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STRUCTURAL AND LUMINESCENT DIVERSITIES OF Eu^{3+} ACTIVATED Gd_2O_3 NANOPHOSPHORS

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Abstract: In this work, the synthesis of $Gd_2(OH)_3:Eu^{3+}$ nanowires via hydrothermal reaction at 200 °C and pH 12. Cubic $Gd_2O_3:Eu^{3+}$ nanowires with high aspect ratio of ~ 266.7 were formed after subsequent calcination of the as-synthesised hexagonal $Gd_2(OH)_3:Eu^{3+}$ at 750 °C. The cubic $Gd_2O_3:Eu^{3+}$ shows larger band gap than that of the as-synthesised $Gd_2(OH)_3:Eu^{3+}$ because of its reduced structural order-disorder. The origin of the dominant red emission for $^5D_0$ - $^7F_2$ transition between the $Gd_2(OH)_3:Eu^{3+}$ and $Gd_2O_3:Eu^{3+}$ does not solely rely on the manifold *f-f* transitions of Eu^{3+} dopants but depends on the crystallographic symmetry and structural imperfection of Gd_2O_3 host.

Keywords: Photoluminescent, hydrothermal synthesis and nanowires

Introduction

The discovery of nanostructured rare-earth oxides has revolutionized related research on optoelectronic devices and biomolecule labelling due to their unique properties such as excellent photochemical stability, manifolds *f-f* transition and high refractive index ($n \sim 2$) (Guo *et al.*, 2004; Lee *et al.,* 2010; de Moura *et al.*, 2014). In addition, the rare-earth oxides have been perceived as a prominent replacement for currently available fluorescent probes used in the fluorescent displays and magnetic resonance imaging (MRI) namely organic dyes, rare-earth doped oxysulfide, vanadates, ferrites and chelates (Jeong *et al.*, 2006; Goldys *et al.*, 2006; Shim *et al.*, 2007; Grandhe *et al.*, 2013).

However, all of the aforementioned materials exhibit low photothermal stability. Some of them (particularly oxysulfide and chelates) emit corrosive gas under electron bombardment (Rajan & Gopchandran, 2009). Furthermore, the high magnetic susceptibility of ferrites influences the MRI signal of neighbouring normal tissues, resulting in unclear images (Grandhe *et al.*, 2013). In order to mitigate the problems, cubic Eu-doped Gd_2O_3 (denoted as $Gd_2O_3:Eu^{3+}$) has been studied intensively due to its durable photothermal and chemical stability, narrow band gap and large Stokes shifts (Rajan & Gopchandran, 2009; Dhananjaya *et al.*, 2010). The excellent chemical stability characteristics of $Gd_2O_3:Eu^{3+}$ enable it to be adopted into the *in vivo* and *in vitro* biological labelling studies. The researchers also indicated the biocompatibility of $Gd_2O_3:Eu^{3+}$ where there is no signicant cytotoxic effect occuring inside the biological cells in long term (Luo *et al.*, 2014). Furthermore, there is a finding indicates that the Gd based compounds can be effectively removed by the wastewater treatment plants (Telgmann, *et al.*, 2013). Hence, we believe that $Gd_2O_3:Eu^{3+}$ would have low ecotoxicity and less environmental impact, leading towards environmental sustainability.

Of all rare-earth oxides, $Gd_2O_3:Eu^{3+}$ demonstrates tunability in luminescence properties by modifying its crystal structure, size and morphology (Lee *et al.*, 2010; Dhananjaya *et al.*, 2010). Knowing that the one-dimensional (1D) silicon nanowires exhibit superior luminescent and anti-reflection

performances (Yang *et al*., 2007; Lee *et al.*, 2010; Kiraly *et al*., 2013; Hazarika & Mohanta, 2016), the Gd_2O_3:Eu^{3+} nanowires might have the similar properties. The unique 1D nanostructure minimises the luminescent scattering and thus enhancing its luminescent intensity (Kiraly *et al.*, 2013). Nevertheless, synthesis of Gd_2O_3:Eu^{3+} phosphorous with controllable size and shape is still a challenge.

