

## Structure and Luminescence of Ce-doped Lu<sub>2</sub>SiO<sub>5</sub> Nanophosphor

Michael Wayne Blair<sup>1</sup>, Luiz G Jacobsohn<sup>2</sup>, Bryan L Bennett<sup>2</sup>, Ross E Muenchausen<sup>2</sup>, Stephanie C Sitarz<sup>2</sup>, James F Smith<sup>2</sup>, D Wayne Cooke<sup>2</sup>, Peter A Crozier<sup>3</sup>, and Ruigang Wang<sup>3</sup>

<sup>1</sup>Earth and Environmental Sciences, Los Alamos National Laboratory, MS J495, Los Alamos, NM, 87544

<sup>2</sup>Materials Science and Technology, Los Alamos National Laboratory, MS E546, Los Alamos, NM, 87545

<sup>3</sup>School of Materials, Arizona State University, Tempe, AZ, 85287

### ABSTRACT

Nanophosphors correspond to nanostructured inorganic insulator materials that emit light under particle or electromagnetic radiation excitation. In this work we investigate the structure and luminescent properties of Ce-doped Lu<sub>2</sub>SiO<sub>5</sub> (LSO) nanophosphors prepared by solution combustion synthesis with the Ce content 0.1 to 12 at. %. Samples were characterized by transmission electron microscopy (TEM), line scan electron energy-loss spectroscopy (EELS), x-ray diffraction (XRD), and electron paramagnetic resonance (EPR) spectroscopy. Photoluminescence excitation and emission spectra are composed of two major bands centered at 360 and 430 nm, respectively. These results reveal a red-shift and enhanced Stokes shift for the nanophosphors when compared to bulk. Ce content was also found to affect photoluminescence emission intensity and fluorescent lifetime. The nanophosphor concentration quenching curve presents a broad maximum centered at 1 at.%. Lifetime measurements show a continuous decrease from 34 to 21 ns as Ce content is increased.

### INTRODUCTION

While an intense investigative effort on the optical properties of nanostructured semiconductors has been carried out for more than a decade, nanophosphors have remained largely unexplored until recently [1]. Of particular interest is the synthesis and characterization of rare-earth (RE) doped nanophosphors with emphasis on optical properties and how these change with reduced dimensionality. Since phosphors play an integral role in modern life, with applications ranging from fluorescent lighting and cathode ray tube displays to medical imaging (i.e., positron emission tomography scanners) and nuclear radiation detectors [2], it is very important to investigate the optical properties of oxyorthosilicates, including Ce-doped Lu<sub>2</sub>SiO<sub>5</sub> (LSO).

In luminescent materials, the electronic and optical properties of the luminescent centers are affected by the local symmetry, crystalline structure, degree of structural disorder, defects and chemical composition. In addition, the presence of other dopants/impurities can alter energy transfer processes. In nanophosphors, myriad surface effects are possible related to structural relaxation, reconstruction, dangling bonds, aging, etc, that arise from the high surface-to-volume ratio of nanoparticles. In this paper, we first examine how the structural properties of Ce-doped Lu<sub>2</sub>SiO<sub>5</sub> (LSO) nanophosphors differ from the bulk samples. Then, we focus on the unique luminescence properties of nanophosphor LSO that arise largely from the structural changes.

## EXPERIMENT

Bulk samples of LSO were obtained by grinding single crystal specimens that had been grown by the Czochralski method to  $< 40\text{-}\mu\text{m}$  particle size. The small distribution coefficient for Ce in LSO is the limiting factor for the Ce concentration, and the Ce concentration is approximately 0.055 at.% relative to Lu. This structure is comprised of  $\text{SiO}_4$  tetrahedra with four different oxygen ions and one non-Si-bonded oxygen that is surrounded by four Lu ions [3]. Lu ions occupy two crystallographic sites coordinated with either six or seven oxygen ions. Nanophosphor LSO samples were prepared by the glycine-nitrate solution combustion technique [4]. Cerium concentration of the nanophosphors varied from 0.1 to 12 at. %.

