Doped oxide nanoparticles: From local structure to long – range perspective via luminescence

Financial support: UEFISCDI

Executive Agency for Higher Education, Research, Development and Innovation Funding

Project code: PN-III-P4-ID-PCE- 2016-0305 (67/2017)

Website: http://nanolumin.inflpr.ro/PCE2017.html

Project timespan: 2017 - 2019

Project Team

Project leader: Dr. Carmen Tiseanu

Members:

- Dr. Bogdan Cojocaru
- Drd Daniel Avram
- Msc student Caludiu Colbea
- Msc student Alin Broasca
- Msc student Diana Damian

Project Budget

No.	BUDGET CHAPTER (EXPENSES)	2017 (RON)	2018 (RON)	2019 (RON)	TOTAL (RON)
1	SALARIES	106 000	160 242	225 758	492 000
2	INVENTORY	175 000	6 000	5 000	186 000
3	MOBILITY	8 000	16 000	12 000	36 000
4	OVERHEAD	29 750	45 560	60 690	136 000
	TOTAL BUDGET	318 750	227 802	303 448	850 000

Abstract

In the recent years, lanthanide doped wide band gap semiconductor and oxide nanoparticles have become one of the fastest growing areas of scientific research. There are two main challenges when doping nanoscale materials with Ln ions. The first is host specific and concerns the huge surface/volume ratio. The second main challenges concern the "marriage" between the host and the lanthanide dopants. In the case of aliovalent doping, the misfit in the valence but also the ionic radii of the bulkier dopants and host cations can lead to reduced complex distribution of lanthanide as isolated substitutional /interstitial centres or associates with defects or/and reduce solubility. So, the first question to be answered when studying lanthanide doped nanoparticles is the following: How do we know if the nanoparticles have been successfully doped? Since the dopants class is represented by optically active dopants, a "natural" selection of a local structure oriented technique would be the luminescence spectroscopy based on use of the lanthanide as luminescence probe.

The project aims at clarifying the local structure around lanthanide dopants in three outstanding wide bandgap oxides SnO_2, TiO_2 and HfO_2. Our luminescence approach based on the simultaneous analysis of the site selective and time-gated luminescence allows an exceptional insight into the photophysics of doped nanoparticles. As lanthanide dopants with local probe properties, we select the Eu, Sm, Tb, Dy and Er ions with relevant emission in the visible and near – infrared, respectively. The project will address also the current limitations existing in the literature and which regard, essentially, the correlation between the local structure and long - range properties. To this aim, we will correlate the *in situ* luminescence with *in situ* X – ray diffraction and *in situ* Raman data to get in depth insight into the order/disorder, doping and surface effects during amorphous/crystalline to crystalline phase transition.

