Sonochemical Synthesis of Highly Luminescent $\text{Ln}_2\text{O}_3:\text{Eu}^{3+}$ (Y, La, Gd) Nanocrystals

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Sonication of $\text{Ln}(\text{CH}_3\text{COO})_3 \cdot \text{H}_2\text{O}$, $\text{Eu}(\text{CH}_3\text{COO})_3 \cdot \text{H}_2\text{O}$ and NaOH dissolved in the ionic liquid -butyl-3-methylimidazolium bis(trifluoromethane)sulfonylamide lead to $\text{Ln}(\text{OH})_3:\text{Eu}$ (Ln: Gd, La, Y) nanoparticles. Subsequent calcination at 800°C for 3h allowed to obtain $\text{Ln}_2\text{O}_3:\text{Eu}$ nanopowders. Gd_2O_3 and Y_2O_3 were obtained in the C-type lanthanide sesquioxide structure, whereas La_2O_3 crystallized in the A-type. Structure, morphology, and luminescent properties of the nano-oxides were investigated by powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), dispersive X-ray (EDX), and photoluminescence (PL).

SEM studies revealed that the synthesized $\text{Gd}_2\text{O}_3:\text{Eu}$, $\text{La}_2\text{O}_3:\text{Eu}$, and $\text{Y}_2\text{O}_3:\text{Eu}$ formed nano-spindle, -sheets, and -rods in shape, respectively. The nanoscale materials show very efficient red emission due to the intraconfigurational f-f transitions of Eu^{3+} . The quantum yields for $\text{Ln}_2\text{O}_3:\text{Eu}(5\%)$ were determined to 4.2% for Ln=Gd, 13.8% for Ln=Y and 5.2% for Ln=La. The asymmetric ratio I_{02}/I_{01} ratio of Eu^{3+} varies from 5.3 for Gd_2O_3 , to 5.6 for Y_2O_3 to 6.5 for La_2O_3 , which increased the color chromaticity.

1. Introduction:

Rare earth oxides have been widely studied because of their importance in many applications as highly luminescent materials, catalysts, magnets, medical diagnostics, and other functional materials.^[1] The oxides of rare earth elements such as Y_2O_3 , La_2O_3 , Gd_2O_3 belong to a group of wide bandgap semiconductor materials (La_2O_3 with value of 4.3 eV possesses the largest energy gap among the rare earth oxides).^[2] They can serve as very efficient host matrices for optical active lanthanide ions because they are transparent for visible and infrared radiation and they have no low energy levels that could interfere with the rare-earth activator ion level. For this reason, Y_2O_3 , La_2O_3 , Gd_2O_3 doped with Eu^{3+} are widely used as red-light emitting phosphors in display devices such as field emission displays (FEDs), plasma display panels (PDPs) or cathode-ray tubes (CRT).^[3] Three basic structure types are known for lanthanide sesquioxides: the trigonal A-type (P-3m1) which is the most stable form for the larger and lighter rare earth elements, the monoclinic B-type (C2/m) which is found for mid-sized rare earth elements and the cubic C-type (Ia-3) which is adopted by the smaller, heavier lanthanide elements.^[4] La_2O_3 is a representative for the A-type sesquioxides, Gd_2O_3 for the B-type, and Y_2O_3 is a C-type structure representative.^[5-7] The different structure types feature different lanthanide ion surroundings. In the A type, a capped octahedron of oxygen atoms surrounds the Ln^{3+} (Ln^{3+} = lanthanide) cation. In the B-type three different oxygen coordination polyhedra exist, of which one can best be described as a capped octahedron and the two others as capped trigonal prisms. The C-type features two different Ln^{3+} sites, each with 6-fold oxygen coordination. The different Ln^{3+} environments gives rise to different spectroscopic properties when optically active ions such as Eu^{3+} substitute Y^{3+} , La^{3+} or Gd^{3+} in the respective host lattice. For the three different sesquioxides Y_2O_3 , La_2O_3 and Gd_2O_3 , all three crystal structures have been realized depending on the synthesis conditions, as the relative energies of the the polymorphs are relatively close.