The structural characteristics of the nanopowders were characterized by XRD, TEM, and EPR spectroscopy at Los Alamos National Laboratory (LANL). EPR spectroscopy was carried out on a Bruker EleXsys E-500 X-band spectrometer equipped with an Oxford cryostat. The elemental analysis of the samples was obtained by EELS and performed at Arizona State University. Excitation (PLE) and emission (PL) photoluminescence measurements were obtained in ambient conditions using a Photon Technology International TimeMaster<sup>TM</sup> fluorimeter and lifetime spectrometer at LANL.

## DISCUSSION

### Structural analysis

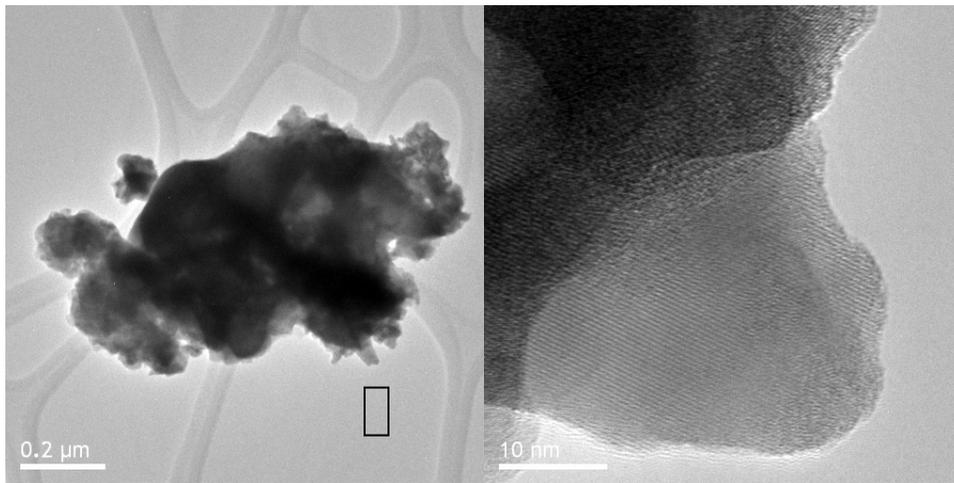
X-ray diffraction data confirmed the structure and phase purity of both bulk and nanophosphor LSO:Ce and TEM showed micron sized particles of agglomerated crystallites with average crystallite size  $\sim 30$  nm. Figure 1 (a) shows the agglomerated crystallites and (b) shows one of the individual crystallite from the agglomerate for nanophosphor LSO. The crystallite size has also been confirmed by Debye-Scherrer analysis of the XRD data [5]. Bulk LSO forms a monoclinic structure with  $C2/c$  space group whereby the Lu ions occupy two crystallographic sites coordinated with either six or seven oxygen ions. Nanophosphor LSO forms a monoclinic structure with  $P2_1/c$  space group, in contrast to the  $C2/c$  structure of bulk samples, with seven and nine oxygen coordination. Although energy dispersive x-ray analysis (EDX) with scanning transmission electron microscopy (STEM) found that the dopant concentration was uniform in the samples [6], EELS analysis has revealed elemental inhomogeneities at the atomic level for nanophosphor LSO.

Further structural analysis was undertaken using EPR spectroscopy. Figure 2 shows EPR spectra for both bulk and nanophosphor LSO:Ce measured at temperatures below 10 K. the Ce lines can only be detected below approximately 50 K due to lifetime broadening of the lines above this temperature [7]. Although there is a slight shift in the g-values between the bulk and nanophosphor samples, of more significance is the broader linewidths displayed by the nanophosphor which are indicative of increased crystal disorder. In order to quantify the disorder, we studied the Orbach relationship for LSO. The Orbach process is a resonant two-phonon process involving the excited state of  $\text{Ce}^{3+}$  and relaxation from this state instead of the direct relaxation employed in the typical EPR process. The temperature-dependent linewidth of the  $\text{Ce}^{3+}$  EPR resonance in the Orbach process is indicative of the inhomogeneous broadening

