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SYNTHESIS AND CHARACTERIZATION OF RARE EARTH DOPED YAG NANOPOWDERS *VIA* COMBUSTION SYNTHESIS

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Abstract: Yttrium Aluminum Garnet (YAG) powder doped with rare earth (RE) ions (RE= Ce^{3+}, Eu^{3+}, Nd^{3+} and Pr^{3+}) were prepared *via* combustion synthesis at relatively low temperature. The combustion synthesis involves the reaction of aluminum nitrate ($Al(NO_3)_3$), yttrium nitrate ($Y(NO_3)_3$) and the rare earth ion nitrates ($RE(NO_3)_3$) with carbohydrazide ($CO(N_2H_3)_2$) as fuel. As-synthesized YAG:RE powder samples were amorphous or nano-crystalline however, after annealing at 1000 °C temperature throughout one hour their reached a cubic perovskite type structure. The PL spectra of YAG:RE powders synthesized in this work confirmed the incorporation of RE ions in the YAG host lattice. This research showed that the Combustion Synthesis is a low-cost and rapid method to produce high quality YAG:RE powders.

Keywords: YAG powders, rare earth ions, combustion synthesis, luminescence.

BACKGROUND

Inorganic luminescent materials are crystalline compounds that absorb energy and subsequently emit this absorbed energy as light. Phosphors are composed of an inert host lattice and an optically excited activator, typically a 3d or 4f electron metal such as Ce^{3+}, Cr^{3+}, Eu^{3+}, among others[1]. Yttrium Aluminum Garnet or YAG ($Y_3Al_5O_{12}$), which exists in the cubic form with a garnet structure, is one of the most commonly used phosphor materials, especially as a host for rare earth (RE) ions, due to its thermal and chemical stability and optical transparency from ultraviolet to infrared regions. YAG crystals doped with RE ions have a wide range of applications in photonics including solid-state lasers, scintillators, and phosphors, due to the YAG´s chemical stability at high temperatures (besides being one of the best creep-resistant oxides[2]), and their unique fluorescent properties of RE ions[3].

In the 1960s, YAG single crystals, drawn the attention for fluorescence and solid-state laser applications[4]. However, the expensiveness and difficulties of single crystal growth, caused the development of different ceramic processing techniques to obtain polycrystalline YAG; having advantages in cost, preparation time and scale production. Recently, transparent polycrystalline YAG ceramics have been prepared for their use as solid-state laser materials[5].

YAG and YAG-based phosphors have been synthesized by numerous techniques, such as solid-state reaction (which requires high temperature above 1,600 °C to gain pure phase YAG), sol–gel[3], gel combustion[6], spray pyrolysis, co-precipitation and hydrothermal methods[7]. These techniques have advantages of fine homogeneity, high reactivity of starting materials and lower sintering temperatures. However, they require long times and restricted fabrication techniques. In contrast, the combustion method is very simple, and the combustion reaction takes a few seconds[8].

Combustion synthesis[9] is a relative low temperature technique, which consists on a highly exothermic redox reaction between metal nitrates and an organic fuel. This reaction yields homogenous complex oxides in a very short time. The as-synthesized products show a high purity, typically a one crystalline phase and they are chemically homogenous.

In this research, we report the preparation of YAG:Ce, YAG:Eu, YAG:Nd and YAG:Pr powders *via* combustion synthesis in a single step. Structural, morphological and luminescent studies of the as-synthesized and the annealed products are presented.

EXPERIMENTAL PROCEDURE

REACTANTS

The precursors used for the synthesis of $Y_{2.97}Al_5O_{12}:RE_{0.01}$ were yttrium nitrate hexahydrate [$Y(NO_3)_3 \cdot 6H_2O$, 99.99%] Sigma-Aldrich, aluminum nitrate nonahydrate [$Al(NO_3)_3 \cdot 9H_2O$, 99%] Sigma-Aldrich, cerium nitrate hexahydrate [$Ce(NO_3)_3 \cdot 6H_2O$, 99%] Sigma-Aldrich, europium nitrate hexahydrate [$Eu(NO_3)_3 \cdot 6H_2O$, 99.9%] Alfa Aesar, neodymium nitrate hexahydrate [$Nd(NO_3)_3 \cdot 6H_2O$, 99.9%] Sigma-Aldrich, praseodymium nitrate hexadydrate [$Pr(NO_3)_3 \cdot 6H_2O$, 99.9%], carbohydrazide [$CO(NHNH_2)_2$, 98%] Sigma-Aldrich and deionized water.

