Defect Evolution in Eu^{3+}, Nb^{5+} Doped and Co-doped CeO_2: X-ray Diffraction, Positron Annihilation Lifetime and Photoluminescence Studies

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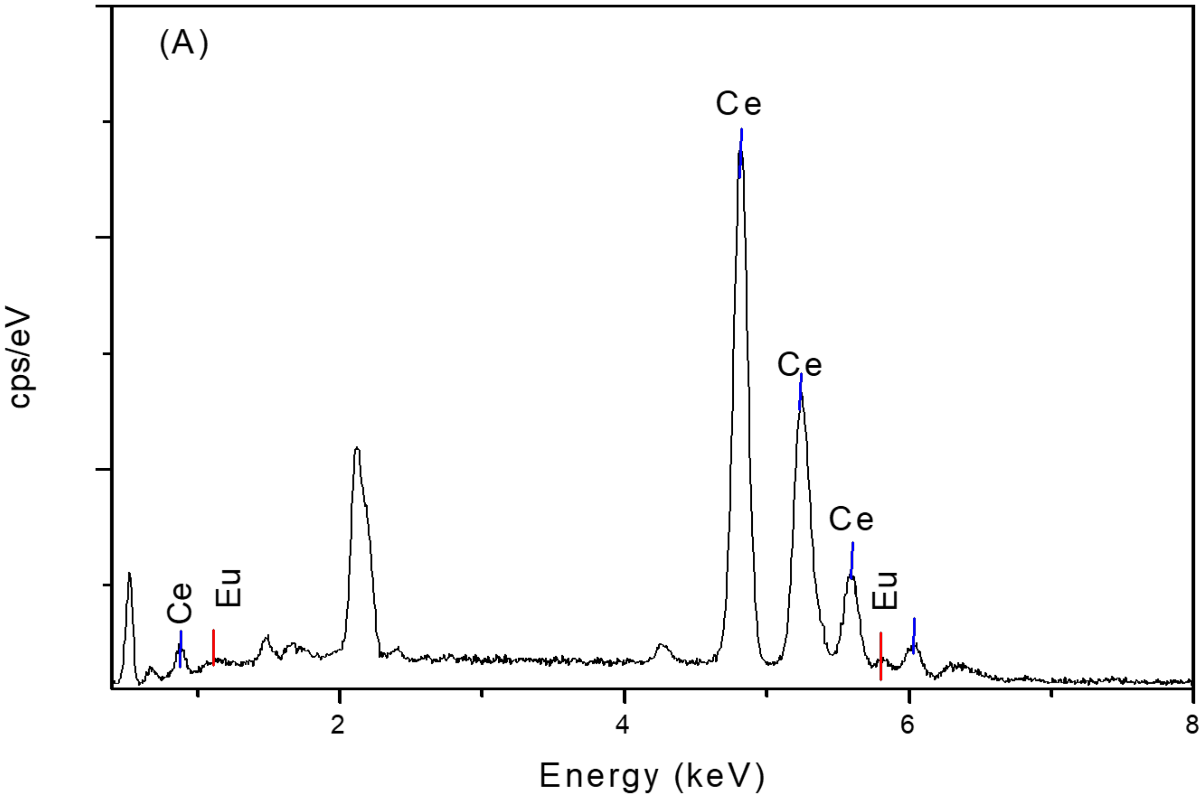
S1. Sample Preparation

Ceria samples were prepared by precipitating cerium hydroxide [1]**.** For undoped sample, $Ce(NO_3)_3.6H_2O$ was first dissolved in minimum quantity of deionized water. The ammonia was added slowly to it till pH 8 reached to precipitate cerium hydroxide. The precipitate was removed by centrifugation dried using IR lamp. The precipitate was calcined in air to obtain fine powder of ceria. The furnace temperature was raised to 1000 ^{0}C from room temperature in three hours and held at 1000 ^{0}C for one hour. To prepare Eu^{3+} doped ceria, stock solution of $Eu(NO_3)_3$ in deionized water was prepared and then requisite amount of this solution was added to cerium nitrate solution before precipitating. Nb^{5+} doped ceria was prepared by the same procedure as above, only difference was that the stock solution of $NbCl_5$ was prepared in by dissolving $NbCl_5$ in HCl. Using the above procedure sample with different mole % of Eu^{3+} and Nb^{5+} doping with respect to moles of Ce^{4+} are prepared. 2% Eu^{3+} and 10% Eu^{3+} doped samples are also codoped with Nb^{5+}. The EDX spectra were recorded for typical samples using a Bruker Nano GmbH XFlash detector 410-M attached to Mini SNE-4500 M Tabletop Scanning Electron Microscope instrument. Typical EDX spectra for Eu doped, Nb doped and codoped samples are shown in Fig. S1. The incorporation of Eu and Nb into the matrix was confirmed by these measurements.


