# A strategy to increase phosphor brightness: Application with $Ce^{3+}$-doped $Gd_3Sc_2Al_3O_{12}$

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## ARTICLE INFO

## ABSTRACT

$Y_3Al_5O_{12}$ (YAG) doped with $Ce^{3+}$ ions is widely used as a phosphor for the generation of white light in LEDs. However, the material presents intrinsic drawbacks: (1) a yellow emission band lacking a red component, leading to a "cold" white light and (2) limited cerium incorporation (∼ 3 mol%), resulting in poor absorption and thus limiting the external quantum efficiency (EQE) of the LED device. In order to increase phosphor absorption and thus phosphor brightness, we propose here an original strategy based on the increase of Ce content in a phosphor compound, while preserving a high internal luminescence quantum yield. For this purpose, we introduce $Ce^{3+}$-doped $Gd_3Sc_2Al_3O_{12}$ (GSAG: Ce). $Gd_{3(1-x)}Ce_{3x}Sc_2Al_3O_{12}$ polycrystalline samples were prepared through a solid-state microwave-assisted reaction, with $x$ varying from 0 to 0.5; $Ce^{3+}$ ions can be incorporated into the GSAG matrix with a concentration up to approximately $x = 0.18$ (i.e. 18 mol%) without the formation of a parasitic phase. The maximum emission wavelength is located at 573 nm for a doping concentration of $x = 0.1$, giving an orange feature to the emission. The internal luminescence quantum yield ($\Phi$) is 52% for Ce concentration up to $x = 0.03$. The EQE, which is proportional to the product of $\Phi$ by the Ce concentration when considering a thin transparent phosphor layer is predicted to be about 30% stronger when using GSAG doped with 10 mol% Ce ($x = 0.1$), with respect to YAG doped with 2 mol% Ce ($x = 0.02$).

## 1. Introduction

Yttrium aluminium garnet (YAG) doped with $Ce^{3+}$ is known as an efficient yellow phosphor with high internal luminescence quantum yield (> 90%) and perfect photostability [1]. One of its broad absorption bands peaks at 450 nm and matches perfectly the blue-emitting LEDs for the generation of white light. However, the emission wavelength lacks a red component, producing a so-called "cold" white light. Moreover, the quantity of $Ce^{3+}$ ions that can be incorporated into the YAG matrix is small due to the mismatch between the $Ce^{3+}$ ionic radius (1.143 Å for a coordination number of 8) and the substituted $Y^{3+}$ ionic radius (1.019 Å for a coordination number of 8): the maximum concentration is reported as 3 at% when YAG:Ce is synthesized by solid state reaction [2]. This results in a small absorption of the blue light of the GaN diode, and a large amount of powder or ceramics is required to acquire the appropriate yellow component from the device. Additional drawbacks include re-absorption and strong scattering that reduces the external quantum efficiency (EQE) of these white LED devices.

Several strategies have been employed to increase the phosphor absorption. T. Hussain *et al.* report the grafting of Au nanoparticles onto YAG nanoparticles in order to enhance absorption via plasmonic effects [3]. Their results indicate a large enhancement of the PL intensity of YAG:Ce after Au nanoparticle modification. Other groups propose to control the size of YAG grains to limit light back-scattering [4]. Another method consists of controlling light propagation within the phosphor film to generate light in the desired direction [5,6].

Herein we investigate a different strategy which consists in increasing the phosphor brightness by increasing the Ce doping concentration while ensuring that the internal luminescence quantum yield remains high. For this purpose, we use the $Gd_3Sc_2Al_3O_{12}$ matrix, also called GSAG, as an alternative to YAG for the incorporation of the doping ions. GSAG has a larger unit cell parameter than that of YAG ($a = 12.39$ Å [7] versus 12.01 Å [2], respectively) that favors the insertion of $Ce^{3+}$ ions. One would thus expect a higher solubility of $Ce^{3+}$ ions into the structure and thus a stronger absorption that could lead to a higher EQE. In addition, GSAG crystallizes in the garnet structure, which