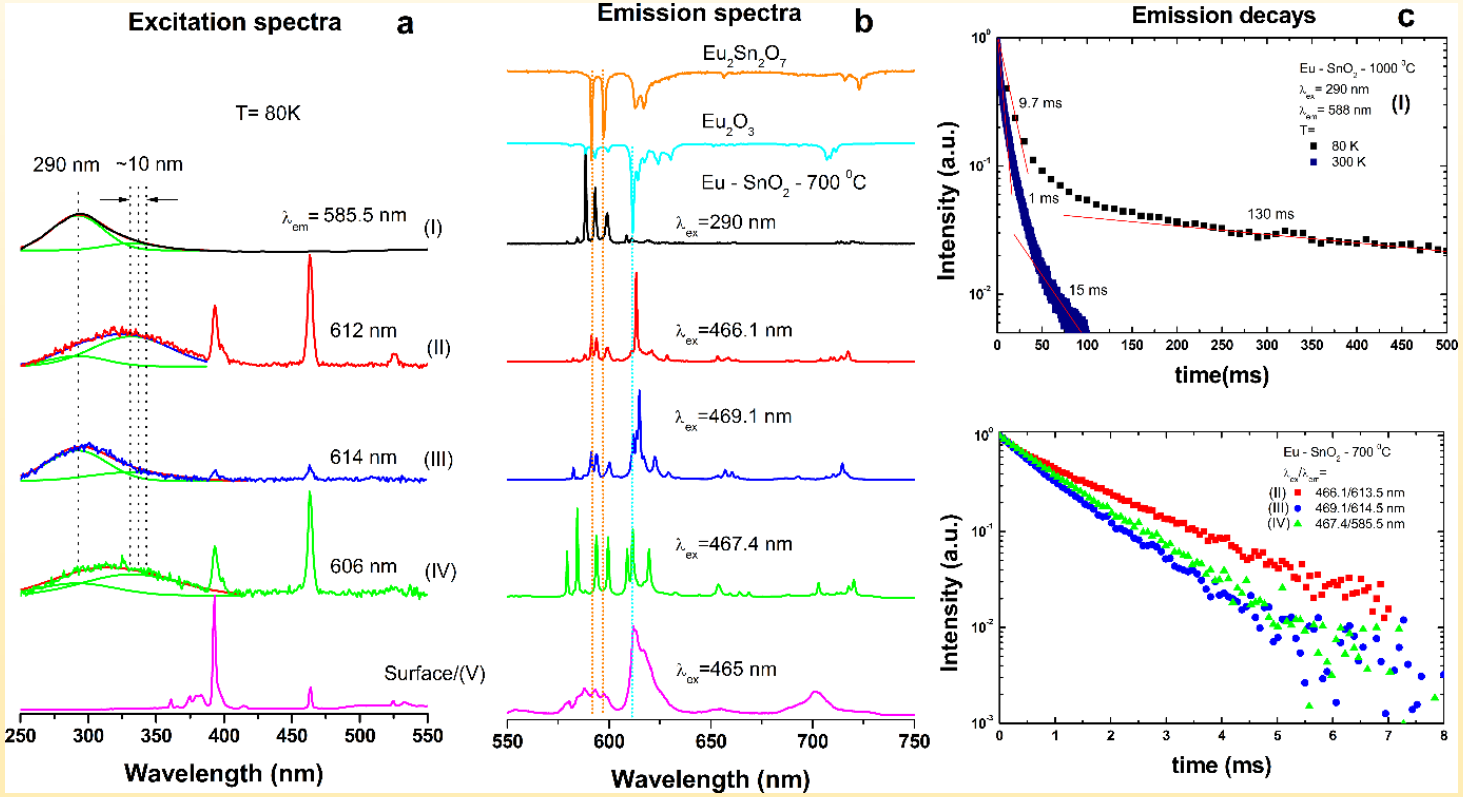
Objectives

The project aims at clarifying the local structure around lanthanide dopants in three outstanding wide bandgap oxides SnO_2, TiO_2 and HfO_2. Our luminescence approach based on the simultaneous analysis of the site selective and time-gated luminescence allows an exceptional insight into the photophysics of doped nanoparticles. As lanthanide dopants with local probe properties, we select the Eu, Sm, Tb, Dy and Er ions with relevant emission in the visible and near – infrared, respectively.

The project will address also the current limitations existing in the literature and which regard, essentially, the correlation between the local structure and long - range properties. To this aim, we will correlate the *in situ* luminescence with *in situ* X – ray diffraction and *in situ* Raman data to get in depth insight into the order/disorder, doping and surface effects during amorphous/crystalline to crystalline phase transition.

Major Scientific Results

1. We evidence for the first time a complex distribution of intrinsic nature composed of substitutional isolated, substitutional associates with defects as well as surface centers. Such multi-modal distribution is revealed for Eu and Sm, while Pr, Tb and Dy appear to be distributed mostly on the SnO_2 surface.