Over the past years much effort has been made to synthesize nano-sized phosphor $\text{Ln}_2\text{O}_3:\text{Eu}^{3+}$ materials by a wide variety of synthetic methods such as hydrothermal, sol-gel techniques^[8,9], spray pyrolysis,^[10] combustion routes using different reducing agents such as urea, glycine or citric acid,^[11] or via co-precipitation processing.^[12] Increasing awareness of

environmental safety risks that could be created by the use of traditional routes to produce nanoparticles, which use toxic and volatile solvents as well as longer periods of conventional heating, leads to the pursuit of alternative, potentially safer and greener productions methods. The application of ultrasound as an economic alternative to traditional routes remains a subject of intense research. Ultrasound heating relies on acoustic cavitation, which involves the formation, growth and collapse of bubbles induced in the liquid. When the induced bubbles collapse suddenly in the small bubble volume high temperatures (up to 5000 K) and high pressures (up to 1000 atm) are generated for a short time. The rates of temperature change are estimated to be larger than 10^9 K/s.^[13] In the context of alternative solvents, ionic liquids (ILs) are often discussed. Ionic liquids (ILs) are salts composed of only ions, which are liquid at relatively low temperatures (under 100°C). Because of their modular character, interesting solvent properties can be realized.^[14] On the one hand, ILs are highly structured solvents, which can influence the evolution of nanoparticles^[15] and finally lead to an efficient size^[16] and morphology control.^[17] On the other hand, the cations and anions of ionic liquids are highly surface active and play a substantial role in phase evolution. Thus, it is also possible to steer polymorph formation and use ILs for phase selective synthesis.^[18]

Herein, we report an easy template and surfactant-free sonochemical method for the fabrication of $\text{Ln}_2\text{O}_3\text{:Eu}$ (Ln : Y, La, Gd) nanoparticles in the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethane)sulfonylamide serving as the solvent and structure directing agent. The influence of the environment and the local symmetry of the Eu^{3+} in the different lanthanide sesquioxide nano-hostmaterials, Ln_2O_3 (Ln : Gd, La, Y) as well as the dopant concentration for Gd_2O_3 on structure, morphology, and the photoluminescence behavior is discussed.

2. Experimental

All reagents employed were commercially available and directly used without further purification. $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ (1-butyl-3-methylimidazoliumbis(trifluoromethanesulfonylamide) was synthesized according to a literature procedure.^[28] Lithiumbis(trifluoromethanesulfonyl)amide (Iolitec), 1-methylimidazole (Sigma-Aldrich, 99%) and 1-chlorobutane (Sigma-Aldrich, 99%). $\text{Y}(\text{CH}_3\text{COO})_3$ (99.9%), $\text{La}(\text{CH}_3\text{COO})_3$ (99.9 %), $\text{Eu}(\text{CH}_3\text{COO})_3\cdot\text{H}_2\text{O}$ (99.9%), were purchased from ABCR, $\text{Gd}(\text{CH}_3\text{COO})_3\cdot 4\text{H}_2\text{O}$ (99.9%) was purchased from Alfa aesar and NaOH from J.T.Baker.

2.1 Preparation of Ln_2O_3 (Ln = Y, La, and Gd) and Eu (5%) doped Ln_2O_3 (Ln = Y, and La), and Eu (5, 10, 15 %) doped Gd_2O_3 .

In a typical synthesis, 1 mmol of $\text{Ln}(\text{CH}_3\text{COO})_3\cdot x\text{H}_2\text{O}$ and 2.5 mmol NaOH fine powder were added to 2 ml of $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$. The reaction mixture was then stirred for 30 min, and irradiated for 6 h in a glass tube sealed with a screw cap in an ultrasound bath (USC200T, VWR International, 45 KHz and 60 W) at room temperature in ambient air. The products were washed thoroughly with ethanol and deionized water, separated by centrifugation, and dried overnight at 90 °C. The dried solids were calcined in air at 800 °C for 3 h. To prepare Eu^{3+} doped materials the required stoichiometric amount of $\text{Eu}(\text{CH}_3\text{COO})_3\cdot\text{H}_2\text{O}$ was added to the reaction mixture before ultrasound treatment.