should allow preserving the spectroscopic properties of $Ce^{3+}$ in terms of excitation and emission wavelengths. Relatively few papers report the formation of the GSAG phase. Most report on GSAG doped with $Cr^{3+}$ for laser applications [8–10], while others utilize GSAG doped with $Ce^{3+}$ for scintillation applications for conversion of the γ-rays and neutrons into light [11–13], Here we present the synthesis of GSAG:Ce crystalline powders as well as their structural and optical characteristics. As the goal is to find an alternative to YAG:Ce for lighting applications, the results obtained on GSAG:Ce will be discussed with respect to those obtained with YAG: Ce.

## 2. Experimental methods

### 2.1. Microwave-assisted GSAG:Ce preparation [14]

Samples were prepared by mixing $Gd_2O_3$ (Alfar Aesa, 99.99%), $CeO_2$ (Cerac, 99.9%), $Sc_2O_3$ (Stanford Materials Corporation, 99.99%), $Al_2O_3$ (Sumitomo AKP-50, > 99.99%) in stoichiometric proportions for $Gd_{3(1-x)}Ce_{3x}Sc_2Al_3O_{12}$ with $x = 0$, 0.005, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.1, 0.2, and 0.5 for a total mass of 1 g. These samples will be referred to as GSAG:$x$Ce in the following. The powders were ground in an alumina mortar with 5 wt% $BaF_2$ (Cerac, 99%) and 0.5 wt% $NH_4F$ (Sigma-Aldrich, 99.9%) as flux. The mixture was decanted into a small alumina crucible and inserted into a larger alumina crucible filled with 6.5 g of granular carbon (Darco 12–20 mesh, Sigma-Aldrich) used as the microwave susceptor. Both crucibles were capped with an alumina lid. The system was placed in a high temperature alumina isolator and heated in a domestic microwave oven for 18 min at a power level between 750 and 850 W.

### 2.2. YAG:Ce preparation

The properties of the Ce-doped GSAG are compared to those of the Ce-doped YAG synthesized by solid state according to the procedure reported in [2]. Briefly, $Y_2O_3$, $Al_2O_3$ and $CeO_2$ were ground together with 5% by mass $BaF_2$ and 0.5% by mass $NH_4F$ acting as sintering agents. The mixture was then placed in alumina crucibles and fired at 1500 °C for 5 h in an alumina tube furnace under 0.2 L/min 5% $H_2/N_2$ gas flow. $Y_{3(1-x)}Ce_{3x}Al_5O_{12}$ with $x = 0.01$, 0.02 and 0.03 were prepared. These samples are referred to as YAG:$x$Ce in the following. It is reported that conventional solid state and microwave assisted methods lead to YAG:Ce compounds with identical structural and optical properties [14], allowing for the direct comparison of solid state YAG to microwave-assisted GSAG.

### 2.3. X-Ray diffraction

X-ray diffraction was performed on the GSAG:$x$Ce samples using two different instruments. Samples where $x = 0$, 0.005, 0.01 – 0.06, 0.1, 0.2, and 0.5 were analysed using a Philips XPert diffractometer ($λ_{Cu} = 1.54056$ Å). Samples where $x = 0.005$, 0.03, 0.06, and 0.1 were characterized using the 11-BM beamline at the Advanced Photon Source (APS) at Argonne National Laboratory ($λ = 0.412154$ Å). Lattice parameters and phase purity was determined through the LeBail method using the GSAS software package with EXPGUI [15–17], Crystal structures were visualized using the VESTA suite of programs [18]. The interatomic distances in YAG and GSAG were calculated using Gretep software [19].

### 2.4. Optical characterization

Luminescence properties were characterized on a Perkin-Elmer LS55 spectrophotometer on pellets. The pellets were prepared by grinding and pressing 200 mg of KBr (≥99%, FT-IR grade, Sigma-Aldrich) with 20 mg of every sample. The excitation was measured with an emission wavelength ($λ_{em}$) of 564 nm and by scanning from 300 nm

to 540 nm. The emission was collected from 480 nm to 800 nm with an excitation wavelength ($λ_{ex}$) of 450 nm.

