Lanthanide–lanthanide and lanthanide–defect interactions in co-doped ceria revealed by luminescence spectroscopy

Daniel Avram [a], Cristina Gheorghe [a], Codruta Rotaru [b], Bogdan Cojocaru [b], Mihaela Florea [b], Vasile Parvulescu [b], Carmen Tiseanu [a,*]

[a] National Institute for Laser, Plasma and Radiation Physics, P.O. Box MG-36, RO 76900 Bucharest-Magurele, Romania
[b] University of Bucharest, Department of Chemical Technology and Catalysis, 4–12 Regina Elisabeta Bvd., Bucharest, Romania

ARTICLE INFO

ABSTRACT

Here, we present a first study on the local structure properties, lanthanide–lanthanide and lanthanide–defect interactions in lanthanide (Sm^{3+}/Nd^{3+} and Sm^{3+}/Eu^{3+}) co-doped CeO_2 nanoparticles by use of luminescence spectroscopy. By comparing the emission/excitation spectra and decays measured with the single doped and co-doped ceria, it is established that the local structure at Sm^{3+} sites is not affected by the presence of the Nd^{3+} or Eu^{3+} co-dopant irrespective of concentration. The results suggest that the excess of oxygen vacancies generated by the co-dopant is not associated with Sm^{3+}, being more probably associated with the Nd^{3+}/Eu^{3+} or/and Ce^{4+} cations. It is also observed that Sm^{3+} is not involved in significant non-radiative energy transfer to Nd^{3+} or Eu^{3+} while the relative strong shortening of Nd^{3+} luminescence decay with concentration is most probably related to cross-relaxation in Nd^{3+}–Nd^{3+} pairs.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

It is well known that the oxide ionic conductivity of ceria-based compounds doped with lanthanide ions is influenced greatly by the ionic radius of the dopant [1]. An increased ionic conductivity requires minimization of interactions between the dopants and defects, the latter being considered mainly of the oxygen vacancy ($V_Ö$) nature type [2]. Density function theory work [3] has shown that around Pm^{3+} there will be no site preference for oxygen vacancies, which facilitate the oxygen vacancy diffusion, determining thus a high ionic conductivity. Co-doping ceria with equal quantities of Sm^{3+} and Nd^{3+} mimics best the (radioactive) Pm^{3+} doped ceria since the resulted weighted average dopant ionic radius of 1.094 Å is close to that of Pm^{3+} of 1.093 Å [4] leading to increased ionic conductivity over singly doped systems. Based on extended X-ray absorption fine structure (EXAFS) study of both single and double doped ceria, it was found that, besides the global lattice strain induced by doping, the local structure at each co-dopants sites also influences strongly the ionic conductivity [5]. Recently, the traditional synergistic co-doping effect established for ceria is challenged by computer simulations, in favor of an average effect,

meaning that the conductivity of the co-doped ceria is the average of the two values corresponding to single doped systems [6].

There is an extensive experimental and theoretical research connecting the structural and conductivity properties of trivalent lanthanide (Ln^{3+}) doped ceria materials [7–12]. The results of these studies which have a particular relevance for our luminescence investigation, can be summarized as follows. For the Ln^{3+} bulkier than Gd^{3+} (ionic radius in 8-fold coordination of 1.053 Å) i.e. located to the left of Gd^{3+} in the 4f series (such as Nd^{3+}, Sm^{3+} and Eu^{3+} with ionic radii in 8-fold coordination of 1.109, 1.079 and 1.066 [4]) the association between Ln^{3+} and oxygen vacancy is expected to occur in the next-nearest-neighbor (NNN) mode. The Ln^{3+} substitutes for the 8-fold coordinated Ce^{4+} ions and the LnO_8 polyhedron preserves the cubic (O_h symmetry) of CeO_8. For the lanthanides with an ionic radius smaller that of Gd^{3+}, i.e. the located to the right of Gd^{3+} in the 4f series the association between Ln^{3+} and oxygen vacancy occurs in the nearest-neighbor (NN) mode as seven coordinated LnO_7. Among the luminescent lanthanide ions, especially Eu^{3+}, and to a lesser extent Sm^{3+}, show strong sensitivity to their nearest local environment, due to a mixing of magnetic dipole and hypersensitive electric dipole emission transitions. In our recent investigations on lanthanide doped CeO_2, besides the Eu^{3+} or Sm^{3+} located in the NNN location to oxygen vacancy (denoted as cubic centre), a second type of centre assigned to lanthanide in NN association with the oxygen vacancy (denoted

as perturbed centre) were clearly identified by use of luminescence spectroscopy with both spectral and temporal resolution. The different nature of the two centres was described in relation with their characteristic emission, excitation and emission decay properties. It is worth mentioning that the existence of these two centres does not depend on the synthesis mode, size of nanoparticles and dopant concentration.

