

**Project title** Temporally and spectrally resolved luminescence of lanthanide doped tetravalent nano-oxides: A unitary approach

**Project Code** PN-II-ID-PCE-2011-3-0534

**Project duration** 2011 - 2016

**Funded by** UEFISCDI, Ministry of Education, Research, Youth and Sport, Romania

**Project leader** Dr. Carmen Tiseanu

**Website:** <http://nanolumin.inflpr.ro/idei.html>

## Project Summary

Our proposal is focused on a particular class of luminescent nano-oxides, namely trivalent lanthanide ions (Ln) doped CeO<sub>2</sub>, (I) ZrO<sub>2</sub> (II) and Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> (III) which attract tremendous attention as advanced ceramics, catalysts, sensors and luminescent materials. These applications rely on their unique, but still not well understood, structures and physical properties. The broad aim of the project is to identify, describe and provide novel insights on the structure - luminescence relationships occurring in the lanthanide doped I - III. Our original approach is based on the unitary investigation of their luminescence and structural properties. The lanthanide dopants will exhibit VIS to NIR emission via down- and up-conversion excitation. At the heart of our studies are the temporally and spectrally resolved luminescence investigations. We believe that our proposal will deepen the fundamental knowledge on the Ln<sup>3+</sup>- I - III host interactions at the nanoscale with strong impact on luminescence and structure-derived applications.

## Project Objectives

**I. In-depth description of the nanoscale environments at the lanthanides sites in CeO<sub>2</sub> (I), ZrO<sub>2</sub> (II) and Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> (III)**

**II. Luminescence of redox active lanthanides doped I - III**

**III. Novel insights into the Ln - Ln and Ln - host (I – III) interactions**

**IV. Assessment of the potential of I - III hosts as emission up- converters**

### **I. In-depth description of the nanoscale environments at the lanthanides sites in CeO<sub>2</sub> (I), ZrO<sub>2</sub> (II) and Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> (III)**



Temperature induced conversion from surface to “bulk” sites in Eu<sup>3+</sup>-impregnated CeO<sub>2</sub> nanocrystals

Carmen Tiseanu<sup>1,a)</sup>, Vasile I. Parvulescu<sup>2</sup>, Margarita Sanchez-Dominguez<sup>3,4</sup> and Magali Boutonnet<sup>5</sup>

+ VIEW AFFILIATIONS

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J. Appl. Phys. **112**, 013521 (2012); <http://dx.doi.org/10.1063/1.4730609>

Evolution with calcination temperature of Eu<sup>3+</sup> sites in CeO<sub>2</sub> nanocrystals has been investigated by time-resolved photoluminescence spectroscopy. In the as-synthesized Eu<sup>3+</sup> impregnated CeO<sub>2</sub>, most of

$\text{Eu}^{3+}$  ions reside on surface (**S**) sites. The  $\text{Eu}^{3+}$  emission in **S** sites is broad and short-lived ( $\tau = 240 \mu\text{s}$ ) being dominated by the electric dipole (ED)  ${}^5\text{D}_0\text{-}{}^7\text{F}_2$  emission with little evidence for clustering. After calcination (between 500 and 1300 °C),  $\text{Eu}^{3+}$  is distributed on surface, cubic and up to three additional crystalline sites. Surface type emission could be detected until 1100 °C. In cubic sites,  $\text{Eu}^{3+}$  substitute for the lattice  $\text{Ce}^{4+}$  with  $\text{O}_h$  symmetry (**O** sites). The emission of  $\text{Eu}^{3+}$  in **O** sites is characterized by relative long-lived ( $\tau = 1.8 - 2 \text{ ms}$ ) and ultra-narrow (FWHM = 7  $\text{cm}^{-1}$ ) magnetic dipole (MD)  ${}^5\text{D}_0\text{-}{}^7\text{F}_1$  emission centered at  $\sim 591 \text{ nm}$ . Three more crystalline sites are attributed to the oxygen vacancy charge-compensated defects. Overall, the results show that the oxygen vacancies are distributed around both  $\text{Eu}^{3+}$  and  $\text{Ce}^{4+}$  and the  $\text{Eu}^{3+}$  - oxygen vacancy interaction mode as next-neighbour or nearest-next-neighbour depend on the calcination temperature (*see, for example C. Tiseanu, V. Parvulescu, M. Sanchez Dominguez, M. Boutonnet, "Temperature induced conversion from surface to bulk sites in  $\text{Eu}^{3+}$ -impregnated  $\text{CeO}_2$ " J. Appl. Phys. 112(1), 013521 (2012).*

The screenshot shows the IOPscience website interface. At the top, there is a navigation bar with 'IOPscience', 'Journals', 'Books', and 'Login' links, along with a search box containing 'Search all IOP'. Below this, the journal title 'Journal of Physics D: Applied Physics' is displayed. The main content area features the word 'PAPER' followed by the article title 'Isolated centres versus defect associates in  $\text{Sm}^{3+}$ -doped  $\text{CeO}_2$ : a spectroscopic investigation'. The authors listed are Carmen Tiseanu<sup>1</sup>, Bogdan Cojocaru<sup>2</sup>, Daniel Avram<sup>1</sup>, Vasile I Parvulescu<sup>2</sup>, Andrea V Vela-Gonzalez<sup>3</sup> and Margarita Sanchez-Dominguez<sup>3</sup>. The publication date is 'Published 19 June 2013 • 2013 IOP Publishing Ltd' and the journal details are 'Journal of Physics D: Applied Physics, Volume 46, Number 27'. A button labeled 'Article PDF' is visible. At the bottom of the article preview, there are links for 'Figures', 'References', 'Citations', and 'Metrics'.