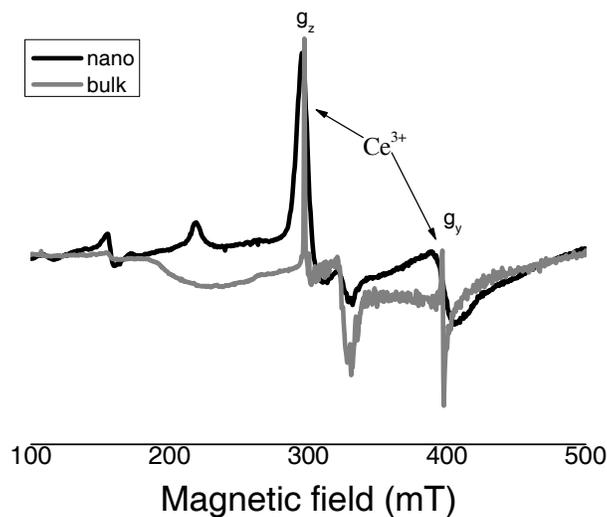
due to crystal disorder [7]. The linewidth for the  $g_z$  resonance was measured for LSO spectra taken at various temperatures and fit to the relationship:

$$(1) \quad \Delta w = A + C\Delta E^3 \exp(-\Delta E / k_B T)$$

where  $\Delta w$  (Gauss) is the FWHM of the resonance,  $A$  (Gauss) is the inhomogeneous broadening due to lattice disorder,  $C$  is a constant, and  $\Delta E$  ( $\text{cm}^{-1}$ ) is the energy splitting between the excited states. The energy splittings for bulk ( $159 \pm 8 \text{ cm}^{-1}$ ) and nanophosphor ( $153 \pm 9 \text{ cm}^{-1}$ ) LSO are consistent with each other, but the lattice disorder for the nanophosphor sample ( $81.8 \pm 1.5$  Gauss) is over fifteen times larger than the bulk sample ( $5.0 \pm 0.8$  Gauss). The increase in crystal disorder is expected as a result of the SCS method and has large implications for the luminescence properties.



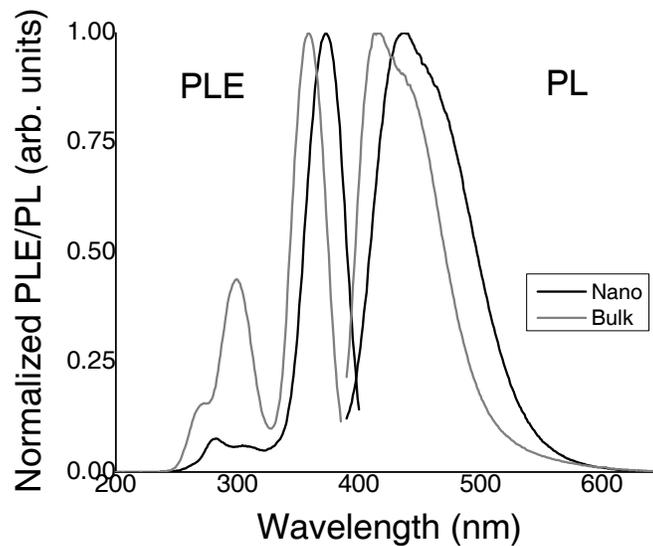
**Figure 1.** TEM of nanophosphor LSO showing (a) micron sized agglomerated crystallites and (b) a single crystallite. The box in (a) shows the area that was scanned in detail to produce (b) image in (b).