SYNTHESIS

The YAG:RE ($Y_{2.97}Al_5O_{12}:RE_{0.01}$) powders were prepared by combustion synthesis. The required mass of each reactant was stoichiometrically calculated from the desired mass of products. The nitrates were dissolved in a beaker using 10 mL of deionized water until a transparent solution was formed. Therefore the carbohydrazide (fuel) was added and dissolved as well. After that, the beaker was introduced in a pre-heated furnace at 500 °C in an air atmosphere to supply the conditions for a highly exothermic redox reaction between the nitrates and the carbohydrazide. The product was cooled down at ambient temperature for 20 min. The products were white flaky textured material for all cases. Subsequently the samples were annealed at 800 °C and 1000 °C to obtain polycrystalline YAG powders.

CHARACTERIZATION

Different techniques were used to perform the characterization of $Y_{2.97}Al_5O_{12}:RE_{0.01}$ stoichiometric powders: X-ray diffraction (XRD), scanning electron microscopy (SEM) and photoluminescence (PL). The XRD study was performed in a Philips X'pert MPD (XRD) model with a high intensity ceramic sealed tube (3kW) and a wavelength of 1.5405 Å, which is especially for powders and thick films. The SEM analysis was done using a JEOL JIB-4500 SEM. For YAG:RE(1%) powder doped with Ce, Eu, and Pr, the photoluminescence effect was observed with a fluorescence spectrophotometer model HITACHI F-7000 provided with a 150 W xenon lamp as light source, which can carry out measurements in a wavelength range of 200 to 750 nm. In order to observe the photoluminescence of the YAG:Nd sample it was necessary to use a more powerful spectrophotometer, because of the excitation wavelength needed (above 800 nm). The model used in this particular case was a Double Beam Spectrophotometer UH5300, with a measuring wavelength range of 190 to 1100 nm.

RESULTS AND DISCUSSION

CRYSTALLINE STRUCTURE

Figure 1 shows the XRD patterns for YAG powders as-synthesized. It is observed that for all cases no diffraction peak appears for the phosphors obtained at 500 °C, which indicates that the phosphors are amorphous or nano-crystalline at this temperature. On the other hand, as observed in figure 2, YAG:RE powders annealed at 1000 °C demonstrate the presence of a cubic crystalline structure. Particularly for YAG:Nd, the XRD pattern confirms the existence of a predominant perovskite phase called YAP and the existence in a minor proportion of the cubic phase. It is well known that, there are two different processes widely accepted about the phase transition during synthesis of YAG powders: (a) direct crystallization from the amorphous and (b) transformation from an intermediate phase, like YAP as in the present case. In several studies, the formation of transitional phases (YAP and YAM) has been attributed to the inhomogeneity of the precursors.

However, there is no explanation for this happening to YAG:Nd only. Both phases can

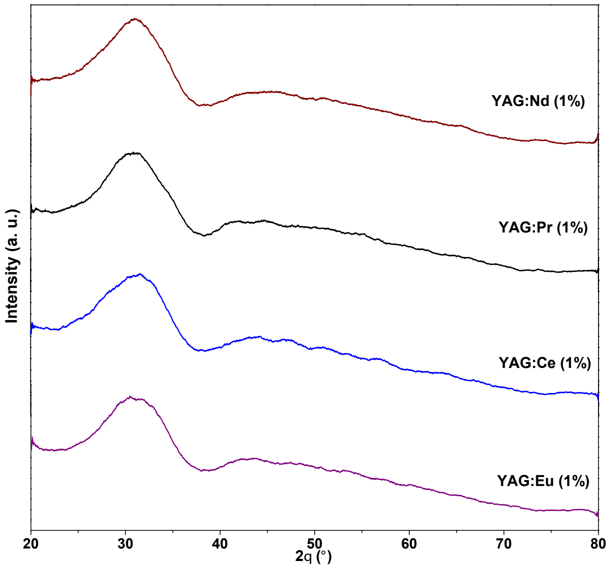


Fig. 1. XRD patterns for YAG:RE(1%) powders as-synthesized at 500 °C.