2.2 Characterization

XRD measurements were carried out on a Huber G670 diffractometer (Huber, Rimsting, Germany) with Mo-K α radiation ($\lambda = 0.07107$). Scanning electron microscopy measurements (SEM) were performed with a high resolution thermally aided field SEM (Zeiss, LEO 1530 Gemini) with a field emission gun (FEG) and an acceleration voltage of $U_{\text{acc}} = 0.2\text{-}30$ KV. For the SEM measurements the sample was put on a carbon-film, dried under vacuum for 20 min and covered with gold to allow for a better electronic conductivity. Attenuated total reflection (ATR) spectroscopy was carried out on an Alpha ATR spectrometer equipped with a diamond crystal (Bruker, Karlsruhe, D). Solid samples were pressed on the crystal. Thermogravimetry (TG) analysis was performed with a Cahn TG 2131 thermobalance. Approximately 25 mg of the sample were heated up to 1000 °C under helium with a heating rate of 5 °C min⁻¹.

Fluorescence and phosphorescence measurements were performed on a Fluorolog FL 3-22 spectrometer (Horiba Jobin Yvon, Unterhachingen, D). A choice between a continuous xenon lamp with 450 W for fluorescence and a pulsed xenon lamp for

phosphorescence measurements is possible. Double gratings for the excitation and emission spectrometer are applied as monochromators. The signal is detected with a photomultiplier. For measurement, powdered samples were filled into silica tubes and carefully positioned in the incoming beam in the sample chamber. For quantum yield measurements, an integrating sphere was used.

The quantum yields of $\text{Ln}_2\text{O}_3:\text{Eu}^{3+}$ were calculated using the following formula

$$\Phi = \frac{E_c}{I_a - I_c}$$

where E_c is the integrated area under the emission spectrum of the investigated sample. I_a , and I_c are the reflectance of the investigated and standard samples at the excitation wavelength. BaSO_4 with a refractive index 0.91 was used in this study as reflectance standard to estimate the amount of light absorbed by the sample. Due to the poor lamp intensity at 250 nm the QY measurements were carried out exciting directly into Eu at 393 nm.

3. Results and discussion

3.1 Phase identification, and morphology of Eu (5%) doped Ln_2O_3 ($\text{Ln} = \text{Y}$, and La), and Eu (5, 10, 15 %) doped Gd_2O_3 .

1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ was used as the ionic liquid in this study as it is one of the most common room temperature ionic liquids with an appreciably low viscosity. It is based on a short-chain alkyl methylimidazolium cation and exhibits a high electron acceptor potential due to the delocalized aromatic system, which is highly likely to create electrostatic attractions on the surface of the oxide particles. H-bond-like interactions may also occur as a result of the acidic character of the imidazolium ring-bound hydrogen atoms.^[19] Appropriate amounts of the respective lanthanides acetate hydrates were dissolved together with sodium hydroxide in the ionic liquid and then sonicated. XRD analysis was used to identify the reaction products.

Figure 1. XRD patterns of the as-prepared $\text{Gd}(\text{OH})_3$ (b), $\text{Y}(\text{OH})_3$ (d), $\text{La}(\text{OH})_3$ (f), and database patterns $\text{Gd}(\text{OH})_3$ (JCPDS 83-2037) (a), $\text{Y}(\text{OH})_3$ (JCPDS 73-1795) (c), and $\text{La}(\text{OH})_3$ (JCPDS 36-1481) (e).

