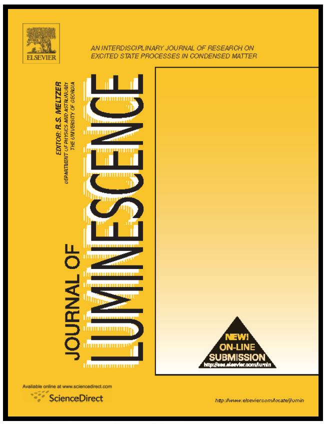

www.elsevier.com/locate/jlumin

# Sonochemical Synthesis of Highly Luminescent $Ln_2O_3:Eu^{3+}$ (Y, La, Gd) Nanocrystals

Tarek Alammar, Joanna Cybinska, Paul S. Campbell, Anja-Verena Mudring

PII: S0022-2313(15)00251-3
DOI: http://dx.doi.org/10.1016/j.jlumin.2015.05.004
Reference: LUMIN13335

To appear in: *Journal of Luminescence*

Received date: 18 November 2014
Revised date: 20 April 2015
Accepted date: 4 May 2015

Cite this article as: Tarek Alammar, Joanna Cybinska, Paul S. Campbell and Anja-Verena Mudring, Sonochemical Synthesis of Highly Luminescent $Ln_2O_3:Eu^{3+}$ (Y, La, Gd) Nanocrystals, *Journal of Luminescence,* http://dx.doi.org/10.1016/j.jlumin.2015.05.004

# Sonochemical Synthesis of Highly Luminescent $Ln_2O_3$:$Eu^{3+}$ (Y, La, Gd) Nanocrystals

**Tarek Alammar, Joanna Cybinska,[b] Paul S. Campbell,[c] and Anja-Verena Mudring[a],***

a Materials Science and Engineering, Iowa State University and Critical Materials Institute, Ames Laboratory, Ames, IA, USA; mudring@iastate.edu; phone +1 515 509 5616
b University of Wroczlaw, Faculty of Chemistry, Joliot-Curie 14, PL-50383 Wroczaw, Poland
c The European Patent Office, Patentlaan 2, 2288 EE Rijswijk, The Netherlands

**Keywords:** ceramics / inorganic compounds / nanostructures / oxides / photoluminescence spectroscopy

Sonication of $Ln(CH_3COO)_3\cdot H_2O$, $Eu(CH_3COO)_3\cdot H_2O$ and NaOH dissolved in the ionic liquid -butyl-3-methylimidazolium bis(trifluoromethane)sulfonylamide lead to $Ln(OH)_3$:Eu (Ln: Gd, La, Y) nanoparticles. Subsequent calcination at 800°C for 3h allowed to obtain $Ln_2O_3$:Eu nanopowders. $Gd_2O_3$ and $Y_2O_3$ were obtained in the C-type lanthanide sequioxide 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 $Gd_2O_3$:Eu, $La_2O_3$:Eu, and $Y_2O_3$: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 $Ln_2O_3$: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-raytubes (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 $Ln_3O_3$:$Eu^{3+}$ materials by a wide varierty 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