



Effect of the PVA (polyvinyl alcohol) concentration on the optical properties of Eu-doped YAG phosphors



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ABSTRACT

The influence of the polyvinyl alcohol (PVA) concentration on the synthesis and structural, morphological and optical properties of $Y_3Al_5O_{13}$: Eu (Eu-doped YAG) was systematically investigated in this work. The final concentration of PVA in the preparation step influenced the crystallite size and also the degree of particle agglomeration in Eu-doped YAG phosphors. X-ray excited optical luminescence (XEOL) emission spectra results indicated typical Eu^{3+} emission lines and an abnormally intense ${}^3D_0 \rightarrow {}^7F_4$. The intensity parameters Ω_2 and Ω_4 were calculated and indicated the PVA concentration affects the ratio $\Omega_2:\Omega_4$. X-ray absorption spectroscopy (XAS) results showed Eu valence did not change and the symmetry around the Eu^{3+} is influenced by the PVA concentration. XEOL-XAS showed the luminescence increases as a function of energy.

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1. Introduction

Yttrium aluminate garnet ($Y_3Al_5O_{12}$ -YAG) has been largely investigated for application as a host to prepare photonic sources. It has a high thermal stability and its crystalline structure present two trivalent cationic sites able to accommodate doping ions such as rare earths, which are, for example, responsible for luminescence properties [1–5]. Doped YAG has been applied in X-ray tubes, low voltage field emission displays (FEDs), vacuum fluorescent displays [6–10], X-ray digital imaging detectors, X-ray micro-radiography and it is also suitable for X-ray imaging with high spatial resolution [11–13]. Particularly, Eu-doped YAG has been cited as a red emitter phosphor, which has potential applications in photonics, mainly in optical display and lighting, such as light emitting diodes (LEDs), plasma panel displays (PDPs), FEDs [3,14–16], fluorescence thermometry [17], etc.

YAG is a versatile host, which can be obtained as crystal or ceramic powders [18–20]. In both cases, it is possible to manipulate its properties by the insertion of impurities on the host structure.

However, the ceramics can be produced by simpler methods than the crystals and their characteristics may be strongly affected by the way they are grown. For example, for nanosized grains, when compared to the bulk ones, they can present completely new properties [21]. In this case, the surface/volume ratio is high and the surface effects, which come from the surface dangling bonds, or quantum confinement effects may determine the material properties [21,22].

Several works report methodologies to synthesize luminescent materials in ceramic powder form, for example, solid state reaction [23], co-precipitation [24], solvothermal [25], combustion [26], glycolthermal treatment [27], spray pyrolysis [28], conventional sol-gel [29], sol-gel assisted by organic molecules, polymers [30–35], etc. The conventional sol-gel route uses alkoxides for the hydrolysis and condensation of the precursors. However, this method has been recently modified by the use of other organic agents containing alcohol and/or carboxylic acid groups, such as ethylene glycol, coconut water [30,31], natural organic matter [32], PVA (polyvinyl alcohol) [33–36], etc. The sol-gel assisted by PVA, $[C_2H_4O]_n$, for example, has been used in order to produce magnetic, biocompatible, and luminescent materials [33–36] and this method was employed to produce the Eu-doped YAG phosphors

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investigated in this work.

The general aim of this work is to study the effect of PVA concentration in the step synthesis on structural, morphological, and optical properties of Eu-doped YAG. For this, the samples' properties were evaluated with X-ray powder diffraction (XRD), scanning electron microscopy (SEM), X-ray excited optical luminescence (XEOL) excitation and emission around the Eu L_{III}-edge (6.977 keV). XEOL excitation spectra, XEOL yield or XEOL-XAS were collected simultaneously with the X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) signals. Those last signals (XANES and EXAFS) were recorded to investigate the valence and the symmetry of Eu sites on Eu-doped YAG.

2. Methodology

Eu-doped YAG powders were synthesized via sol-gel method using PVA as the condensation agent. The starting reactants were polyvinyl alcohol (PVA) (Proquímios), yttrium nitrate tetrahydrate (Sigma-Aldrich, 99.99%), aluminum nitrate nonahydrate (Sigma-Aldrich, 99.9%), and europium nitrate pentahydrate (Sigma-Aldrich, 99.9%). The first step was the preparation of a PVA solution (0.1 g/cm³), in which the PVA was dissolved in distilled water and continuously stirred and heated at 100 °C until solution was transparent and homogeneous. The second step was the preparation of three starting solutions to get Eu-doped YAG samples. The starting reactants (nitrates), in stoichiometric amounts, were dissolved in distilled water and different volumetric ratios of PVA solution/distilled water (PVA/DW, in ml) – 5/25, 10/20 and 15/15 – were added to obtain the final solution. The following step involved heating (100 °C) and stirring these solutions in order to get sols; gels were achieved after approximately 6 h. These samples were dried at 100°C/24 h to get xerogels, which were homogenized in agate mortars and calcined in an electric furnace at 1100°C/2 h [37,38] in static air atmosphere.