(A)
cps/eV
Ce
Ce
Ce
Ce
Eu
Eu
2
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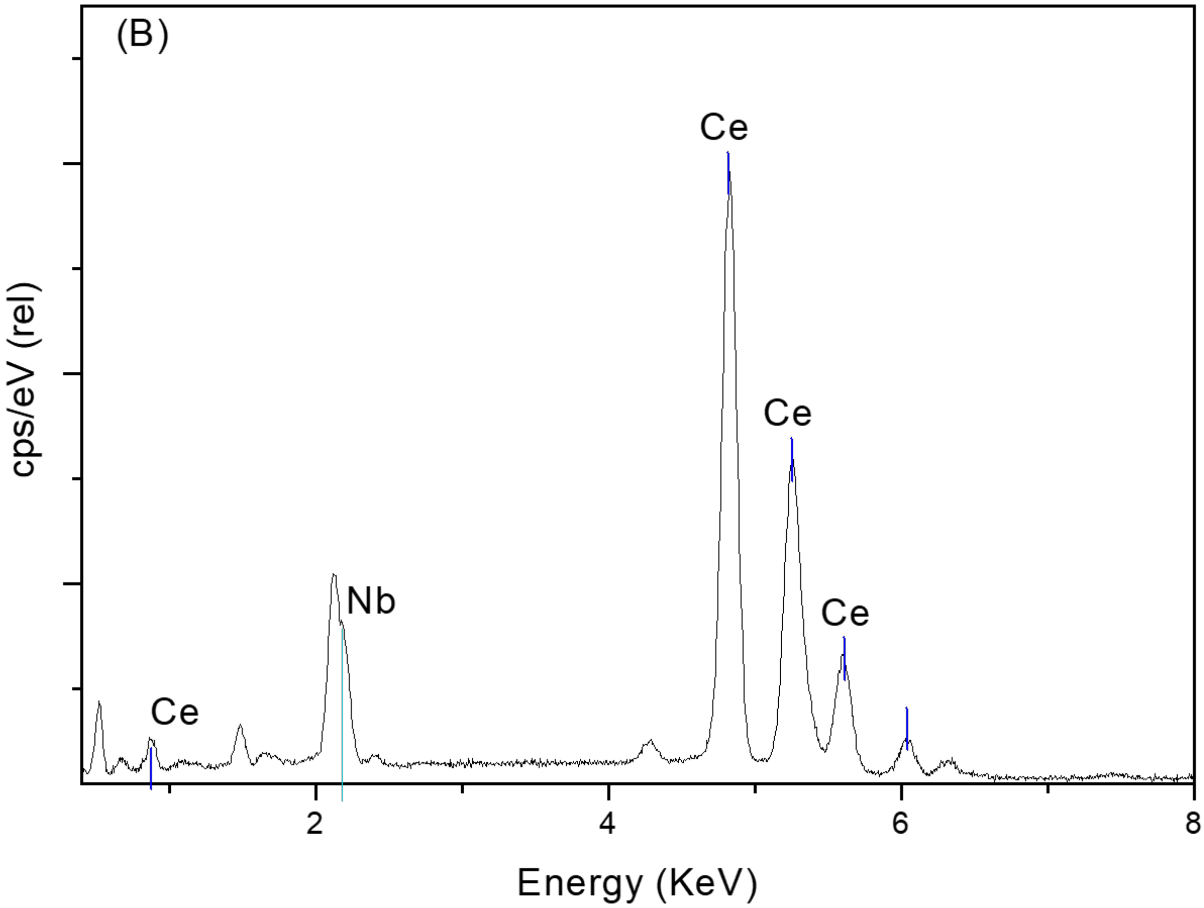
Energy (keV)


(B)
cps/eV (rel)
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Ce
Ce
Ce
Nb
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4
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Energy (KeV)

