Order and Disorder Effects in Nano- ZrO$_2$ Investigated by

Micro- Raman and Spectrally and Temporarily Resolved Photoluminescence

Carmen Tiseanu $^a$, Bogdan Cojocaru $^b$, Vasile I. Parvulescu $^b$, Margarita Sanchez Dominguez $^{a,d}$, Philipp A. Primus $^e$, Magali Boutonnet $^f$

$^a$ National Institute for Laser, Plasma and Radiation Physics, P.O.Box MG-36, RO 76900, Bucharest-Magurele, Romania; $^b$ University of Bucharest, Department of Chemical Technology and Catalysis 4 – 12 Regina Elisabeta Bvd., Bucharest 030016, Romania; $^c$ Instituto de Química Avanzada de Cataluña, Consejo Superior de Investigaciones Científicas (IQAC-CSIC), CIBER en Biotecnología, Biomateriales y Nanomedicina (CIBER BBN), Jordi Girona 18-26, 08034 Barcelona, SPAIN; $^d$ Centro de Investigación en Materiales Avanzados, S. C. (CIMAV), Unidad Monterrey; GENES-Group of Embedded Nanomaterials for Energy Scavenging, Alianza Norte 202, Parque de Investigación e Innovación Tecnológica, 66600 Apodaca, Nuevo León, MEXICO; $^e$ Institute of Chemistry, Physical Chemistry, University of Potsdam, Karl-Liebknecht-Str. 24-25, 14476 Potsdam-Golm, Germany; $^f$ Kungliga Tekniska Högskolan (KTH), School of Chemistry, Div. of Chemical Technology, Teknikringen 42, SE-10044, Stockholm, Sweden.

Supplemental Information
Figure S1. STEM images of calcined pure zirconia samples (ZE) synthesized in o/w microemulsions. ZE-500: (a) bright field and (b) dark field. ZE-1000: (c) bright field and (d) dark field.

Figure S2. STEM images of calcined europium-doped zirconia (ZEB) samples synthesized in o/w microemulsions. 500/ZEB-500: (a) bright field and (b) dark field. 1000/ZEB-1000: (c) bright field and (d) dark field.
Textural characterization. Pure zirconia, ie ZE sample, after calcining at 350 °C exhibited a surface area of 253 m²g⁻¹ with an average pore size of 26.9 Å. Further calcinations at 500 and 1000 °C led to a strong decrease of the surface areas to 24 and 4 m²g⁻¹, respectively. Doping with europium (ZEB sample) was not generating important differences in the texture of these materials. Thus, the surface areas of the samples calcined at 350, 500 and 1000 °C corresponded to 248, 31 and 5 m²g⁻¹, that are in fact very similar.

**Figure S3.** TGA and DTA curves for pure (ZE, a) and europium doped zirconia (ZEB, b) samples.

**Figure S4.** PL excitation spectra of europium in ZEB-500 and ZEB-1000.
Figure S5. (a) Steady state PL spectra of ZEB-500 and ZEB-1000; (b) Time-resolved PL spectra of ZEB-1000 upon excitation at 240 nm.

Figure S6. From Left to Right: PL decays of ZEB-750, ZEB-900 and ZEB-1000. Emission and excitation wavelengths are indicated on the Figures.

Figure S7. Evolution with delay time of the asymmetry ratio, R, of ZEB-500 and ZEB-1000.