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Supporting information for

A positron annihilation spectroscopic investigation of europium-doped cerium oxide nanoparticles

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Synthesis of ceria nanoparticles:

The solvothermal method is used to synthesize undoped and Eu-doped cerium oxide nanoparticles. A closed cylindrical Teflon lined stainless steel chamber with 45 ml capacity was used. 0.1 M of $Ce(NO_3)_3.6H_2O$ and an appropriate amount of 28% aqueous ammonium hydroxide (1-2 g) were dissolved in 35 ml of anhydrous ethanol in a Teflon bottle. This mixture was stirred for 5 min. Various concentrations of $Eu(NO_3)_3.5H_2O$ (0.1 - 50 atom%) were added in the above mixture. The solution was stirred for another 15 min with the formation of milky slurry. Subsequently, the closed Teflon chamber was transferred into a temperature-controlled preheated electric oven, and was subjected to solvothermal treatment at 180 °C for 12 h. Yellowish precipitates were collected, washed with deionized water and absolute ethanol several times by centrifugation and followed by drying at 50 °C in air. Samples with varying concentrations of Europium doping will be subsequently represented as CEX, where X = 0, 0.1, 0.5, 1, 5, 10, 20, 30, 40, and 50 atom%.

Particle size distribution of undoped and doped ceria nanoparticles:

The crystallite sizes were calculated from the XRD pattern. Three different XRD spectra obtained from three different sets of samples (experiment was repeated 3 times) were taken into account. The patterns are similar, no shift in the peak position was observed. This confirms the reproducibility of the synthesis process. The higher intense peaks were considered for the calculation of crystallite sizes. Figure S1 shows the particle size distribution for the undoped, 1% and 20% Eu doped ceria samples. The plot shows ± 0.4 nm disparity in the particles sizes.

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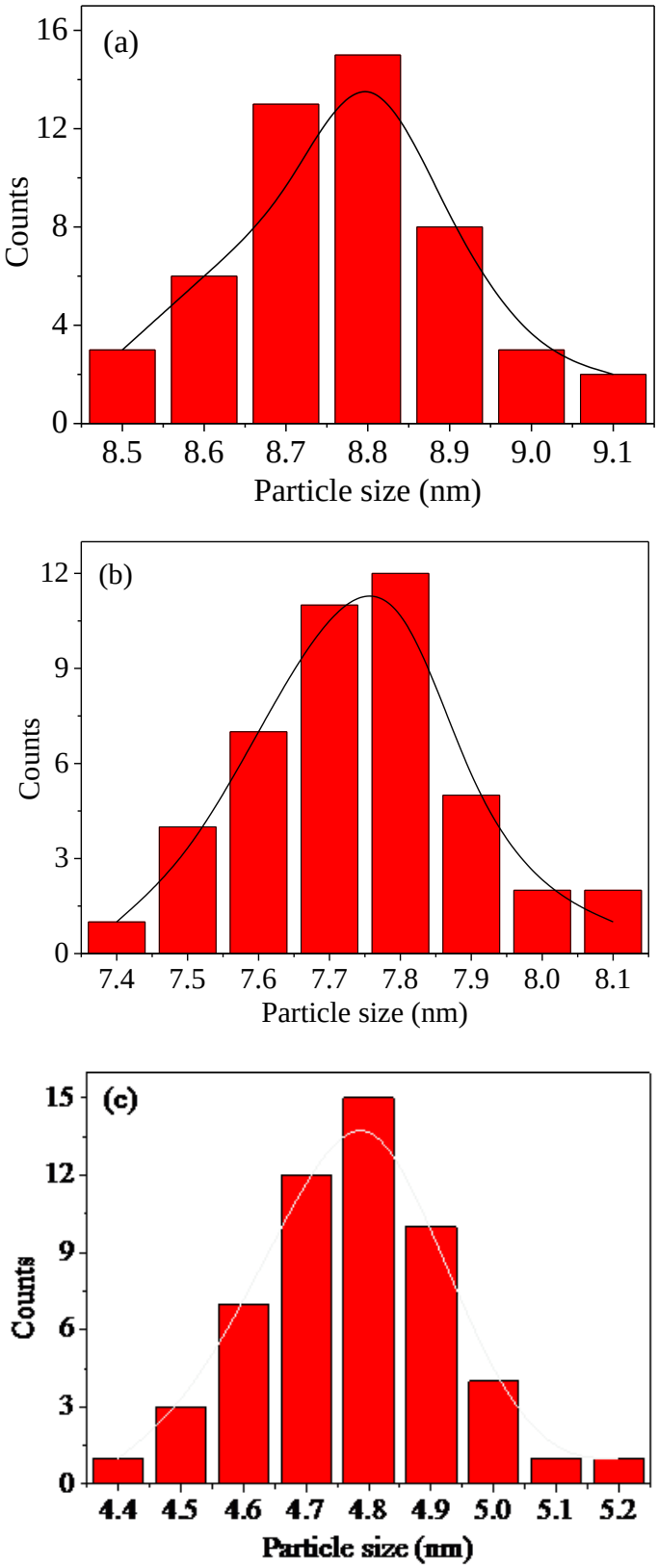