Here, we propose a first study on the local structure properties of lanthanide co-doped CeO_2 by use of luminescence spectroscopy. Sm^{3+} (5%) and Nd^{3+} (1% and 5%) co-dopants were incorporated in CeO_2 *via* wet impregnation followed by calcinations in air at 1000 °C in an effort to confirm the remarkable capability of preformed nanosized CeO_2 to dissolve high concentrations of lanthanide oxides added *via* impregnation [13]. Sm^{3+} (1%) and Eu^{3+} (1% and 5%) were incorporated *via* bulk doping followed also by calcination in air at 1000 °C.

It is established that there are three types of interactions with relevance for the ionic conductivity properties of the lanthanide doped CeO_2 [14]: interaction between the oxygen vacancies in the anion sublattice ($V_{\ddot{O}} - V_{\ddot{O}}$), interaction between the lanthanide ions in the cation sublattice ($Ln^{3+} - Ln^{3+}$) and interaction between the lanthanide ions and oxygen vacancies connecting the sublattices ($Ln^{3+} - V_{\ddot{O}}$). According to EXAFS data, it is the nearest (oxygen) neighbor (NN) environment which responds the most strongly to a change in the number of oxygen vacancies [15]. Here, we show that by use of Sm^{3+} or/and Eu^{3+} as luminescence probes, a wealth of information on the lanthanide–oxygen vacancy and the lanthanide–lanthanide interactions in CeO_2 can be obtained. Both the lanthanide–$V_{\ddot{O}}$ and the lanthanide–lanthanide interactions were investigated by use of the emission/excitation spectra and excited state dynamics. Routine characterization was performed by X-ray diffraction (XRD), diffuse reflectance and Raman spectroscopies.

2. Experimental

2.1. Samples synthesis

The preparation of citrate CeO_2 support was performed as reported in literature [16]. For the preparation of co-impregnated samples, 1 g of CeO_2 was impregnated with the required amounts of 0.004 M solutions of $Nd(NO_3)_3 \cdot 6H_2O$ and $Sm(NO_3)_3 \cdot 6H_2O$ respectively. The suspension was stirred 12 h at 60 °C and then water was evaporated at 80 °C. Drying of the samples was continued at 80 °C in vacuum for 4 h. In this way, samples 5% Sm, 1% Nd–CeO_2 and 5% Sm, 5% Nd–CeO_2 were prepared, being denoted as 5Sm1Nd–CeO_2 and 5Sm5Nd–CeO_2, respectively. In a typical preparation of citrate 1% Sm, 1% Eu–CeO_2 and 1% Sm, 5% Eu–CeO_2 samples, a corresponding amount of $Ce(NO_3)_3 \cdot 6H_2O$ was dissolved in 50 mL of distilled water heated at 60 °C, $Sm(NO_3)_3 \cdot 6H_2O$ in 25 mL of hot distilled water (60 °C) and $Eu(NO_3)_3 \cdot 6H_2O$ in 25 mL of hot distilled water (60 °C). Then the solutions were mixed together and stirred for 10 min. Citric acid was added to this mixture and the stirring was continued for 1 h at 60 °C. After stirring, the solution was submitted to water evaporation in a vacuumed rotary evaporator resulting in a colorless gel. The gel was then dried for 5 h under vacuum at 60 °C and then at 120 °C in air for another 12 h. A pale yellow solid powder was obtained. The 1% Sm, 1% Eu–CeO_2 and 1% Sm, 5% Eu–CeO_2 samples were denoted as 1Sm1Eu–CeO_2 and 1Sm5Eu–CeO_2, respectively. All samples were calcined for 4 h at 1000 °C with a heating rate of 10 °C/min.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Schimadzu XRD-7000 diffractometer using Cu Kα radiation (λ = 1.5418 Å, 40 kV, 40 mA) at a step of 0.2° and a scanning speed of 2° min^{-1} in the 10–90° 2Θ range. Crystalline phase were identified by comparison of the XRD patterns with the JCPDS database. Diffuse reflectance in the UV–Vis range (DR-UV–Vis) spectra were recorded at room temperature on a Analytik Jena Specord 250 spectrophotometer with an integrating sphere for reflectance measurements and Spectralon as the reflectance standard. DR-UV–Vis spectra were recorded in reflectance units and were transformed in Kubelka–Munk remission function $F(R)$. The Raman spectra were acquired in the extended spectral region from 150 up 4000 cm^{-1}. Raman analysis was carried out with a Horiba JobinYvon–Labram HR UV–Visible–NIR Raman Microscope Spectrometer, at 488 and 514 nm. The photoluminescence (PL) measurements were carried out using a Fluoromax 4 spectrofluorometer (Horiba) operated in both the