The results of X-ray powder diffraction, give evidence that the mere sonication process did not yield Ln_2O_3 directly as shown in Fig. 1. Rather the diffraction patterns of the as-prepared products can be indexed to the respective hydroxides (JCPDS No. 73-1795 for $\text{Y}(\text{OH})_3$, 36-1481 for $\text{La}(\text{OH})_3$, and 83-2037 for $\text{Gd}(\text{OH})_3$ crystallizing isotypically in $P6_3/m$. Thus, further calcination is needed to convert the obtained $\text{Ln}(\text{OH})_3$ to the sesquioxide. To investigate the thermal decomposition of the hydroxides to the respective sesquioxides the thermal behaviour of $\text{Gd}(\text{OH})_3$ may serve as an example (Fig. 2).

Figure 2. TGA curve of the obtained $\text{Gd}(\text{OH})_3$.

Thermogravimetric (TG) experiments (Fig. 2) show that the dehydration takes place in two steps. The weight loss between 70 and 145 °C is ascribed to removal of surface-adsorbed H_2O . The first dehydration occurs from 145 to 333 °C with weight loss of 8.56 %, due to the decomposition of $\text{Gd}(\text{OH})_3$ to GdOOH .^[20] The second dehydration step is caused by the further decomposition of GdOOH to Gd_2O_3 and takes place from 333 °C up to 760 °C with a total weight loss of 4.43 %. The theoretical weight losses for the first and second dehydrations step are 8.70% and 4.35%, respectively,^[21] which matches quite well with the experimental data obtained from the TG experiment.

Figure 3. XRD patterns of Gd_2O_3 (b), Y_2O_3 (d), and La_2O_3 (f), in comparison with the respective database patterns of Gd_2O_3 (JCPDS 86-2475) (a), Y_2O_3 (JCPDS 41-1105) (c), and La_2O_3 (JCPDS 74-2430) (e).

On the basis of TGA data the $\text{Y}(\text{OH})_3$, $\text{La}(\text{OH})_3$, and $\text{Gd}(\text{OH})_3$ samples were calcinated in air at 800 °C for 3 h to ensure their complete decomposition, and, indeed, phase-pure Y_2O_3 , La_2O_3 , and Gd_2O_3 were obtained, respectively. Figure 3 shows the XRD patterns of Gd_2O_3 , Y_2O_3 , and La_2O_3 after calcination. The respective diffraction patterns of the corresponding Eu (5, 10, 15 %)-doped Gd_2O_3 , Eu (5%)-doped Y_2O_3 , and Eu(5%)-doped La_2O_3 samples can be found in SI-Fig. 1. For the gadolinium and yttrium sesquioxide samples all diffraction peaks can be indexed to the cubic C-type phase in agreements with the JCPDS cards [JCPDS No. 41-1105 (Y_2O_3), 86-2475 (Gd_2O_3)]. For the larger lanthanum analogue, the diffraction

pattern shows, as expected, the formation of the thermodynamically stable trigonal A-phase. All observed diffraction peaks match the standard JCPDS card [JCPDS No. 74-2430 (La_2O_3)]. No additional peaks for other phases were found, indicating that complete conversion of the lanthanide hydroxides to the oxides was achieved and the samples are phase pure. This is further supported by infrared spectroscopy. The infrared spectra of the as-prepared nanopowders $\text{Ln}(\text{OH})_3 \cdot \text{Eu}$ (5%) and $\text{Ln}_2\text{O}_3 \cdot \text{Eu}$ (5%) after calcination at 800 °C for 3 h are presented in Figure 4 in the 4000-350 cm^{-1} range. The sonochemically derived as-prepared $\text{Ln}(\text{OH})_3 \cdot \text{Eu}$ (5%) show O-H bands at 3615 cm^{-1} along with Ln-O bands at 643 cm^{-1} for Gd-OH, 704 cm^{-1} for Y-OH, at 713 cm^{-1} for La-OH which agrees with literature reports.^[22] No obvious bands for impurities or IL were observed. After calcination at 800 °C, the IR spectra show Gd-O bands at 546 and 440 cm^{-1} , Y-O absorption bands at 572 and 475 cm^{-1} and La-O bands at 537 and 432 cm^{-1} .^[23] The disappearance of the OH bands centered at 3615 cm^{-1} at the end of calcination indicates that the the respective $\text{Ln}(\text{OH})_3 \cdot \text{Eu}$ were completely converted to $\text{Ln}_2\text{O}_3 \cdot \text{Eu}$.