In this regard, hydrothermal method is a promising approach to synthesize isotropic and anisotropic Gd_2O_3:Eu^{3+} nanostructures compared with other synthesis routes like combustion, sol-gel, pyrolysis, precipitates and polyol chemical methods etc (Yang *et al.*, 2005; Goldys *et al.*, 2006; Lin *et al.*, 2007; Dhananjaya *et al.*, 2010; Maalej *et al.*, 2015). This route offers various advantages including simplicity, high yield and low cost in sample preparation (Lee *et al.*, 2008). It has been found that the synthesis temperature and pH are the key parameters which enable the diversity of nanostructures. As reported previously, 1D Gd_2O_3:Eu^{3+} nanowires can be obtained when the synthesis temperature was maintained at 180 °C while the pHs were regulated in the range of 11 – 12 (Lee *et al.*, 2008). Gd_2O_3:Eu^{3+} nanorods can be formed either at lower synthesis temperature of 145 °C in strong alkaline solution (pH 12) or at 180 - 200 °C in mild alkaline solution (pH 8 - 10) (Yang *et al.*, 2007; Lee *et al*., 2008; Dhananjaya *et al.*, 2010; Hazarika & Mohanta, 2016).

In this work, we focus on the hydrothermal synthesis of hexagonal $Gd_2(OH)_3$:Eu^{3+} at temperature 200 °C and pH 12 with longer synthesis duration (72 hours) as compared to the synthesis conditions reported in previous studies (Yang *et al.*, 2007; Lee *et al.*, 2008). We demonstrate the formation of cubic Gd_2O_3:Eu^{3+} 1D nanowires when the as-synthesised $Gd_2(OH)_3$:Eu^{3+} was subsequently underwent dehydration and calcination at 750 °C for 5 hours. The morphological evolution and luminescence features of the 1D Gd_2O_3:Eu^{3+} nanowires are discussed and highlighted.

Experimental

Gd_2O_3 and Eu_2O_3 with analytical grade of 99.99% and 99.90% purity; respectively, were used as starting powders to synthesize Gd_2O_3:Eu^{3+} using hydrothermal method. The stoichiometric amounts of Gd_2O_3 and 8 mol% Eu_2O_3 were dissolved in 1.0 M HNO_3 to form a clear solution. An aqueous 1.0 M NaOH was then added to adjust the pH of the solution to be in the range of alkaline (pH ~12) for the formation of colloidal hydroxide precipitates. The resulting precipitates were then loaded into a teflon-lined stainless steel autoclave to be placed into an oven which had been preset to 200 °C for 72 hours. The reaction product $Gd_2(OH)_3$: Eu^{3+} obtained in this way was washed with ethanol, collected through centrifugation and dried at 60 °C (hereafter denoted as as-synthesised $Gd_2(OH)_3$:Eu^{3+}) The $Gd_2(OH)_3$:Eu powder was calcined at 750 °C for 5 hours with the ramping rate of 3 °C/min in order to yield Gd_2O_3:Eu^{3+}. The phase and structural identification of the as-synthesised $Gd_2(OH)_3$:Eu^{3+} and Gd_2O_3:Eu^{3+} powders were performed by using the Rigaku Miniflex X-ray diffractometer with Cu Kα ranging from 20° to 80°. The nanostructural and surface morphology of the samples were imaged using a JEOL scanning electron microscope (SEM) operated at 15 kV. The samples were sputter-coated with a thin layer of Au before the imaging process was carried out. Measurements of UV-Vis absorption and photoluminescence emission spectra were performed at room temperature using Perkin Elmer Lambda 25 UV-vis spectrometer and Perkin Elmer LS 55 Fluorescence spectrometer; respectively. The UV-vis absorbance were obtained in the range of 200 nm - 900 nm. The photoluminescence emission spectra were measured at room temperature with Xenon flash lamp radiation in the range of 560-720 nm under the excitation wavelength of 257 nm

Result and Discussion

Figure 1 shows the X-ray diffraction (XRD)

patterns of the as-synthesised $Gd_2(OH)_3:Eu^{3+}$ and $Gd_2O_3:Eu^{3+}$ powders. The $Gd_2O_3:Eu^{3+}$ exhibits cubic phase with preferential orientation of (222) plane after calcination at 750 °C for 5 hours whereas the as-synthesised $Gd_2(OH)_3:Eu^{3+}$ forms hexagonal phase. No trace of Eu_2O_3 as secondary phase was observed in the XRD patterns of these two powders. The as-synthesised $Gd_2(OH)_3:Eu^{3+}$ and $Gd_2O_3:Eu^{3+}$ were indexed according to JCPDS file no. 83-2037 and 73-6280, respectively.