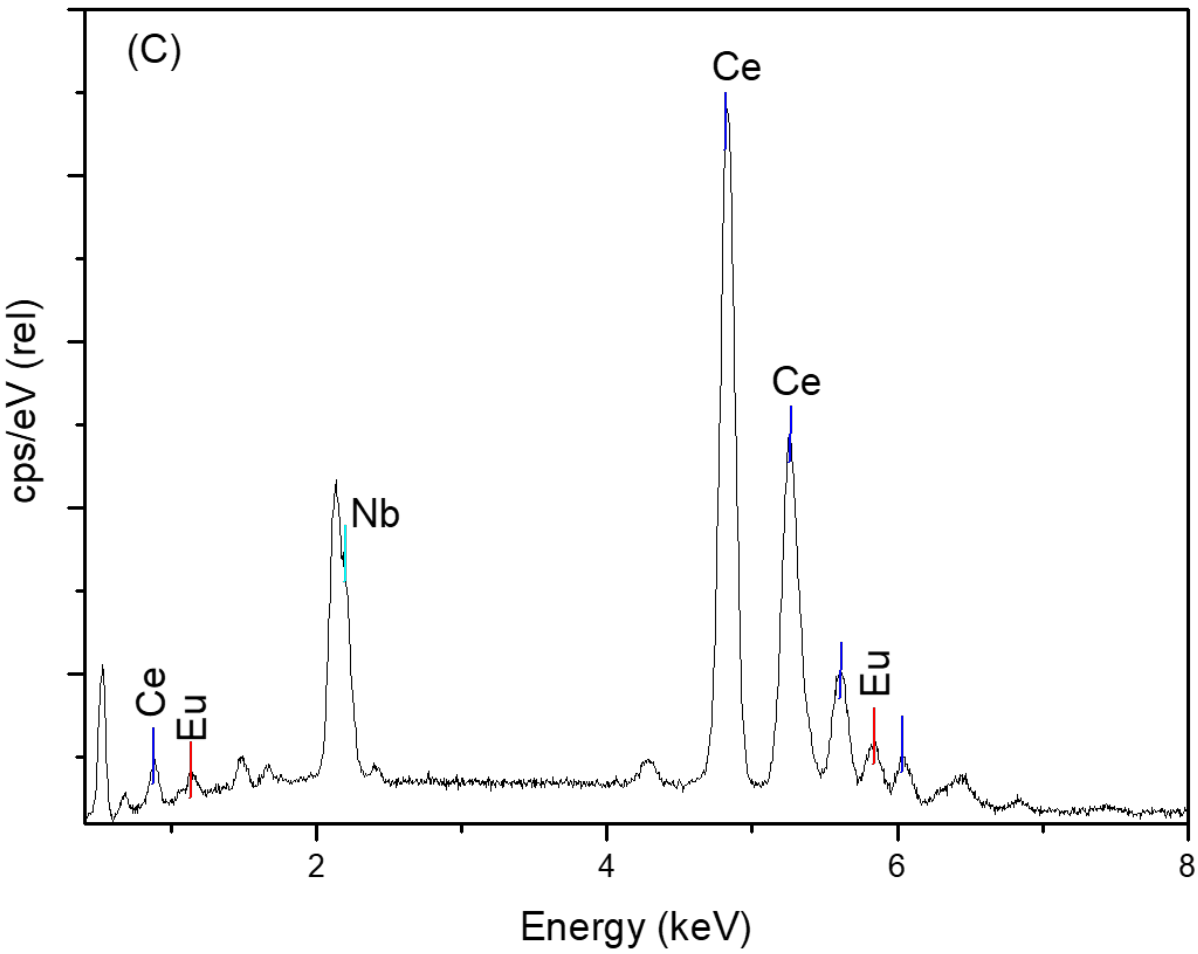

Figure S1. EDX spectra from (A) Eu doped (B)Nb doped and (C) Eu+Nb codoped ceria**.**

S2. Powder X-ray Diffraction (XRD)

The X-ray powder diffraction(XRD) pattern of the samples were obtained using a Proto AXRD X-ray diffractometer with CuK$_\alpha$ radiation of wavelength 0.15406 nm at 30kV and 20mA in 20°–80° 2θ range to identify crystal structure of powder samples. The scan rate of the sample was ~1 deg/min. Rietveld refinement of the recorded XRD patterns was carried out using FULLPROF software [2]. XRD pattern from LaB$_6$ standard sample was used in the FULLPROF program in profile matching mode in order get initial estimates of the instrumental parameters to start fitting the diffraction pattern of ceria sample.

S3. Positron annihilation lifetime spectroscopy (PALS)

PALS measurements were carried out using a Na-22 radioisotope-based positron lifetime spectrometer consisting of two plastic scintillation detectors. The time resolution of the spectrometer measured using gamma-rays of ^{60}Co was 280ps. The source of positrons was 15 μCi Na-22 encapsulated between two polyimide films of 8micron. The source was immersed in the sufficient quantity of powder samples to stop positron. The fraction of positrons annihilating in the polyimide films used in encapsulating Na-22 were estimated using positron annihilation lifetime spectra of silicon as reference and accounted for in analyzing the positron annihilation spectra from the samples, as is the standard practice. The lifetime spectra were analyzed using *PALSfit* **[3]** for extracting different lifetime components.

S4. Photoluminescence Studies

The photoluminescence (PL) emission spectrums were recorded using Edinburgh F900 spectrometer. The instrument was equipped with M 300 grating monochromators. The data acquisition and analysis were done by F-900 software. A 150 W Xenon flash lamp (excitation source) having variable frequency range of 10–100 Hz was used. The powder sample was mixed with few drops of collodion solution and the resulting slurry was pasted over a glass plate using spatula. This was dried at room temperature and used for the PL measurements. Fluorescence lifetime measurements were carried out using time correlated single photon counting technique at lamp frequency of 10 Hz while the excitation and emission spectra were recorded at lamp frequency of 100Hz. Multiple scans were averaged for obtaining better signal to background ratio.

