S.1 Data correction at ID11

From the analysis of the G(*r*) curves, we observed that the *r*-position of the G(*r*) peaks were larger than expected, this effect amplifying with increasing *r*. In order to correct for this aberration, we collected a XRPD pattern at the ID31 beamline of the ESRF [27] at an incident wavelength 0.31912 Å at *T*=100°C on $Ce_{0.75}La_{0.25}O_{1.875}$. Due to its very narrow instrumental resolution function, at ID31 it is possible to determine the cell parameter with very high accuracy. Once known the cell parameter, a G(*r*) was calculated based on the fluorite structural model and using proper thermal parameters to simulate the experimental G(*r*) curves.

Based on our experience on doped ceria materials, from ~10 Å on, the G(*r*) can be correctly described by the fluorite structure. For this reason the calculated PDF can be used a reference. Note that peak positions deriving from the average structure cannot be used directly as reference, since both Ce-Ce and Ce-O pairs contribute to some G(*r*) peaks.

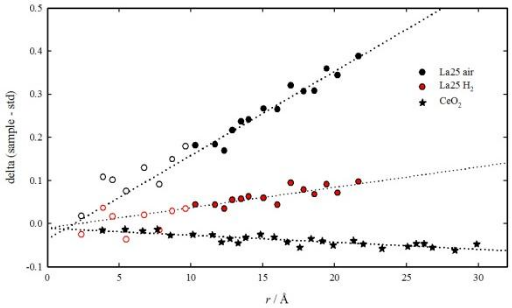

Fig. S.1. *r*-position mismatch between observed and calculated peak positions. Black circles: La25air, red circles: La25H2, stars: ceria. Empty circles are points not considered in the linear regression.

In Fig. S.1 the mismatch between the peak *r*-positions observed in the collected PDF and those calculated is plotted as a function of *r*. The data in the 10 < *r* < 25 Å range were fitted with a linear regression.

The *r* position in G(*r*) was then corrected with the equation

$$r_N = r_E - m r_E - q \qquad \text{(SI1)}$$

where r_N stands for normalized *r* peak position, r_E for observed peak position, *m* is the slope of the regression line and *q* its intercept. This correction is based on the assumption that no reduction occurs at *T*=100°C, that is La25air and La25H2 exhibit the same structure.

It should be noted that this correction does not modify the temperature evolution of a peak, but rather it is fundamental in order to compare sample distances and for fitting a structural model over a wide *r* range. This is the case, for example, of the determination of instrumental related parameters (e.g. Q_{damp} and Q_{broad} in PDFGUI), which require the refinement of a reference structure over a wide *r*-range.