The lattice parameters and unit cell volumes were calculated according to the interplanar *d*-spacing equations for hexagonal and cubic structures, respectively (Cullity, 2001). The hexagonal $Gd_2(OH)_3:Eu^{3+}$ has a unit cell volume of 125.828(0) $Å^3$ with its lattice parameters $a = b = 6.316(7)$ Å and $c = 3.6413(8)$ Å. The cubic $Gd_2O_3:Eu^{3+}$ is under tensile strain due to doping as its lattice parameters and unit cell volume are expanded to $a = b = c = 10.810(3)$ Å and 1263.305(6) $Å^3$, respectively. For pure Gd_2O_3 with cubic crystal structure, its lattice parameters are $a = b = c = 10.790(0)$ Å. Such an expansion is evidenced by the marginal shifting of $Gd_2O_3:Eu^{3+}$ (222) peak towards lower angle in the XRD pattern (inset of Figure 1) in comparison with that of the pure Eu_2O_3 and Gd_2O_3. These observation indicates the doping effect of Eu^{3+} into the Gd_2O_3 structure when the smaller Gd^{3+} (ionic radius = 0.94 Å) is substituted by larger Eu^{3+} (ionic radius = 1.07 Å) (Shin *et al.*, 2005; Mukherjee *et al.*, 2009). In addition, the relatively narrower XRD peaks of $Gd_2O_3:Eu^{3+}$with full width at half maximum (FWHM) in the range of 0.31° – 0.36° suggest the highly crystalline nature of the $Gd_2O_3:Eu^{3+}$ in contrast to the as-synthesised $Gd_2(OH)_3:Eu^{3+}$ with higher FWHM of 0.43°-0.76°. The larger FWHMs of $Gd_2(OH)_3:Eu^{3+}$ is attributed to the higher degree of structural order-disorder in its lattices.

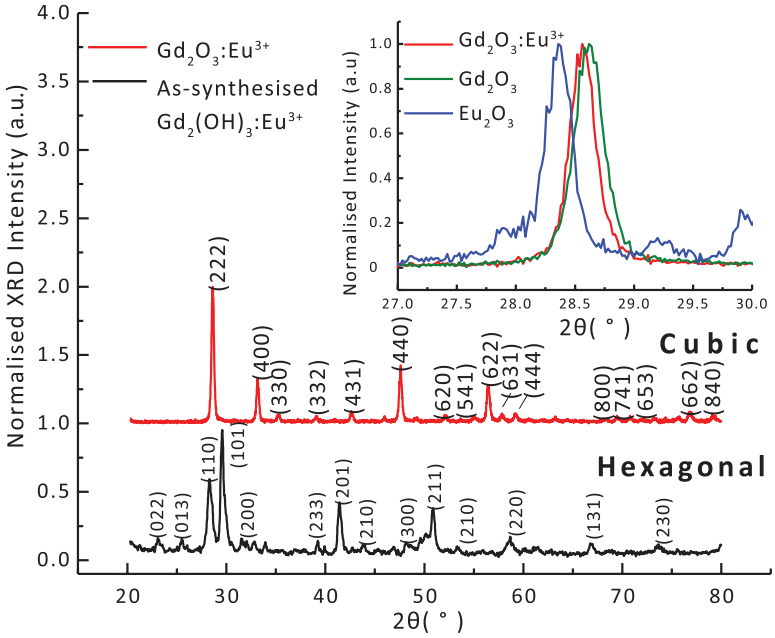

Figure 1: X-ray diffraction patterns of the as-synthesised $Gd_2(OH)_3:Eu^{3+}$ and $Gd_2O_3:Eu^{3+}$ nanophosphors. The inset shows the peak shifting of $Gd_2O_3:Eu^{3+}$ around (222) reflection as compared to pure Gd_2O_3 and Eu_2O_3