The excitation wavelength of 250 nm is in UV (or high energy) and corresponds to band to band excitation of ceria where in the reported band gap in the ceria samples range around 3 to 3.5 eV [4, 5]. The emission spectrum of undoped ceria is shown in Fig. S2. The emission spectrum consists of a broad band in 400 to 550nm range and prominent peaks at 443nm, 487nm, 533 nm and 622 nm. The observed peaks in the photoluminescence spectrum are similar to the spectrum reported [6-8] though relative intensities are quite different. The photoluminescence characteristics are sensitive to preparation and processing conditions of the samples. The synthesis conditions introduce different kinds of defects in the materials. Based on the literature various peaks observed in the current PL spectrum of ceria can be described as follows. The broad band in 400 nm- 500 nm is arising due to charge transfer from Ce 4f level to O 2p level [8]. As prepared samples of CeO2 also contain oxygen vacancies and Ce3+. The peak around 443 nm is arising due to the presence of Ce3+ in the samples. The emission peak around 487 nm is attributed to F centres [6] while peaks around 470 nm has been reported to be due to surface defects, dislocations etc [9]. The emission in this The presence of peak around 533nm is attributed to radiative recombination where in Ce3+ acts as hole trap while oxygen vacancy acts as electron trap by Malleshappa et al. [6]. Similar peak around 530 nm is reported by Tamizhdurai et al [9].The peak at 622 nm is due to O2- to Ce4+ charge transfer [10].The PL emission spectrum of Nb^{5+} doped ceria is shown in Fig.S3. The major peaks in the doped sample are marked. A broader band appears in the region of 400 to 500 nm instead of peak around 445nm in undoped samples. The positions of emission peaks are also sensitive to crystallite sizes. The peak around 440nm is higher in 1% Nb^{5+} doped samples probably due to presence of higher Ce^{3+} concentration and other peaks attributable to intrinsic oxygen vacancies and other defect centres. The relative intensities may also indicate that the initial doping of Nb^{5+} may reduce the oxygen vacancies and at higher concentration a variation in Ce^{3+} concentration can't be ruled out.

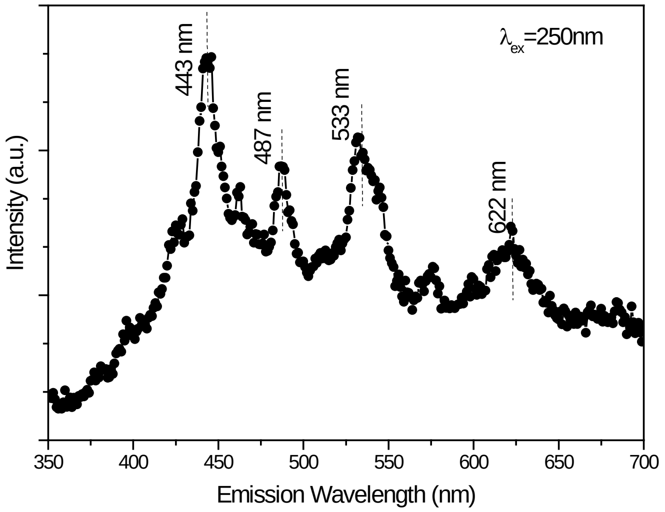

Fig. S2. Emission spectra of CeO_2 with excitation wavelength at 250 nm

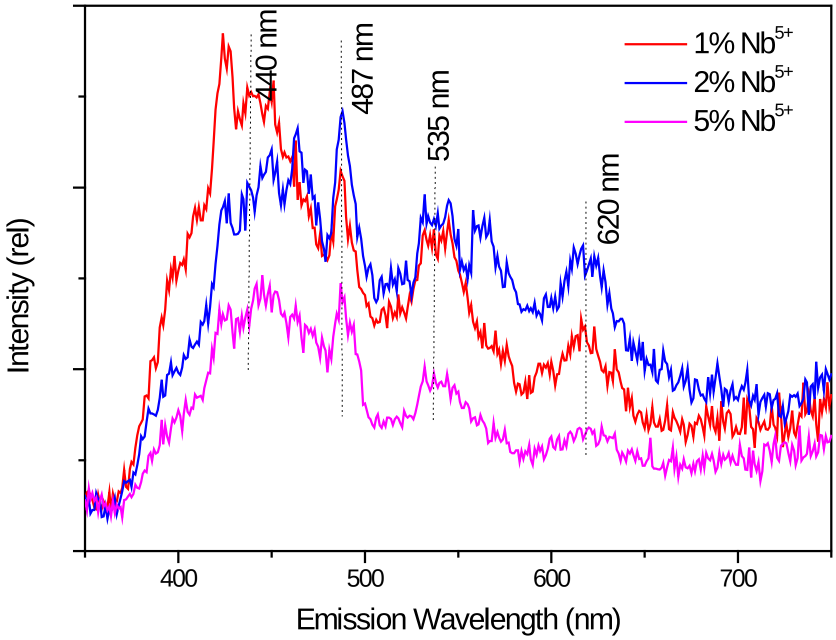

Fig. S3. Emission spectra of Nb^{5+} doped CeO_2 with excitation wavelength at 250 nm

