

## Enhanced luminescence of $Y_3Al_5O_{12}:Ce^{3+}$ nanophosphor for white light-emitting diodes

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Results pertaining to the development of highly dispersible stand-alone particles of  $Ce^{3+}$ -doped  $Y_3Al_5O_{12}$  nanophosphor and their luminescence are presented. The yellow light-emitting nanophosphor was produced as a result of a single-step auto-combustion process, which requires no auxiliary annealing treatments prior to any practical application. The structure, photoluminescence, and chromaticity of the powder nanophosphor samples with the compositions  $Y_{(3-x)}Al_5O_{12}:xCe^{3+}$  ( $x=0.01-1$ ) are featured in the letter. The nanophosphor absorbs light efficiently in the visible region of 400–500 nm, and shows single broadband emission peaking at  $\sim 560$  nm. The luminescence yield is almost analogous to the samples made from other conventional methods. Hence, it could be an apt candidate for generating white light when coupled to a blue light-emitting diode ( $\lambda_{em}=450$  nm). © 2006 American Institute of Physics. [DOI: 10.1063/1.2367657]

Light-emitting diodes (LEDs) are solid-state devices that can generate light having a peak wavelength in a specific region of the electromagnetic spectrum. LEDs are typically used as illuminators and indicators and used in displays due to low power efficiency, high brightness levels, low operating voltages and longer lifetimes.<sup>1,2</sup> Traditionally, the most efficient LEDs emit radiance in the red region. Recently, a LED based on GaN has been developed. It emits blue light typically in the range of 400–480 nm.<sup>3–5</sup> Since blue LEDs emit light with a shorter wavelength than red ones, it is possible to develop a suitable and intense yellow light-emitting phosphor that can complement the blue emission to yield ideal white light.<sup>6</sup> Shimizu *et al.*<sup>7</sup> reported various phosphor LEDs that generate white light having a color temperature between 5000 and 6000 K. Out of all the phosphor LEDs described, cerium-doped yttrium–aluminum–garnet (YAG:Ce) phosphor was found to be the most suitable phosphor satisfactorily tested on GaN LEDs for the production of white light.<sup>8–11</sup> Therefore, any improvement in the luminescence of YAG:Ce phosphor and its degree of dispersal in a polymer matrix would be extremely valuable for scientific, technological and commercial exploitation.

In this letter we disclose a unique method of making high-brightness YAG:Ce phosphor in the nano-form by a single-step auto-combustion process. The methodology adapted by us results in stand-alone nanoparticles with appreciable luminescence characteristics in the yellow region, which could be due to the advantages associated with nanotechnology. Further, it is observed that the blue light from commercial LED combined with the yellow light simulated from the nanophosphor generated a white light that has colorimetric coordinates very close to the “ideal white” region of the chromaticity diagram.

$Ce^{3+}$ -doped  $Y_3Al_5O_{12}$  (YAG:Ce) nanophosphor powders with the composition of  $Y_{(3-x)}Al_5O_{12}:xCe^{3+}$  ( $x=0.01-1$ ) were prepared from the nitrates of yttrium, aluminum and cerium dissolved in ethanol-water mixture (2:1). The well-mixed nitrate solution was heated to boiling and concen-

trated to some extent through evaporation. The required amount of urea (combustible fuel) was added. This was calculated from the valencies of the precursor materials as per standard procedures.<sup>12</sup> Liquor ammonia was added to facilitate the formation of nitrate–ammonium hydroxide complex. This, upon burning, minimizes the evolution of hazardous  $N_xO_x$  gases and makes the process eco friendly. The combustion process was carried out in an indigenous apparatus<sup>13</sup> consisting of a quartz firing tube with single-way output valve and a furnace pre-heated up to  $\sim 600$  °C. Upon sudden heating of the reactants, there was vigorous evolution of gases with subsequent appearance of flame. The mass swelled, expelled and dried into yellow colored foam within 2–5 minutes. The end product was comprised of highly dispersible, stand-alone particles of  $Ce^{3+}$ -doped YAG nanophosphor.