Investigation of the local structure around  $\text{Sm}^{3+}$  dopant in  $\text{CeO}_2$  was performed by the use of tunable laser excited time-resolved luminescence and micro-Raman spectroscopies. Both cubic and low-symmetry  $\text{Sm}^{3+}$  centres co-exist, their nature being tentatively assigned to  $\text{Sm}^{3+}$  in the next-nearest neighbour or nearest-neighbour positions to the oxygen vacancy positions, respectively. The local environment around cubic  $\text{Sm}^{3+}$  centres is not changed with  $\text{Sm}^{3+}$  concentration (varying between 0.1 and 5 wt%) and ceria size (varying between  $\sim 5$  and 62 nm). The cubic  $\text{Sm}^{3+}$  centres are sensitized *via* the charge-transfer absorption band of  $\text{CeO}_2$ , whereas the  $\text{Sm}^{3+}$ -oxygen vacancy associates are preferentially excited *via* the f-f absorption transitions of  $\text{Sm}^{3+}$ . The luminescence properties evidence that the interactions between the trivalent dopant and oxygen defects in  $\text{CeO}_2$  appear stronger for  $\text{Eu}^{3+}$  in comparison with  $\text{Sm}^{3+}$ , a phenomenon which is probably related to the enhanced sensitivity of the electronic transitions of  $\text{Eu}^{3+}$  to its local environment (*see, for example, C. Tiseanu, B. Cojocaru, D. Avram, V. Parvulescu, M. Sanchez Dominguez "Isolated versus  $\text{Sm}^{3+}$ -defect associations in  $\text{CeO}_2$ : a spectroscopic investigation" J. Phys. D: Appl. Phys. 46, 275302 (2013).*

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Article

**Toward a Unified Description of Luminescence–Local Structure Correlation in Ln Doped CeO<sub>2</sub> Nanoparticles: Roles of Ln Ionic Radius, Ln Concentration, and Oxygen Vacancies**

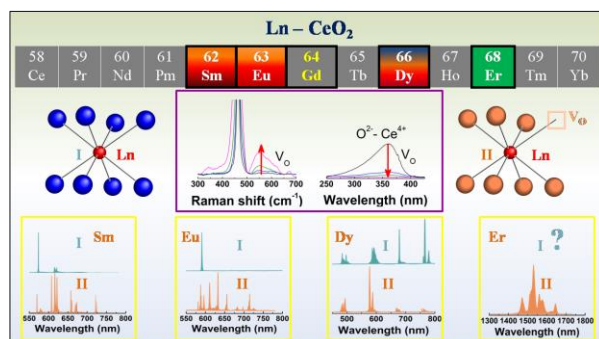
Daniel Avram<sup>†</sup>, Margarita Sanchez-Dominguez<sup>‡</sup>, Bogdan Cojocaru<sup>§</sup>, Mihaela Florea<sup>§</sup>, Vasile Parvulescu<sup>§</sup>, and Carmen Tiseanu<sup>†</sup>

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We have also propose a physical model for luminescence properties of trivalent lanthanide (Ln) doped into CeO<sub>2</sub> by use of low temperature, site selective, time-gated luminescence spectroscopy seconded by X-ray diffraction, Raman, and Fourier transform infrared spectroscopy and transmission electron microscopy. The main findings can be summarized as follows: (i) Ln situated to both the left and right sides to Gd in the Ln series exhibit a two-center distribution. Both Ln centers substitute for the tetravalent Ce fluorite sites being differentiated by the local symmetry: cubic, as a result of zero vacancy in the nearest-neighbor oxygen shell (cubic Ln center), and low symmetry, likely due to one vacancy in the nearest-neighbor oxygen shell (Ln–defect associate center). (ii) A first example of Dy emission in an inversion (cubic) symmetry, characterized by relatively strong lines at 679 and 764 nm, is reported. This result is expected to challenge the way this lanthanide is currently used as a luminescence probe. (iii) The relative contribution of the Ln centers to the overall emission depends on the Ln ionic radius: Sm exists predominantly as a cubic center, while Er is found mostly as a vacancy associate. (iv) Er, La codoped CeO<sub>2</sub> can be used as an effective model system to separate the effects of Ln concentration and subsequently induced oxygen vacancies on the efficiency of CeO<sub>2</sub> sensitization of Ln emission. (v) Zr codoping of CeO<sub>2</sub> obstructs the formation of Ln–defect associates. The implications of our findings for the interpretation of data already present in the literature are also discussed.



(See for example, D. Avram, M. Sanchez-Dominguez, B. Cojocaru, M. Florea, V. Parvulescu, C. Tiseanu "[Toward a Unified Description of Luminescence – Local Structure Correlation in Ln Doped CeO<sub>2</sub> Nanoparticles: Roles of Ln Ionic Radius, Ln Concentration and Oxygen Vacancies](#)", J. Phys. Chem. C 119(28), 16303-16313 (2015))

# THE JOURNAL OF PHYSICAL CHEMISTRY C

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## Article

### *In situ* Raman and Time-Resolved Luminescence Investigation of the Local Structure of ZrO<sub>2</sub> in the Amorphous to Crystalline Phase Transition

Carmen Tiseanu<sup>†</sup>, Vasile I. Parvulescu<sup>‡</sup>, Bogdan Cojocaru<sup>‡</sup>, Kelly Pemartin<sup>§</sup>, Margarita Sanchez-Dominguez<sup>§</sup>, and Magali Boutonnet<sup>¶</sup>

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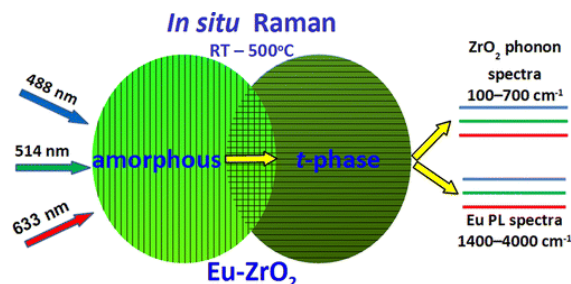
J. Phys. Chem. C, 2012, 116 (31), pp 16776–16783

DOI: 10.1021/jp3040538

Publication Date (Web): June 5, 2012

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The local structure of europium doped and impregnated ZrO<sub>2</sub> in the amorphous state and during crystallization is investigated by using *in situ* X-ray diffraction and *in situ* Raman, high-resolution transmission electron microscopy (HRTEM) and time-resolved photoluminescence spectroscopy. From Raman spectra excited at three different wavelengths ( $\lambda_{\text{ex}} = 488, 514$  and  $633$  nm), both phonons modes and photoluminescence (PL) corresponding to europium electronic transitions were investigated. In the as-synthesized state, samples were X-ray and Raman amorphous with few tetragonal (also monoclinic) crystallites being observed under HRTEM microscopy. *In situ* XRD patterns show that all samples crystallize in the tetragonal phase around  $450$  °C. The time-resolved PL spectra of europium doped and impregnated ZrO<sub>2</sub> show spectral dynamics with time delay after lamp/laser pulse which is assigned to the co-existence of the different amorphous and crystalline components or unreacted europium precursor. From *in situ* Raman spectra, crystallization was detected at  $\sim 300$ - $350$  °C, monitoring for the characteristic tetragonal like <sup>5</sup>D<sub>0</sub>-<sup>7</sup>F<sub>2</sub> emission of europium at  $606$  nm. The ratio of tetragonal to amorphous emission increased abruptly from ca. 2- 4 % at  $300$ -  $400$  °C to almost 25 % at  $400$ -  $450$  °C whereas at  $500$  °C the emission is mostly tetragonal.