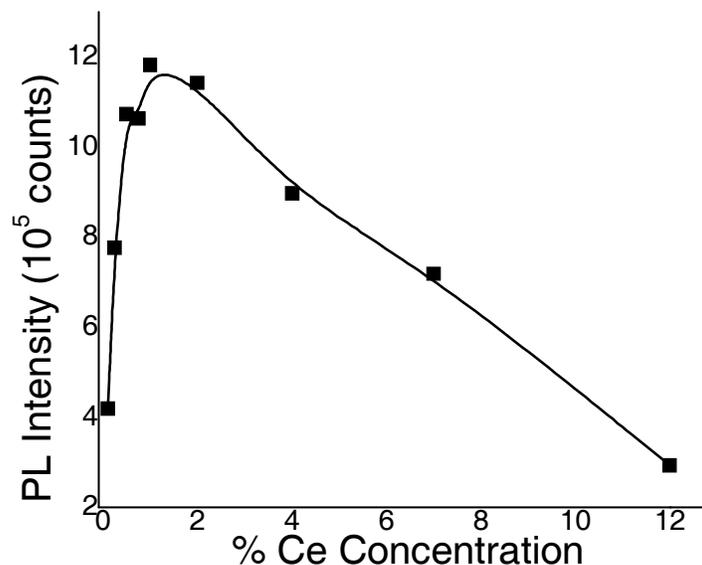
**Figure 2.** EPR spectra of bulk (measured at 6 K) and nanophosphor (measured at 9K) LSO: Ce. The  $g_z$  and  $g_y$  resonances of  $\text{Ce}^{3+}$  are labeled in the figure.

## Luminescence properties

The luminescence properties of bulk and nanophosphor LSO:Ce have been investigated using PLE, PL, and lifetime measurements. The PLE and PL spectra for nanophosphor LSO shown in Figure 3 display an increased Stokes shift as compared to data from the bulk sample. These shifts result in less self-absorption within the nanophosphor materials. The reduced self-absorption in the nanophosphor contributes to a PL intensity that is the same order of magnitude as the bulk. The reduced self-absorption also contributes to the greater-than-expected light yield found from other luminescence experiments.



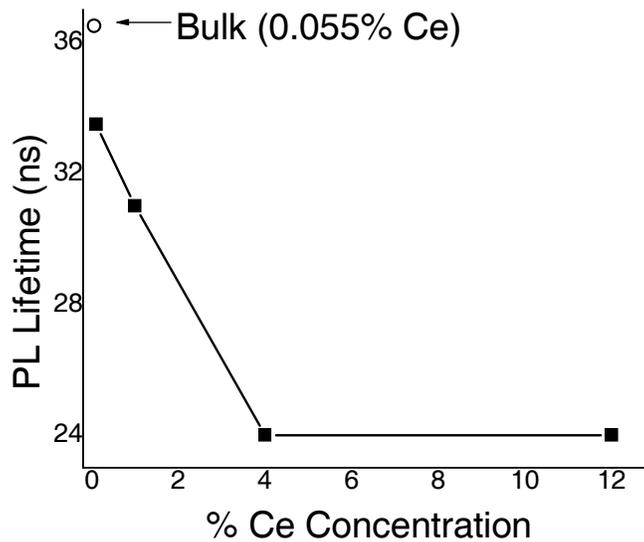
**Figure 3** Normalized PLE (left curve) and PL (right curve) for nanophosphor LSO (1 % Ce) and bulk LSO. Note that the nanophosphor displays a larger Stokes shift and less self-absorption than the bulk sample.



**Figure 4** PL quenching curve for nanophosphor LSO as a function of Ce concentration. Note that the curve peaks around 1 % Ce concentration.

The amount of Ce incorporated in the nanophosphor crystal structure also affects the luminescence properties. The PL quenching curve is shown in figure 4 and was obtained using the PL intensity at the maximum emission. The quenching curve peaks at around 1 at. %, which is a higher value than expected. This phenomenon is probably due to the reduced dimensionality of the nanophosphor. Quenching occurs due to energy transfer between Ce ions and the energy transfer is confined within the nanoparticle unlike the bulk sample where energy transfer is not as spatially confined. A higher Ce concentration is therefore required in the nanophosphors for quenching effects comparable to the bulk samples to be seen.