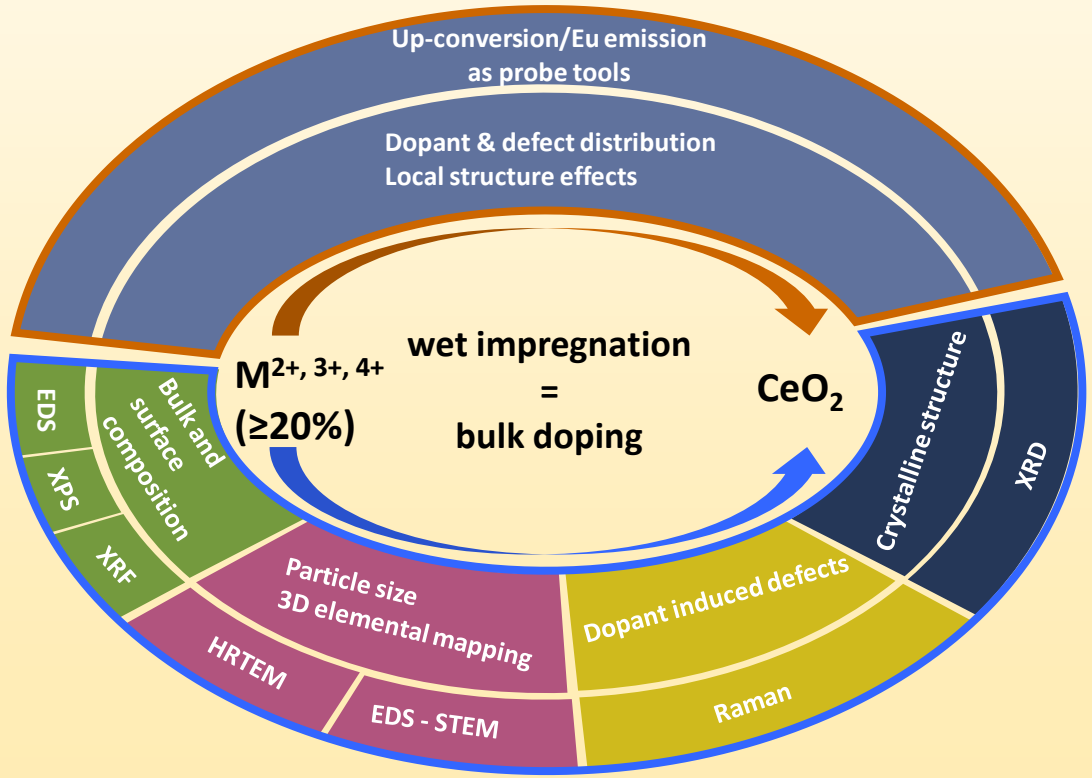


Summary of the emission properties of Eu-SnO_2 calcined at 700 /1000 °C and measured at 80 and 300 K. Characteristic excitation spectra (**a**), emission spectra (**b**) and emission decays (**c**) of Eu centers labelled as **I–V centers**.

Major Scientific Results

2. Heavy (>20%) wet impregnation of ceria with metals of various valences represents a viable alternative to bulk doping methods.

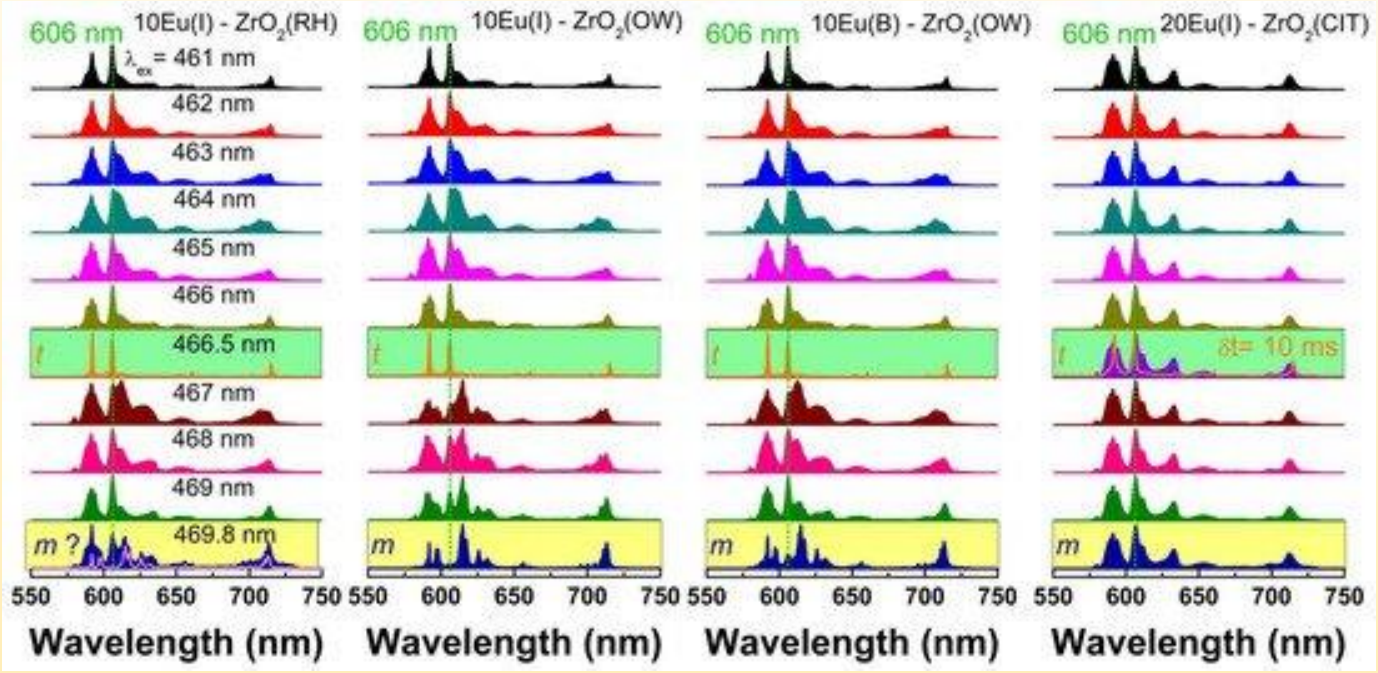
3. Using for the first time up-conversion as a probe tool for the location and distribution of dopant(s) in nanoscale systems and to identify the opposite roles of Ca and Zr as the repeller and the scavenger of oxygen vacancies in ceria, respectively.