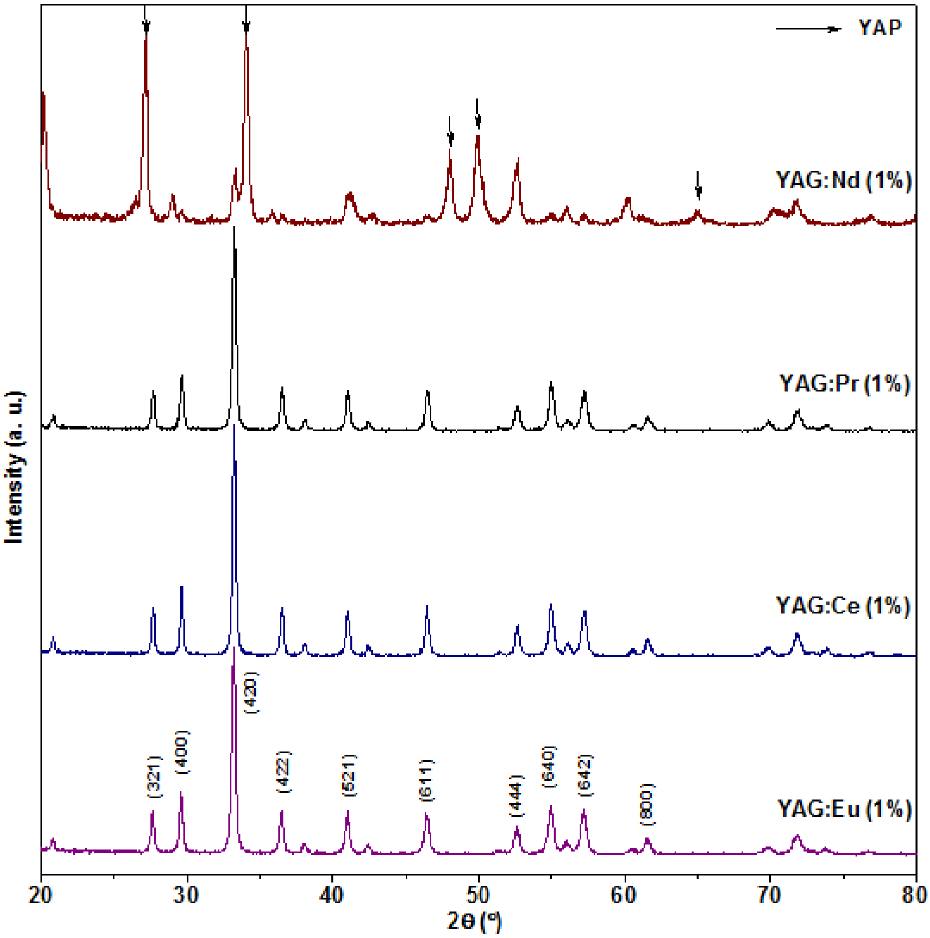


Fig. 2. XRD patterns for YAG:RE(1%) powders annealed at 1000 °C.

be observed since YAP (JCPDS Card No. 16-219) crystallizes at 900 °C and it is persistent at 1000 °C when YAG (JCPDS Card No. 33-40) is detected[10,11].

