To correlate the oxidation state modification of the elements with annealing, XPS studies were carried out using Al Kα source. The XPS spectra were charge corrected with respect to C 1s peak. The high resolution Ce 3d spectra is shown in Figure S1 for EFCR and EFC9 along with the deconvoluted peaks. The multiple peaks arise after deconvolution due to the presence of cerium in +3 and +4 oxidation states as well as multiple d-splitting.

**Figure S1:** XPS spectra of Ce 3d for EFCR and EFC9
The high resolution Ce 3d spectrum showed a significant change in the valley of V’ with respect to EFCR and EFC9 which denotes the change in Ce$^{3+}$ concentration. The increase in the intensity of V’ in EFCR shows the presence of higher Ce$^{3+}$ concentration in comparison to EFC9. The quantitative calculation of Ce$^{3+}$ concentration from XPS was done as per our previous report. The calculated concentration for EFCR was found to be 29% while that of EFC9 showed 9%. Generation of Ce$^{3+}$ results in the formation of oxygen vacancy (to compensate the charges in ceria lattice). Hence higher Ce$^{3+}$ concentration leads to more oxygen vacancy concentration. On annealing (EFC9), the observed reduction in Ce$^{3+}$ concentration indicates the oxidation of Ce$^{3+}$ to Ce$^{4+}$ and possible segregation of Fe$^{3+}$ from the host lattice. Thus XPS and Raman spectroscopic result complements the observed trend and oxygen vacancy concentration.

The changes in the oxidation state of iron was analysed from Fe 2p XPS spectra of for EFCR and EFC9. The two main peaks of Fe 2$p_{3/2}$ and 2$p_{1/2}$ were clearly observed at ~709 and 725 eV, respectively, for both EFCR and EFC9 which can be attributed to the presence of iron in Fe$^{3+}$ oxidation state. However no significant shift in peak position in Fe 2$p$ level indicates the absence of any changes in oxidation state. A similar observation was made by Perez-Alonso et al., in Fe 2$p$ region for iron doped ceria. Formation of α- and γ-$\text{Fe}_2\text{O}_3$ could not be identified in XPS for EFC9 due to identical core level spectra for Fe 2$p$. 
The oxygen (O1s) peak was analysed in order to study the local environment changes around the oxygen for the as prepared (EFCR) and annealed (EFC9) samples. The Gaussian-Lorentzian function was used to deconvolute the O1s peak and it showed four peaks differing in binding energy. Four deconvoluted peaks codes as O_a (529 eV), O_b (529.6 eV), O_c (531.4 eV) and O_d (533.5 eV) are shown in Figure S3. The binding energy follows the order of: Ce^{4+} - O^2\text{-} (O_a) < Ce^{3+} - O^2\text{-} (O_b) < Fe^{3+} - O^2\text{-} (O_c) based on the electronegativity difference between the respective ions.\(^3\) Thus the integrated peak intensity (IPI) of deconvoluted peaks represent the concentration of oxygen species with respect to their local bonding environment. Annealing (EFC9) lead to an increase in IPI of O_a (0.51 to 0.56) while decreasing that of O_b (0.25 to 0.07) in comparison to the as prepared sample which denotes a reduction in Ce^{3+} concentration (with a corresponding increase in Ce^{4+} concentration) with annealing temperature. With increase in annealing temperature, the O_c peak showed a significant increase in IPI from 0.16 to 0.32 which indicates the probable diffusion of Fe^{3+} ion to form the Fe_2O_3. The O_d peak belong to the hydroxyl group (H^+\text{-}O^2\text{-}) which decreases upon annealing from 0.07 to 0.03 indicating the removal of surface hydroxyl or water moiety at higher temperatures.
**Figure S3:** Deconvoluted XPS spectrum of O 1s peak for EFCR and EFC9

**References:**