(See, for example, C. Tiseanu, V. Parvulescu, B. Cojocaru, Kelly Pemartin, M. Sanchez Dominguez, M. Boutonnet, "[In situ Raman and Time-Resolved Luminescence Investigation of Local Structure of ZrO<sub>2</sub> in the Amorphous to Crystalline Phase Transition](#)" J. Phys. Chem. C. 116(31), 16776-16783(2012)).



Paper

### Order and disorder effects in nano-ZrO<sub>2</sub> investigated by micro-Raman and spectrally and temporarily resolved photoluminescence

Carmen Tiseanu,<sup>\*a</sup> Bogdan Cojocaru,<sup>b</sup>  
Vasile I. Parvulescu,<sup>b</sup> Margarita Sanchez-Dominguez,<sup>cd</sup>  
Philipp A. Primus,<sup>e</sup> and Magali Boutonnet<sup>f</sup>

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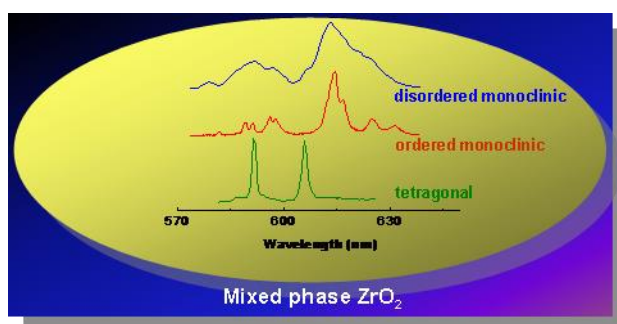
Phys. Chem. Chem. Phys., 2012, 14, 12970-12981

DOI: 10.1039/C2CP41946G

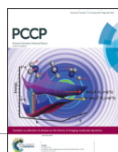
Received 11 Jun 2012, Accepted 23 Jul 2012

First published online 24 Jul 2012

Based on the Raman spectra excited at three different wavelengths *i.e.* 488, 514 and 633 nm and measured in the spectral range of 150–4000 cm<sup>-1</sup> the correlation between the phonon spectra of ZrO<sub>2</sub> and luminescence of europium has been revealed. After annealing at 500 °C, the overall Eu<sup>3+</sup> emission is dominated by Eu<sup>3+</sup> located in tetragonal symmetry lattice sites with a crystal-field splitting of the <sup>5</sup>D<sub>0</sub>–<sup>7</sup>F<sub>1</sub> emission of 20 cm<sup>-1</sup>. Annealing of ZrO<sub>2</sub> at 1000 °C leads to a superposition of Eu<sup>3+</sup> emissions from tetragonal and monoclinic lattice sites with monoclinic crystal-field splitting of 200 cm<sup>-1</sup> for the <sup>5</sup>D<sub>0</sub>–<sup>7</sup>F<sub>1</sub> transition. At all temperatures, a non-negligible amorphous/disordered content is also measured and determined to be of monoclinic nature. It was found that the evolutions with calcination temperature of the average PL lifetimes corresponding to europium emission in the tetragonal and monoclinic sites and the monoclinic phase content of the Eu<sup>3+</sup> doped ZrO<sub>2</sub> samples follow a similar trend. By use of specific excitation conditions, the distribution of europium on the amorphous/disordered surface or ordered/crystalline sites can be identified and related to the phase content of zirconia. The role of zirconia host as a sensitizer for the europium PL is also discussed in both tetragonal and monoclinic phases



Under selective and time-resolved luminescence excitation, distribution of europium in a mixed phase ZrO<sub>2</sub> is associated with ordered/disordered monoclinic and tetragonal sites. (See, for example, C. Tiseanu, B. Cojocaru, V. Parvulescu, M. Sanchez Dominguez, P. A. Primus, M. Boutonnet, "[Order and disorder effects in nano-ZrO<sub>2</sub> investigated by micro-Raman and spectrally and temporarily resolved photoluminescence](#)" Phys. Chem. Chem. Phys. 14(37), 12970-12981(2012)).



Paper

**Local structure and nanoscale homogeneity of  $\text{CeO}_2\text{-ZrO}_2$ : differences and similarities to parent oxides revealed by luminescence with temporal and spectral resolution**

Carmen Tiseanu,<sup>\*a</sup> Vasile Parvulescu,<sup>b</sup> Daniel Avram,<sup>a</sup>

Bogdan Cojocaru,<sup>b</sup> Magali Boutonnet<sup>c</sup> and

Margarita Sanchez-Dominguez<sup>de</sup>

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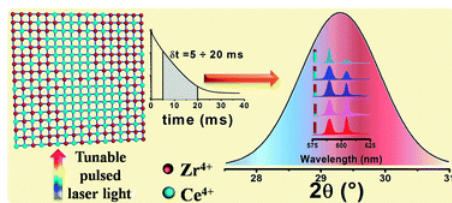
*Phys. Chem. Chem. Phys.*, 2014, **16**, 703-710

DOI: 10.1039/C3CP52893F

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First published online 21 Nov 2013

Although homogeneity at the atomic level of  $\text{CeO}_2\text{-ZrO}_2$  with a Ce/Zr atomic ratio close to unity is considered to be one of the main causes for the increased total oxygen storage capacity (OSC), the characterization approaches of homogeneity remain a major challenge. We propose a simple, yet effective method, to assess both structural and compositional homogeneity of  $\text{CeO}_2\text{-ZrO}_2$  by using  $\text{Eu}^{3+}$  luminescence measured with time and dual spectral resolution (emission and excitation). For  $\text{Eu}^{3+}\text{-CeO}_2\text{-ZrO}_2$  calcined at 750 °C, the X-ray diffraction, Raman and High-Resolution Transmission Electron Microscopy data converge to a single pseudo-cubic phase. However, the evolution of  $\text{Eu}^{3+}$ - delayed luminescence from cubic ceria-like to tetragonal zirconia-like emission reveals the formation of  $\text{CeO}_2$ - and  $\text{ZrO}_2$ -rich nanodomains and provides evidence for early phase separation. For  $\text{Eu}^{3+}\text{-CeO}_2\text{-ZrO}_2$  calcined at 1000 °C, the emission of  $\text{Eu}^{3+}$  reveals both structural and compositional inhomogeneity. Our study identifies the differences between the local structure properties of  $\text{CeO}_2$  and  $\text{ZrO}_2$  parent oxides and  $\text{CeO}_2\text{-ZrO}_2$  mixed oxide, also confirming the special chemical environment of the oxygen atoms in the mixed oxide as reported earlier by Extended X-ray Absorption Fine Structure investigation



(See, for example, C. Tiseanu, V. Parvulescu, D. Avram, B. Cojocaru, M. Boutonnet, M. Sanchez-Dominguez "[Local structure and nanoscale homogeneity of  \$\text{CeO}\_2\text{-ZrO}\_2\$ : Differences and similarities to parent oxides revealed by luminescence with temporal and spectral resolution](#)", *Phys. Chem. Chem. Phys.* **16**, 703-710 (2014)).

