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# SYNTHESIS BY A CITRATE SOL-GEL METHOD AND CHARACTERIZATION OF $EU^{3+}$-DOPED YTTRIUM ALUMINUM GARNET NANOCRYSTALS

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*Abstract*. In the present work, we synthesized YAG:Eu by nitrate–citrate sol–gel process and the structure of the materials was analyzed by means of X-ray diffraction (XRD), showing the cubic garnet phase of YAG. We studied the effect of thermal treatment on crystalline size and we distinguished the $Eu^{3+}$ ion presence by means of optical spectroscopic measurements

*Key words:* nanocrystals, YAG, $Eu^{3+}$, sol- gel method

## 1. INTRODUCTION

Small crystalline materials with particle diameters of 100 nm or less exhibit many novel physical properties (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, $Y_3Al_5O_{12}$ (YAG), existing in a cubic form with a garnet structure, has received much attention because of interesting optical and mechanical properties. Single crystal is widely used in solid- state lasers. Rare-earth doped YAG powders are promising phosphors for displays. YAG doped with lanthanide ions such as $Nd^{3+}$ and $Ce^{3+}$ is already used in the construction of dye lasers and new generation lighting devices. $Ce^{3+}$-activated YAG is a very stable and long-life phosphor used in liquid crystal light valve projection display [1,2].

YAG:Tb is a characteristic narrow-band phosphor suitable for contrast-enhanced display application in high ambient illumination conditions. Hence, YAG:Tb is one of the potential phosphors which may be used in projection CRT's [3]. $Eu^{3+}$-doped YAG phosphors also have the potential for application in field emission devices. Phosphors for field emission and vacuum fluorescent display devices have critical dependence on their particle sizes, the quantum efficiency of the luminescence 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.

YAG phosphors doped with activators are mainly synthesized by solid-state reaction techniques which require high sintering temperatures (above 1600ºC), long reaction times (10 - 20h) and extensive ball milling, which generally

introduces additional impurities and defects. It is reported that two detrimental phases, YAM (yttrium aluminum monoclinic- $Y_4A_{l2}O_9$) and YAP (yttrium aluminum perovskite - $YAlO_3$), often coexist with YAG [4]. In order to obtain sharp powders, several chemical synthesis techniques, such as sol–gel [5-14], coprecipitation [15,16], precipitation of hydroxides [17], spray pyrolisis [18,19] and combustion methods [20], hydrothermal syntheses [21] 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.

## 2. EXPERIMENTAL

### 2.1. Materials and sample preparation

In the sol–gel process for preparing YAG:$Eu^{3+}$ 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 $Eu^{3+}$:YAG nanocrystals, aqueous solutions of $Y(NO_3)_3{\cdot}5H_2O$ 1.93M, $Al(NO_3)_3{\cdot}9H_2O$ 2.12M, and $Eu(NO_3)_3{\cdot}5H_2O$ 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 ($C_6H_8O_7{\cdot}H_2O$) 2M, in molar ratio citric acid: nitrates of 3:1. The mixture was evaporated at 80°C until a transparent viscous gel was obtained. The gel was decomposed at 600°C for 6h obtaining a black powder, which then was calcinated at ~900°C for 6 h in air, achieving this way a white powder implying that organic compounds were burned away during calcination.

### 2.2. XRD measurements

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

### 2.3. Optical spectroscopy

The luminescence spectrum of $Eu^{3+}$ substituted for $Y^{3+}$ in YAG 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.

## 3. RESULTS AND DISCUSSION

The gel was annealed at various temperatures. Since no obvious diffraction peaks are observed for the samples heat-treated up to 900°C, it can be concluded that the powders are still amorphous. The YAG crystallization occurs at ~ 930°C. The XRD pattern shows YAG to be the only crystalline component (Fig. 1).

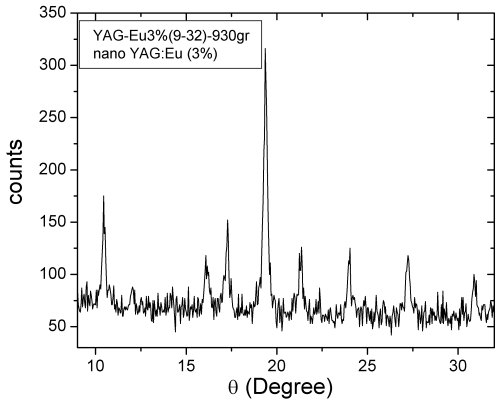


Fig. 1. XRD patterns of the sample heated at 900°C.

