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Effect of the europium doping on the structural and luminescent properties of yttrium aluminum garnet

L.E. Muresan[a,*], E.J. Popovici[a], I. Perhaita[a], E. Indrea[b], T.D. Silipas[b]

[a] *"Babes-Bolyai" University, "Raluca Ripan" Institute for Research in Chemistry, Fantanele 30, 400294 Cluj-Napoca, Romania*
[b] *National Institute for R&D for Isotopic and Molecular Technologies, Donath 71-103, 400293, Romania*

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ABSTRACT

Europium activated yttrium aluminate (YAG:Eu) phosphors were synthesized using urea by wet chemical synthesis route. The luminescent behavior and the microstructural changes are monitored, depending on the amount of europium. The luminescent spectra of YAG:Eu phosphors possess four major emission bands in the range of 570–700 nm with maxima situated at 592 nm 598 nm, 611 nm and 631 nm. The intensity ratio between the 611 nm band as red component ($^5D_0 \rightarrow {}^7F_2$) and 592 nm band as orange component ($^5D_0 \rightarrow {}^7F_1$) is discussed, in order to obtain information about the chemical surroundings of the luminescent centers and their symmetry. X-ray diffraction showed that the main crystalline phase of the phosphors is yttrium aluminum garnet $Y_3Al_5O_{12}$ with cubic structure. Monoclinic $Y_4Al_2O_9$ phase was also found as impurity. The effect of the europium content on the microstructural parameters is revealed. The luminescent characteristics depend strongly on the structural purity, activator concentration and incorporation of europium ions in the host lattice. Additional investigations as FT-IR, BET, ICP-OES were performed for a better understanding of the luminescent and structural characteristics of YAG:Eu phosphor.

1. Introduction

Phosphors are well known materials due to their utilization in displays and traditional lighting devices, like cathode-ray tubes, fluorescent lamps, light emitting diode or field emission displays. Recent progress and future prospects show that, luminescent materials remain not only interesting from a scientific perspective but also relevant from an applicative point of view [1,2].

Yttrium aluminate doped with rare-earth (RE) ions are interesting compounds, which have been extensively used as lasers and phosphors [3,4]. Literature describes that yttrium-aluminum oxide based compounds possess different kinds of crystal phases such as: cubic-$Y_3Al_5O_{12}$ (YAG, garnet), hexagonal-$YAlO_3$ (YAP, perovskite) and monoclinic-$Y_4Al_2O_9$ (YAM) [5–7].

Among the rare earth ions, Eu^{3+} is mostly used as activator, due to both the narrow-bands emission spectra and the long lifetime of the optically active states. Eu^{3+} ions have been often used for estimation of local environment in different matrices. Useful information about the local structure around Eu^{3+} ions can be obtained easily from its f–f electron transition spectra.

YAG has a cubic crystal structure with aluminum ions located in the center of octahedral and tetrahedral sites with coordination number (CN) 6 and 4 respectively. Yttrium ions (CN = 8) are situated in the middle of the dodecahedral interspaces composed of regular aluminum tetrahedrons and octahedrons [8]. Generally in the YAG host lattice, Eu^{3+} ions replace the Y^{3+} ions, occupying the dodecahedral site with D2 symmetry, generating luminescent centers [9].

The luminescent emission of YAG:Eu is the result of the electron transitions that take place in Eu^{3+} ions namely: $^5D_0 \rightarrow {}^7F_1$ magnetic dipole transition (~590 nm) and $^5D_0 \rightarrow {}^7F_2$ electric dipole transitions (~609 nm) [10,11]. Literature provides some information regarding the site symmetry of Eu^{3+} based on the luminescent properties of YAG:Eu [12].

Europium activated yttrium aluminate phosphors (YAG:Eu) can be obtained by different ways like sol–gel, co-precipitation, pyrolysis, combustion or solid state reaction [13–17]. Various studies regarding the luminescence and structural characteristics of YAG:Eu phosphor were performed in order to highlight the influence of different preparative factors as concentration of the europium [18,19], source of aluminum [20] or firing temperature [13,21]; as well as the effect of phosphor particle size [22,23].We report the synthesis of YAG:Eu phosphor ($Y_3Al_5O_{12}$:Eu) by an original wet-chemical synthesis route using the reactants simultaneous addition technique (SimAdd). Previous studies showed that the SimAdd method was successfully used to obtain YAG phosphors doped with cerium [24–26]. In order to obtain new phosphors with high phase purity and tunable photoluminescence some studies referring to the doping of YAG with Ce, Eu and/or Tb were initiated. The present paper is focused on the influence of europium

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[*] Corresponding author.
E-mail address: laura_muresan2003@yahoo.com (L.E. Muresan).