The PL lifetimes also show a continuous decrease with increasing Ce concentration (figure 5). This effect is probably due to the high surface-to-volume ratio of the nanophosphor LSO and its effect on the local electric field and hence effective index of refraction [8]. The luminescence of nanophosphor LSO then shows at least two effects directly related to reduced dimensionality.



**Figure 5** PL lifetime of nanophosphor LSO as a function of % Ce concentration. The lifetime of bulk LSO (0.055 % Ce) is also shown for comparison.

## CONCLUSIONS

We have successfully synthesized nanophosphor crystallites (approximately 30 nm) of LSO:Ce, and the nanophosphor samples display different structural and luminescence properties as compared to the bulk samples. The nanophosphors form a monoclinic structure with  $P2_1/c$  space group with seven and nine oxygen coordinated Lu as opposed to the  $C2/c$  space group with six and seven oxygen coordinated Lu for the bulk samples. EPR measurements revealed slight shifts in the  $g$  values and much broader resonances. The slight shifts in  $g$  values are indicative of changes in the local environment and may reflect the change in crystal structure. The broader resonances indicate increased crystal disorder, and this effect was quantified by studying the Orbach relationship for both bulk and nanophosphor LSO [7]. However, it is not clear if these structural changes are due to the reduced dimensionality of the crystals or the synthesis process.

Luminescence properties were also found to differ between nanophosphor and bulk LSO. Both the excitation and the emission maxima shift to longer wavelengths (increased Stokes shift) for the nanophosphor. These shifts result in reduced self-absorption for the nanophosphor and partially explain the increased light yield, resulting in surprisingly bright luminescence comparable to the bulk sample. An affect of reduced dimensionality is seen in the PL quenching curve where the nanophosphor PL is seen to quench at a higher Ce concentration than expected due to the limited range of energy transfer among Ce ions. The decrease in PL lifetimes with an increase in Ce concentration is also due to reduced dimensionality.

## ACKNOWLEDGMENTS

This research was supported by the DOE Office of Basic Energy Sciences (#07SCPE972).

## REFERENCES

1. H. Chander, "Development of nanophosphors-A review," *Mat. Sci. Eng. R* **49**, 113 (2005).
2. P. Dorenbos, "Light output and energy resolution of Ce<sup>3+</sup>-doped scintillators," *Nucl. Instrum. Meth. Phys. Res. A* **486**, 208 (2002).
3. J. Felsche, "The crystal chemistry of the rare-earth silicates," *Structure and Bonding* **13**, ed. J. Dunitz, P. Hemmerich, J. Ibers, C. Jorgensen, J. Neilands, R. Nyholm, D. Reiner, and R. Williams (Springer-Verlag, 1973), pp. 99-197.
4. J. J. Kingsley and K. C. Patil, *Mater. Lett.* **6**, 427-432 (1988).
5. B. D. Cullity, *Elements of X-ray Diffraction*, (Addison-Wesley, 1956) ch. 3.
6. R. E. Muenchausen, E. A. McKigney, L. G. Jacobsohn, M. W. Blair, B. L. Bennett, and D. W. Cooke, "Science and application of nanophosphors, *IEEE Trans. Nuc. Sci.* (in press).
7. L. Pidol, O. Guillot-Noël, A. Kahn-Harari, B. Viana, D. Pelenc, and D. Gourier, "EPR study of Ce<sup>3+</sup> ions in lutetium silicate scintillators Lu<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> and Lu<sub>2</sub>SiO<sub>5</sub>," *J. Phys. Chem. Solids* **67**, 643 (2006).
8. D. W. Cooke, J. K. Lee, B. L. Bennett, J. R. Groves, L. G. Jacobsohn, E. A. McKigney, R. E., Muenchausen, M. Nastasi, K. E. Sickafus, M. Tang, and J. Valdez, "Luminescent properties and reduced dimensional behavior of hydrothermally prepared Y<sub>2</sub>SiO<sub>5</sub>:Ce nanophosphors." *Appl. Phys. Lett.* **88**, 103108 (2006).