

Local structure and nanoscale homogeneity of CeO₂ - ZrO₂: Differences and similarities to parent oxides revealed by luminescence with temporal and spectral resolution

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I. *In situ* XRD patterns and Raman spectra measured in the temperature range of 50 - 1000 °C and 50 - 550 °C, respectively.

The *in situ* X-ray diffraction (XRD) patterns (Figure S1, temperature range $T = 50$ - 1000 °C) show three main reflections (111), (200) and (220) characteristic of CeO_2 cubic phase with fluorite structure. The lines gain intensity with increasing calcination temperature whereas the widths are narrowed as a result of better crystallization and crystallite size increase. No phase transformation is visible.

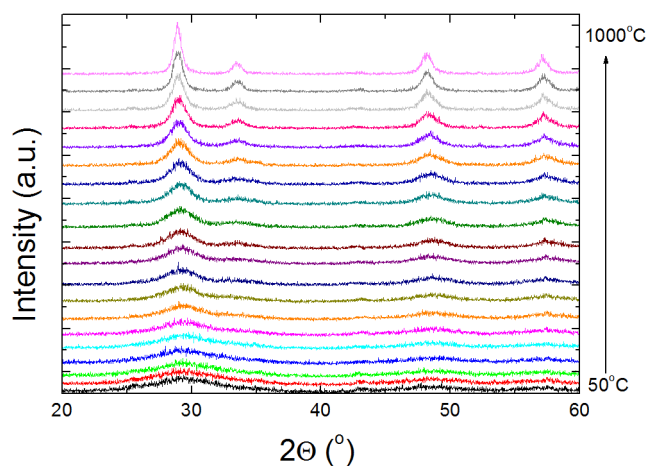


Figure S1. *In situ* XRD patterns of Eu^{3+} doped CeO_2 - ZrO_2 .

II. HRTEM analysis of Eu^{3+} - CeO_2 - ZrO_2 calcined at 750 °C (CZE- 750)

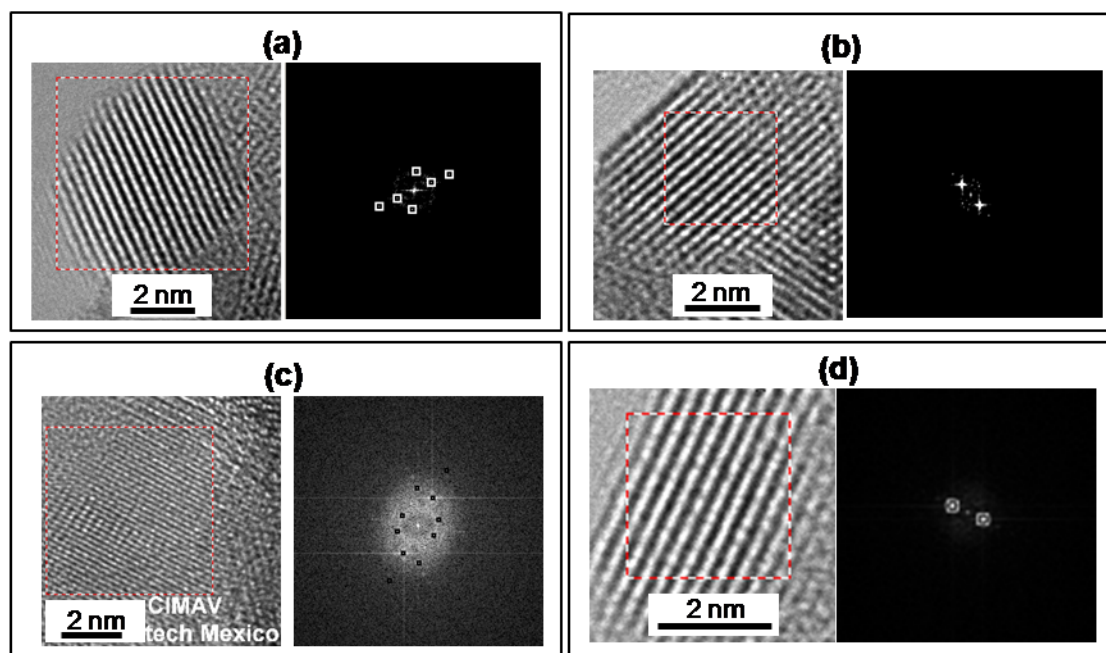


Figure S2. HRTEM images and their corresponding FFT analysis of CZE-750. d-spacings: (a) and (b) 3.1 Å and 1.55 Å (consistent with hkl 311 and 444 of cubic $\text{Ce}_2\text{Zr}_2\text{O}_7$, card number 00-052-1104); (c) 3.1 Å, 2.7 Å, 1.88 Å, 1.58 Å, and 1.55 Å (consistent with hkl 111, 200, 220, 311 and 222 of cubic $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$, card number 00-038-1439); (d) 3.1 and 3.2 Å (consistent with hkl 311 of cubic $\text{Ce}_2\text{Zr}_2\text{O}_7$, card number 00-052-1104)