The crystallographic phase purity of YAG:Ce nanophosphors was checked by x-ray diffraction (XRD). The YAG crystal belongs to the cubic structure with  $a=1.2009$  nm and  $Ia\bar{3}d$  lattice symmetry. It is well known that only pure YAG phase is favorable for luminescence.<sup>14</sup> But, the liberation of gases such as  $NH_3$ ,  $N_2$ , oxides of  $N_2$  and  $CO/CO_2$  during the auto-combustion process, created *in-situ* a mild reducing atmosphere that resulted in pure-YAG phase at temperatures as low as 600 °C. The coexistence of

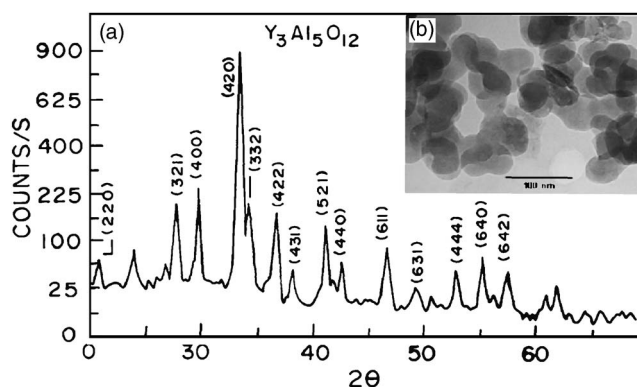


FIG. 1. (a) XRD pattern of  $Y_3Al_5O_{12}$  (YAG) host lattice and (b) TEM image (at magnification of 73 kX) of YAG:Ce nanophosphor.

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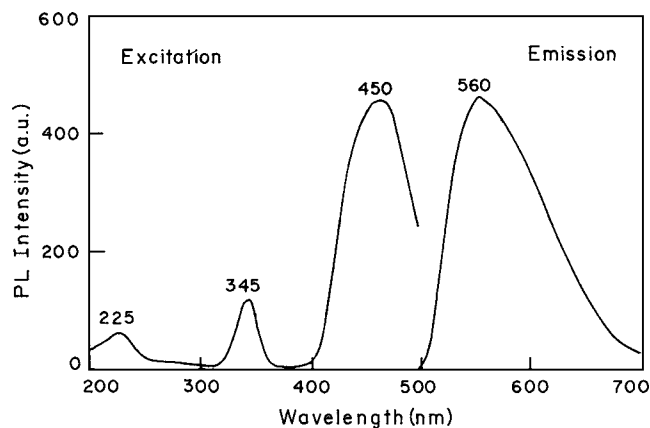


FIG. 2. Room-temperature excitation and emission spectra of YAG:Ce nanophosphor.

phases like  $\text{YAlO}_3$  (YAP, polymorph) and  $\text{Y}_4\text{Al}_2\text{O}_9$  (YAM, monoclinic), which do not favor luminescence are completely eliminated in this process. The YAG phase thus obtained shows good agreement with Joint Committee on Powder Diffraction Standards card No. 33-40. Moreover, the broadening of major diffraction peaks shown in Fig. 1 indicates the ultrafine nature of the particles present in the powder. When  $\text{Ce}^{3+}$  was added ( $>10$  mol % with respect to  $\text{Y}^{3+}$  ions) and fired in air instead of in a reducing atmosphere, the diffraction lines pertaining to the  $\text{CeO}_2$  peaking at  $28.5^\circ$  and  $47.5^\circ$  appeared in the XRD profile. This indicates that dopant concentration of  $\sim 10$  mol % is the limit for the proper incorporation of  $\text{Ce}^{3+}$  ions in the YAG system.

Trivalent Ce ion has only one electron in the  $4f$  state. The ground state of  $\text{Ce}^{3+}$  is split into  $^2F_{7/2}$  and  $^2F_{5/2}$  with an energy difference<sup>15</sup> of about  $2200\text{ cm}^{-1}$ . The next higher state originates from the  $5d$  state and  $4f$ - $5d$  transitions are parity and spin allowed.<sup>16</sup> The  $5d$  state is split by crystal field and, hence, there are three  $\text{Ce}^{3+}$  absorption bands in the excitation spectrum located at 225, 345 and 450 nm (see Fig. 2). This is because  $\text{Ce}^{3+}$  occupies the octahedral site of the strong crystal field of  $\text{O}^{2-}$  in the YAG host crystal.<sup>15</sup> The band at 225 nm is very weak because the upper  $5d$  states of  $\text{Ce}^{3+}$  in YAG have energies within the conduction band of the host and, therefore, excitation in these levels results mainly

