Cubic and low symmetry centres of Eu³⁺ doped CeO₂ nanoparticles: micro-Raman and luminescence spectroscopic study



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Introduction:

Among the trivalent lanthanides dopants for ceria, europium (Eu³⁺) is used mostly as a luminescence probe, whereas ceria beyond its classical use as catalyst or catalyst support, present also interest for biomedicine, radical scavenging antioxidants and biological labels applications.

Objective:

Investigation of the multicenter distribution of Eu³⁺ doped CeO₂ and its dependency on sample type, size and Eu³⁺ concentration.

Materials and Methods:

Three types of ceria nanoparticles were investigated such as commercial (com) or obtained by microemulsion (ow) and citrate (cit) methods. Sizes of nanoparticles varies between 30 and 55 nm. **Europium was incorporated in CeO₂ nanoparticles** via wet impregnation in three concentrations of 1, 5 and 10 wt.% with subsequent calcination at 1000 °C.

Samples Notations: CE(Eu³⁺-CeO₂)-1,5,10(dopant concentration wt.%)

Study Design :

XRD (X-ray diffraction) and Raman spectra measured in the whole range of 0-4000 cm⁻¹ with excitation at 488 and 514 nm

Steady state and time-resolved photoluminescence (PL) (emission and excitation) spectroscopy

Time-resolved PL spectra = PL spectra measured at different delay times, δt, after the laser/lamp pulse.

Excitation into O²⁻ Ce⁴⁺ charge-transfer band (CT) and f-f absorptions of Eu³⁺. Follow the evolution of the intensity of magnetic dipole (MD) PL transitions (at 591 nm) relative to the intensity of dipole electric (ED) transitions (~611and ~632 nm) respectively, with dopant concentration and nanoparticle size.



In all cases the diffraction peaks can be indexed as a pure cubic fluorite CeO₂. Except for CE(com) for which a strong asymmetry was observed around 220 reflection at 47.5°, no other phases were observed irrespective of Eu³⁺ concentration. With increase of Eu³⁺ amount from 1% to 10wt.%, the crystallite size decreased from 41 to 30 nm in CE(cit) sample and from 38 to 30 nm in CE(ow) samples as determined with Debye-

No significant changes of the particle size were observed for CE(com) samples, with crystallite size varying slightly from 52 to 55 nm for the similar concentration range of Eu³⁺. This is probably due to the thermal pretreatment done by the manufacturer which prohibits the full incorporation of Eu³⁺ dopants.



The Raman spectra are characterized in the spectral range of phonon bands, by a strong, narrow phonon band around 460-470 cm⁻¹ which corresponds to the F_{2q} mode of the CeO₂ fluorite phase along with weaker bands around 250, 600 and 1165 cm⁻¹, due to secondorder transverse acoustic (2TA) defect-induced (D) and second-order longitudinal optical (2LO) modes. Further, the enhancement of the spectral feature around 550 cm⁻¹ together with the F_{2q} band shift by ~ 1.5 cm⁻¹ (citrate) or 4 cm⁻¹ (ow) to lower energy are evident for the concentrated samples. The spectral feature at 550 cm⁻¹ is assigned to the oxygen vacancies which are generated upon Ce⁴⁺ substitution by Eu³⁺. With increasing Eu³⁺ concentration, the F_{2q} mode becomes asymmetric, broader and slightly shifted to lower wavenumber which is related to the combined effects of strain and phonon confinement resulted from the decrease of the crystallite size.

CE(ow)-1 CE(ow)-1 - CE(ow)-5 -CE(ow)-10 = 350 nm =464 nm

Here, R refers to an "average" local symmetry, as emission spectra are related to a sum of emissions corresponding to cubic (isolated) and low symmetry (perturbed) Eu³⁺ centers. The perturbation is most probably related to short-range interaction between Eu³⁺ and oxygen vacancy located in the NN site which lowers the symmetry, remove the inversion center, allowing thus the observance of the ED transitions.







The sensitization pathway of emissions related to the two main Eu³⁺ centers is clarified with the excitation spectra measured around the emission of the cubic center (around 591 nm) and perturbed center (around 611 or 632 nm), being exemplified with CE(ow) samples in(c, d).

different shapes and decay times. At short delays, the emissions of both Eu³⁺ centers are measured. The emission of the low symmetry center prevails for the concentrated sample up to 2 ms after the laser pulse for excitation into CT band and up to 5 ms for excitation at 466.6 nm, whereas the emission characteristic of the cubic center dominates the emission of the diluted sample when excited into the CT band. The "true" emission of the cubic center is extracted from the delayed PL spectra measured at delay times longer than 10-20 ms and by use of up to 500 accumulations per pulse laser.



spectra excited at 514 nm) gives a four peaks structure which is indicative of four low symmetry centers (a).

The lineshape of ⁵D₀- ⁷F₀ emission was alternatively analyzed by selective excitation into the profile of ${}^{7}F_{0}$ - ${}^{5}D_{2}$ absorption centered at 466 nm. With change of the excitation wavelength between 465.5 and 467.4 nm the shape (b), peak position and width of this emission changes reflecting the co-existence of at least four perturbed centres with distinct oxygen environments (peaks at 578.78±0.4; 579.19±0.4; 579.63±0.4; 580.06±0.4 nm).

Overall emission properties agree with a structure composed of one dominating cubic center, one dominating low symmetry center and three minor low symmetry centers which we found to be intrinsic to Eu³⁺ doped ceria solid solutions.

The low symmetry at the main perturbed Eu³⁺ center is most probably defined by a short-range interaction between Eu³⁺ and nearest-neighbour oxyygen vacancies.

The local oxygen environments at Eu³⁺ cubic and major low symmetry sites do not depend on size and dopant concentration.

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