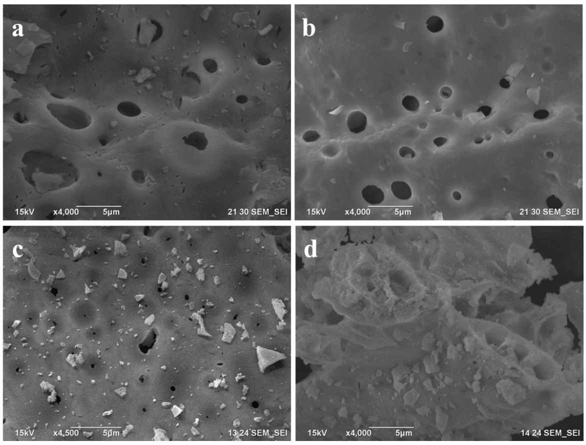
Particle size distribution has been calculated using the Scherrer's formula:

$$\tau = \frac{0.9(\lambda)}{(B)\cos\theta},$$

where λ is the wavelength of the applied XRD, *B* is the full width at half maximum expressed in radians and Θ is the Bragg angle of the considered diffraction peak. After applying the Scherrer's formula to the YAG:RE(1%) data, it was found that the average particle size was 27.64 nm for the powders annealed at 1000 °C.

MORPHOLOGY

SEM micrographs of the $Y_{2.97}Al_5O_{12}:RE_{0.01}$ powder is depicted in figure 3. For all samples, the images indicate irregular shapes with well-defined structure consisting of flakes with micropores. This structure is probably due to the escaping of gases during combustion reaction and that is the same for the samples without heat treatment. Only for the sample YAG:Nd annealed at 1000 °C there is a change in the morphology of the surface, and also various sub-microsized particles are observed; probably that is due to the formation of the YAP phase.



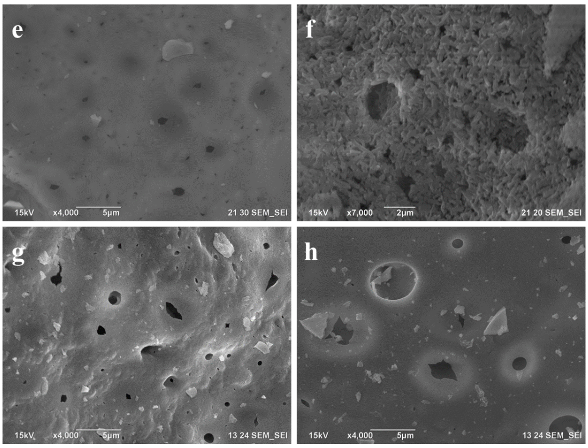
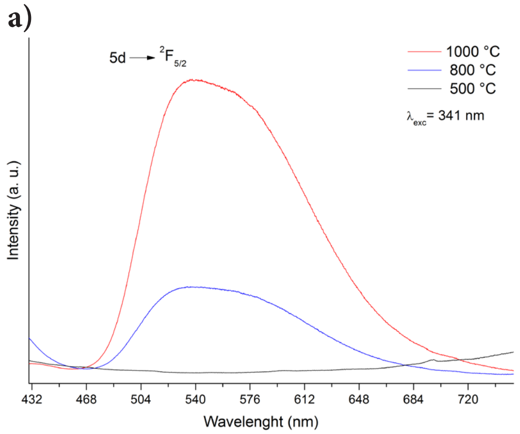


Fig. 3. SEM images for samples YAG:Ce, YAG:Eu, YAG:Nd and YAG:Pr as-synthesized (a, c, e, and g, respectively) and after annealing at 1000 °C (b, d, f, and h, respectively).

LUMINESCENCE

The emission spectra for YAG:Ce powder at 500 °C, 800 °C and 1000 °C, are shown in figure 4a. The emission spectra show the characteristic 4f to 5d transitions of Ce^{3+} in YAG:Ce crystals which corresponds to the ground state of Ce^{3+} ($4f^1$ electronic configuration) consisting of a doublet ($2F_{5/2}$ and $2F_{7/2}$) splitted due to the spin–orbit interaction, while the lower excited states are the 5d levels split by the crystal field. This transitions can be found elsewhere in the literature[3,12]. Under an excitation wavelength of 341 nm the PL spectrum shows a broad peak maximum at 520 nm, which is in the green region.



