Yttrium nitrate used in the combustion synthesis does not have exothermic reaction with urea which is commonly used fuel. Aluminum nitrate, on the other hand, has such reaction. Glycine had been successfully used as a fuel for combustion synthesis of yttrium compound. Use of Glycine + Urea mixed fuel may lead to maximum exothermicity and one may obtain the desired compound in one step.

In this paper we describe one step combustion synthesis of YAG, YAP and YAM carried out at 500 C furnace temperature. Activation with  $Eu^{3+}$  could also be achieved during the synthesis without taking recourse to any post-combustion thermal treatment.

#### **Experimental**

Instead of the conventional solution combustion synthesis, we used the modified procedure which led to the formation of the desired compounds in a single step. Reagent grade (Indian Rare Earths, Ltd.) rare earth oxides/carbonates were converted to the corresponding nitrates by dissolving in nitric



acid. The nitrates were dried by prolonged, gentle warming. Stoichiometric amounts of hydrated nitrates of yttrium, aluminium and europium were thorougly mixed with urea/glycine. Due to the presence of large water of crystallization in aluminium nitrate, a thick paste was formed. A china dish containing the paste was inserted in a furnace heated to 500 <sup>o</sup>C. Within minutes the paste foamed and a flame was produced which lasted for several seconds. The china dish was immediately removed from the furnace. X-ray diffraction patterns were recorded on Philips PANalytical X'pert Pro diffractometer. PL characteristics were studied using a Hitachi F-4000 spectrofluorimeter, at room temperature, using 1.5 nm spectral slit width in the range of 200–700 nm.

#### **Results and discussions**

## Eu<sup>3+</sup> activation

Yang et al[30], prepared YAG using combustion synthesis with urea as a fuel. However, the combustion product was admixture of YAG and YAP. Repeated sintering for 5 hrs at 1000 C was necessary to obtain YAG. More or less similar results were obtained by Pan et al[27]. Fu et al[36] used carbohydrazide fuel, but annealing at 1150 C for 6 hours was required to achieve good crystallinity and PL intensity. In our experiments, when urea was used as a fuel, the combustion products were poorly crystallized. Yttrium nitrate does not have exothermic reaction with urea. Hence we tried mixed (Glycine + urea) fuel. Glycine has exothermic reaction with Yttrium nitrate and urea with aluminum nitrate. XRD pattern of the product obtained with this fuel is shown in Fig.4.



Figure4:- XRD Results for YAG XRD data for YAG is compared with the ICDD data file 88-2048.

An excellent match is obtained with ICDD file 88-2048 corresponding to YAG. No lines corresponding to YAP (2 theta 34.236), YAM (2 theta 29.289) or YAH (2 theta 32.832) could be seen. Phase pure YAG is thus obtained in a single step combustion process without any additional thermal treatment when mixed fuel (Glycine + urea) was used. In most of the previous works on the combustion

synthesis of YAG, a single fuel was used. This had exothermic reaction with one of the nitrates (Y or Al). Use of mixed fuel has optimized the combustion reaction, thus resulting into phase pure YAG in a single step.

The Eu<sup>3+</sup> ions usually occupy the dodecahedral c site with D<sub>2</sub> symmetry in YAG host and thus replacing Y<sup>3+</sup>, and the exact local symmetry is only a small distortion of the centrosymmetric D<sub>2h</sub> point symmetry[37]. The emission spectrum of Eu<sup>3+</sup> doped YAG is shown, in Fig. 7a. It can be seen that the Stark splittings of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  and  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  emission lines are 3 (590, 591 and 596 nm) and 2 (610 and 630 nm), respectively. The strongest emission peak situated at 590 nm showing prominent and bright orange light is due to the magnetic dipole transition ( ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ ) and the 610 nm attributed to Eu<sup>3+</sup> forced electric dipole transition  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  is relatively weak, which indicates the Eu<sup>3+</sup> site has inversion symmetry and  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  electric dipole transition absent.

YAP was also successfully prepared by one step combustion with mixed (Glycine + urea) fuel. It can be seen from Fig.5 that the XRD pattern matches excellently with the stick pattern of ICDD file 33-0041 corresponding to the perovskite phase. No lines corresponding to YAG (2 theta 33.36), YAM (2 theta 29.289) or YAH (32.832) could be seen.