Heavy (>20%) wet impregnation of ceria with metals of various valences represents a viable alternative to bulk doping methods.

Major Scientific Results

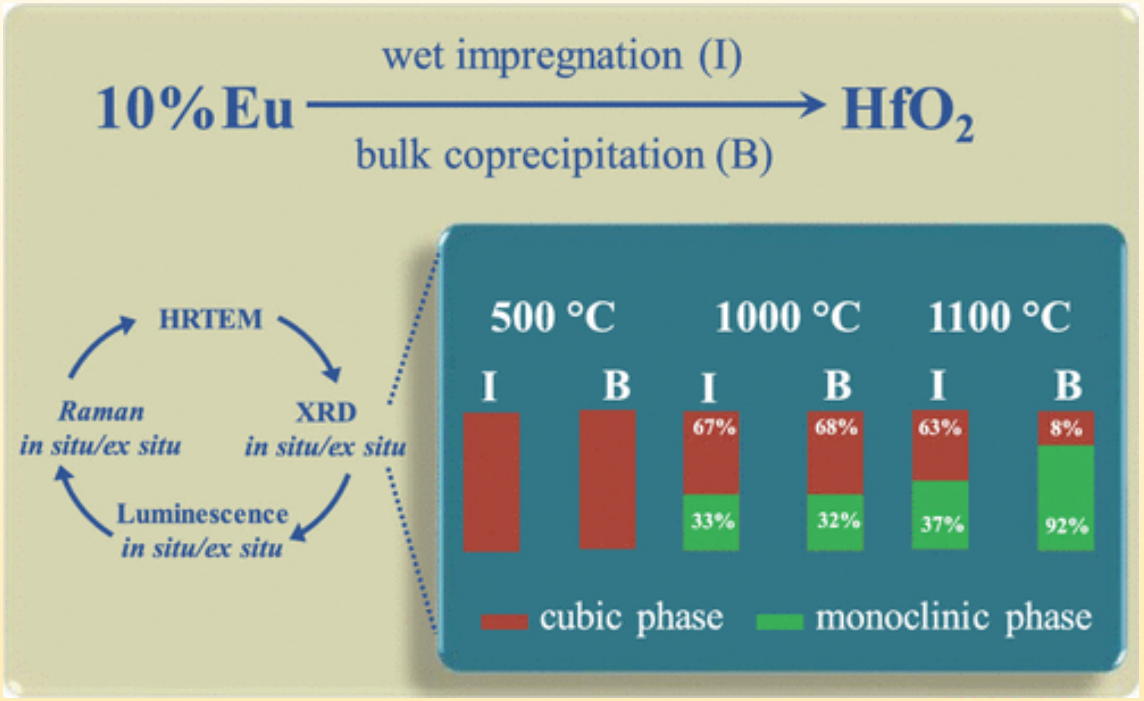
4. Wet impregnation with 10 and 20% Eu followed by calcination in air above 500 °C produces a full tetragonal phase stabilization of ZrO_2 nanoparticles in the bulk.



Comparison between the site-selective emission spectra of 10Eu(I)–ZrO_2 (OW, RH) and 20Eu(I)–ZrO_2 (CIT) performed at low temperature (T = 80 K). The green highlighted spectra correspond to well-separated tetragonal emission. The yellow highlighted spectra represent the contribution from the monoclinic fingerprint mission.

Major Scientific Results

5. CeO_2, ZrO_2, and HfO_2 represent a unique case of a family of oxides that is extremely tolerant to heavy doping by wet impregnation.