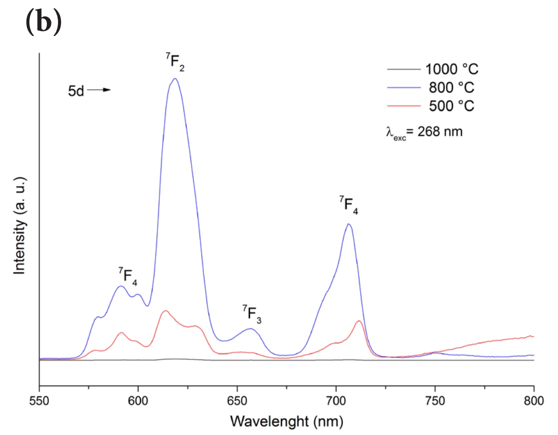


Fig. 4. Emission spectra for (a) YAG:Ce(1%) and (b) YAG:Eu(1%) samples at different temperatures.

Figure 4b shows the emission spectra for YAG:Eu at the same temperatures than those for YAG:Ce. The spectra of YAG:Eu with a 268 nm excitation wavelength shows the typical emission peaks for Eu^{3+}, which correspond to the transition states $^5D_0$-$^7F_1$ at 590 nm, $^5D_0$-$^7F_2$ at 608 nm and $^5D_0$-$^7F_4$ at 705 nm[13], giving an intense red fluorescence characteristic of Eu^{3+}.

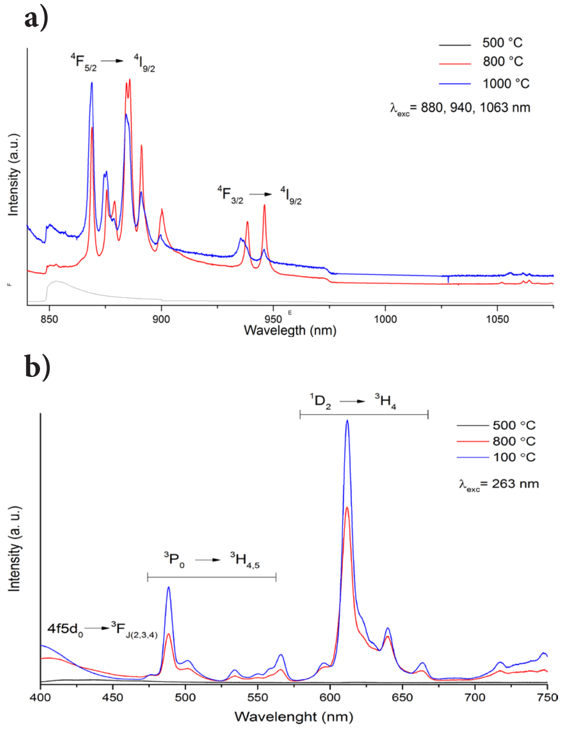


Fig. 5. Emission spectra for (a) YAG:Nd(1%) and (b) YAG:Pr(1%) samples at different temperatures.

The emission spectra for YAG: Nd powder is shown in figure 5a. The observed luminescence bands were assigned to the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ and $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transitions. The assignment of Stark components of the observed luminescence lines is identical to those observed for the single Nd:YAG crystal. That emission is has been associated to the thermalization of the $^4F_{3/2}$ orbitals as it has been not seen at low temperatures[14].

Figure 5b shows the emission spectra of YAG:Pr powder at the same temperatures mentioned before using a 263 nm excitation wavelength. The resulting emission spectra shows two main groups: one in the range of 450–600 nm that is originated from $^3P0 \rightarrow {}^3H_{4,5}$ transitions dominated by an intense blue emission line at 488 nm due to the $^3P0 \rightarrow {}^3H_4$ transition; and the other group in red originates from $^1D_2 \rightarrow {}^3H_4$ transition dominated by an intense red emission line at 610 nm with emission at 640 nm[15].