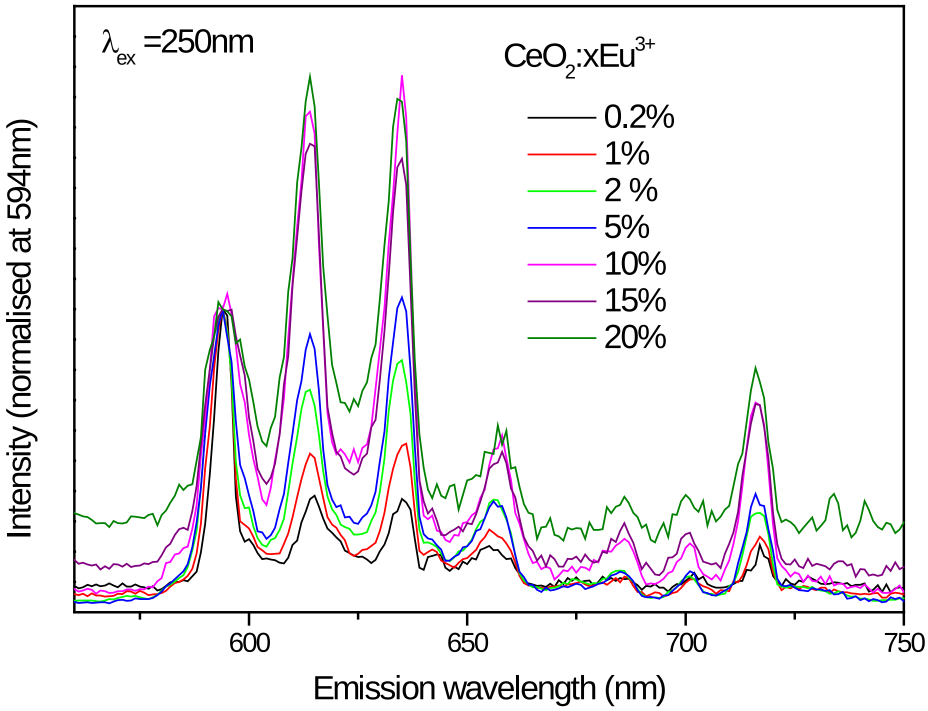

Fig. S4. Emission spectra of Eu^{3+} doped ceria samples with emission intensity normalized at 594nm. The intensity of emission is normalized at 594 nm corresponding to $^5D_0$ to $^7F_1$ transition, a magnetic dipole transition (MDT) which is expected to be high when Eu3+ is in centrosymmetric environment. It is seen from the figure that the intensity of electric dipole transitions (EDT), corresponding to $^5D_0$ to $^7F_2$ (615 nm and 635 nm) which is signature of asymmetry in the environment around the Eu^{3+} ion increases with increase in doping.

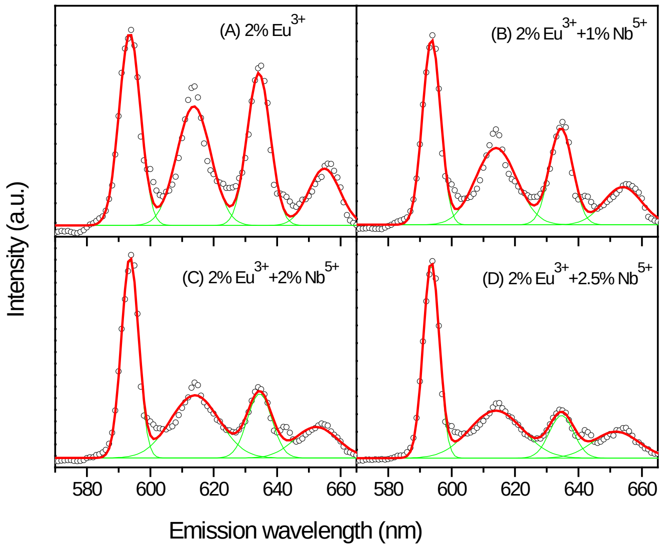

Fig. S5. Typical fitting of the emission spectra corresponding to Eu^{3+} emission line to extract the emission intensities for evaluating asymmetry ratio i.e. MDT/EDT intensity.