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doping on the structural and luminescent properties of yttrium aluminum garnet. Our previous researches showed that, among urea, oxalic acid and ammonium carbonate, the first precipitant agent (urea) leads to the formation of europium doped yttrium aluminate with garnet structure [27]. In this paper we discuss some aspects concerning the luminescent properties of YAG:Eu phosphors with variable activator amounts, in correlations with their phase purity and microstructural parameters. New physical-chemical aspects regarding YAG:Eu phosphors prepared by wet chemical synthesis route are revealed.

2. Experimental

Europium activated yttrium aluminate phosphors (YAG:Eu) were prepared by reactants simultaneous addition technique (SimAdd) [24–26], using urea as precipitating agents. In this purpose, Y–Al–Eu precursors were prepared from $Y(NO_3)_3 \cdot 5H_2O$ (99.9% Aldrich); $Al(NO_3)_3 \cdot 9H_2O$ (98%, Alfa Aesar); $Eu(NO_3)_3 \cdot 5H_2O$ (extra pure Merck) as metallic ion sources and urea (99.3% AlphaAesar) as anion source.

The synthesis of YAG:Eu was carried out in two stages. In the first stage Y–Al–Eu precursors were prepared by precipitation at 80 °C and pH 8 (kept constant by addition of ammonia), using equal volumes of yttrium–aluminum–europium nitrate (0.5 M) and urea (2 M) solutions, which were simultaneously added into a diluted solution (1:10) of urea. In the precipitation process, turbidity was observed after 5 min from the beginning of the reagents additions and the pH tends to decrease slowly from 8.0 to 7.7. The nitrate solution mixture contains Y^{3+}, Eu^{3+} and Al^{3+} in stoichiometric amounts. The precursor post precipitation stage consists in 24 h aging, washing, centrifugation and drying.

The second stage of the method was the thermal treatment of the precursors that was carried out at 1200 °C, in nitrogen atmosphere, for 2 h. The as obtained phosphor powders were water washed, dried and sieved.

Samples with the general formula $Y_{3-x}Eu_x\,Al_5O_{12}$ ($x = 0.0$, 0.03, 0.09, 0.15 and 0.21) were prepared. The YAG:Eu phosphors with different europium concentration were codified as follows: EAG0.1 (0 mol% Eu) EAG1.1 (1 mol% Eu), EAG11.1 (3 mol% Eu), EAG12.1 (5 mol% Eu) and EAG13.1 (7 mol% Eu).

In order to evaluate the incorporation degree of the Eu^{3+} ions into the YAG host lattice, chemical analysis was performed by inductively coupled plasma-optical emission spectrometry (ICP-OES). Therefore the corresponding precursors were precisely weighed (0.2 g), dissolved in 10 ml mixture of 3:1:0.5 nitric acid (65%); hydrochloric acid (35%) and sulphuric acid (95%) and boiled for 30 min. After the samples were dissolved, the solutions were diluted and measured.

Precursors and phosphors were investigated by Fourier-Transform infrared absorption spectroscopy (Thermo Scientific Nicolet 6700 FT-IR Spectrometer; KBr pellet technique), surface area measurements (TriStar II3020 - Micromeritics, nitrogen adsorption at 77 K; sample decontamination at 150 °C for 24 h in nitrogen flow) and ICP-OES spectrometry (PerkinElmer, OPTIMA 2100DV). The characterization of phosphors was also performed by photoluminescence measurements (JASCO FP-6500 Spectrofluorimeter Wavel; Glass filter WG 320) and X-ray diffraction (BRUKER D8 Advance X-ray diffractometer, 40 kV, 40 mA, $\lambda_{CuK\alpha1} = 1.54056$ Å, 2θ range 15–85° step of $\Delta 2\theta = 0.01°$)

