



Morphological optimization and (3-aminopropyl) trimethoxy silane surface modification of $Y_3Al_5O_{12}:Pr$ nanoscintillator for biomedical applications



Prakhar Sengar^{a,*}, G.A. Hirata^b, Mario H. Farias^b, Felipe Castellón^b

^a Centro de Investigación Científica y de Educación Superior de Ensenada, Posgrado en Física de materiales, Carretera Ensenada-Tijuana No. 3918, Zona Playitas, C.P. 22860 Ensenada, B.C., Mexico

^b Universidad Nacional Autónoma de México—Centro de Nanociencias y Nanotecnología, Km. 107 Carretera Tijuana-Ensenada, Ensenada, B.C. 22860, Mexico

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ABSTRACT

The present work details the effect of synthesis route on the morphology, luminescence property and surface functionalizability of Pr^{3+} doped $Y_3Al_5O_{12}$ (YAG:Pr) as a potential nanoscintillator for biomedical applications. Highly crystalline and pure YAG:Pr nanocrystals were synthesized via sol–gel (YAG:PrSG) and combustion synthesis (YAG:PrCB) techniques by using metal nitrates as the precursors. The surface of the YAG:Pr nanophosphors was successfully modified with aminopropyltrimethoxysilane (APTMS) and a comparative analysis of the synthesized nanocrystals displayed narrower size distribution, regular morphology and better surface chemistry of YAG:PrSG. Thus, sol–gel method produced better nanophosphors with improved properties for further surface functionalization with biomolecules required in biomedical applications.

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1. Introduction

Nanoscintillators have gained a considerable attention in biomedical applications over the past few decades [1–3]. The light emitting property of nanoscintillators in response to ionizing radiation can not only applied in radiation detection but also in various biomedical applications [4–6] such as photodynamic therapy (PDT) for cancer treatment. PDT involves generation of reactive oxygen species from the irradiated photosensitive nanoscintillators localized at the tumor site [7]. The classical PDT employs a long wavelength excitation source thereby limiting the depth of penetration in tissues to ~ 1 cm. Recently, a pioneer work reported excellent therapeutic results of the new combinatorial systems, where X-ray tissue penetrability was harnessed through nanoscintillator core mesoporous system loaded with MC-540 photosensitizer [8]. Nanoscintillator core acted as a nanotransducer that converted X-ray photons to visible photons with wavelength equivalent to the absorption wavelength of the utilized photosensitizer.

In our previous collaborative work, 1% Pr^{3+} doped $Y_3Al_5O_{12}$ (YAG:Pr) nanoscintillator synthesized by combustion method was proposed to be an excellent candidate for radiation mediated PDT.

The proposal was made on the basis of high light output with emission in the ultraviolet (UV) range (300–400 nm) upon irradiation with X-rays [9]. Thus, the YAG:Pr nanoscintillator may act as a nanotransducer for converting X-ray photons into UV photons which can initiate the photosensitizing action of different photosensitizers [10,11]. Furthermore, YAG based nanoscintillators are reported to show low cytotoxicity which makes them a potential candidate for biomedical applications [12].

To date, various surface functionalization strategies have been followed to make the nanoscintillator target specific and compatible with biological environments [13,14]. The most common approach involves the surface modification of nanoscintillators with silicon-based ligands such as silica (SiO_2), aminosilanes like (3-aminopropyl) triethoxysilane (APTES) [15,16] and trimethoxy analog (APTMS) [17]. The aminosilanes introduce amine groups on the surface of nanoscintillators for further chemical and biofunctionalization. The surface modification of the nanoscintillators by aminosilanes mainly rely on the particle size, surface chemistry and morphology of nanoscintillators.

Morphology, size, surface area and luminescence property of the YAG based nanoscintillators are largely dependent on their synthesis route like combustion [9,18], sol–gel [19], hydrothermal [17], and spray pyrolysis [20]. YAG based nanoparticles synthesized by combustion method are reported to show irregular

* Corresponding author. Fax: +52 16461750650.

E-mail addresses: prakharsengar@gmail.com, sengar@cicese.edu.mx (P. Sengar).

morphology and larger particle size. While hydrothermal synthesis is a useful technique for obtaining small and homogenous nanoscintillators as shown in the case of YAG:Ce where mean particle size was reported to be ~ 46 nm [17]. However, therapeutic applications require nanoscintillators with 50–150 nm particle size for prolonged circulation time in the bloodstream [21]. Also, the hydrothermal route requires a very high temperature and pressure to produce single phase nanocrystals [22]. In this regard, sol–gel synthesis is considered to be a very effective and widely utilized method for the synthesis of nanoscintillators for biomedical purposes [23].

In this work, we report the synthesis of YAG:Pr nanoscintillator by carbohydrazide assisted combustion (YAG:PrCB) and tartaric acid assisted sol–gel (YAG:PrSG) methods. YAG:Pr nanoscintillators synthesized by the two methods were compared for their luminescence, structural and morphological properties. The condensation of APTMS on the surface of nanocrystalline YAG:PrCB and YAG:PrSG was further examined to assess the effect of morphology and surface chemistry of nanoscintillators on silanization.