Figure 4. IR spectra of as-prepared $\text{Ln}(\text{OH})_3 \cdot \text{Eu}$ (5%), and $\text{Ln}_2\text{O}_3 \cdot \text{Eu}$ (5%) calcined at 800 °C for 3 h in ambient air.

In addition, EDS (energy-dispersive X-ray) spectra of the Ln_2O_3 samples (SI-Fig. 2) were recorded during SEM (scanning electron microscopy) measurement to confirm the sample purity and complete removal of the ionic liquid. SEM imaging was used to investigate the sample morphology and estimate the particle size of the as-prepared samples. It can be seen from Fig. 5(-1, -2, -3, -4) that the Gd_2O_3 and $\text{Gd}_2\text{O}_3 \cdot \text{Eu}^{3+}$ nanomaterial forms as spindle-shaped particles with a width of about 200 nm at the center and lengths ranging from 1 to 2 μm . For Y_2O_3 smaller, more rod-like particles with ~50 nm diameter and lengths that vary from 200 to 500 nm are observed as shown in Fig. 5(-5, -6). As for Gd_2O_3 there is no remarkable change in the morphology of the particles upon incorporation of Eu^{3+} . In case of La_2O_3 and $\text{La}_2\text{O}_3 \cdot \text{Eu}^{3+}$ Fig. 5(-7, -8) nanoplates of hexagonal shape which agglomerate parallel to each other, with an average diameter of 100-200 nm and with a thickness up to ≈ 30 nm are formed, in agreement with the hexagonal A-type form.

Figure 5. SEM images of as-prepared Gd_2O_3 (1), $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ 5% (2), 10% (3), 15% (4), Y_2O_3 (5), $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ 5% (6), La_2O_3 (7), and $\text{La}_2\text{O}_3:\text{Eu}^{3+}$ 5% (8).

3.2 Luminescence Properties

The XRD patterns of the $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ and $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ samples evidence the formation of the cubic C-type crystal structure. Even for samples containing relatively high concentrations of Eu^{3+} dopant ions (15%), only diffraction peaks of the cubic Gd_2O_3 phase are observed. The C-type structure of lanthanide sesquioxides (isotypic with bixbyite) offers two possible nonequivalent sites for the metal ions – a non-centrosymmetric C_2 and a centrosymmetric S_6 (C_{3i}) site. The ratio between the number of the rare-earth ions occupying the C_2 and S_6 (C_{3i}) sites is equal to 3:1. In both structures the coordination environment of the rare earth ions is formed by six oxygen atoms. Although $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ and $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ crystallize isotypically and the Eu^{3+} occupy sites with same symmetry, different optical properties are expected. In case of $\text{Gd}_2\text{O}_3:\text{Eu}$ the ionic radii of for both lanthanide ions are almost the same ($0.947 \text{ \AA}$ for Eu^{3+} and $0.938 \text{ \AA}$ Gd^{3+}),^[24] the introduction of the active ions into this host lattice does not lead to any distortion of the Gd_2O_3 crystal structure and there is not preferential site occupation for Eu^{3+} ions.^[25] A different scenario is found for $\text{Y}_2\text{O}_3:\text{Eu}$, where the Y^{3+} radius is much smaller ($0.900 \text{ \AA}$) compared to Eu^{3+} and the substitution of Y^{3+} by Eu^{3+} consequently leads to distortions, which influences the optical properties. The room and low temperature excitation spectra (Fig. 7, and SI. 3) of all samples consist of narrow bands which can be assigned to the transitions within the $4f^6$ configuration of Eu^{3+} ions (Fig.6). The UV range is dominated by a broad and intense band with maximum around 250 nm due to the $\text{O}^{2-}-\text{Eu}^{3+}$ charge transfer band (see Fig. 6 for an illustration). Thus, the ultraviolet radiation is efficiently absorbed by this charge transfer state. SI. 6 and SI. 7 show the excitation spectra of $\text{Y}_2\text{O}_3:\text{Eu}$ and $\text{La}_2\text{O}_3:\text{Eu}$. These spectra show similar features to that of $\text{Gd}_2\text{O}_3:\text{Eu}$, consisting of a very intense broad band in the higher energy part of the spectra, while the lower energy region is dominated by narrow f-f transitions of Eu^{3+} ions. The broad band in UV region results from an electron transfer from the O^{2-} ($2p$) states to the empty states of the $\text{Eu}^{3+}-4f^6$ configuration. The location of the maximum of this band varies with the metal ions in the host lattice. For $\text{Y}_2\text{O}_3:\text{Eu}$ it is found