## II. Luminescence of redox active lanthanide doped I – III

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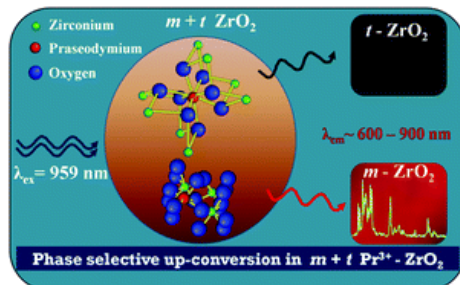
**Structural, down- and phase selective up-conversion emission properties of mixed valent Pr doped into oxides with tetravalent cations**

Carmen Tiseanu,<sup>\*a</sup> Vasile Parvulescu,<sup>b</sup> Daniel Avram,<sup>a</sup>  
Bogdan Cojocaru,<sup>b</sup> Nicoleta Apostol,<sup>c</sup>  
Andrea V. Vela-Gonzalez<sup>d</sup> and  
Margarita Sanchez-Dominguez<sup>d</sup>

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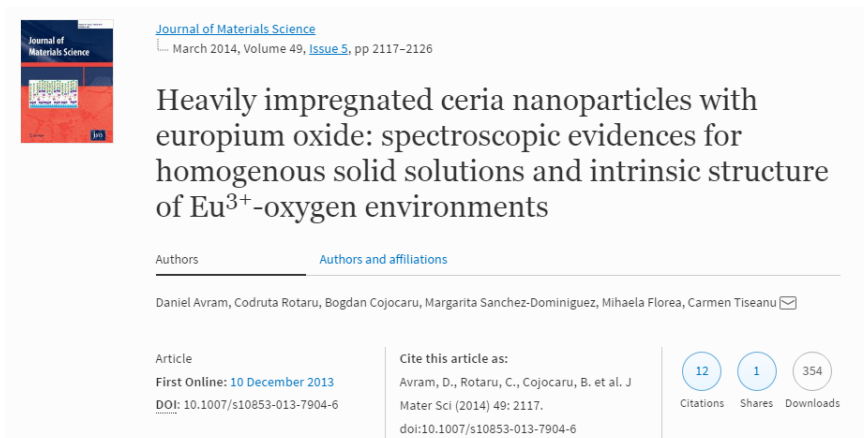
*Phys. Chem. Chem. Phys.*, 2014, 16, 5793-5802  
DOI: 10.1039/C3CP54899F  
Received 21 Nov 2013, Accepted 20 Jan 2014  
First published online 18 Feb 2014

We have investigate the structure–property relationships in Pr-doped CeO<sub>2</sub> and ZrO<sub>2</sub> using X-ray diffraction (XRD), Raman, UV to Vis Diffuse Reflectance (DR-UV/Vis), X-ray Photoelectron (XPS), and luminescence (PL) spectroscopies. Both 3+ and 4+ valence states of Pr are evidenced, irrespective of the host and calcination temperature,  $T$  ( $T= 500$  and  $1000$  °C) with consequences on absorption, surface, vibrational and luminescence properties. Only zirconia represents a suitable host for Pr<sup>3+</sup> luminescence. The distinct trivalent Pr centers and their excitation mechanism are identified in relation to the tetragonal and monoclinic phases of ZrO<sub>2</sub>. A near-infrared to visible up-conversion (UPC) emission of Pr<sup>3+</sup> is observed upon excitation at 959 nm which occurs, most probably, *via* a two-photon excited state process. By using a multi-wavelength, time-gated excitation, the UPC process is established as phase selective, *i.e.* only Pr<sup>3+</sup> located in the monoclinic sites of the mixed phase, monoclinic and tetragonal ZrO<sub>2</sub> ( $T= 1000$  °C) contribute to the UPC emission. We believe that, besides the local symmetry, a key role in phase selective UPC is played by the presence of Pr<sup>3+</sup> low-lying 4f 5d levels. To the best of our knowledge, this is the first report of phase selective up-conversion emission in a lanthanide doped multi-phase host.

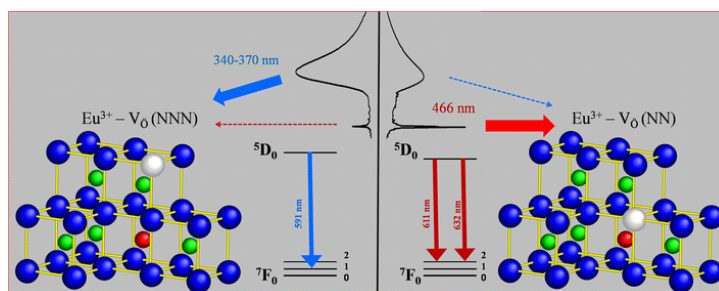


(See, for example, C. Tiseanu, V. Parvulescu, D. Avram, B. Cojocaru, N. Apostol, A. V. Vela-Gonzalez, M. Sanchez-Dominguez, "[Structural down- and phase selective up-conversion emission properties of mixed valent Pr doped into oxides with tetravalent cations](#)", *Phys. Chem. Chem. Phys.* 16, 5793-5802 (2014)).