2. Experimental

2.1. Synthesis

2.1.1. Chemicals and materials

Gadolinium(III) nitrate hexahydrate (Sigma–Aldrich, 99.9%), aluminum nitrate hydrate puratronic (Alfa Aesar, 99.999%), yttrium(III) nitrate hexahydrate (Alfa Aesar, 99.9%), praseodymium(III) nitrate (Alfa Aesar, 99.9%), carbohydrazide (Alfa Aesar, 97%), L-tartaric acid (Alfa Aesar, 97%), and (3-aminopropyl) trimethoxysilane (APTMS) solution (97% Sigma–Aldrich) were used as the raw materials.

2.1.2. Synthesis of YAG:Pr by combustion method (YAG:PrCB)

The YAG:PrCB was synthesized by using carbohydrazide ($\text{CH}_6\text{N}_4\text{O}$) as the fuel [24]. The exothermic reaction between the precursors of metal nitrates and the fuel at a relatively low temperature ($\sim 500^\circ\text{C}$) is the main principle behind combustion

synthesis. All the constituents were weighed according to the stoichiometry and dissolved in deionized (DI) water. The solution containing the precursor was placed in a pre-heated furnace and incubated to boil the solution and ignite the fuel. The molar production of gas per mole of solid was high in the reaction (102 moles) which exerted high pressure by the escaping gases and thus gave an extremely porous product. Also, due to the short duration time at high temperatures (flame temperatures $>1500^\circ\text{C}$), the powders produced were nanocrystalline [25]. Therefore, combustion synthesis is a straightforward method to produce a nanocrystalline oxide. The product was annealed at 1200°C in air for 2 h and grounded with a mortar and pestle.

2.1.3. Synthesis of YAG:Pr by sol–gel method (YAG:PrSG)

YAG:Pr nanoscintillator was synthesized according to the tartaric acid assisted method as reported earlier [26]. Nitrates were utilized as the precursors; all the constituents were weighed according to the stoichiometry and dissolved in DI water. The above solution was continuously stirred for 24 h at room temperature. The stirring was further continued for 2 h at 80°C after the pH of the solution reached to ~ 0.5 which made the mixture denser forming a sol-phase. Sol-phase was further stirred at 120°C until gel-phase was formed. The dried gel was collected and annealed at 1200°C for 2 h to obtain YAG:Pr nanocrystals. Obtained YAG:Pr nanocrystals were further grounded with mortar and pestle.

2.1.4. YAGPr@APTMS core–shell synthesis

The surface of YAG:Pr nanoscintillators synthesized by both the methods were modified by reaction with APTMS. The mixture of 50 mg YAG:Pr powder in the water:ethanol (3:7, (v/v)) solution was subjected to high power ultrasonication in (600 W) ultrasonicator (Sonics & Materials, Inc., Model VCX600) operated at 24 kHz for 30 min to obtain a homogenous dispersion. After the ultrasonication, $150\ \mu\text{l}$ of APTMS was added dropwise over an hour on the nanoscintillator suspension with constant stirring. The reaction was stirred at room temperature for overnight. The functionalized nanoparticles were separated by centrifugation, at 10,000 rpm for 10 min, from the solution and washed five times

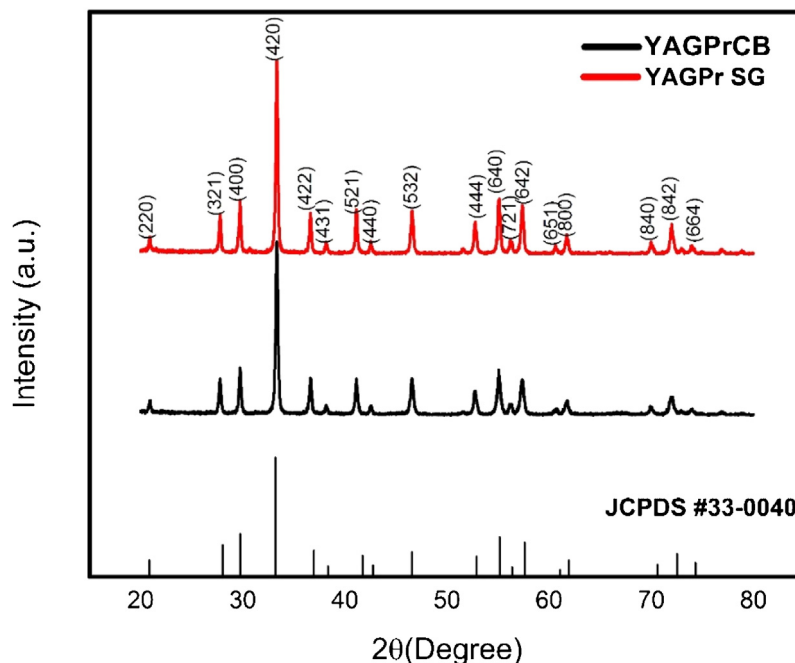


Fig. 1. XRD patterns of YAG:PrCB and YAG:PrSG nanoscintillators.

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