Figure 5:- XRD Results for YAP XRD data for YAP is compared with the ICDD data file 33-0041. However, the emission spectrum of Eu<sup>3+</sup> doped YAP (Fig. 7c) is dominated by the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  (615 nm) forced electric-dipole transition accompanied by the presence of  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  transition at 581 nm. Also, it can be seen that the Stark splittings of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ ,  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  and  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  emission lines are 1 (581 nm), 3 (590, 593 and 597 nm) and 5 (610, 615, 616, 618 and 627 nm), respectively.

YAM is a yttrium rich phase and due to exothermic reaction between glycine and yttrium nitrate, high temperatures may be anticipated during the combustion process. This may lead to decomposition of YAM and formation of YAP and YAG. Earlier, Han et al[38] prepared YAM by combustion synthesis. In the noisy XRD of the as-prepared materials they observed few weak lines. Crystallinity was attained only after 1100 C reheating. On the other hand, phase pure YAM was obtained by the combustion synthesis with mixed (Glycine + urea) fuel. It can be seen from Fig.6 that the XRD pattern matches excellently with the stick pattern of ICDD file 83-0935 corresponding to the YAM phase. No lines corresponding to YAG (2 theta 34.236), YAP (2 theta 33.614) or YAH (32.832) could be seen.



Figure 6:- XRD Results for YAM XRD data for YAM is compared with the ICDD data file 83-0935.

The emission spectrum of  $Eu^{3+}$  doped YAM is shown in Fig. 7(e). It can be seen that the Stark splittings of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ ,  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  and  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  emission lines are 2 (579 and 582 nm), 6 (585, 587, 590, 594, 596 and 598 nm) and 7 (607, 610, 612, 614, 617, 618 and 629 nm), respectively. The maximum splitting of the F<sub>J</sub> levels for a given site is 2J+1, where J is the angular momentum. So, it is obvious that the Eu<sup>3+</sup> ions occupy atleast two different sites.



Figure 7:- PL spectra for Eu<sup>3+</sup> activated samples a> YAG:Eu<sup>3+</sup> Emission for 395 nm excitation b> Excitation for 610 nm emission of YAG:Eu<sup>3+</sup> c> YAP:Eu<sup>3+</sup> Emission for 395 nm excitation d> Excitation for 610 nm emission of YAP:Eu<sup>3+</sup> e> YAM:Eu3+ Emission for 395 nm excitation f> Excitation for 610 nm emission of YAM:Eu<sup>3+</sup>

Fig. 8 shows an emission mechanism of  $Eu^{3+}$  ion in YAG, YAP and YAM phosphors by monitoring 395 nm excitation. Upon excitation at 395 nm, the  $Eu^{3+}$  ions are promoted from the ground state to  ${}^{5}L_{6}$  state. Then, the excited  $Eu^{3+}$  ions relax to the  ${}^{5}D_{0}$  energy level following a non-radiative process. The  ${}^{5}D_{0}$  level is populated and is responsible for the fluorescence at  ${}^{7}F_{J}$  (J = 0–2) energy levels.



Figure 8:- Emission mechanism of Eu<sup>3+</sup> ion in YAG, YAP and YAM phosphors under 395 nm excitation.

## **Conclusions:**

Phase pure YAG, YAP and YAM could be pepared by a one step combustion synthesis employing (Glycine+ urea) mixed fuel at the furnace temperature 500 C. No further heat treatment was needed. Preparation of  $Eu^{3+}$  activated phosphors was also attempted.  $Eu^{3+}$  was successfully doped into YAG, YAP and YAM as indicated by observation of PL spectra characteristic to these phases.

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#### **References:**

[1]Zhao W, Mancini C, Amans D, Boulon G, Epicier T, Min Y, Yagi H, Yanagitani T, Yanagida T, and Yoshikawa A, Optical Ceramics, *Jpn J. Appl. Phys*, 2010, *49*, 022602

[2]Fadlalla H.M.H and Tang C, J.Crystal Growth, 2009, 311, 3737

[3]Goel P, Mittal R, Choudhury N and Chaplot S.L , J. Phys.: Condens. Matter ,2010, 22, 065401.

[4] Cuche A, Masenelli B, Ledoux G, Amans D, Dujardin C, Sonnefraud Y, Melinon P, and Huant S,

Nanotechnology, 2009, 20,015603

[5]Jung K.Y and Kang Y.C, Physica B: Condensed Matter, 2010, 405,1615

[6]Liu Z, Liu S, Wang K and Luo X, Applied Optics, 2010, 49, 247



[7]Carvalho J.F, Vicente F.S.D, Pairis S, Odier P, Hernandes A.C, Ibanez A, J. Eur. Cer. Soc, 2009, 29, 2511

[8] Gao H, and Wang Y, Mater. Res. Bull, 2007, 42, 921.