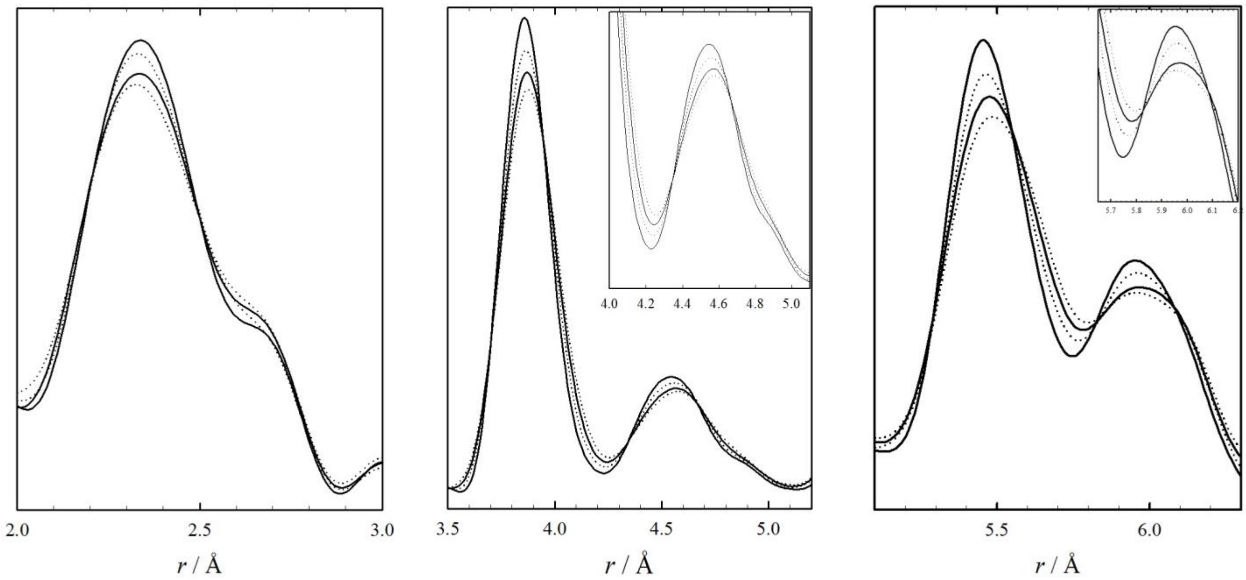

Fig. S.2 G(*r*)curves for CeO_2 related to the 1st M-O pair (*left*), 1st M-M and 2nd M-O pairs (*middle*) and 2nd M-M and 3rd M-O pairs (*right*) recorded every 100°C from 450 to 750 °C. The peak amplitude decrease with temperature. The pairs are referred to an undistorted fluorite structure. It is clear that neither peak anisotropies or splits are induced by increasing temperature.

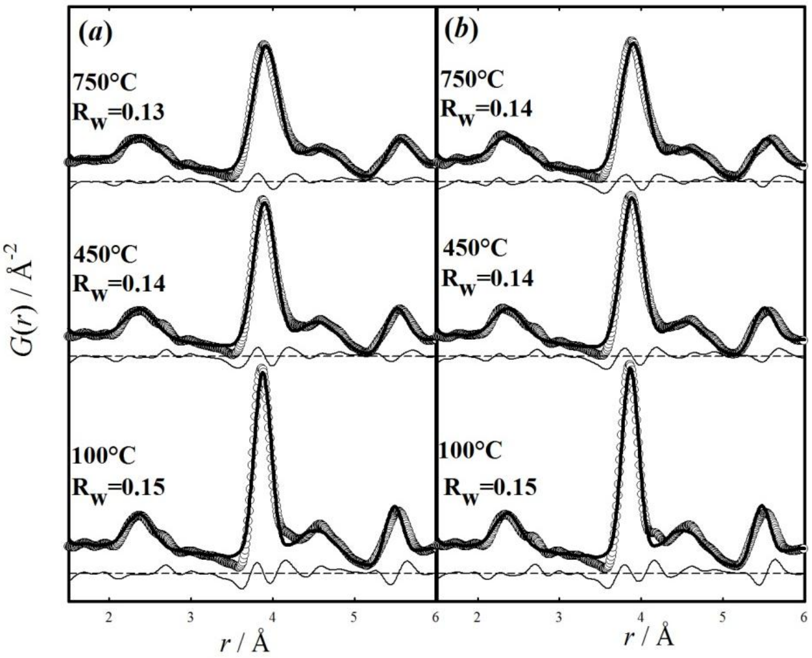

Fig. S.3 PDF refinements at *T*=100, 450 and 750°C on La25air (*a*) and La25H2 (*b*) performed by means of the *fluorite* model. At low temperature the model is clearly wrong, whilst by increasing temperature the peak broadening improves the fit quality. The fluorite model, though, is still wrong even at high temperature, because, as discussed in the main text (see Fig. 7), a G(*r*) contribution, hidden by an excessive peak broadening, is still present.