### III. Novel insights into the Ln - Ln and Ln - host (I – III) interactions



We have investigated the homogeneity, structural and luminescence properties of ceria nanoparticles doped with  $\text{Eu}^{3+}$ .  $\text{Eu}^{3+}$  in concentration of 1, 5 and 10 wt% was incorporated via wetness impregnation into preformed ceria nanoparticles followed by calcination in air at 1000 °C. A remarkable homogeneity of  $\text{Eu}^{3+}$ -ceria solid solutions is measured for ceria grown by citrate and micro-emulsion methods using Raman, Diffuse Reflectance in UV–Vis, photoluminescence spectroscopies and X-ray diffraction, even for the  $\text{Eu}^{3+}$  concentration of 10 wt%. The emission properties of all  $\text{Eu}^{3+}$ -doped ceria samples are well-characterized by a two main centre model assigned to perturbed and isolated  $\text{Eu}^{3+}$  centres. It is established that the characteristic emission and excitation spectra of the two main  $\text{Eu}^{3+}$  centres as well as the overall multisite distribution of  $\text{Eu}^{3+}$  within ceria lattice are intrinsic properties of  $\text{Eu}^{3+}$ -doped ceria since these do not depend on synthesis route, nanoparticle size and  $\text{Eu}^{3+}$  concentration.



Two centre model in  $\text{Eu}^{3+}$  doped ceria nanoparticles. These centres correspond to  $\text{Eu}^{3+}$  located in the nearest (local symmetry lower than cubic and  $\text{Eu}^{3+}$ -oxygen coordination lower than eight) and next-nearest-neighbour positions (cubic local symmetry and eightfold  $\text{Eu}^{3+}$ -oxygen coordination) to oxygen vacancy, respectively (See, for example, D. Avram, C. Rotaru, B. Cojocaru, M. Sanchez-Dominguez, M. Florea, C. Tiseanu "[Heavily impregnated ceria nanoparticles with europium oxide: spectroscopic evidences for homogenous solid solutions and intrinsic structure of  \$\text{Eu}^{3+}\$  - oxygen environments](#)", *J. Mater. Sci.*, 49(5), 2117-2126 (2014)).





Paper

## Exceptional capability of nanosized CeO<sub>2</sub> materials to “dissolve” lanthanide oxides established by time-gated excitation and emission spectroscopy

Carmen Tiseanu,<sup>\*a</sup> Vasile Parvulescu,<sup>b</sup> Daniel Avram,<sup>a</sup>

Bogdan Cojocaru,<sup>b</sup> and Margarita Sanchez-Dominguez<sup>c</sup>

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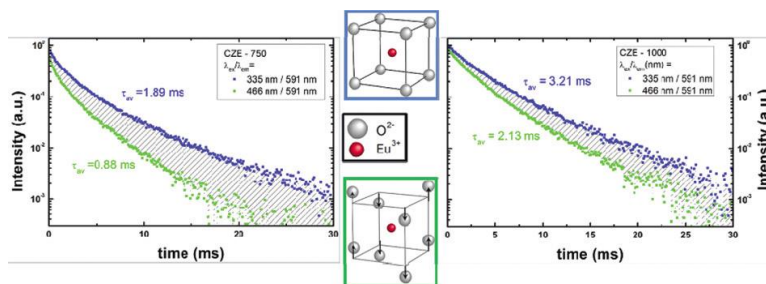
*Dalton Trans.*, 2014, 43, 7622-7630

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The atomic scale homogeneity of Ce and Zr oxygen bonds represents the main reason for enhanced total oxygen storage capability of CeO<sub>2</sub>-ZrO<sub>2</sub> (Ce/Zr = 1) as compared to that of CeO<sub>2</sub>. Here, we demonstrate that the addition of 10% Eu<sup>3+</sup> by wet impregnation on preformed nanosized CeO<sub>2</sub>-ZrO<sub>2</sub> (Ce/Zr = 1) followed by calcination induces a remarkable homogeneity of 10% Eu<sup>3+</sup>-CeO<sub>2</sub>-ZrO<sub>2</sub> solid solution. By use of time-resolved emission and excitation spectroscopies, the improvement of the nanoscale chemical and structural homogeneity of 10% Eu<sup>3+</sup>-CeO<sub>2</sub>-ZrO<sub>2</sub> calcined at 1000 °C as compared to sample calcined at 750 °C is demonstrated. Based on the comparison of luminescence properties of 10% Eu<sup>3+</sup> impregnated on preformed nanosized CeO<sub>2</sub>-ZrO<sub>2</sub> and CeO<sub>2</sub>, we also show that the presence of zirconium does not only preserve the ability of cerium oxide to “dissolve” lanthanide oxide, but also determines an important stabilization of defects (oxygen vacancies) generated upon Eu<sup>3+</sup> doping.



(See, for example, C. Tiseanu, V. Parvulescu, D. Avram, B. Cojocaru, M. Sanchez-Dominguez ["Exceptional capability of CeO<sub>2</sub>-ZrO<sub>2</sub> to "dissolve" europium oxide established by X-ray Diffraction, Raman and time-resolved luminescence spectroscopy"](#), *Dalton Trans.* 43(20), 7622-7630 (2014)).



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

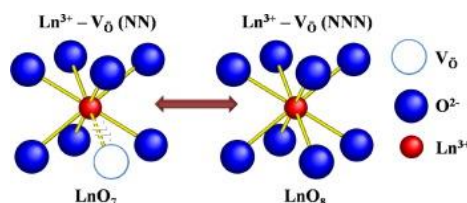
Daniel Avram<sup>a</sup>, Cristina Gheorghe<sup>a</sup>, Codruta Rotaru<sup>b</sup>, Bogdan Cojocaru<sup>b</sup>, Mihaela Florea<sup>b</sup>, Vasile Parvulescu<sup>b</sup>, Carmen Tiseanu<sup>a</sup>  

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We have reported a first study on the local structure properties, lanthanide–lanthanide and lanthanide–defect interactions in lanthanide ( $\text{Sm}^{3+}/\text{Nd}^{3+}$  and  $\text{Sm}^{3+}/\text{Eu}^{3+}$ ) co-doped  $\text{CeO}_2$  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  $\text{Sm}^{3+}$  sites is not affected by the presence of the  $\text{Nd}^{3+}$  or  $\text{Eu}^{3+}$  co-dopant irrespective of concentration. The results suggest that the excess of oxygen vacancies generated by the co-dopant is not associated with  $\text{Sm}^{3+}$ , being more probably associated with the  $\text{Nd}^{3+}/\text{Eu}^{3+}$  or/and  $\text{Ce}^{4+}$  cations. It is also observed that  $\text{Sm}^{3+}$  is not involved in significant non-radiative energy transfer to  $\text{Nd}^{3+}$  or  $\text{Eu}^{3+}$  while the relative strong shortening of  $\text{Nd}^{3+}$  luminescence decay with concentration is most probably related to cross-relaxation in  $\text{Nd}^{3+}$ – $\text{Nd}^{3+}$  pairs.



