Table S1. Gauss+Lorentz fitting parameters of the Pd3d doublet photoelectron line. The spin-orbit splitting and intensity ratio was set to 5.30±0.02 eV and 0.66±0.01. Lorentzian contribution was set to 0.2 due to dielectric character of the analyzed samples.

Specimen	Doublet 1			Doublet 1			Doublet 2			Doublet 3		
	Rel. int.	BE	FWHM	Rel. int.	BE	FWHM	Rel. int.	BE	FWHM	Rel. int.	BE	FWHM
CP-450	-	-	-	0.14	336.1	1.86	-	-	-	0.86	338.0	1.86
CP-600	-	-	-	0.28	336.1	1.95	-	-	-	0.72	338.0	1.95
CP-1000	0.21	335.3	1.95	-	-	-	0.48	337.0	1.95	0.31	338.1	1.95
IWI-450	-	-	-	0.11	335.9	1.90	0.48	337.0	1.90	0.41	338.1	1.88
IWI-600	-	-	-	0.13	335.9	1.91	0.40	337.0	1.90	0.47	338.1	1.89
IWI-1000	0.51	335.1	2.00				0.24	336.9	2.00	0.25	338.1	1.95

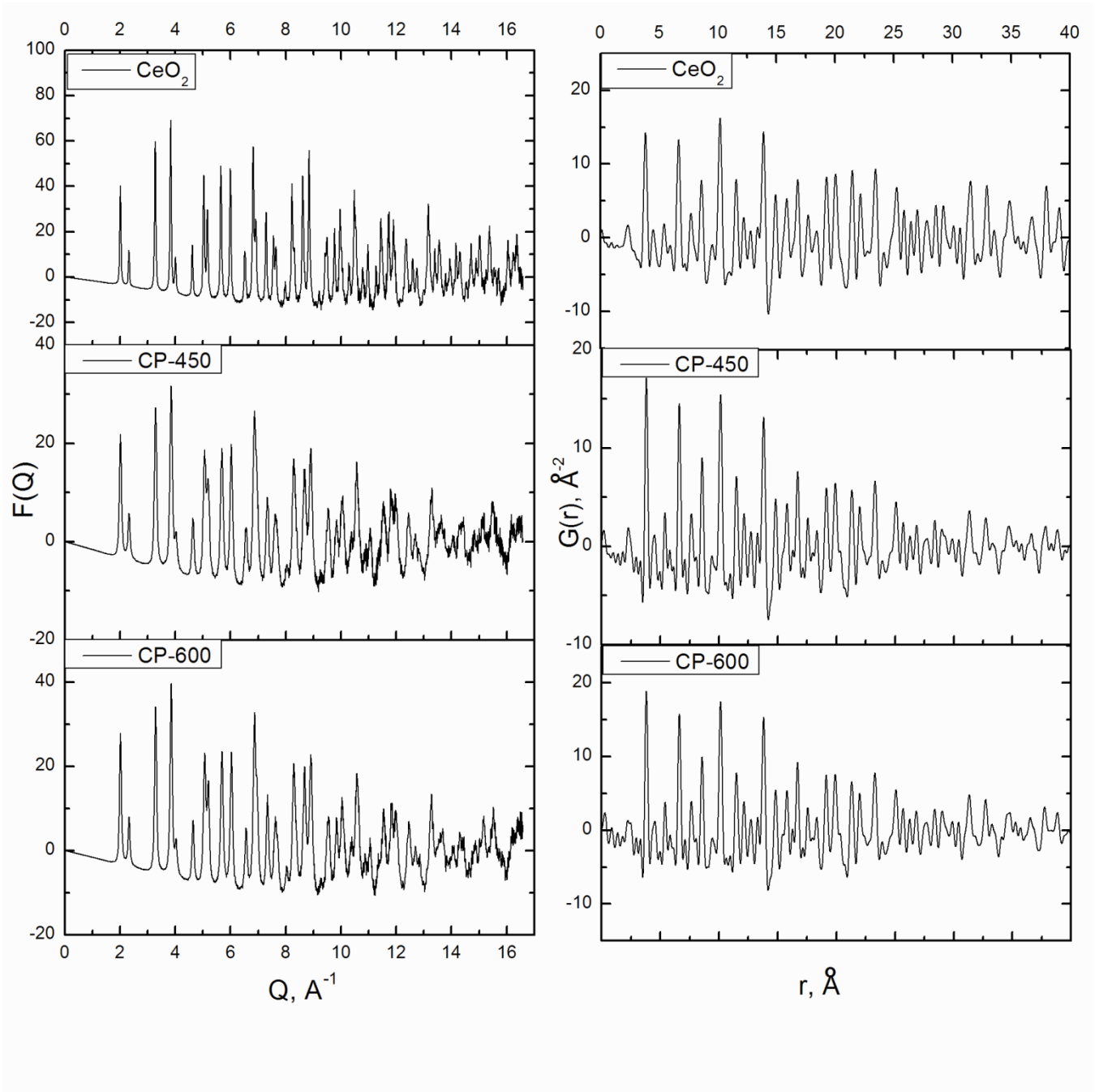


Fig S2. Left panel: Q^2 weighted experimental scattering curves obtained for the CP-450 and CP-600 samples compared with that one for clean ceria CeO_2. Right panel: experimental PDF curves obtained for corresponded samples