The characterization step started with the powder X-ray diffraction (XRD) and was performed in continuous scan mode, using Co K_α (1.79 Å) radiation in a Rigaku RINT 2000/PC diffractometer in the Bragg-Brentano geometry, operating at 40 kV/40 mA. The particle size and shape were evaluated by scanning electron microscopy (SEM) using a Jeol JSM-7500F from the Multiuser Center of Nanotechnology at the Federal University of Sergipe (CMNano/UFS). The samples for SEM measurements were dispersed in isopropyl alcohol (P.A.) and a single drop for each sample was collected and deposited on a conductive substrate. X-ray absorption spectroscopy (XAS: XANES and EXAFS) and XEOL experiments were performed at the X-ray absorption fine structure (D08B-XAFS-2) beamline at the Brazilian Synchrotron Light Laboratory (LNLS). The XAS data were recorded around the Eu-L_{III} edge (6.977 keV) in fluorescence mode and the signal was collected using a Ge15 detector from Specs. The total XEOL yield, or XEOL excitation spectra, and the XANES/EXAFS spectra were obtained simultaneously. This data will be referred as XEOL-XAS in the following text. The XEOL-XAS setup was composed of an optical fiber (1 mm aperture) coupled to a Hamamatsu R928 photomultiplier. The XEOL emission spectra were recorded using a specific excitation energy (6.977 keV). The setup was composed of an optical fiber and an Ocean Optics HR2000 spectrometer.

3. Results

Fig. 1 shows the X-ray powder diffraction of the Eu-doped YAG precursor, as prepared calcined at 1100°C/2 h. The diffractograms patterns exhibit only the YAG crystalline phase when compared to the standard pattern [39], indexed at the Inorganic Crystal Database

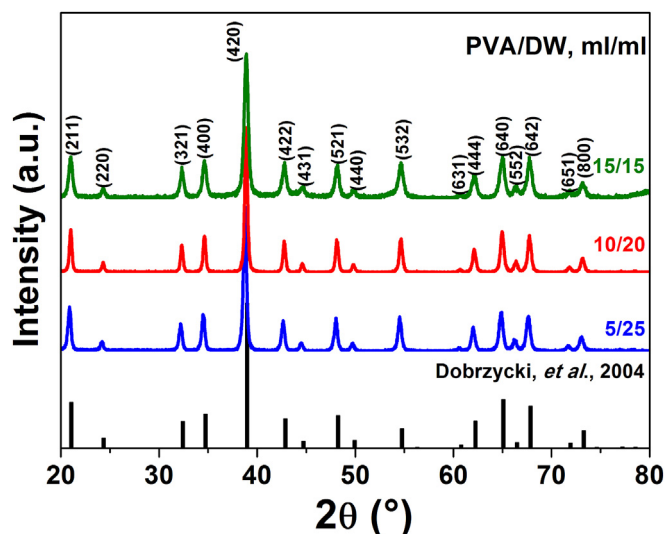


Fig. 1. XRD patterns of the calcined YAG precursor, as prepared, prepared using different PVA/DW (in ml/ml) compared to the indexed pattern (ICSD 17058) [39].

Structure (ICSD) under collection code#17058. This result suggests the PVA/DW ratio did not influence the YAG synthesis and all precursors reacted completely until the oxide single phase formation.

According to the literature, at this synthesis process, the three dimensional structure of PVA acts as a confined space, which allows high contact among the solvated ions, favoring the synthesis process and also minimizing the precipitation of the precursors. Consequently, it also minimizes the formation of spurious phases [40]. After the thermal treatment, the YAG particles are formed with high crystallinity.

Changes in the particle size are related to the modification of the surface energy. This thermodynamic parameter depends on the surface tension of the curved interfaces and also on the particles surface area [41]. Surface tension is a variable governed by the chemical nature of ions present on the particle surface and the PVA role is associated with the capability of H-bonding with its solvents, inducing modifications on their surface tension and in turn influencing the crystallite and the particle size [42]. To evaluate the YAG particles and crystallite size, both Scanning Electron Microscopy (SEM) and Scherrer's calculations were employed.

Eu-doped YAG crystallite size was evaluated using Scherrer's equation [43] (Eq. (1)):

$$d = k \cdot \lambda / \beta \cdot \cos \theta_B \quad (1)$$

where **d** is the crystallite size, **k** is the shape coefficient for the reciprocal lattice point (in this work it was considered $k = 0.89$, for spherical crystallites), λ is the X-ray wavelength ($\lambda = 1.79$ Å for Co-K_α), **B** is the full width at half maximum (FWHM) of the main diffraction peak, which was calculated removing the instrumental broadening obtained using a micrometric LaB₆ standard; and θ_B corresponds to the diffraction angle of the more intense Bragg peak (420), presented in Fig. 1. The summarized results are presented in Table 1, where the biggest crystallite size was observed for the

Table 1
Crystallite sizes calculated using the XRD patterns of Eu-doped YAG samples.

(PVA/DW, ml/ml)	5/25	10/20	15/15
Crystallite sizes (nm)	28	34	22

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