Increasing the annealing temperature, the diffraction pattern shows higher intensity and narrower diffraction lines. It denotes that the YAG crystallites grow as the annealing temperature increases. Thus, in Fig. 2 we show the XRD patern of an YAG:Eu powder annealed at 1300ºC.

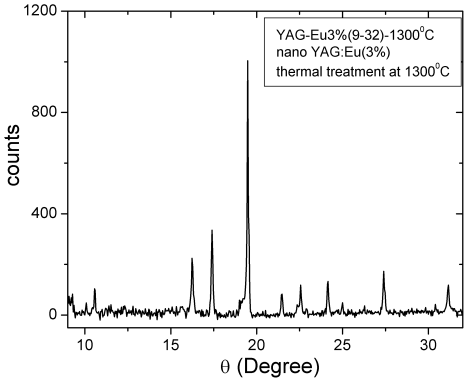


Fig. 2. XRD patterns of the sample heated at 1300°C.

The presence of the $Eu^{3+}$ ion in the YAG nanocrystals was evidenced using optical spectroscopy measurements. The fluorescence spectrum of $Eu^{3+}$ in samples annealed at 900ºC (Fig. 3) is characteristic for the amorphous state.

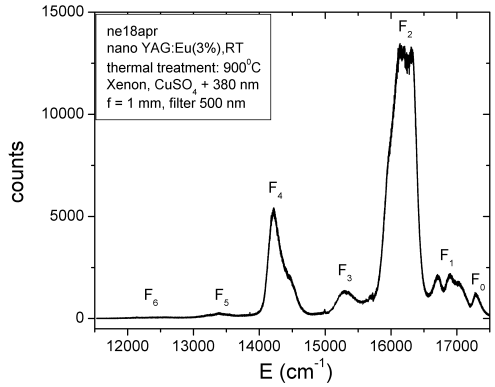


Fig. 3. The fluorescence spectrum ($^5D_0 \rightarrow {}^7F_j$) of $Eu^{3+}$ in samples annealed at 900°C – amorphous state.

When heated at 930°C the fluorescence spectrum of $Eu^{3+}$ in YAG is obtained (Fig. 4).

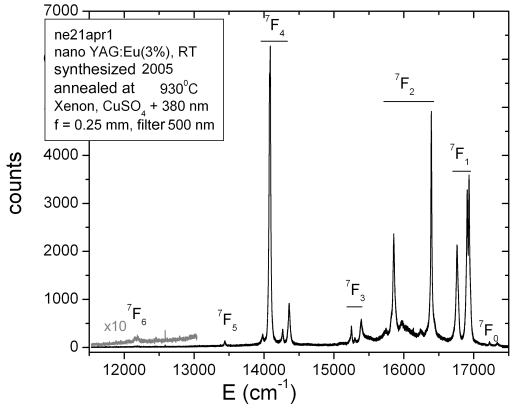


Fig. 4. The fluorescence spectrum ($^5D_0 \rightarrow {}^7F_j$) of $Eu^{3+}$ in samples annealed at 930°C - the fluorescence spectrum of $Eu^{3+}$ in YAG

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 $^5D_0 \rightarrow {}^7F_4$ (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.

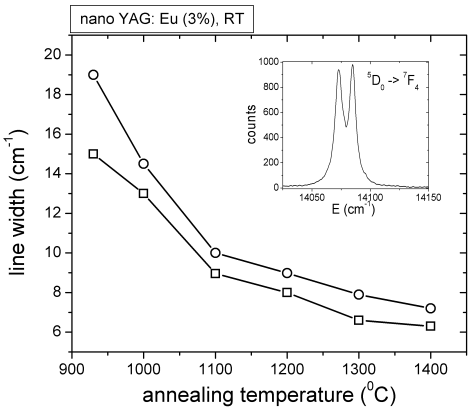


Fig. 5. Dependence of line width with annealing temperature of two isolated fluorescence lines belonging to the transition $^5D_0 \rightarrow {}^7F_4$. Inset: the two analyzed lines

## 3. CONCLUSIONS

Pure garnet phase YAG:Eu phosphor can be synthesized at calcination temperatures ~ 900°C by nitrate–citrate sol–gel process. Single-phase cubic YAG: Eu is formed by direct crystallization from amorphous materials and no intermediate phase (such as YAM or YAP) is observed. YAG:Eu powders of various particle sizes can be synthesized by varying the calcination temperature.

Both XRD and optical spectroscopy measurements illustrated the YAG phase.

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