In order to obtain an insight into the morphology of the as-synthesised $Gd_2(OH)_3:Eu^{3+}$ and $Gd_2O_3:Eu^{3+}$ nanostructures, their SEM images were captured and shown in Figure 2. The as-synthesised $Gd_2(OH)_3:Eu^{3+}$ appeared in the form of nanowires embedded within the randomly distributed two and three dimensional (2D and 3D) nanoflakes as shown in Figure 2 (a). The nanoflakes were grown from the $Gd_2(OH)_3:Eu^{3+}$ nuclei via 1D growth and subsequently agglomerated into 2D and 3D clusters. A similar 1D nucleation and growth was observed in ZnO synthesised by microwave-assisted hydrothermal method (Kharisov *et al.,* 2012). The 1D $Gd_2(OH)_3:Eu^{3+}$ nanowires shown in Figure 2 (b) have the average diameter of 30 nm and length of 200 nm that gives the aspect ratio (height/width) of 6.7. However, upon calcination at 750 °C the 1D nanowires elongated to ~ 8 µm in length whereas their diameters remained the same (Figure 2 (c)). The average length of these nanowires is about two times longer than that of the $Gd_2O_3:Eu^{3+}$ (2 - 3 µm in length) prepared by Lee *et al*. (2008) via hydrothermal reaction at 180 °C (Lee *et al*., 2008). It is noteworthy that similar pH 12 was used in this work and their studies (Lee *et al*., 2008). These calcined 1D nanowires possess a high aspect ratio of 266.7.

A key reason for this is that the surface energy along the preferential direction is lowered and thus assisting the elongation (Hazarika & Mohanta, 2016). Besides the elongation, the anisotropic distribution of these 1D nanowires was reduced considerably. Multiple $Gd_2O_3:Eu^{3+}$ nanowires rearranged themselves into arrays or bunch of nanowires, affirming the presence of 1D preferential growth. Both $Gd_2(OH)_3:Eu^{3+}$ and $Gd_2O_3:Eu^{3+}$ nanowires were relatively straight unlike the winding and curvy growth of $Gd_2O_3:Eu^{3+}$ nanotubes with the aid of multi