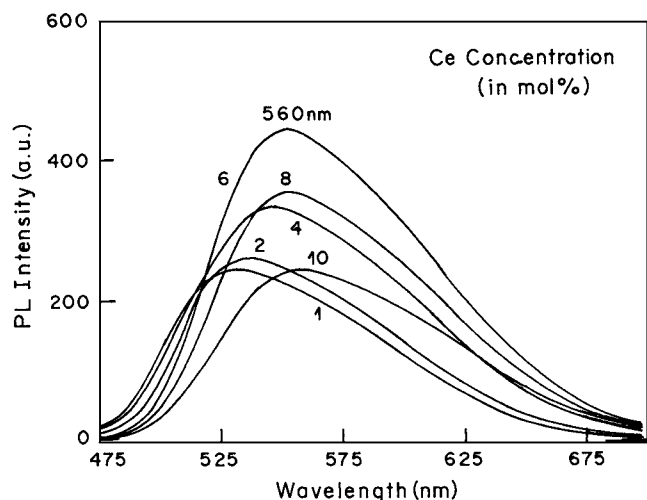


FIG. 3. Emission spectra of YAG:Ce nanophosphor with different  $\text{Ce}^{3+}$  ion concentrations recorded at 450 nm.

TABLE I. Comparison of relative efficiencies of bulk and nanophosphors.

Company name	Product name	Relative quantum efficiency (%) at $\lambda_{\text{ex}}=430$ nm
NICHIA	YAG:Ce (bulk)	70
OSRAM	YAG:Ce (bulk)	67
CREE	YAG:Ce (bulk)	61
LUMINOX	P-20	12
Our sample	YAG:Ce (nano)	54

in quenching.<sup>17</sup> The  $5d$  level of  $\text{Ce}^{3+}$  populated by the transition occurring at 345 nm is just below the YAG conduction band and will also be quenched to some extent at room temperature.<sup>17</sup> The excitation band covering 400–500 nm is the most intense band and provides a strong basis to make use of this nanophosphor to GaN based blue LED for white light generation.<sup>18</sup> The emission of commercially available blue LEDs is in the range 400 and 480 nm. This is in perfect match with the excitation band of YAG:Ce, as mentioned above. In the emission spectrum, the band located between 500 and 700 nm is an ideal yellow light, complementary to the blue light emitted by blue LEDs to generate white light.<sup>19</sup>

Figure 3 shows the concentration effects of  $\text{Ce}^{3+}$  in YAG nanophosphors. This forms the basis of our study to optimize the  $\text{Ce}^{3+}$  ion concentration. It is interesting to note that an increase in  $\text{Ce}^{3+}$  concentration progressively shifted the photoluminescence (PL) peak towards the red region with a regular variation in brightness levels. It is known that  $5d$ - $4f$  emission of  $\text{Ce}^{3+}$  depends strongly on the strength of the crystal field and its surroundings.<sup>20</sup> Hence, with an increase in crystal field, the  $\text{Ce}^{3+}$  emission moved towards the red region. A maximum PL intensity was obtained at 560 nm for about 6–7 mol %  $\text{Ce}^{3+}$  additions. Concentration quenching effect was observed when  $\text{Ce}^{3+}$  amount was increased beyond this limit due to the increase of intra ionic nonradiative relaxation between adjacent  $\text{Ce}^{3+}$  ions.