at 230 nm, for Gd₂O₃:Eu at 250 nm, and for La₂O₃:Eu 275 nm. These bands are very important for potential applications as the formally allowed CTS (charge transfer state) is able to efficiently absorb the excitation energy and subsequently transfer this energy to lower lying 4f levels leading to red emission by the Eu³⁺ ions. The position of the CT band depends on the electronegativity of the bonding partners and their interatomic distances. Shortening of this distance leads to a larger energy separation between the Ln-4f and O-2p states. If the metal ion is more electropositive, this facilitates charge transfer as acceptor levels are located at lower energy. The position of the observed CT band for Y₂O₃:Eu, La₂O₃:Eu and Gd₂O₃:Eu is in good agreement with the expectations based on the ionic radii and with literature reports.^[26]

Figure 6. Energy level diagram with all possible radiative and non-radiative transitions of Eu³⁺ ions in Gd₂O₃:Eu³⁺.

The resulting emission spectra consist of narrow bands assigned to emission of the Eu³⁺ ions. Thus, all the samples under investigation show, both at room (Fig.7, SI. 3) as well as at low temperature, a very strong red emission of Eu³⁺ under excitation into the CT band at 270 nm. For the Gd₂O₃:Eu³⁺, direct emission from higher lying excited levels of Eu³⁺ (⁵D₁, ⁵D₂) occurring in the range between 450-550 nm in addition to the emission from the ⁵D₀ level was also observed (Fig. 8, inset).

Fig. 7. Room temperature emission spectra of Gd_2O_3 doped by Eu^{3+} ions under excitation at 270 nm.

As expected, an increase in the concentration of active ions causes a decrease in the emission intensity in the 450-550 nm spectral range (in comparison to the much stronger main emission from $^5\text{D}_0$ level). For Eu_2O_3 no emission from $^5\text{D}_2$ or $^5\text{D}_1$ level could be detected. At higher Eu^{3+} dopant ion concentrations strong concentration quenching is expected, due to fact that each Eu^{3+} ion finds itself in close proximity to relatively large number of Eu^{3+} neighboring ions, facilitating energy migration processes. In terms of application, it is very important that, as we observe here, that the most intense emission band is located at 612 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) and that it is much stronger than the one observed around 590 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_1$) as this guarantees a good chromaticity. For all the investigated samples excited at 270 nm, the wavelength which corresponds to the $\text{O}^{2-}\text{-Eu}^{3+}$ CT of the ion, a similar observation was made.