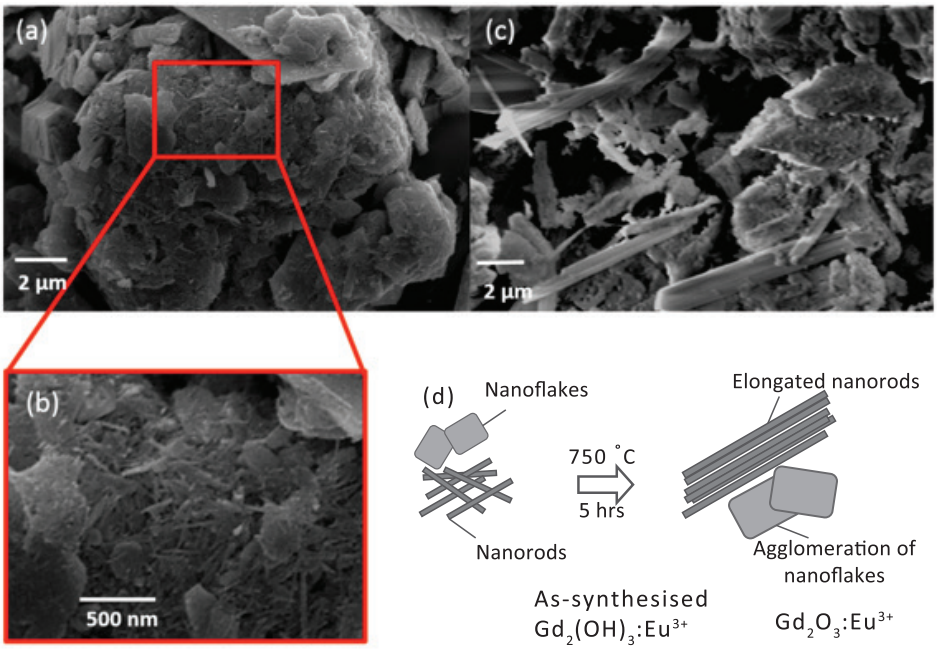

Figure 2: Structural morphology of the as-synthesised $Gd_2(OH)_3:Eu^{3+}$ and $Gd_2O_3:Eu^{3+}$ nanophosphors. (a) as-synthesised $Gd_2(OH)_3:Eu^{3+}$; (b) magnified image of $Gd_2(OH)_3:Eu^{3+}$ as shown in (a); (c) high aspect ratio $Gd_2O_3:Eu^{3+}$ nanowires embedded in the matrix of $Gd_2O_3:Eu^{3+}$ nanoflakes obtained after calcination at 750 °C. (d) Schematic diagrams for the structural evolution of the as-synthesised $Gd_2(OH)_3:Eu^{3+}$ and calcined $Gd_2O_3:Eu^{3+}$ nanophosphors

wall carbon nanotubes (MWCNTs) which act as templates (Grandhe *et al*., 2013). Agglomeration of the $Gd_2(OH)_3$:Eu^{3+} nanoflakes towards micron sized Gd_2O_3:Eu^{3+} flakes also took place after the calcination. The growth of these nanostructures is schematically illustrated in Figure 2 (d).

Figure 3 shows the Tauc plots of the as-synthesised $Gd_2(OH)_3$:Eu^{3+} and Gd_2O_3:Eu^{3+} powders. The optical band gaps were estimated from the Wood and Tauc relation (Dhananjaya *et al*., 2010) with the indirect allowed electronic transition, n = 2. The indirect band gap herein refers to forbidden electrical dipole transitions which are phonon assisted transitions (Shinde *et al.,* 2012). The straight line segments indicated the optical energy band gap, E_g of 4.95 eV, and 5.31 eV for the as-synthesised $Gd_2(OH)_3$:Eu^{3+} and Gd_2O_3:Eu^{3+} powders, respectively. The discrepancy of optical band gap between them is due to the different degree of structural order-disorder in their lattices (Krishna *et al*., 2013). As indicated by the larger FWHM of the as-synthesised $Gd_2(OH)_3$:Eu^{3+} compared to the Gd_2O_3:Eu^{3+}, the former has a higher degree of structural defects (Dhananjaya *et al*., 2010). An intermediate energy level can be introduced by the structural defects. This intermediate energy level facilitates a two-step excitation causing a reduction of E_g in $Gd_2(OH)_3$:Eu^{3+}. The as-synthesised hexagonal $Gd_2(OH)_3$:Eu^{3+} transformed into highly Crystalline cubic Gd_2O_3:Eu^{3+} with fewer defects upon calcination. The hexagonal is compsed of $[Gd(OH)_3]$-clusters connected to each other. Since the The Eu^{3+} dopant is a lattice modifier (Volanti *et al*., 2009), the addition of Eu^{3+} in the hexagonal $Gd(OH)_3$ promotes the expansion of $Gd(OH)_3$ unit cell with high concentration of structural defects (Volanti *et al*., 2009., Omar *et al*., 2016). When the hexagonal $Gd(OH)_3$:Eu^{3+} is subjected to a calcination, the crystallinity is promoted to form $[GdO_{10}]$ cluster with random dispersion of Eu^{3+} substitution that connected to each other in