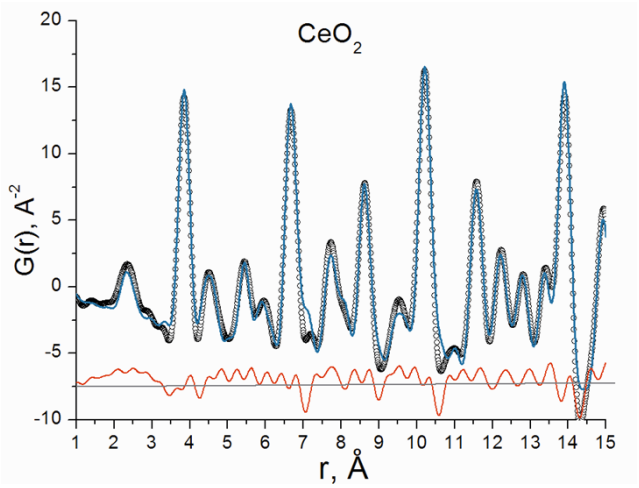


Fig S3. Refinement of the clean ceria structure within fluorite model with 10% anion vacancies (model II without substituting of cerium by palladium)

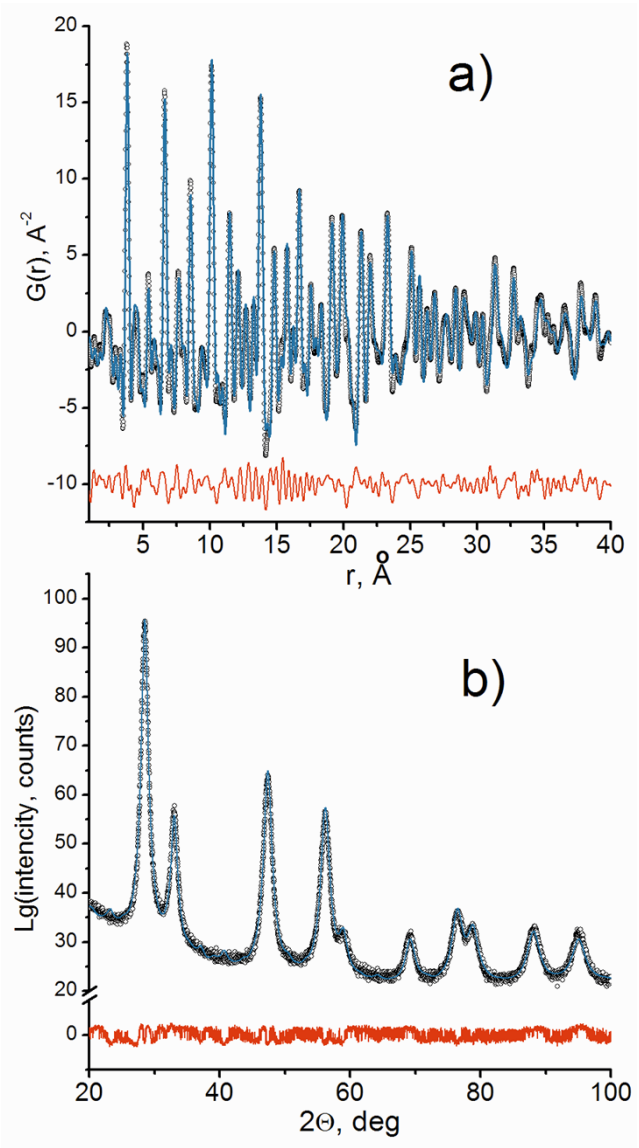


Fig.S4. Refinement of the solid solution structure within model V for a wide range of interatomic distances (1-40 Å) with respect to the X-ray PDF for CP-600 sample.