It is important to note that commercial YAG:Ce (Nichia, Japan) phosphor has  $\sim 70\%$  quantum efficiency at the excitation of 430 nm. Following the method of de Mello Donega *et al.*,<sup>21</sup> which is accurate within 10%, we have calculated the relative efficiency of our YAG:Ce nanophosphor with respect to bulk-YAG:Ce phosphors supplied by OSRAM and CREE; and also a sulfide-based standard yellow light-emitting P-20 phosphor from LUMINOX. Table I shows the relative efficiencies of bulk commercial phosphors and nanophosphors. One can observe that our YAG:Ce nanophosphor

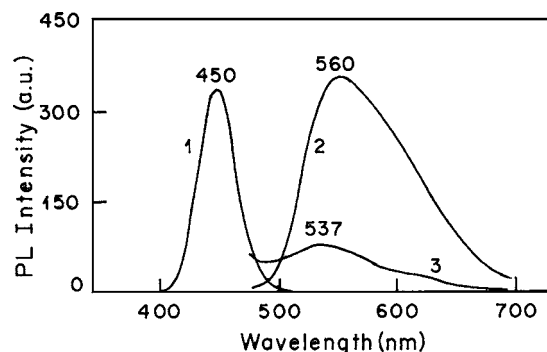


FIG. 4. (1) Photoluminescence spectra of GaN blue LED, (2) YAG:Ce nanophosphor and (3) commercial yellow-emitting sulfide (P-20) phosphor.

TABLE II. Comparison of colorimetric coordinates ( $x, y$ ) for commercial blue-emitting LED, YAG:Ce nanophosphor, and its simulated white light using phosphor and LED; and CIE ideal white light conditions at  $\lambda_{\text{ex}} = 450$  nm.

Sample	Colorimetric coordinates ( $x, y$ ) at $\lambda_{\text{ex}} = 450$ nm
GaN blue LED	(0.15, 0.02)
YAG:Ce nanophosphor	(0.43, 0.54)
Simulated white light (blue LED+nano-YAG:Ce)	(0.28, 0.31)
CIE Ideal white light	(0.33, 0.33)

has fairly comparable quantum efficiency to that of bulk commercial phosphors of the same kind. In addition, it is undoubtedly far better than the standard yellow light-emitting P-20 phosphor. Due to the process limitations of auto combustion, the smallest particle size we could achieve for YAG:Ce nanophosphor is  $\sim 40$  nm. But we believe that further reduction in particle sizes to the quantum confinement regime, i.e., 2–5 nm could improve the efficiency to better than the bulk commercial counterparts as has been evidenced by Bhargava *et al.*<sup>22</sup> for other nanophosphor systems. This is possible if the activator (dopant) atom gets incorporated within the smallest of the nanoparticles and experiences strong confinement effects<sup>23</sup> to exhibit the finest possible luminous efficiency. Efforts are being made in this direction to reduce the particle size to below 10 nm, by using methods such as sol-gel thermolysis. Details of these are beyond the scope of this letter.

Figure 4 shows the PL spectra of GaN blue LED, YAG:Ce nanophosphor and commercially available yellow-emitting sulfide (P-20) phosphor. The colorimetric coordinates ( $x, y$ ) for both blue LED and YAG:Ce nanophosphor were calculated using equidistant wavelength method.<sup>24</sup> These coordinates are very useful in determining the exact emission color of the sample, as per the chromaticity diagram of the Commission Internationale de l'Eclairage (CIE).<sup>25</sup> Table II summarizes the comparison of CIE colorimetric coordinates ( $x, y$ ) for ideal white light, commercial blue-emitting LED ( $\lambda_{\text{em}} = 450$  nm), simulated white light using YAG:Ce nanophosphor and the nanophosphor itself at  $\lambda_{\text{ex}} = 450$  nm. If a straight line is drawn between the coordinates of blue LED and YAG:Ce nanophosphor, it passes very close to the "ideal white" site of the CIE chromaticity diagram. The above observations hint at the promising application of YAG:Ce nanophosphor to produce white light from GaN-based blue LED.

In summary, a simple and unique methodology of preparing bright yellow-emitting YAG:Ce nanophosphor with bespoke luminescence is presented. Precise control over the size and uniform distribution of nanoparticles has been achieved quantitatively. XRD and transmission electron mi-

croscopy (TEM) observations have been used to verify the crystalline phase, particle size and their distribution, respectively. Enhancement in PL intensity indicated reduced dimensionality. The quality of white light emission was evaluated using CIE chromaticity diagram. Furthermore, we have also demonstrated that YAG:Ce nanophosphor could be simulated to produce general-purpose white light. The methodology shown has the potential to be easily scaled up for mass production and also for duly incrementing white LED technology.

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