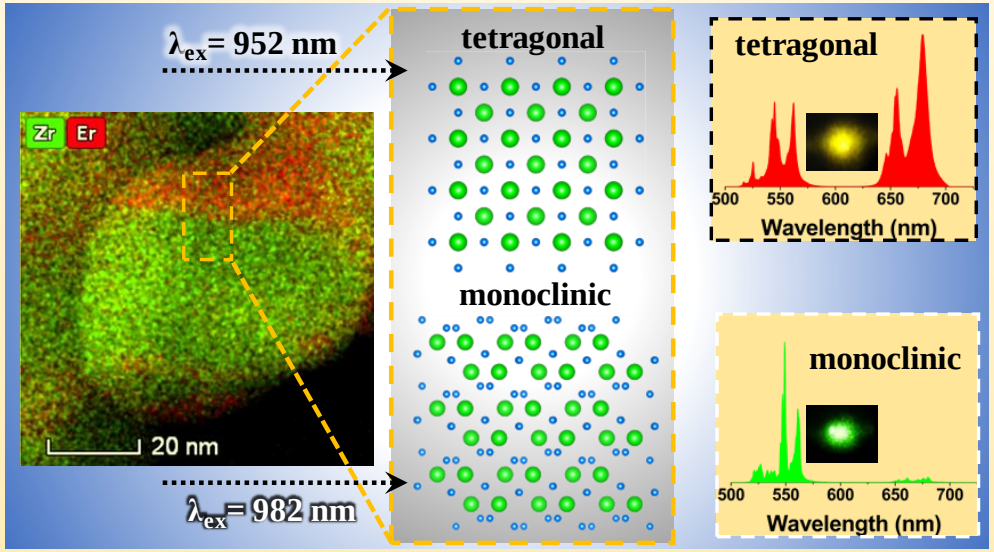


Effect of Eu Insertion Mode (Wet Impregnation/Bulk Coprecipitation) on Cubic Phase Stabilization of Hafnia Nanoparticles

Major Scientific Results

6. Rare evidence of a heterogeneous (Er enriched/Er depleted) distribution leading to the coexistence of two polymorphs in a single nanoparticle is revealed by phase and Z contrast TEM while the absence of the energy transfer between Er of the two polymorphs was confirmed by UPC emission measurements.

7. The outstanding sensitivity of combined TEM and UPC emission to subtle deviations from uniform doping in the diluted concentration regime renders such an approach relevant for various functional oxides supporting lanthanide dopants as emitters.



The distribution of a lanthanide (Er) dopant, be this enriched, depleted or surface segregated, is associated to its optical response across full tetragonal to monoclinic phase transformation of ZrO_2. This illustration depicts how the combination of upconversion (UPC) emission and advanced transmission electron microscopy (TEM) disentangles the structural phases and UPC emission determined by Er distribution in mixed phase nanoparticles.

Major Scientific Results

8. Local symmetry influences not only the emission intensity but also the relative contribution of the upconversion mechanisms, which can be spectrally tuned by the excitation wavelength. Our findings are relevant in the developing context of use of pulsed excited UPC emission of lanthanide doped nanoparticles in bioimaging, thermometry and lifetime multiplexing applications.

Under pulsed excitation, the upconversion emission intensity is comparable/110 times greater

in higher com-pared to in lower local symmetry, in contrast to cw excited upconversion.

Dissemination of Results – 2017
Articles in ISI Journals

Authors: Bogdan Cojocaru, Daniel Avram, Vadim Kessler, Vasile Parvulescu, Gulaim Seisenbaeva & Carmen Tiseanu