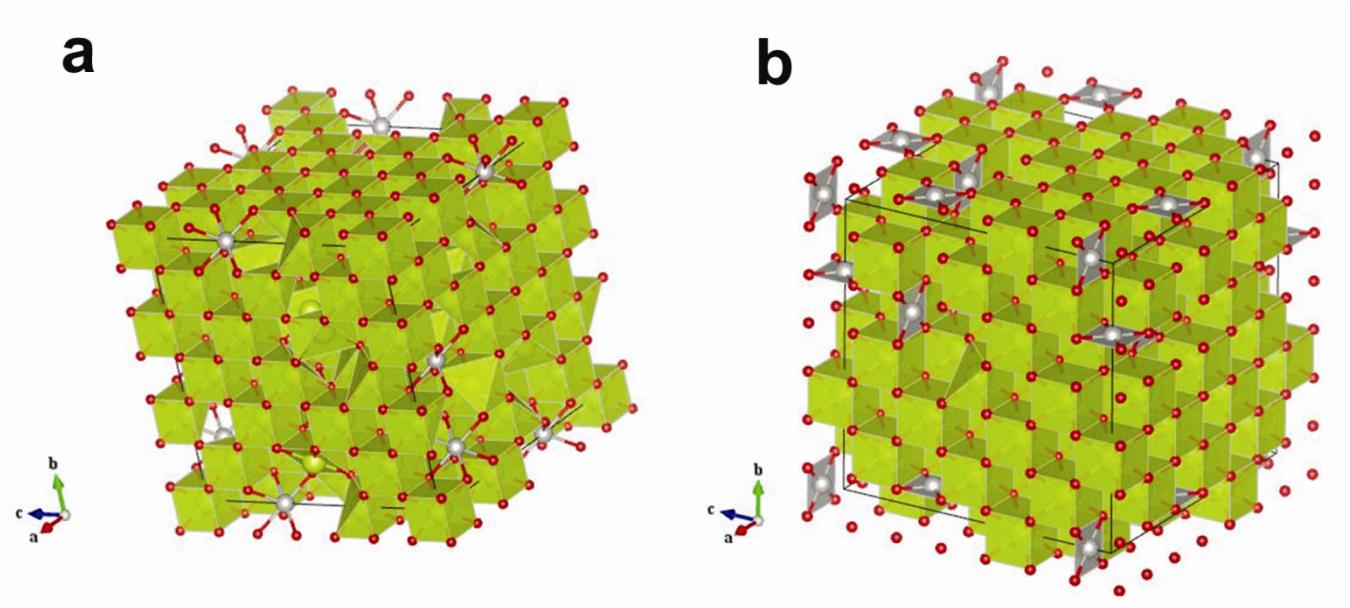
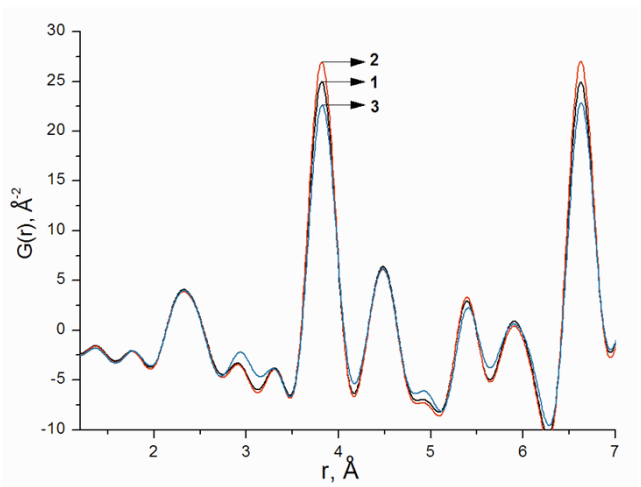


Fig. S5. Schematic representations of the solid solution models built from 3x3x3 units of fluorite structure. a) Model I – Pd in a Ce position and 10% anion vacancies are introduced. b) Model VI – Pd substituting of Ce shifted from Ce position to O_8 cube face and 10% anion vacancies are introduced. Direction of Pd ion shift is randomly selected from six possible (100) family directions. CeO_8 polyhedrons a represented by dark-yellow, Pd ions are grey spheres, while oxygen inns are red spheres.



FigS6. Theoretical PDF curves for Q_{max}=16 Å^{-1} and for main considered models: 1 – model I: $Pd^{4+}_xCe^{4+}_{1-x}O_2$, Pd in Ce position; 2 – model II: $Pd^{2+}_xCe^{4+}_{1-x-y}Ce^{3+}_yO_{2-x-y/2}$, Pd in Ce position and 20% oxygen vacancies are introduced; 3 – Model V: $Pd^{2+}_xCe^{3+}_yCe^{4+}_{1-x-y}O_{2-x-y/2}\bullet xH_2O$ based on DFT geometry with Pd displacement from Ce position and water molecule introduced.