[9] Nikl M, Yoshikawa A, Vedda A and Fukuda T, J.Crystal Growth, 2006, 1292, 416.

[10] Zhydachevskii Y, Suchocki A, Berkowski M, Sugak D, Bilski P and Warchol S, Radiat. Meas,

2010 : Article in Press

[11] Loutts G. B, Warren M, Taylor L, .Rakhimov R. R, Ries H. R, Miller G. et al., *Phys. Rev. B*, 1998, 57,3706.

[12] Shirpour M, Faghihi Sani M, and Mirhabibi A, Ceramics International, 2007, 33, 1427.

[13] Vasylechko L, Senyshyn A and Bismayer U, Handbook on the Physics and Chemistry of Rare Earths, 2009, 39,

[14] Liu G, Wang H, Makino H, H.J.Ko, Hanada T and Yao T, Appl. Surf. Sci, 2002, 190, 408.

[15] Hariharan R and Gopalan P, J. Alloys Compd, 2010:Article in Press

[16] Noginov M, Loutts G, Jones D, Turney V, Rachimov R, Herbert L and Truong A, *J.Appl. Phys*, 2002, *91*, 569.

[17] Bachmann V, Ronda C, and Meijerink A, Chem. Mater, 2009, 21, 2077.

[18] Huang C and Chen Y, Mater. Res. Bull, 2002, 37, 3, 563.

[19] FELDMANN C, JUSTEL T, RONDA C.R, SCHMIDT P.J, INORGANIC LUMINESCENT

MATERIALS: 100 YEARS OF RESEARCH AND APPLICATIONADV. FUNCT. MATER. 2003,13,511.

[20] ZHANG Q.Y, PITA K, YE W, QUE W.X, CHEM. PHYS. LETT. 2002,351, 163.

[21] Park J.K, Lim M.A, Kim C.H, Park H.D, Park J.T, Choi S.Y, Appl. Phys. Lett, 2003, 82, 683.

[22] Wu C, Qin W, Qin G, Zhao D, Zheng J, Huang S, Lu S, Liu H, Lin H, *Appl. Phys.Lett.* 2003, *82*, 520.

[23] Surendra Babu S, Babu P, Jayasankar C.K, Sievers W, Troster Th, Wortmann G, *J. Lumin*, 2007,126, 109.

[24] Edita Garskaite, Mikael Lindgren, Mari-Ann Einarsrud, Tor Grande, *J. Eur. Cer. Soc*, 2010, *30*, 1717.

[25] Zorenko Y.V and Gorbenko V.I, Physics of the Solid State, 2009, 51, 1800.

[26] Ohno K and Abe T, J.Electrochem.Soc.:Solid-StateSci.Technol, 1986, 133, 638.

[27] Yuexiao Pan, Mingmei Wu and Qiang Su, J. Phys. Chem. Solids, 2004, 65. 845.

[28] Yuexiao Pan, Mingmei Wu, Qiang Su, Mater. Sci. Engg. B, 2004, 106, 251.

[29] Zhang J, Ning J, Liu X, Pan Y and Huang L, Mater. Lett, 2003, 57, 3077

[30] Zhiping Yang, Xu Li, Yong Yang, and Xingmin Li, Proc. SPIE, 2006, 6033 60330N.

[31] Yang Z, Li X, Yang Y, and Li X, J. Lumin, 2007, 126, 707.



[32] Tao Feng, JianLin Shi and Danyu Jiang, J. Eur. Cer. Soc, 2008, 28, 2539.

[33] Jiao H, Ma Q, He L, Liu Z and Wu Q, Powder Technology, 2010, 198, 229.

[34] Taspinar E and Tas A, J. Am. Ceram. Soc, 1997, 80, 133.

[35] Han S, Kharkar S, Taxak V, Kumar D and Park Y, Mater. Sci. Eng. B, 2006, 127, 272.

[36] Fu Y.P, Wen S.B and Hsu C.S, J.Alloys. Compd, 2008, 458, 318.

[37]Ravichandra D, Roy R, Chakhovskoib A.G, Hunt C.E, White W.B, Erdei S, J.Lumin. 1997, 71,

291.