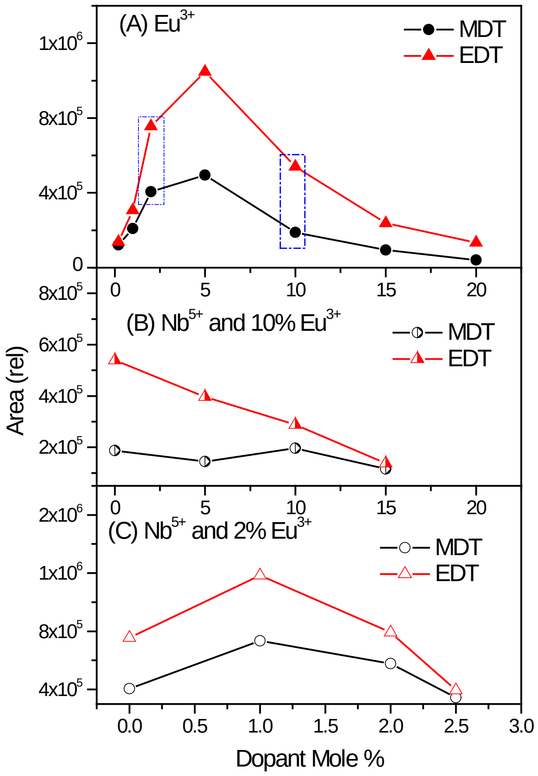

Fig. S6. Intensity corresponding to MDT and EDT in Eu^{3+} doped and Nb^{5+} codoped samples. The areas are evaluated from fittings similar to shown in Fig. S5. The marked points in (A) correspond to Eu^{3+} concentration in which Nb^{5+} is codoped and their data is shown in B and C.

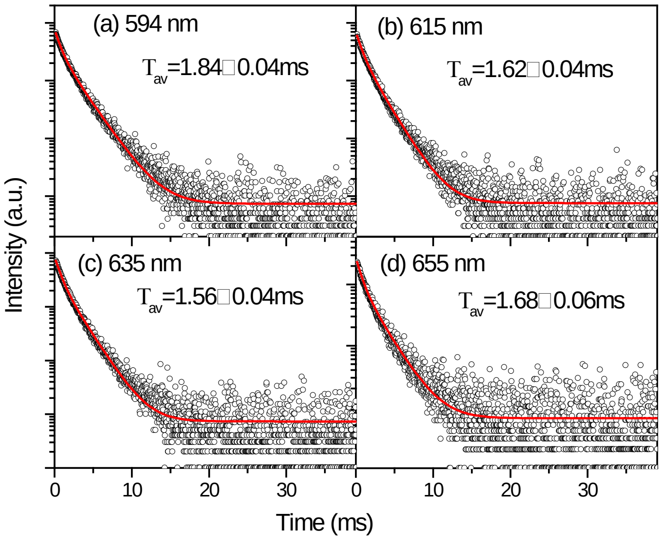

Fig. S7. Typical biexponential fitting of the luminescence lifetime spectra of different emission lines in 5% Eu^{3+} doped CeO_2. The excitation wavelength is 250 nm. The emission wavelengths and the obtained average lifetimes from fitting are indicated in the figure.

The emission lifetime could not be fitted to single lifetime component and a bi- exponential gave good fitting of the spectra. All the spectra were fitted into

$$I(t) = A_1 \exp\left(-\frac{t}{T_1}\right) + A_2 \exp\left(-\frac{t}{T_2}\right) + C_B$$

where I(t) is intensity at time t, T_1 and T_2 are luminescence lifetime and A_1& A_2 are their relative magnitudes. The C_B is the background counts. The average lifetimes are calculated from the above parameters as

$T_{av} = \frac{A_1 T_1^2 + A_2 T_2^2}{A_1 T_1 + A_2 T_2}$, while the relative intensities are calculated as $I_2(\%) = \frac{A_2 T_2}{A_1 T_1 + A_2 T_2} \times 100$

and I_1+I_2 =100%. The summary of the lifetimes and the intensities obtained are given below in Figs. S8.