III. Luminescence properties of Eu^{3+} - CeO_2 - ZrO_2 calcined at 750 °C (CZE- 750)

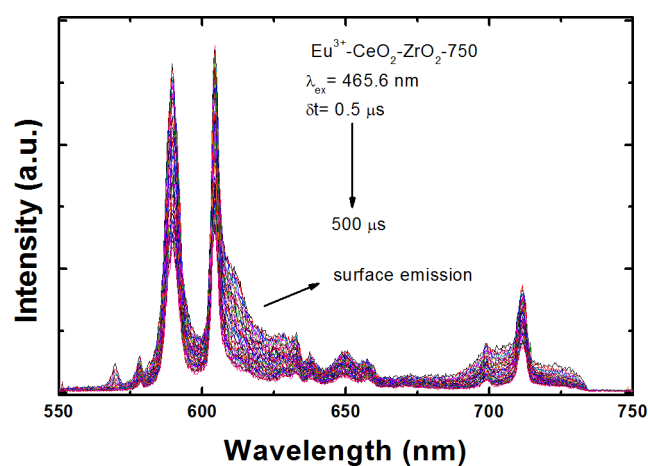


Figure S3. Temporal evolution of the peak normalized emission spectra of Eu^{3+} - CeO_2 - ZrO_2 - 750. The spectra evidence for the presence of a broad, surface type emission which is quenched at delays greater than 500 μs.

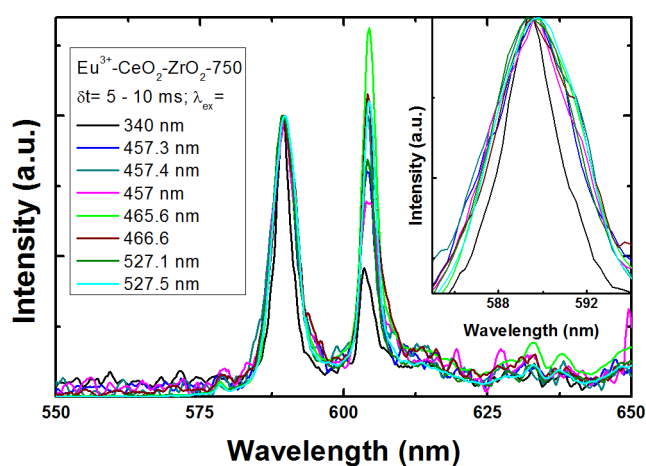


Figure S4. Dependency of the asymmetry ratio of Eu^{3+} doped $\text{CeO}_2\text{-ZrO}_2 - 750$ on the excitation wavelength. Inset shows the dependency of the emission peak at 590 nm and broadness (FWHM corresponding to 590 nm emission) on the excitation wavelength. The FWHM varies from ~ 2.8 nm (excitation wavelength at 340 nm) to ~ 4.3 nm (excitation wavelength at 465.6 nm)

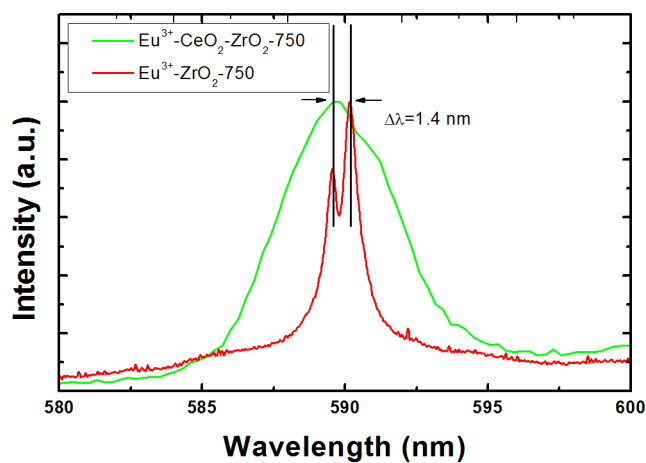


Figure S5. Figure S7. (a) Comparison between high resolution emission spectra around 590 nm of Eu^{3+} doped $\text{CeO}_2\text{-ZrO}_2$ and ZrO_2 calcined at 750 °C.