Fig S1. Particle size distribution of (a) undoped (b) 1% Eu doped (c) 20% Eu doped ceria samples.

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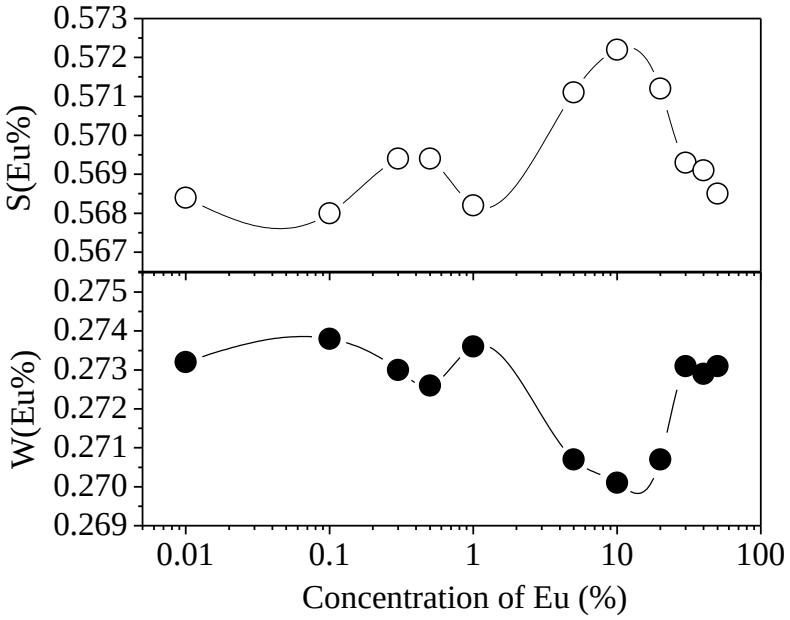


Fig S2 The *S* and *W* parameters versus the concentrations of Eu doping in the CeO_2 nanocrystalline samples. The values shown against 0.01 stand for the undoped sample. In both the cases, the errors (~ ± 0.0008) are within the sizes of the points.

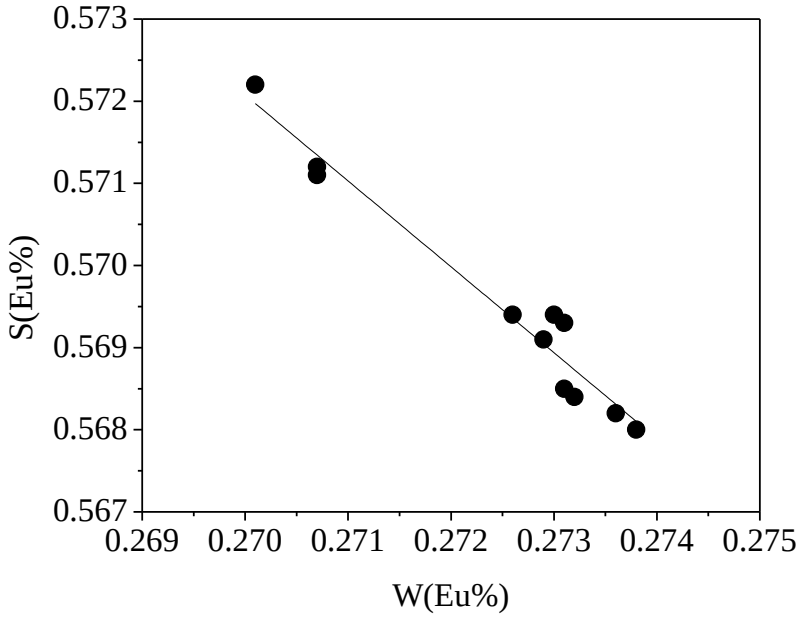


Fig S3. The *S* – *W* plot illustrating the linear relationship between the two parameters.