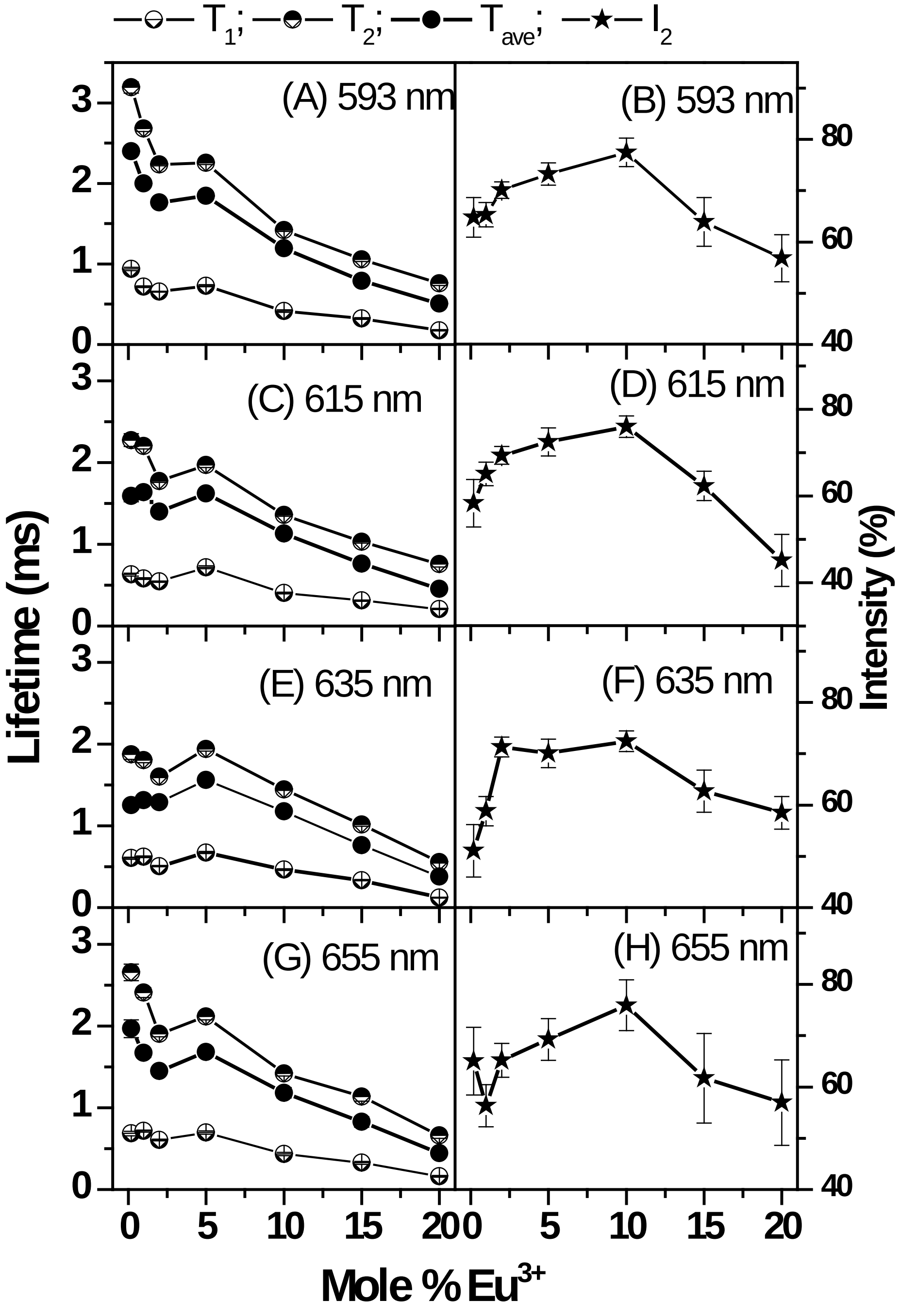

Fig. S8 (A). Summary of the luminescence lifetimes and intensities obtained from the biexponential fitting of the lifetime data in Eu^{3+} doped ceria samples. Left hand side of the figure (A, C, E and G) show the lifetimes while right layers in the figure (B, D, F and G) show intensity corresponding to the longer of the two components.