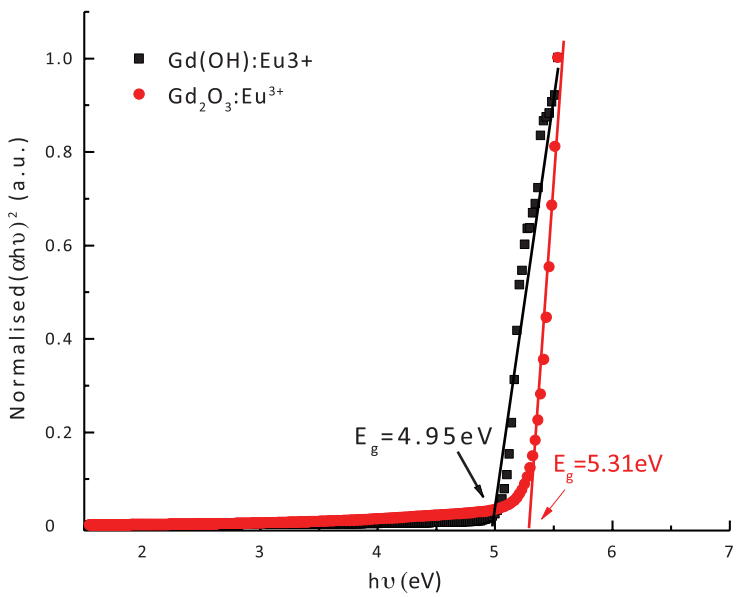

Figure 3: Tauc plots of the as-synthesised $Gd_2(OH)_3$:Eu^{3+} and Gd_2O_3:Eu^{3+}. The optical band gaps of 4.95 eV and 5.31 eV for the $Gd_2(OH)_3$:Eu^{3+} and Gd_2O_3:Eu^{3+}, respectively, were estimated from the Wood and Tauc relation with n = 2 for the indirect allowed electronic transition

compact cubic crystal structure (de Moura *et al*., 2014). The quantity of surface structural defects is reduced as affirmed by the nanostructures evolution mentioned previously. Consequently, the intermediate energy levels within the absorption band of Gd_2O_3:Eu^{3+} is minimized, leading to an increase of E_g.

The photoluminescence (PL) of the $Gd_2(OH)_3$:Eu^{3+} and Gd_2O_3:Eu^{3+} powders were compared to that of the pure Gd_2O_3 and Eu_2O_3. Figure 4 shows the PL emission spectra of these compounds measured in the range of 560-720 nm under the excitation wavelength of 257 nm. This excitation wavelength corresponds to the charge transfer band of Eu^{3+} where the charge is transferred from O^{2-} 2p orbital to Eu^{3+} 4f orbital (Dhananjaya *et al*., 2012). The emission spectra depict the manifolds of Eu^{3+} transitions with $^5D_0$ to ^7F_i transition where i is 1, 2, 3 and 4. For the pure Gd_2O_3, no significant emission was observed from its spectrum. The cubic Gd_2O_3:Eu^{3+} exhibits strong emission at 612 nm with the intensity two times higher than that of the commercially available Eu_2O_3. The peak at 612 nm is responsible for the dominant red emission associated with the $^5D_0$ - $^7F_2$ transition of the Eu^{3+} ions only (Rajan & Gopchandran, 2009; Maalej *et al*., 2015).

Based on the Judd-Ofelt theory (Rajan & Gopchandran, 2009; Shinde *et al*., 2012; Maalej *et al*., 2015), the intensity of $^5D_0 \rightarrow {}^7F_2$ transition is hypersensitive to the symmetry of the surrounding Eu^{3+}. Therefore, the asymmetry ratio, R for $^5D_0 \rightarrow {}^7F_2$ to $^5D_0 \rightarrow {}^7F_1$ transition or $R = \frac{I(^5D_0 \rightarrow {}^7F_2)}{I(^5D_0 \rightarrow {}^7F_1)}$ can be used as a parameter to estimate deviation of the asymmetric coordination polyhedron of Eu^{3+}. The R values for the Gd_2O_3:Eu^{3+}, $Gd_2(OH)_3$:Eu^{3+} and Eu_2O_3 are tabulated in Table 1. The higher R value shown in the cubic Gd_2O_3:Eu^{3+} indicates that majority of Eu^{3+} dopants occupy C_2 sites rather than S_6 (or C_{3i}) sites due to the dominant presence of allowed $^5D_0 \rightarrow {}^7F_2$ electric dipole transition. On the other hand, the hexagonal $Gd_2(OH)_3$:Eu^{3+} and cubic Eu_2O_3 spectra show broader and shifted $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transition peaks with lower intensities. The lower R values and comparable intensities for both $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions confirm that the occupancy of Eu^{3+} in $Gd_2(OH)_3$ and Eu_2O_3 are relatively random between the C_2 and S_6 sites. The discrepancy of the R values also implies the presence of weaker Eu-O covalent bonding in $Gd_2(OH)_3$:Eu^3 and Eu_2O_3 (Rajan & Gopchandran, 2009).