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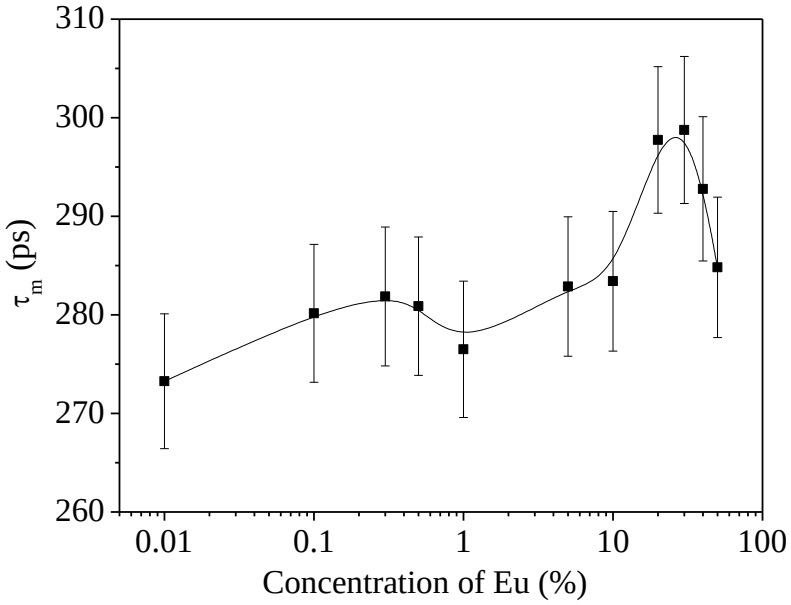


Fig S4 The positron mean lifetime τ_m versus the concentrations of Eu doping in the CeO_2 nanocrystalline samples. The values shown against 0.01 stand for the undoped sample.

The lineshape parameters *S* and *W* derived from the projected one-dimensional spectra described above, according to the relations

$$S = \frac{\sum_{i=-2}^{2} N_i(\Delta E)}{\sum_{i=-50}^{50} N_i(\Delta E)} \qquad \text{(a)}$$

and

$$W = \frac{\sum_{i=-12}^{-4} N_i(\Delta E) + \sum_{i=4}^{12} N_i(\Delta E)}{\sum_{i=-50}^{50} N_i(\Delta E)} \qquad \text{(b)}$$

In these equations, $i = 0$ corresponds to $E_1 - E_2 = 2\Delta E = 0$ and each channel was calibrated for 400 eV. The calculated *S* and *W* parameters are plotted against the Eu doping concentration and shown in Fig. S2. Both the parameters vary complementarily as illustrated

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by plotting one against the other and results the straight line (Fig. S3). The *S* parameter plot in Fig. S2 show two distinct peaks at low (around 0.05%) and high (10%) loadings. It is suggested that the lower feature reflects a small increase of anion vacancies being added as the Eu is added but this is compensated for by changing crystalline size as described above. The peak at higher Eu loadings is due to increased vacancy defect concentration until the formation of an ideal M_2O_3 structure begins to form. These are the regions of increasing particle size accompanied by the generation of additional oxygen vacancies and their complex formation with existing cationic vacancies and quantum confinement effects leading to increase of the band gap energy. These observations further support the findings of the positron lifetime measurements too, as illustrated by the variation of the positron mean lifetime τ_m in Fig. S4. τ_m is defined as the weighted average of the positron lifetimes. The similarity of variation of τ_m and *S* derived from two independent experiments cannot be missed in this context.

$$\tau_m = \frac{\sum_{i=1}^{3} \tau_i I_i}{\sum_{i=1}^{3} I_i} \qquad \text{(c)}$$