IV. HRTEM analysis of Eu^{3+} - CeO_2 - ZrO_2 calcined at 1000 °C (CZE- 1000)

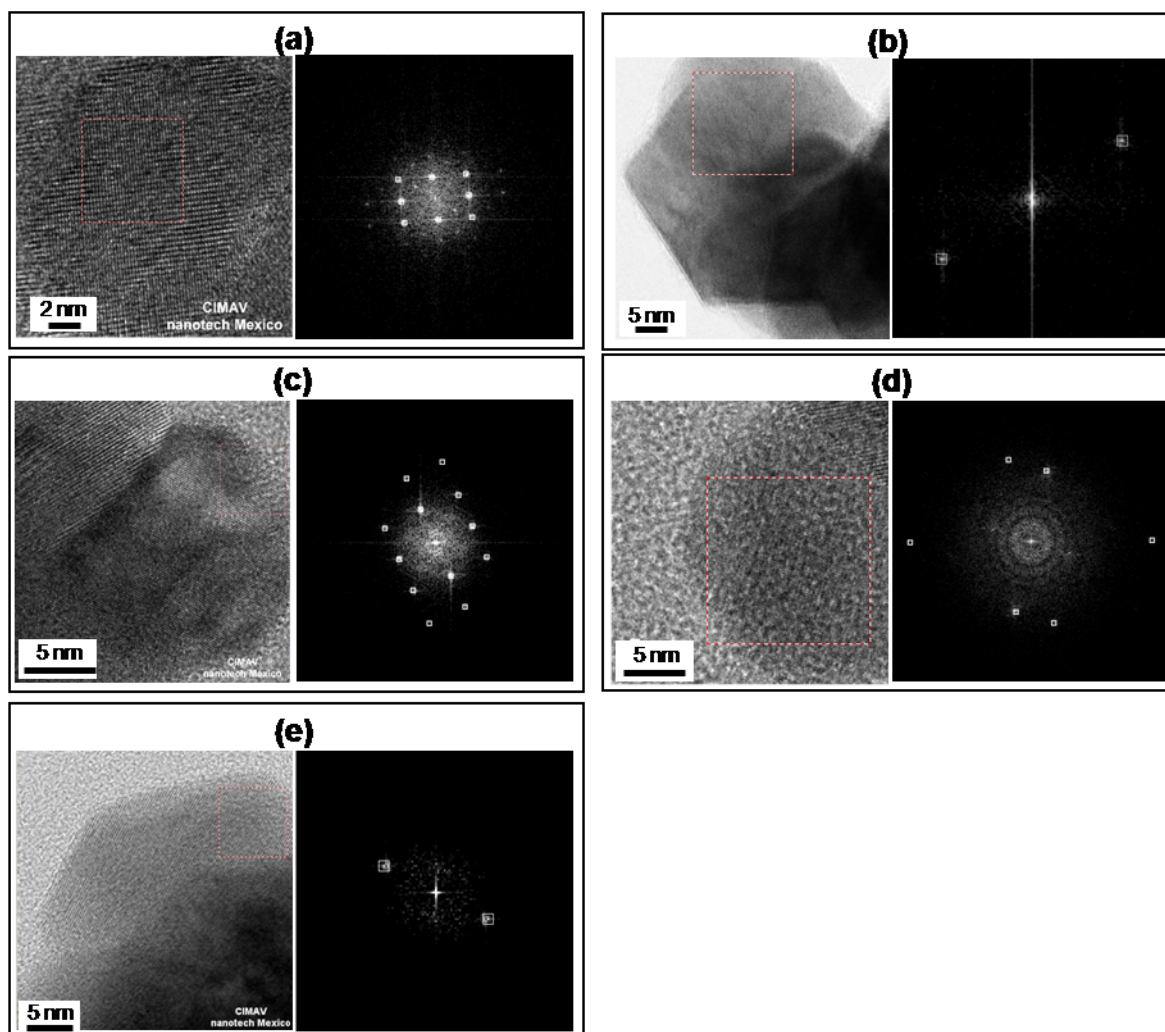


Figure S6. HRTEM images and their corresponding FFT analysis of CZE-1000. d-spacings (d(Å)): (a) 3.08 Å, 1.9 Å, 1.6 Å, and 1.55 Å (consistent with hkl 111, 220, 311 and 222 of cubic $\text{Zr}_{0.4}\text{Ce}_{0.6}\text{O}_2$, card number 00-038-1439); (b) 3.15 Å (consistent with hkl 311 of cubic $\text{Ce}_2\text{Zr}_2\text{O}_7$, card number 00-052-1104); (c) 1.24 Å, 1.22 Å, 1.61 Å, 1.83 Å, 0.93 Å and 0.81 Å, (consistent with hkl 104, 213, 103, 200, 224 and 420 of tetragonal $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$, card number 00-055-0997). (d) 1.62 Å, 1.11 Å and 1.91 Å (consistent with hkl 103, 204, and 112 of tetragonal $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$, card number 