fluorescence and the phosphorescence mode. The repetition rate of the xenon flash lamp was 25 Hz, the integration window varied between 0.1 and 0.5 s, the delay after flash varied between 0.03 and 0.1 ms and up to 50 flashes were accumulated per data point. Slits were varied from 5 to 29 nm for excitation and from 0.3 to 1 nm in emission measurements, respectively. The PL decays were measured by using the "decay by delay" feature of the phosphorescence mode. Time resolved emission spectra (TRES) were recorded using a wavelength tunable (from 210 to 2300 nm) NT340 Series EKSPLA OPO (Optical Parametric Oscillator) operated at 10 Hz as excitation light source and an intensified CCD (iCCD) camera (Andor Technology) coupled to a spectrograph (Shamrock 303i, Andor) as detection system. The TRES were collected using the box car technique. The gain of the micro-channel plate (MCP) varied from 30 to 100, depending on the intensity of the luminescence. PL was detected in the spectral range of 400 nm < λ_{em} < 900 nm with a spectral resolution from 0.05 nm to 0.88 nm. The delay after pulse varied from 0.001 to 20 ms, with 10–200 μs gate and 100–300 accumulations per laser pulse depending on the signal to noise ratio. The average PL lifetime was calculated as integrated area of normalized decay. The near-infrared emission spectra were recorded with a setup consisting of a Jarell-Ash monochromator, S1 photomultipliers, Ge photodiodes and a Lock-in amplifier on line with a computer and excited with an OPO Rainbow-VIR/S laser at 592 nm. All PL measurements were performed at room-temperature.

3. Results and discussion

3.1. Solid solution formation

X-ray diffractograms (Fig. 1a) of the analysed samples correspond to the cubic fluorite structure (PDF card 00-034-0394) and no diffraction lines associated with samarium, europium or neodymium oxides could be observed. Crystallite sizes determined by the Debye–Scherrer equation using the (1 1 1) plane are 47.3 and 31.2 nm for 5Sm1Nd–CeO_2 and 5Sm5Nd–CeO_2, and 46.9 and 45.1 nm for 1Sm1Eu–CeO_2 and 1Sm5Eu–CeO_2, respectively. The slight shift of the CeO_2 peaks towards lower angles together with the values of the lattice parameters of 5Sm1Nd–CeO_2 and 5Sm5Nd–CeO_2 of 5.417 Å and 5.421 Å which exceed that of undoped CeO_2 (5.415 Å) indicate the existence of a solid solution [17,18].

For all samples, the broadening and shifting of the F_{2g} Raman mode (Fig. 1b) towards smaller energy relative to that of undoped CeO_2 (ca. 473 cm^{-1}), along with enhancement of vibrational modes around 550 cm^{-1} assigned to the generation of oxygen vacancies induced by the insertion of the dopant cations in the CeO_2 structure and around 600 cm^{-1} assigned to the presence of intrinsic oxygen vacancies were observed, [19]. Using Kröger–Vink notation, the dissolution of Ln_2O_3 into CeO_2 can be described by Eq. (1):

$$Ln_2O_3 \xrightarrow{CeO_2} 2Ln'_{Ce} + V_{\ddot{O}} + 3O_O^X \qquad (1)$$

showing that oxygen vacancies (positively charged) are induced to compensate for the introduced negative charge of Ln'_{Ce} cations. No Raman bands characteristic to Sm_2O_3, Nd_2O_3 and Eu_2O_3 parasite phases [20–21] were observed. It is worth noting the marked increase of the intensity of the Raman band at 550 cm^{-1} for the 5Sm5Nd–CeO_2 and 1Sm5Eu–CeO_2 compared to 5Sm1Nd–CeO_2 and 1Sm1Eu–CeO_2, respectively which evidence for the formation of solid solutions. The DR-UV–Vis–NIR spectra show a strong absorption band below 400 nm which is typical for CeO_2, assigned to the charge–transfer transition from O^{2-} (2p) to Ce^{4+} (4f) orbitals in CeO_2 together with some narrow bands assigned especially to the f–f absorption transitions of Nd^{3+} (Fig. 1c). Based on the above XRD and Raman results, we can conclude that the co-doped CeO_2 form satisfactory homogenous solid solutions, irrespective of the co-doping mode (wet impregnation or bulk doping). Our results confirm the observation of Corma et al. [13] regarding the formation of homogenous solid solution upon adding La^{3+} or Zr^{4+} dopants *via* wet impregnation in concentration as high as 30% on preformed nanosized CeO_2 as well as our recent investigations on 10% Eu^{3+} impregnated on CeO_2 and CeO_2–ZrO_2 [22,23]. The present work represents a first demonstration on a homogenous solid solution