As mentioned before, the Eu^{3+} ions may occupy two different sites in the Gd_2O_3 host lattice. Hence, the emission spectra can be rich in lines resulting from transitions from europium ions residing in the C_2 and/or the S_6 (C_{3i}) site. This becomes most evident in the spectral range of 580-605 nm, where the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition occurs. For the Eu^{3+} ions occupying the centrosymmetric S_6 (C_{3i}) sites, only the magnetic dipole f-f transition is observed (two lines in the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition), while for Eu^{3+} ions occupying the non-centrosymmetric C_2 sites, the electric dipole transitions can be also expected (three lines). Very efficient energy transfer between the two different sites S_6 (C_{3i}) $\rightarrow$ C_2 of europium is known to occur. This process strongly depends on the concentration of the Eu^{3+} ions. In Eu_2O_3 energy transfer becomes so dominant, that no lines from $\text{Eu}(\text{S}_6, \text{C}_{3i})$ (even after the selective excitation) can be detected.^[27]

Figure 8. Room temperature emission spectrum of the Gd_2O_3 doped with 5% Eu^{3+} ions, under excitation at 270 nm. The inset shows the concentration dependency of emission from higher Eu^{3+} ion levels.

Table 1. Measured emission lifetimes and quantum yield of $\text{Ln}_2\text{O}_3\text{:Eu}$. under excitation at 393 nm.

Sample	Life time (ms)	Quantum Yield (%)
$\text{Gd}_2\text{O}_3\text{:Eu}^{3+}$ (5%)	1.06	4.24 ± 0.12
$\text{Gd}_2\text{O}_3\text{:Eu}^{3+}$ (10%)	0.92	1.64 ± 0.14
$\text{Gd}_2\text{O}_3\text{:Eu}^{3+}$ (15%)	0.69	0.48 ± 0.01
$\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ (5%)	1.75	13.83 ± 0.43
$\text{La}_2\text{O}_3\text{:Eu}^{3+}$ (5%)	0.88	5.17 ± 0.21

As expected, the lifetimes of Gd_2O_3 doped by Eu^{3+} ions varies from 0.69 (15%) to 0.92 (10%) to 1.06 ms (5%) with decreasing relative mass of europium in the host lattice.

Fig. 8 shows no major differences in the emission spectra of Eu^{3+} in the Y_2O_3 and Gd_2O_3 but for La_2O_3 which crystallizes in a different structure (A-type). In the A-type, Eu^{3+} when substituting La^{3+} in the host material occupies sites with C_{3v} symmetry. As expected the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition with a maximum at 625 nm becomes the most intense, in contrast to that

observed for the C- type host lattices where the $^5D_0 \rightarrow ^7F_2$ transition is more prominent. The chromaticity or saturation of red emitted light is related to the values of the relative intensity for the $^5D_0 \rightarrow ^7F_2$ to $^5D_0 \rightarrow ^7F_1$ (I_{02}/I_{01}) emission transition, which is called the asymmetry ratio, where larger I_{02}/I_{01} values originating from lower site symmetry of the Eu^{3+} ion in the host lead to better color chromaticity.^[31] The I_{02}/I_{01} ratio varies from 5.3 for Gd_2O_3 , to 5.6 for Y_2O_3 to 6.5 for La_2O_3 . The 5D_0 lifetime of $\text{La}_2\text{O}_3:\text{Eu}^{3+}$, $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$, and $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ for $\lambda_{\text{ex, em}} = (295, 626)$, $(263, 611)$, $(270, 611 \text{ nm})$ at room temperature were determined to be 0.88, 1.75, 1.06 ms, respectively as listed in Table 1. The quantum yields of $\text{Ln}_2\text{O}_3:\text{Eu}^{3+}$ with respect to concentration of the dopant ion Eu^{3+} and its site symmetry are listed in Table 1. Quantum yields (QY) range from 4.24% for $\text{Gd}_2\text{O}_3:\text{Eu}(5\%)$ to 0.48% for $\text{Gd}_2\text{O}_3:\text{Eu}(15\%)$, and are 14% for $\text{Y}_2\text{O}_3:\text{Eu}^{3+}(5\%)$, and 5.17% for $\text{La}_2\text{O}_3:\text{Eu}^{3+}(5\%)$. These results show that the quantum yield depends robustly on the Eu^{3+} concentration as well as on the sample structure, where it is seen that with rising the Eu^{3+} concentration from 5% to 15% in the same host lattice led, as expected, to a decrease in quantum yields from 4.24% to 0.48%. The decreased QY for $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ (15%) compared with $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}(5\%)$ is the consequence of the increased concentration quenching. The obtained values in our case for $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ are larger than the quantum yield of $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ nanorods (0.45%) and bulk counterpart (0.7%) reported by A. G. Macedo *et.al.*^[32] Moreover, using different host materials when the concentration of activator is kept unchanged (Eu^{3+} 5%) leads to increased quantum yield from 4.24% for Gd_2O_3 to 5.17% for La_2O_3 and 14% for Y_2O_3 .

