

Structural, down - and phase selective up - conversion emission properties of mixed valent Pr doped into oxides with tetravalent cations

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Supporting Info

X-ray Photoelectron Spectroscopy (XPS). Figure S1 presents the X-ray photoelectron spectra electron distribution curves for the Ce 3d levels in Pr-doped ceria samples. The 3d level consists of a spin-orbit split doublet ($3d_{5/2}$ and $3d_{3/2}$), but the Ce 3d spectrum is further complicated by the existence of shake-up and shake-down satellites. In fact, it was recently demonstrated that Ce 3d in CeO_2 may be reasonably simulated with six components, corresponding to Ce^{4+} (parent, shake-up and shake-down) and Ce^{3+} (same three components).¹ We note also that the general aspect of the Ce 3d spectra is quite different from the published spectra to date.² This may be attributed to the recording of the spectra from Fig. S2 by using monochromatic Al $K_{\alpha 1}$ radiation. This implies that the excitation line has no satellites, as in the case of unmonochromatized Mg K_{α} , used in Refs. 1- 3. Also, the spectra are affected by the presence of a Ce Auger MNN line (885 eV apparent binding energy), represented as a singlet in Figure S1. All six components discussed previously are simulated as Voigt doublets, by using the formula from Ref. 4. The (4+) parent $3d_{5/2}$ binding energies are located at 889.0-890.3 eV, the (3+) parent lines are located at 888.5-888.7 eV. The shake-up satellites are shifted by ~ 7 -9 eV towards higher binding energies, whereas the shake-down satellites are shifted by 5-7 eV towards lower binding energies. The parent doublets for (4+) and (3+) are represented by full lines (blue, respectively green) in Fig. S2, whereas the satellites are represented by dashed lines. As it was commented earlier¹ the satellites are sometimes of larger integral intensity than the parent lines and this makes it difficult an immediate interpretation of the Ce 3d spectrum. A similar difficulty was acknowledged by other authors.²⁻³ However, based on the 'deconvolution' of the spectra one may extract the overall integral intensity of the line corresponding to each ionization state (3+) and (4+) together with the satellites. Hence, the ratio between Ce^{3+} and Ce^{4+} will be given by:

$$\frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]} = \frac{A_p(\text{Ce}^{3+}) + A_{s-u}(\text{Ce}^{3+}) + A_{s-d}(\text{Ce}^{3+})}{A_p(\text{Ce}^{4+}) + A_{s-u}(\text{Ce}^{4+}) + A_{s-d}(\text{Ce}^{4+})} \quad (\text{S1})$$

where A_p , A_{s-u} and A_{s-d} are integral amplitudes of the doublets corresponding to the parent, shake-up and shake-down lines, respectively. Applying the above formula, one obtains the $[\text{Ce}^{3+}] / [\text{Ce}^{4+}]$ ratio as 0.297 for 1 % PrC-500, decreasing to 0.187 for PrC- 1000.

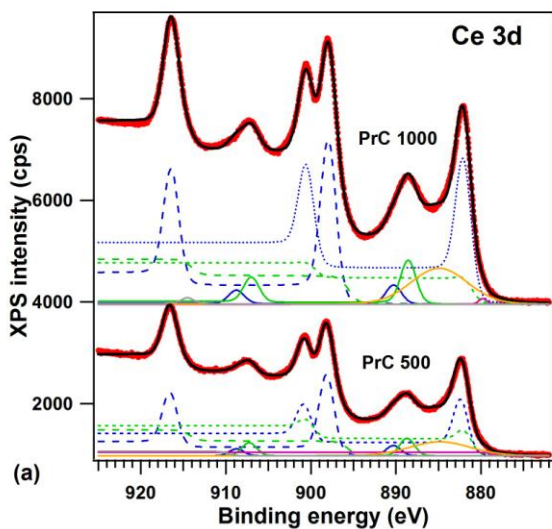


Fig. S1. Ce 3d electron distribution curves (EDCs) for Pr-doped CeO₂ calcined at 500 and 1000 °C. Red dots are experimental data, black curves are fits and the other curves are individual components (see text for details).

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- [4]. C. M. Teodorescu, J. M. Esteva, R. C. Karnatak and A. El Afif, *Nucl. Instrum. Meth. Phys. Res. A*, 1994, **345**, 141.

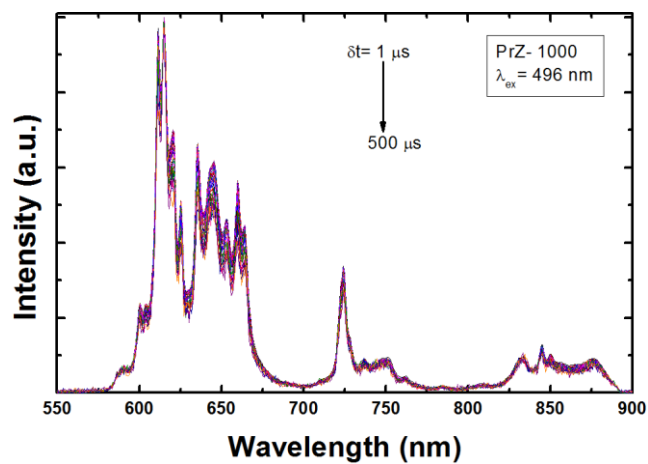


Fig. S2. Time-resolved PL spectra of PrZ-1000 excited at 496 nm.