00-055-0997); (e) 2.99 Å and 2.93 Å (consistent with hkl 101 of tetragonal $\text{Zr}_{0.5}\text{Ce}_{0.5}\text{O}_2$, card number 00-038-1436);

V. Raman spectra of Eu^{3+} - CeO_2 - ZrO_2 calcined at 1000 °C (CZE - 1000)

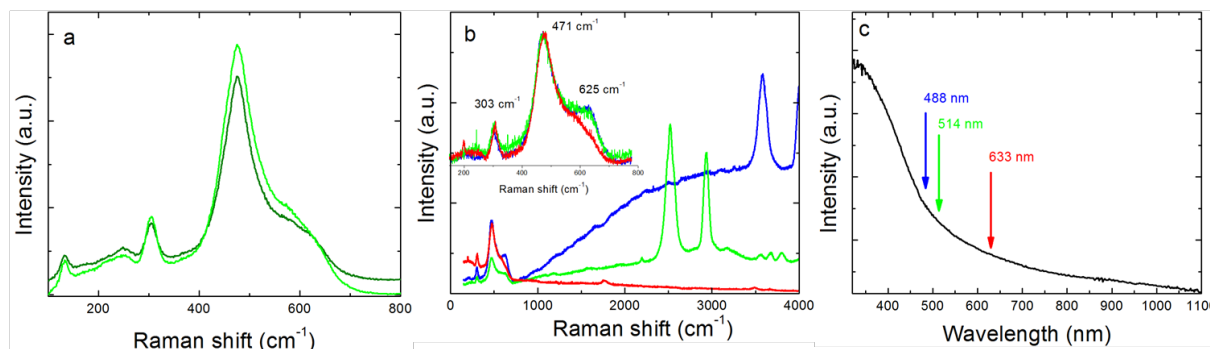


Figure S7. (a) Raman spectra corresponding to different laser spot positions within Eu^{3+} - CeO_2 - ZrO_2 calcined at 1000 °C; (b) Raman spectra of CeO_2 - ZrO_2 calcined at 1000 °C measured with at three laser excitation wavelengths of 488, 514 and 633 nm; (c) Dr-UV/Vis spectrum Eu^{3+} - CeO_2 - ZrO_2 calcined at 1000 °C.

VI. Luminescence properties of Eu^{3+} - CeO_2 - ZrO_2 - 1000

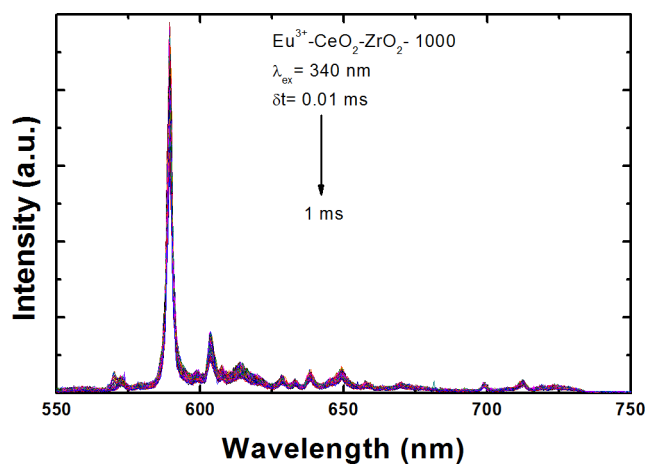


Figure S8. Temporal evolution of the peak normalized emission spectra of Eu^{3+} - Ce- enriched CeO_2 - ZrO_2 - 1000 under excitation at 340 nm.