(See, for example, Avram, C. Gheorghe, C. Rotaru, B. Cojocaru, M. Florea, V. Parvulescu, C. Tiseanu "[Lanthanide - lanthanide and lanthanide - defect interactions in co - doped ceria revealed by luminescence spectroscopy](#)", *J. Alloys Compd.* 616, 535-541 (2014)).



## Local structure in $\text{CeO}_2$ and $\text{CeO}_2$ – $\text{ZrO}_2$ nanoparticles probed by Eu luminescence

Vasile I. Parvulescu<sup>a</sup>, Carmen Tiseanu<sup>b</sup>  

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We have also established that the luminescence of Eu represents an excellent probe for surface *versus* inner lattice sites location, Eu–defects interactions, nanoscale homogeneity and defects (re) configuration


under fuel cell operating conditions in CeO<sub>2</sub> nanoparticles. Moreover, the Eu probe-based site selective, time-gated luminescence spectroscopy can complement significantly the structural information provided by Raman scattering and X-ray diffraction, such as phase content, homogeneity and presence of defects in the diluted doping regime. (See, for example, **II. V. I. Parvulescu, C. Tiseanu** "[Local structure in CeO<sub>2</sub> and CeO<sub>2</sub> - ZrO<sub>2</sub> nanoparticles probed by Eu luminescence](#)", *Catal. Today*, 253, 33-39 (2015)).

#### IV. Assessment of the potential of I - III hosts as emission up- converters



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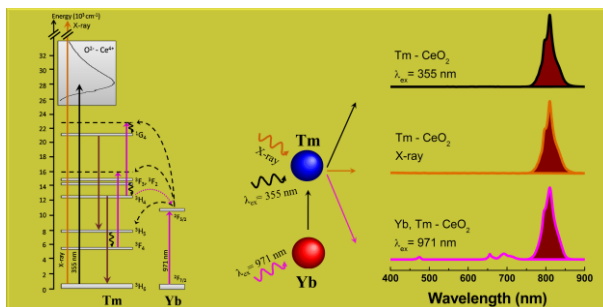
**Pure and almost pure NIR emission of Tm and Tm,Yb-CeO<sub>2</sub> under UV, X-ray and NIR up-conversion excitation: key roles of level selective antenna sensitization and charge-compensation**

Daniel Avram,<sup>a</sup> Bogdan Cojocaru,<sup>b</sup> Adriana Urda,<sup>b</sup>  
Ion Tiseanu,<sup>a</sup> Mihaela Florea<sup>b</sup> and Carmen Tiseanu<sup>\*b</sup>

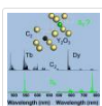
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First published online 15 Sep 2015

We have shown, for the first time, that the structure of CeO<sub>2</sub> host has a significant effect on the down – and up – conversion emission of Ln dopants with at least two properties being notable: the low-lying CT band of CeO<sub>2</sub> that acts as a selective *antenna* sensitizer of Ln (Tm, Er, Ho) emission and the defects induced by substitution of Ce<sup>4+</sup> by trivalent Ln *via* the charge-compensation mechanism. The selective character of CT band sensitization is responsible for the pure NIR emission of Tm - CeO<sub>2</sub> at 807 nm under UV excitation that may be of interest for broad UV to NIR downshifting applications. More interestingly, the NIR emission at 807 nm that is measured under high-energy, X-ray excitation renders Tm - CeO<sub>2</sub> attractive for high - penetration tissue imaging and diagnostics. Relevancy of Tm - CeO<sub>2</sub> for theranostics applications may be significant as nanoceria can act both as a radiosensitizer, by selectively enhancing radiation induced tumour damage and as a radioprotector of the normal tissue against adverse effects of radiotherapy. Upon excitation across Yb absorption profile, a relative intense UPC emission of Tm is observed with a NIR to blue emission ratio ranging from 24 to 100. The optimization of Ln doped CeO<sub>2</sub> NPs for imaging and therapy applications require further knowledge of the impact of the low lying CT band of CeO<sub>2</sub> and charge – compensation on the overall, down- *and* up – conversion emission properties.



A first study that correlates the down and up-conversion emission properties of lanthanide(s)–(co) dopants with CeO<sub>2</sub> structure. (See for example, D. Avram, A. Urda, B. Cojocaru, I. Tiseanu, M. Florea, C. Tiseanu ["Pure and almost pure NIR emission of Tm and Tm, Yb - CeO<sub>2</sub> under UV, X - ray and NIR up - conversion excitation: Key roles of level selective antenna sensitization and charge - compensation"](#), *Phys. Chem. Chem. Phys.* 17(46), 30988-30992 (2015)).



## Advances in luminescence of lanthanide doped Y<sub>2</sub>O<sub>3</sub>: case of S<sub>6</sub> sites

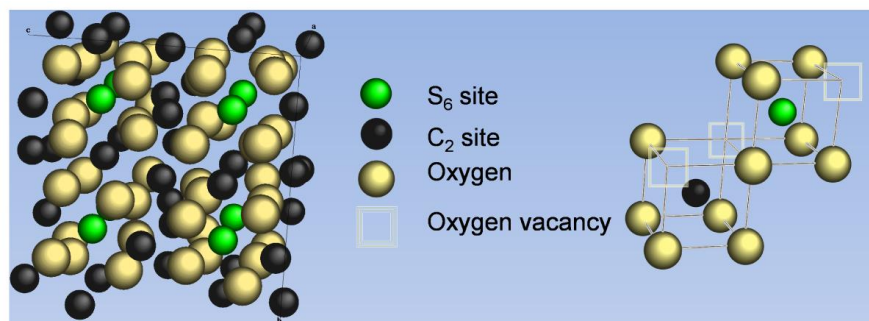
Daniel Avram, Bogdan Cojocaru, Mihaela Florea, and Carmen Tiseanu

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Optical Materials Express Vol. 6, Issue 5, pp. 1635-1643 (2016) • <https://doi.org/10.1364/OME.6.001635>