As observed in the emission spectra for YAG:Ce, YAG:Nd and YAG:Pr, the intensity of the emission peaks increases with the annealing temperatures. However, YAG:Eu showed a different pattern, the sample annealed at 800 °C presented a higher intensity than the sample annealed at 1000 °C. It can be explained by the quenching generated by the particle size and lifetime of Eu^{3+}, which decays according to the annealing temperature[8], as it is well known, the typical emission spectra of YAG:Eu is presented in the amorphous phase and decreases as the particle size increases[16].

Under ultraviolet lamp excitation (365 nm wavelength), the YAG:RE (1%) samples annealed at 1000 °C exhibited high intense visible fluorescence (YAG:Nd as exception because its emission peaks occurs in the infrared region) as observed in figure 6, while the samples as-synthesized do not show any detectable fluorescence. The observation

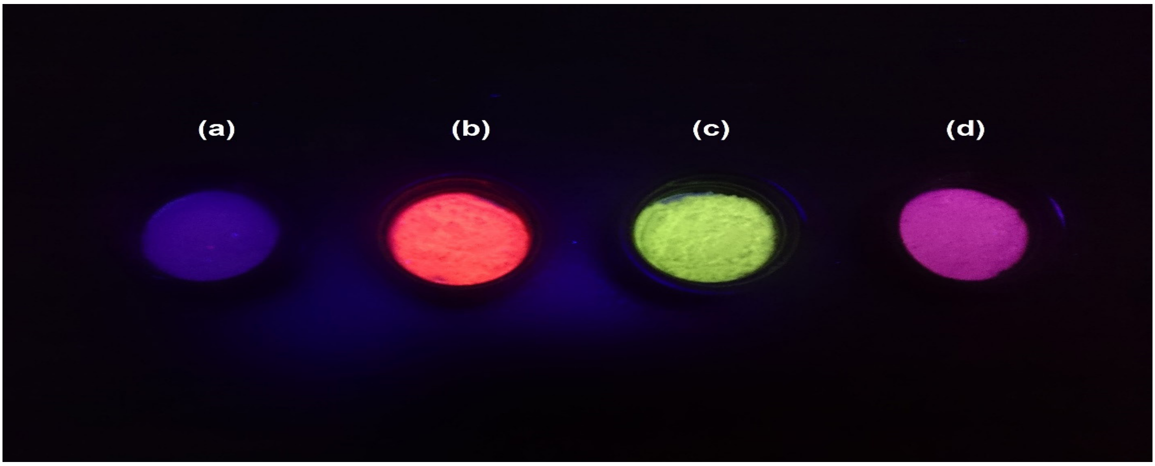


Fig. 6. Images of (a) YAG:Nd, (b) YAG:Eu, (c) YAG:Ce and (d) YAG:Pr powders annealed at 1000 °C under UV lamp at 365 nm wavelength excitation.

of this fluorescence indicates that the RE ions are incorporated into the host YAG crystalline phase[17].

CONCLUSIONS

Ce^{3+}, Eu^{3+}, Nd^{3+} and Pr^{3+} doped YAG powders were obtained by combustion synthesis using carbohydrazide as fuel at 500 °C initial temperature. Further annealing process between 800 and 1000 °C was necessary in order to obtain YAG powders with a perovskite crystalline structure, since below 750 °C the material is amorphous or nanocrystalline. Samples annealed at 1000 °C, the XRD showed the formation of YAG cubic phase and for YAG:Nd, also the formation of YAP phase occur. SEM images showed a slight change in the microporous morphology. The photoluminescence of the YAG:RE powders correspond to those reported for Ce^{3+}, Eu^{3+}, Nd^{3+} and Pr^{3+} ions. For YAG:Eu after sintering process, shows coincidence in emission and morphology as those samples reported with others, more expensive and slower synthesis techniques such as solid-state reaction, where quenching is reported. This work demonstrates that combustion synthesis is an effective, fast and economic technique for the preparation of YAG:RE powders.

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