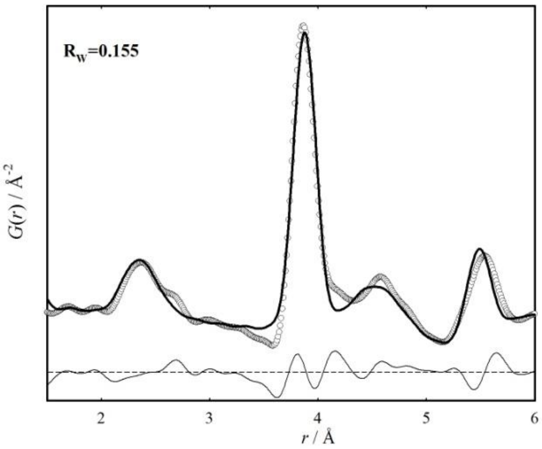

Fig. S.4 PDF refinements at T=70°C performed by means of the *cluster* model described in the text.

The fit is pretty similar to the one obtained with a fluorite structural model and it does not account for the G(r) contribution at ~4 Å, deemed as a fingerprint of structural disorder.

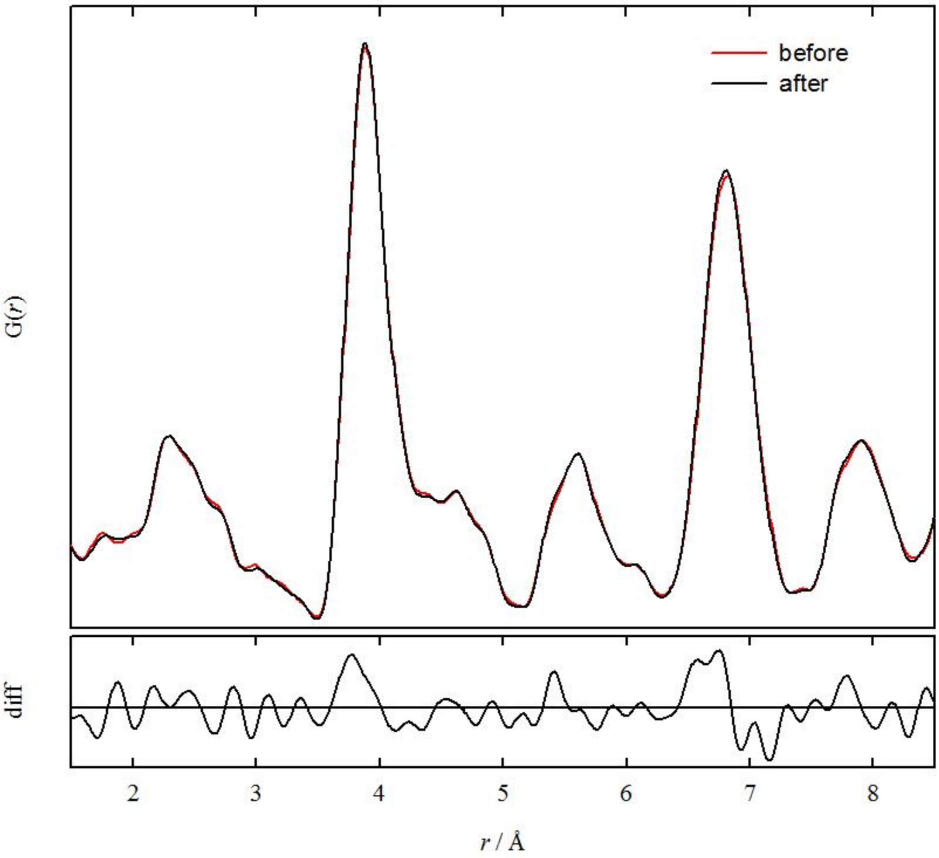

Fig S.5

red solid line: La25H2 once reached T=750°C.
black solid line La25H2 after 3 hours at T=750°C.
The curves look almost superimposed.

Below: magnified (x4) difference curve. Positive not random difference observed before each of the M-M distances (~3.7, ~5.4, ~6.6 and ~7.9 Å).