Although the emission of lanthanide (Ln) ions doped cubic sesquioxides has been subject of extensive studies, there are fundamental issues still to be elucidated. Specifically, compared to the well – understood emission of Ln at C<sub>2</sub> sites, the emission at the inversion S<sub>6</sub> (C<sub>3i</sub>) sites, representing ¼ of the total sites, has been identified only for Pr, Nd, Eu, Sm and Yb. Here, we present a first report and improved identification of the emission, excitation and decay properties of Tb, Dy and Pr at S<sub>6</sub> sites in Y<sub>2</sub>O<sub>3</sub> by use of time-gated luminescence spectroscopy. The emission of Tb at S<sub>6</sub> sites is characterized by an intensity ratio relative to the yellow band at 490 nm of 0.1 compared to 0.5 measured for Tb at C<sub>2</sub> sites. Dy at S<sub>6</sub> sites displays a relatively intense, near-infrared emission at 765 nm which is red-shifted by ca. 200 nm relative to yellow peaked emission of Dy at C<sub>2</sub> sites. The emission lifetimes of 9.4 and 4.8 ms, associated with Tb and Dy at S<sub>6</sub> sites, exceed by a factor of 5 and 10 those of C<sub>2</sub> counterparts. It is also found that Dy may be regarded as a sensitive probe for the inversion symmetry, comparable with the more recognized Eu. The participation of Ln at S<sub>6</sub> sites to the up-conversion emission is revealed for the first time in Sm doped Y<sub>2</sub>O<sub>3</sub> and Eu /Tb, Yb co-doped Y<sub>2</sub>O<sub>3</sub> and explained in terms of successive ground state and excited state absorptions and cooperative energy transfer, respectively.



The scheme of the cubic structure of  $Y_2O_3$  and the schematic representation of  $C_2$  and  $S_6$  sites of  $Y_2O_3$ . ( See for example: D. Avram, B. Cojocaru, M. Florea, C. Tiseanu. [Advances in luminescence of lanthanide doped  \$Y\_2O\_3\$ : case of  \$S\_6\$  sites](#). *Opt. Mater. Express.* 6(5), 1635-1643 (2016))



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Paper



### Defect induced tunable near infrared emission of Er–CeO<sub>2</sub> by heterovalent co-dopants

Mihaela Florea,<sup>a</sup> Daniel Avram,<sup>b</sup> Bogdan Cojocaru,<sup>a</sup>  
Ion Tiseanu,<sup>b</sup> Vasile Parvulescu<sup>a</sup> and Carmen Tiseanu<sup>\*b</sup>

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*Phys. Chem. Chem. Phys.*, 2016, **18**, 18268–18277

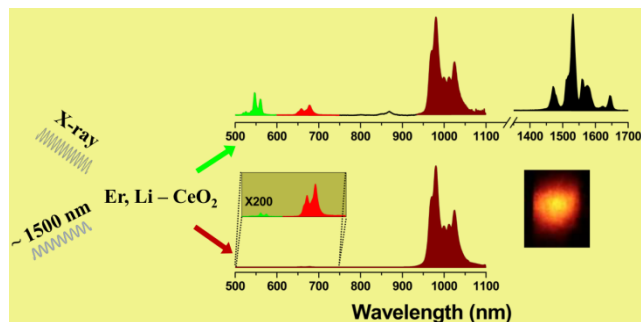
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We investigate the effects of heterovalent co-dopants on the structural and emission properties of 1% Er–CeO<sub>2</sub> nanoparticles. The CeO<sub>2</sub> oxide host was selected on the basis of its fairly well-understood defect chemistry in either a pure or doped state. As a luminescent activator, Er is acknowledged as an interesting element due to its rich luminescence and excitation properties spanning the visible to near-infrared range. The optically inactive trivalent La and monovalent Li metal ions with a concentration of up to 20% were chosen to presumably generate a variable amount of defects in the Er–CeO<sub>2</sub> lattice. It was found that La and Li co-dopants induced distinct changes related to the size, lattice constant, bandgap energy, lattice and surface defects of Er–CeO<sub>2</sub>. As a result of these changes, a strong modulation of the luminescence intensity and shape was measured using a suite of excitation conditions (charge-transfer absorption band of CeO<sub>2</sub>, direct/up-conversion into Er absorptions and X-ray excitation modes). The use of Eu as a luminescent probe offered additional information concerning the effects of La/Li co-doping on the local structure surrounding the luminescent activator. Remarkably high percentages of 90 and 98% of the total emission of Er measured between 500 and 1100 nm are measured in the near-infrared region at 980 nm under X-ray

and up-conversion excitation at  $\sim 1500$  nm, respectively. The optical properties suggest that Li, Er co-doped  $\text{CeO}_2$  has good potential for therapy and biological imaging.




Emission spectra of Er, Li -  $\text{CeO}_2$  obtained under X-ray and infrared excitation (See for example: M. Florea, D. Avram, B. Cojocaru, I. Tiseanu, V. Parvulescu, C. Tiseanu. [Defects induced tunable near infrared emission of Er-CeO<sub>2</sub> by heterovalent co-dopants](#). Phys. Chem. Chem. Phys. 18, 18268-18277 (2016))






Journal of Luminescence

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Full Length Article

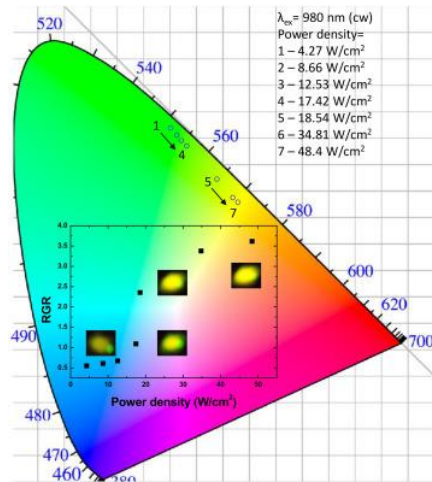
### Time-gated down-/up-conversion emission of Ho– $\text{CeO}_2$ and Ho, Yb– $\text{CeO}_2$ nanoparticles

Daniel Avram<sup>a</sup>, Ioana Porosnicu<sup>a</sup>, Bogdan Cojocaru<sup>b</sup>, Mihaela Florea<sup>b</sup>, Carmen Tiseanu<sup>a</sup>.   

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Herein, we report the luminescence properties of (1%) Ho and (1%) Ho, (20%) Yb– $\text{CeO}_2$  nanoparticles, investigated by time-resolved luminescence spectroscopy at 300 and 80 K temperatures. The emission was measured over a broad detection range, from visible (450 nm) up to infrared (1500 nm) with excitation ranging from 210 to 1000 nm. The structural properties were characterized by X-ray diffraction, Raman, Diffuse Reflectance Optical and Diffuse Reflectance Fourier Transform Infrared spectroscopies. The up-conversion emission of Ho– $\text{CeO}_2$  and Ho, Yb– $\text{CeO}_2$  using excitation wavelengths of 646.6, 759, 918 and 971 nm, respectively, were described in terms of time-gated up-conversion emission and excitation spectra, as well as up-conversion emission decays. Under short gate/ short delay conditions, the contribution of the  $^5\text{F}_3$  and  $^5\text{F}_5$  energy levels to the red emission of Ho at 630–680 nm could be separated. The role of  $\text{CeO}_2$  charge transfer band as a selective antenna sensitizer as well as back transfer of excitation from Ho to Yb was also discussed. The mechanisms involved in the up-conversion emission of Ho and Ho, Yb– $\text{CeO}_2$  were interpreted as ground state absorption followed by excited state absorption and energy transfer, respectively. For Ho, Yb– $\text{CeO}_2$ , a tunable red to green up-conversion emission ratio from 0.5 to 3.6 was also observed by increasing the power density of  $\sim 4$  to  $48 \text{ W/cm}^2$  of a cw laser diode at 980 nm.