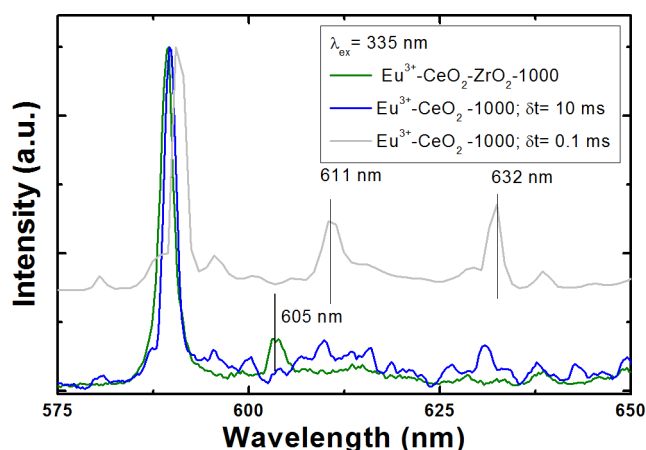


Figure S9 (a, b) Comparison between delayed emission spectra of Eu^{3+} doped $\text{CeO}_2\text{-ZrO}_2$ and CeO_2 calcined at 1000 °C) under excitation at 335. The fingerprint emission of Eu^{3+} in cubic sites of CeO_2 is obtained by use of a delay set at 10 ms (spectrum with blue line) and gate width of 1 ms. The characteristic, shorter -lived emission of Eu^{3+} center in CeO_2 (spectrum with grey lines) is obtained by use of a delay set at 0.1 ms (spectrum with blue line) and gate width of 0.3 ms. The emission spectrum displays typical emission lines around 611 and 632 nm which are no longer observed with $\text{Eu}^{3+}\text{-CeO}_2\text{-ZrO}_2\text{-1000}$ (spectrum with green line).

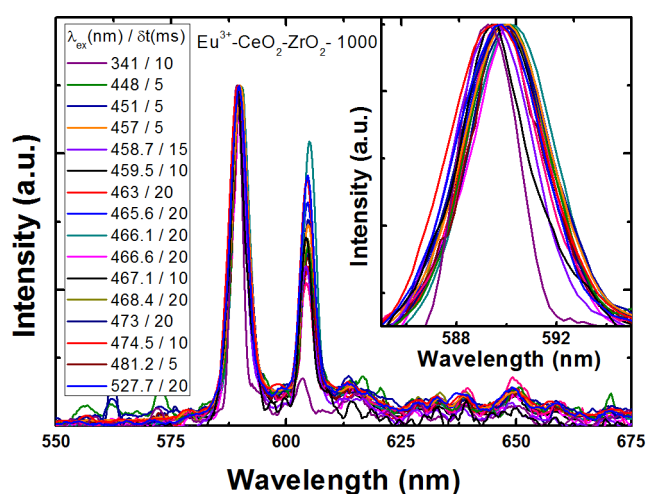


Figure S10. Dependency of the asymmetry ratio of Eu^{3+} doped $\text{CeO}_2\text{-ZrO}_2\text{-1000}$ on the excitation wavelength. Inset shows the dependency of the emission peak at 590 nm and broadness (FWHM corresponding to 590 nm emission) on the excitation wavelength. The FWHM varies from ~ 1.8 nm (excitation wavelength at 340 nm) to ~ 3.5 nm (excitation wavelength at 465.6 nm).

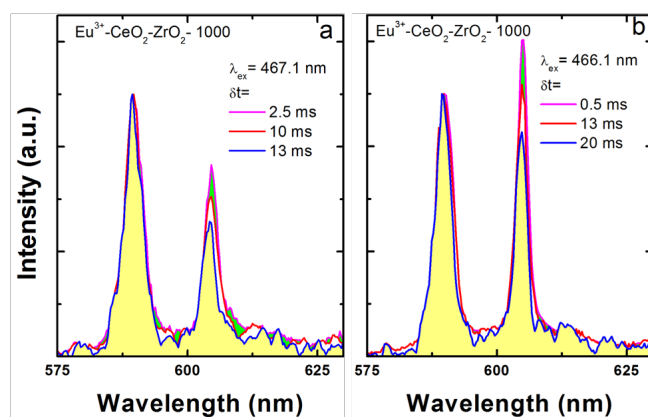


Figure S11. Temporal evolution of the peak normalized emission spectra of Eu^{3+} - CeO_2 - ZrO_2 - 1000 under excitation at two different wavelengths which shows the strong emission superposition from Eu^{3+} located in slightly different tetragonal like oxygen environments.