Figure 9. Low temperature emission spectrum of the Ln_2O_3 ($\text{Ln}=\text{Y, Gd, La}$) doped by 5% Eu^{3+} ions, under excitation at 270 nm. The insert shows the concentration dependency of emission from higher Eu^{3+} ions levels.

The QY of $\text{La}_2\text{O}_3:\text{Eu}$ is found close to the previously determined value for $\text{La}_2\text{O}_3:\text{Eu}(5\%)$ nanoparticles (6%) prepared by Glycine assisted combustion synthesis^[34]. Although the quantum yield of the sononchemically prepared $\text{Y}_2\text{O}_3:\text{Eu}(5\%)$ nanoparticles is significantly lower than that of the commercial powder (90%) of $\text{Y}_2\text{O}_3:\text{Eu}$ ^[35], it is still higher than previously reported quantum yields of $\text{Y}_2\text{O}_3:\text{Eu}$ nanomaterials. For example, $\text{Y}_2\text{O}_3:\text{Eu}$ (5%) nanoparticles prepared by subambient homogeneous reduction using alkalide solution and subsequent oxidation exhibited low quantum yield less than 8%^[36] while $\text{Y}_2\text{O}_3:\text{Eu}$ (0.7-7%) prepared by chemical vapor synthesis (QYs of less than 10%).^[37] Typically lower quantum yields of nanomaterials are related to increased surface-to-volume ratio resulting in an increase of non-radiative surface recombination. Another explanation provided by Schmechel and co-workers is that the lower quantum yields may be caused by a greatly reduced radiative transition rate due to the lattice expansion of nanoparticles and an enhanced non-radiative transition rate due multi-phonon relaxation mediated by surface adsorbates.^[36,37]

4. Conclusions

$\text{Ln}_2\text{O}_3:\text{Eu}$ ($\text{Ln} : \text{Gd, La, Y}$) nanoparticles have been obtained by sonicating a solution of rare earth acetates and NaOH in the ionic liquid $[\text{C}_4\text{mim}][\text{TF}_2\text{N}]$ and subsequent calcination of the material at 800°C for 3h. This novel synthetic route towards

homogeneous, uniform and high quality $\text{Ln}_2\text{O}_3:\text{Eu}$ ($\text{Ln} : \text{Gd, La, Y}$) nanomaterials is simple and easy, and does not involve the used of additional templates or surfactants to control the size, phase and morphology of the finite material. Using different Ln_2O_3 as host materials for Eu^{3+} as the activator ion in a concentration of 5% leads to variations in the asymmetric ratio from 6.5 for $\text{La}_2\text{O}_3:\text{Eu}(5\%)$ (A type) to 5.6 for $\text{Y}_2\text{O}_3:\text{Eu}(5\%)$ (A type) and 5.3 for Gd_2O_3 (C type). The C-type material has the highest color chromaticity. Quantum yields (QY) range from 4.24% for $\text{Gd}_2\text{O}_3:\text{Eu}(5\%)$ over 5.17% for $\text{La}_2\text{O}_3:\text{Eu}^{3+}(5\%)$ to 14% for $\text{Y}_2\text{O}_3:\text{Eu}^{3+}(5\%)$. Raising the Eu^{3+} concentration from 5% to 15% in Gd_2O_3 causes a decrease in the emission intensity in the 450-550 nm spectral range together with a decrease in lifetimes from 1.06 to 0.69 ms, which also finds its expression in a reduction of quantum yields from 4.24% to 0.48%.

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