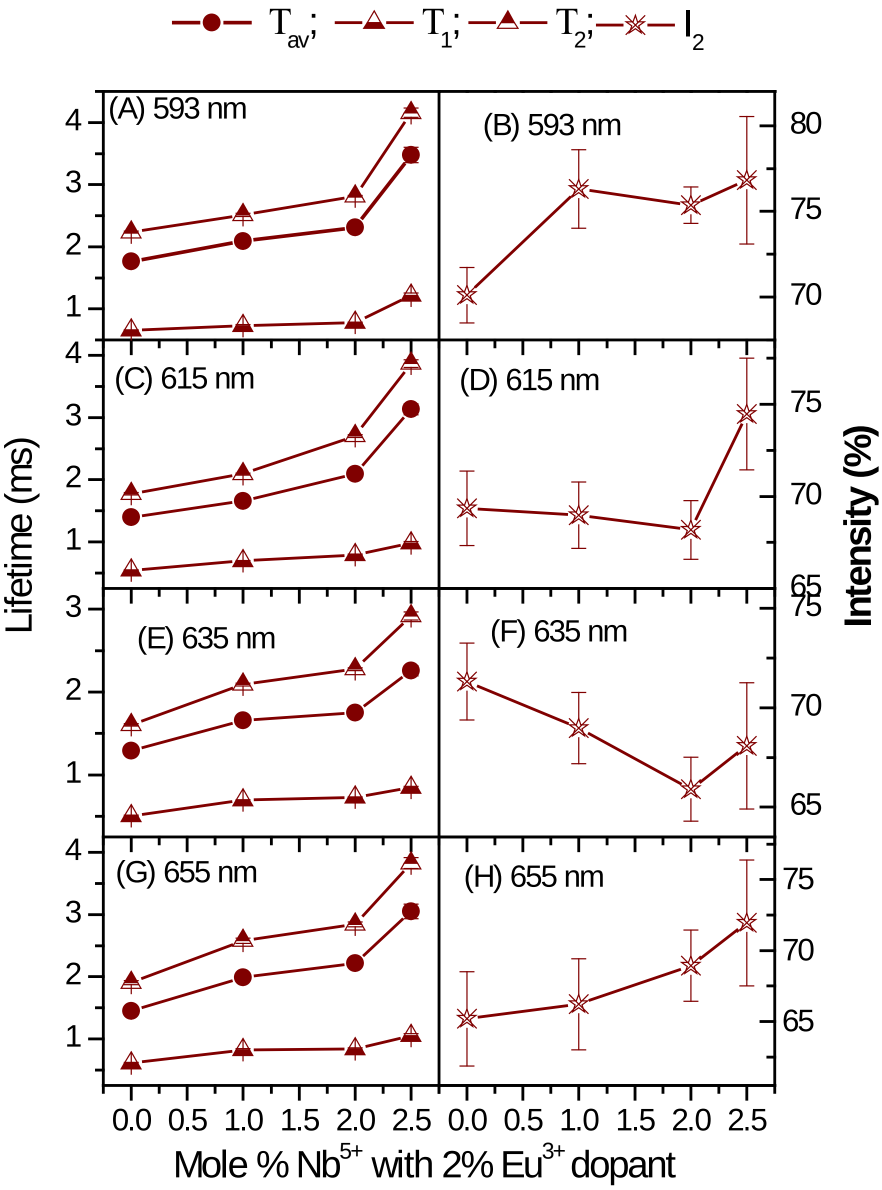

Fig. S8 (B). Summary of the luminescence lifetimes and intensities obtained from the biexponential fitting of the lifetime data in Nb^{5+} codoped with 2% Eu^{3+} in ceria samples. Left hand side of the figure (A, C, E and G) show the lifetimes while right layers in the figure (B, D, F and G) show intensity corresponding to the longer of the two components.

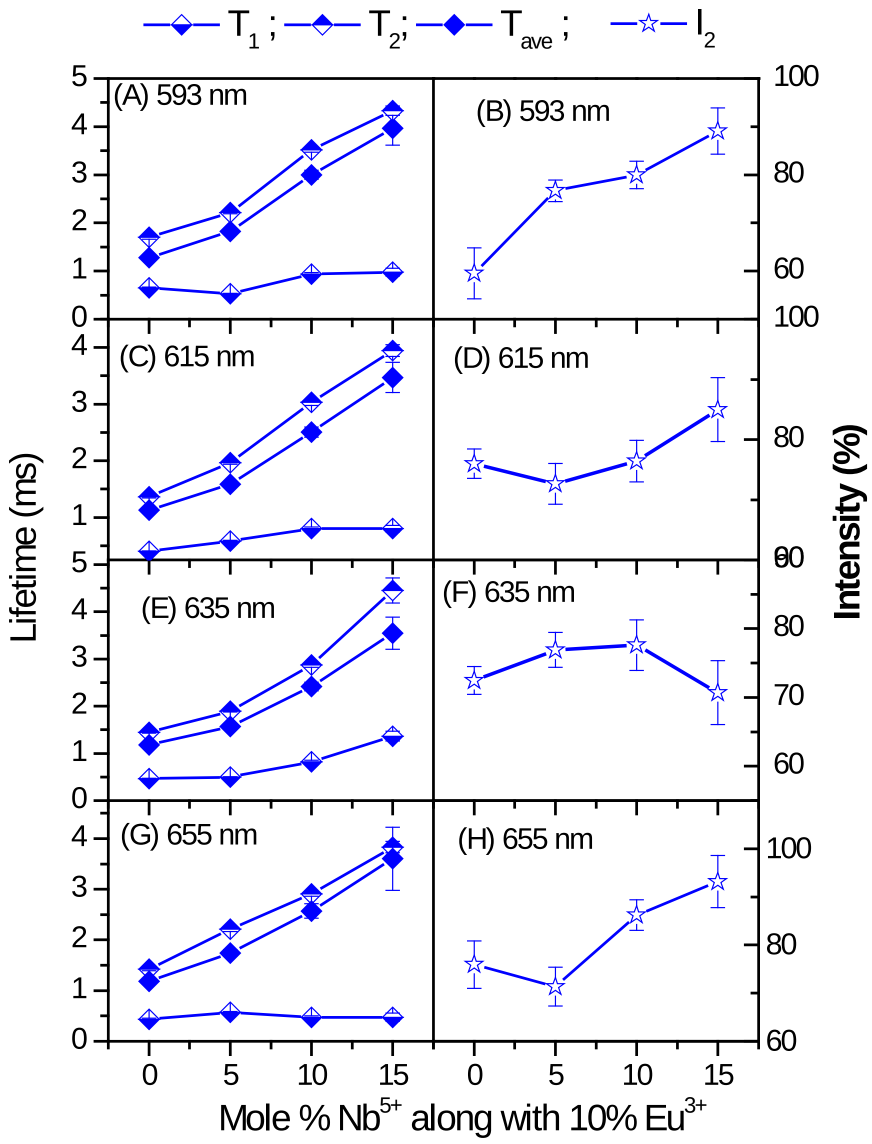

Fig. S8 (C). Summary of the luminescence lifetimes and intensities obtained from the biexponential fitting of the lifetime data in Nb^{5+} codoped with 10% Eu^{3+} in ceria samples. Left hand side of the figure (A, C, E and G) show the lifetimes while right layers in the figure (B, D, F and G) show intensity corresponding to the longer of the two components.

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