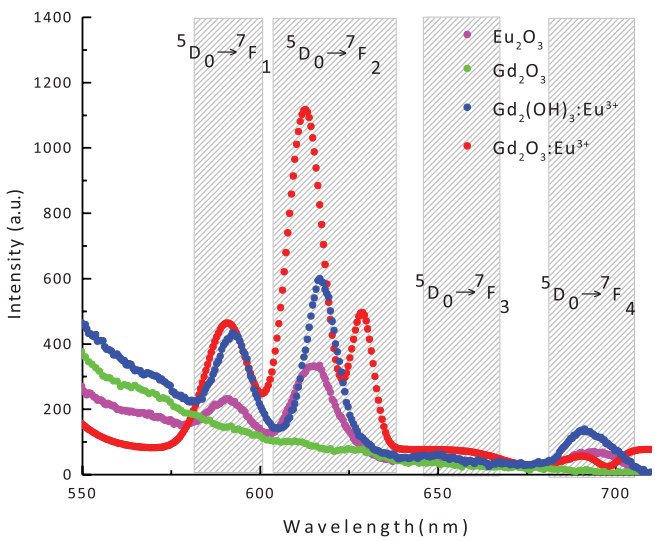

Figure 4: Photoluminescence (PL) emission spectra of the as-synthesised $Gd_2(OH)_3$:Eu^{3+} and calcined Gd_2O_3:Eu^{3+} in comparison to pure Gd_2O_3 and Eu_2O_3. The shaded areas are the emission regions associated with the manifolds of Eu^{3+} with $^5D_0$ to ^7F_i transition where i is 1, 2, 3 and 4

Table 1: Asymmetry ratio, R of $Gd_2O_3:Eu^{3+}$, $Gd_2(OH)_3:Eu^{3+}$ and Eu_2O_3

Compounds	Asymmetric intensity ratio, *R*
$Gd_2O_3:Eu^{3+}$	2.405
$Gd_2(OH)_3:Eu^3$	1.402
Eu_2O_3	1.428

These weak Eu-O bonds act as trapping sites for charge transfer leading to quenching of luminescence. This observation is in fact in good agreement with that found in $Gd_2O_3:Eu^{3+}$ films grown by pulsed laser deposition technique and the $Gd_2O_3:Eu^{3+}$ powders prepared using combustion method (Rajan & Gopchandran, 2009; Dhananjaya *et al*., 2010).

In addition, the results also reveal that the photoluminescence properties are not only rely on the manifold *f-f* transitions of Eu^{3+} dopants but also depend on the crystallographic symmetry and structural imperfection of the Gd_2O_3 host. Owing to the high reflective index and large band gap of Gd_2O_3, the absorption of UV by Gd_2O_3 host lattice is entirely transferred to the Eu^{3+} dopants that are mainly located at the C_2 sites. As a result, a high optical dispersion at 612 nm is induced (Rajan & Gopchandran, 2009). Hence, this profound red emission confirms that Gd_2O_3 is an excellent host which enables efficient energy transfer to the Eu^{3+} dopants.

Conclusion

In summary, this work demonstrates that $Gd_2O_3:Eu^{3+}$ nanowires can be synthesised by means of relatively straightforward hydrothermal route without using any surfactant, catalysts or MWCNTs templates. XRD patterns revealed that the as-synthesised $Gd_2(OH)_3:Eu^{3+}$ evolved from hexagonal structure towards highly crystalline cubic $Gd_2O_3:Eu^{3+}$ after calcination at 750 °C for 5 hours. Simultaneously, the degree of structural order-disorder is reduced leading to the enhancement of band gap of the $Gd_2O_3:Eu^{3+}$ nanophosphors. The $Gd_2O_3:Eu^3$ has a high aspect ratio of 266.7 compared with 6.7 for the as-synthesised $Gd_2(OH)_3:Eu^{3+}$. The combination of symmetric host lattice of Gd_2O_3 and manifold *f-f* transitions of Eu^{3+} stimulate strong red emission associated with $^5D_0 \rightarrow {}^7F_2$ transition at 612 nm. The discrepancy of the *R* values and varied degree of structural imperfections shed some light on the correlation between photoluminescence and structural properties. Hence, controlled growth of nanostructure with high aspect ratio offers a reliable pathway to strongly improve photoluminescence in red region, which is beneficial to biological labelling and optoelectronics.

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