3. Results and discussion

3.1. General characterization

Europium doped yttrium aluminum garnet phosphors with different amount of europium were prepared using urea as precipitating agent and the reactants simultaneous addition technique. During the precipitation process, the urea hydrolyzes providing in the reaction medium some ionic species such as: $CO_3{}^{2-}$, $NH_4{}^+$, HO^- and H_3O^+ respectively [28]. The solution of yttrium–europium–aluminum nitrates supplies the Y^{3+}, Eu^{3+}, Al^{3+} and $NO_3{}^-$ species. Our previous work reported that the composition of Y–Eu–Al based precursor is: $M_2(CO_3)_3 \cdot aM(OH)_3 \cdot cM(NO_3)_3 \cdot dH_2O \cdot eNH_3$ where M = Y, Al, Eu [27]. The thermal treatment leads to the formation of YAG host lattice and to the incorporation of the europium ions. Because the precipitation with urea is performed in a multi-metal containing medium, the phosphor composition can be different from the theoretical one. In order to determine the real content of the europium incorporated into the phosphor lattice, ICP-OES measurements were performed.

Table 1 presents the comparison of the theoretical and experimental composition of the YAG:Eu phosphors calculated on the basis of Y to Eu to Al ratio from precursor precipitate.

Excepting sample EAG13.1, the experimental content of the europium is slightly higher than the theoretical values and varies from 1.06 mol% to 5.18 mol%. The experimental ratio of Y + Eu/Al is smaller than the theoretical value, and tends to decrease slowly with increasing the europium content. This can be explained due to selective and uncontrolled precipitation of metallic ions (Y^{3+}, Eu^{3+} and Al^{3+}). It seems that the precipitation rate of the aluminum is higher than that of yttrium and europium, as the content of the europium increase.

The fact that the yttrium and aluminum compounds precipitate with different rates was also reported in literature [29,30]. Aluminum ions precipitate first, followed by the yttrium and europium ions which precipitate onto the aluminum compound particles to produce fine YAG precursor precipitates. The reason for this behavior is the difference between the solubility products of indissoluble metallic compounds [31]. A good control of the precipitation stage is particularly important because it directly affects the molar ratio between Y, Eu and Al ions and consequently influences the structural and luminescent characteristics of the final product.

3.2. Luminescence characterization

The photoluminescent characteristics of YAG:Eu phosphors were evaluated on the basis of emission (PL) and excitation (PLE) spectra.

Fig. 1 presents the emission and excitation spectra of $Y_3Al_5O_{12}$:Eu samples. The PLE spectra recorded between 200 nm and 400 nm presents two important excitation regions. The first spectral domain is situated between 220 and 250 nm and contains the Eu^{3+} and O^{2-} charge-transfer band (CTB) with maximum intensity at around 238 nm. The second region between 280 nm and 425 nm contains several weak sharp lines associated to the f–f electronic transitions of Eu^{3+} ions with maxima at 266 nm, 298 nm, 319 nm ($^7F_0 \rightarrow {}^5H_{5-7}$), 362 nm ($^7F_0 \rightarrow {}^5D_4$), 379 nm ($^7F_0 \rightarrow {}^5G_{4-6}$), 394 nm ($^7F_{0,1} \rightarrow {}^5L6$) and 405 nm ($^7F_0 \rightarrow {}^5D_3$), in agreement with the literature data [32,33]. The increase of europium concentration brings about the increase of CTB intensity, arising from the enhancement of the energy transfer, and a slight red-shift of CTB maximum from 235 nm (for 0 and 1 mol% Eu) to 238 nm (for 7 mol% Eu). Moreover sample EAG11.1 possess a shoulder in the range 250–280 nm (not observed in other samples) suggesting that, the europium ions form different luminescent centers.

All YAG:Eu samples exhibit an orange-red luminescence with similar characteristic emission bands. In the 580–640 nm domain the PL spectra present five bands with maxima situated at 587 nm, 592 nm, 598 nm, 611 nm and 631 nm which are associated with $^5D_0$–^7F_J ($J = 0, 1, 2$) transitions in Eu^{3+} ions [13,23].

The luminescent emission of YAG:Eu samples is enhanced when the europium content increases from 1 mol% to 7 mol%. This