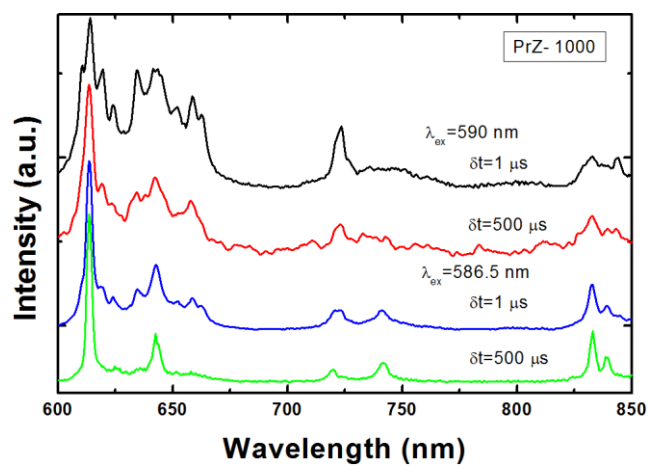


Fig. S3. Time-resolved PL spectra of PrZ-1000 excited into 1D_2 levels.

Table S1. Energy levels corresponding to 3P_0 and 1D_2 states of Pr^{3+} in the monoclinic and tetragonal sites of ZrO_2 (calcined at 1000 C, PrZ-1000) together with measurements details (spectral resolution=0.88 nm).

Electronic level/site	Experimental values	Measurement details
3P_0 (tetragonal sites)	488.5, 502 nm ($^3P_0 - ^3H_4$) 561 nm ($^3P_0 - ^3H_5$)	λ_{ex} = 210, 300 nm gate width = 0.05 μ s δt = 0.05- 0.5 μ s T= 80 and 300K
3P_0 (monoclinic sites)	496 nm ($^3P_0 - ^3H_4$)	λ_{ex} = 453,2 nm gate width = 0.05 μ s δt = 0.05- 0.5 μ s T= 80 and 300K
1D_2 (tetragonal sites)	586.5, 614, 643.2 nm ($^1D_2 - ^3H_4$) 720, 742 nm ($^1D_2 - ^3H_5$) 833, 839 nm ($^1D_2 - ^3H_6$)	λ_{ex} =300, 458.7, 488.5, 586.5, nm gate width= 30-100 μ s δt = 1-2500 μ s T= 80 and 300K
1D_2 (monoclinic sites)	590, 610*, 612.5*, 614.3*, 615.5*, 619, 623, 628, 642.2, 643.5, 651.5, 657.5, 661.5 nm ($^1D_2 - ^3H_4$) 722.5, 726, 734.8, 740.2, 747, 749.2, 759.3 nm ($^1D_2 - ^3H_5$) 832, 838, 843, 848.5 ($^1D_2 - ^3H_6$)	λ_{ex} = 345, 457.9, 453.2, 452.3, 496, 590, 959 nm gate= 30-100 μ s δt = 1-2500 μ s T= 80 and 300K

* - hot bands

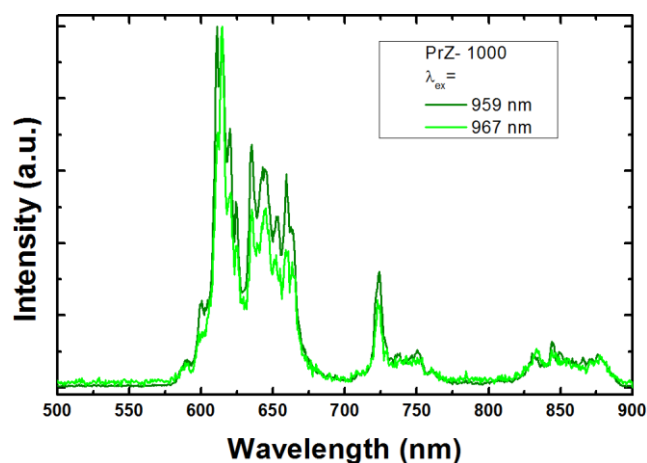


Fig. S4 (in relation to **Fig 6b**). Comparison between the peak normalized (at 619 nm) UPC emission spectra of PrZ-1000 excited at 959 and 967 nm. The occurrence of a tetragonal emission excited at 967 nm was inferred only from slight spectral differences of the peak-normalized spectra excited at 959 and 967 nm. The delay after the laser pulse was set at 1 μ s.