To measure the internal luminescence quantum yield, each sample was mixed with silicone GE RTV615A + B in a 0.2:1 ratio. A drop of the mixture was then deposited on a $1 \times 1$ cm quartz slide and heated at 150 °C for 15 min to cure the silicone. The samples were inserted into an integrating sphere and excited at 457 nm with an Ar laser.

To measure the excited state lifetime as a function of temperature, the powder samples were placed into a cryostat, where the temperature can be varied from 77 to 873 K, and excited by a 444-nm pulsed laser. The emission, selected in a 500–600 nm range by two high- and low-pass filters, was collected into a PhotoMultiplier and amplified. The signal was then histogrammed using a multichannel counter with a resolution of 800 ps. For details of this experimental set-up and interpretation of the data see [20].

## 3. Results

### 3.1. Increased Ce solubility limit in GSAG

The GSAG compound, isostructural with YAG, crystallizes with the cubic garnet structure in $Ia\bar{3}d$ space group. The structure is constituted of $AlO_4$ tetrahedra, $ScO_6$ octahedra and $Gd^{3+}$ in an 8-coordinated site, represented in Fig. 1a. In order to determine the purity and lattice parameters of the synthesized GSAG:$x$Ce samples, powder X-ray diffraction data were recorded utilizing both a laboratory and synchrotron X-ray source. Fig. 1b shows the LeBail fit to the diffraction pattern of $Gd_{2.7}Ce_{0.3}Sc_2Al_3O_{12}$ collected on 11BM, and is representative of the synchrotron data. No impurity phase was detected for this doping concentration ($x = 0.1$).

Laboratory X-ray diffraction data collected on Ce doping concentration $x = 0$, 0.005, 0.01 – 0.06, 0.1, 0.2, and 0.5 are shown in Fig. 2a. In order to determine the maximum Ce concentration in GSAG, the evolution of the unit cell parameter $a$ was studied as a function of the
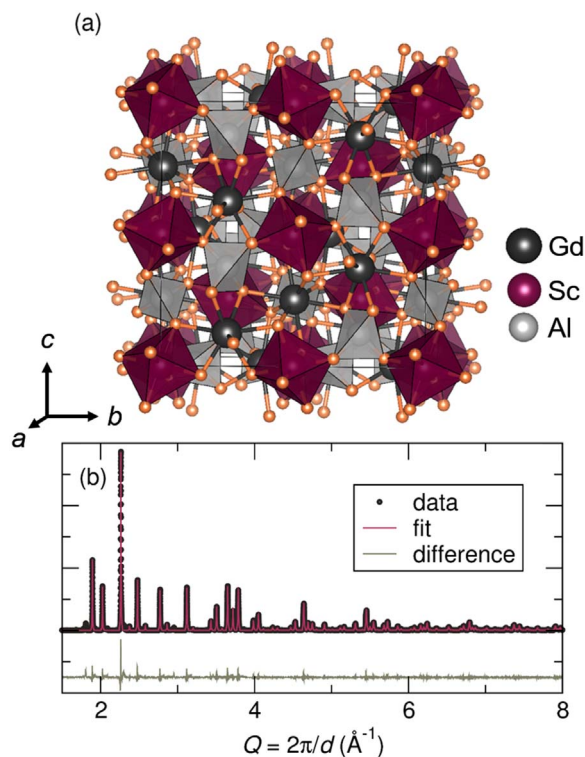


**Fig. 1.** (a) Crystal structure of $Gd_3Sc_2Al_3O_{12}$ in the $Ia\bar{3}d$ space group with $ScO_6$ octahedra shown in maroon, $AlO_4$ tetrahedra in grey, $O^{2-}$ in orange and $Gd^{3+}$ in charcoal. (b) LeBail fit of the 11-BM data for $Gd_{2.7}Ce_{0.3}Sc_2Al_3O_{12}$ indicates the sample is phase pure and properly indexed by this space group.