CIE chromaticity diagram showing the evolution of the (x, y) color coordinates with pumping power density for Ho, Yb - CeO<sub>2</sub> excited at 980 nm. Inset: red to green up - conversion emission ratio (RGR) evolution with pumping power density and the digital photographs showing the transition from green to yellow emission for Ho, Yb - CeO<sub>2</sub> pumped at 980 nm with increasing the power density. (See for example D. Avram, I. Porosnicu, B. Cojocaru, M. Florea, C. Tiseanu. [Time-gated down-/up-conversion emission of Ho-CeO<sub>2</sub> and Ho, Yb-CeO<sub>2</sub> nanoparticles](#). *J. Lumin.*179, 265-271 (2016))

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14. D. Avram, B. Cojocaru, M. Florea, C. Tiseanu. [Advances in luminescence of lanthanide doped Y<sub>2</sub>O<sub>3</sub>: case of S<sub>6</sub> sites](#). Opt. Mater. Express. 6(5), 1635-43 (2016).
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16. D. Avram, I. Porosnicu, B. Cojocaru, M. Florea, C. Tiseanu. [Time-gated down-/up-conversion emission of Ho-CeO<sub>2</sub> and Ho, Yb-CeO<sub>2</sub> nanoparticles](#). J. Lumin. 179, 265-271 (2016)

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1. C. Tiseanu, V. Parvulescu, Magali Boutonnet, B. Cojocaru, M. Sanchez Dominguez "Local structure of Ln<sup>3+</sup>-doped tetravalent nano-oxides" [4<sup>th</sup> International Symposium on Structure-Property Relationships in Solid State Materials](#), Bordeaux, France, 24-29.06.2012 (poster presentation)
2. C. Tiseanu, V. Parvulescu, Magali Boutonnet, B. Cojocaru, M. Sanchez Dominguez "Local structure of Ln<sup>3+</sup>-doped tetravalent nano-oxides" [XI International Conference on Nanostructured Materials](#), Palace Convention Center, Rhodes, Greece, 26-31.08.2012 (poster presentation)
3. D. Avram, B. Cojocaru, N. Gheorghe, C. Tiseanu "Cubic and low symmetry centers in Eu<sup>3+</sup> and Sm<sup>3+</sup> doped CeO<sub>2</sub> nanoparticles. Effects of dopant concentration and thermal treatment" [XI International Krutyn Summer School 2012](#), Krutyn, Poland, 23-29.09.2012 (poster presentation)
4. D. Avram, [10<sup>th</sup> European short course on "Principles and Applications of Time-Resolved Fluorescence Spectroscopy"](#) Berlin, Germany, 29.10-01.11.2012
5. D. Avram, B. Cojocaru, M. Florea, C. Tiseanu "Cubic and low symmetry of Eu<sup>3+</sup> doped CeO<sub>2</sub> nanoparticles: micro-Raman and luminescence spectroscopic study" [12<sup>th</sup> National Seminar of nanoscience and nanotechnology](#), The Romanian Academy Library, Bucharest, 16.05.2013 (poster presentation)
6. D. Avram, C. Tiseanu "Cubic and low symmetry centres in Eu<sup>3+</sup>/Sm<sup>3+</sup> doped CeO<sub>2</sub> nanoparticles: a micro-Raman and luminescence spectroscopic study" [Bucharest University Faculty of Physics 2013 Meeting](#), Bucharest, 21.06.2013 (oral presentation)
7. C. Tiseanu, D. Avram, B. Cojocaru, V. Parvulescu "Nanoscale homogeneity in luminescent lanthanide-doped nano - oxides", [European Congress and Exhibition on Advanced Materials and Processes 2013](#), Sevilla, Spain, 08.09-13.09.2013 (oral presentation)
8. C. Tiseanu "Interactions between ceria host and lanthanide dopants probed by luminescence spectroscopy", [Fundamentals and applications of cerium dioxide in catalysis](#), Udine, Italy, 11-14.07.2014 (invited lecture)
9. D. Avram, C. Tiseanu "IR, NIR and Vis to NIR and Vis up - Conversion Emission in Er doped BiOCl" [2014 JUNIOR EUROMAT 2014](#), Lausanne, Switzerland, 21-25.07.2014 (poster presentation)
10. D. Avram, C. Tiseanu "Infrared and Near-Infrared to Visible and Near-Infrared up-conversion emission of Yb - Ln (Ln= Er, Tm) co-doped CeO<sub>2</sub> nanoparticles for biological applications" [The 4th International Colloquium 'Physics of Materials' - PM-4](#), Bucharest, Romania, 13-14.11.2014 (oral presentation)

11. D. Avram, B. Cojocaru, M. Florea, V. Parvulescu, and C. Tiseanu, "Luminescence properties of CeO<sub>2</sub> doped with Ln ions under optical and X-ray excitation modes," [The 4th International Conference on the Physics of Optical Materials and Devices, ICOM 2015](#), 31 August - 04 September 2015, Budva, Montenegro; Book of Abstracts, ISBN: 978-86-7306-134-4, p. 53, presentation S9-O30-165 (oral presentation)

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### Theses

1. Daniel Avram - "Spectrally and temporally resolved luminescence of lanthanide doped nano-oxides", Faculty of Physics, University of Bucharest (June 2013), Advisor: Dr. Carmen Tiseanu (Master Thesis)

2. Ioana Porosnicu - "Down and Up-conversion processes in Ho and Ho, Yb doped CeO<sub>2</sub> nanoparticles", Faculty of Physics, University of Bucharest (June 2016), Advisor: Dr. Carmen Tiseanu (Master Thesis)

3. Daniel Avram - "Lanthanide doped nanoparticles: From local structure to long - range perspective *via* luminescence", Faculty of Physics, University of Bucharest (October 2016, admitted to doctoral school)