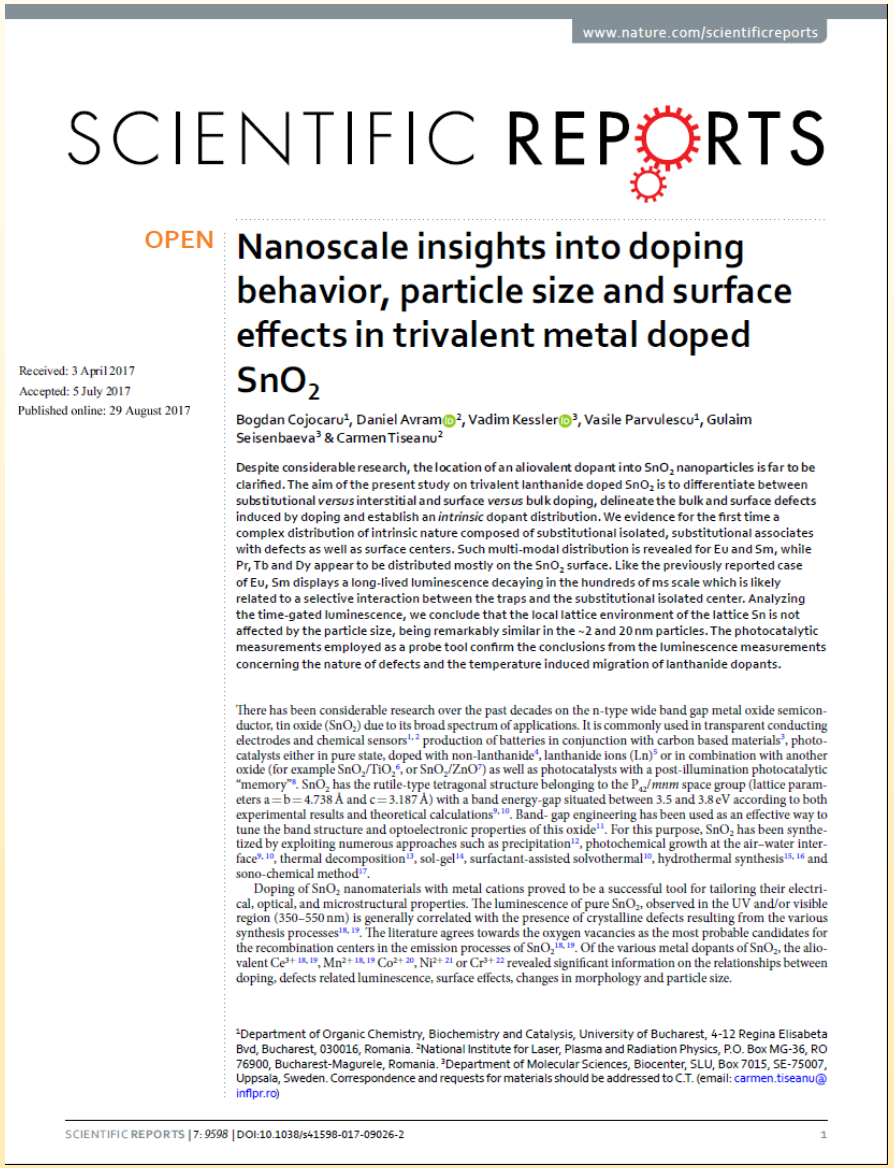
Article Title: Nanoscale insights into doping behavior, particle size and surface effects in trivalent metal doped SnO_2

*Scientific Reports, 2017, **7**, 9598

Acknowledgements

DA and CT acknowledge the Romanian National Authority for Scientific Research and Innovation, the program NUCLEU, contract 4N/2016 and the Romanian National Authority for Scientific Research and Innovation (CNCS-UEFISCDI), project PN-III-P4-ID-PCE-2016-0305 for the partial financial support. GS and VK acknowledge Swedish Research Council (Vetenskapsrådet) for the grant 2014–3938.

Although the article has the appropriate Acknowledgment, it is not part of the official dissemination of results as the accepted date of the article is a week prior the official project start.



www.nature.com/scientificreports

SCIENTIFIC REPORTS

OPEN

Received: 3 April 2017
Accepted: 5 July 2017
Published online: 29 August 2017

Nanoscale insights into doping behavior, particle size and surface effects in trivalent metal doped SnO_2

Bogdan Cojocaru[1], Daniel Avram[2], Vadim Kessler[3], Vasile Parvulescu[1], Gulaim Seisenbaeva[3] & Carmen Tiseanu[2]

Despite considerable research, the location of an aliovalent dopant into SnO_2 nanoparticles is far to be clarified. The aim of the present study on trivalent lanthanide doped SnO_2 is to differentiate between substitutional *versus* interstitial and surface *versus* bulk doping, delineate the bulk and surface defects induced by doping and establish an *intrinsic* dopant distribution. We evidence for the first time a complex distribution of intrinsic nature composed of substitutional isolated, substitutional associates with defects as well as surface centers. Such multi-modal distribution is revealed for Eu and Sm, while Pr, Tb and Dy appear to be distributed mostly on the SnO_2 surface. Like the previously reported case of Eu, Sm displays a long-lived luminescence decaying in the hundreds of ms scale which is likely related to a selective interaction between the traps and the substitutional isolated center. Analyzing the time-gated luminescence, we conclude that the local lattice environment of the lattice Sn is not affected by the particle size, being remarkably similar in the ~2 and 20 nm particles. The photocatalytic measurements employed as a probe tool confirm the conclusions from the luminescence measurements concerning the nature of defects and the temperature induced migration of lanthanide dopants.

There has been considerable research over the past decades on the n-type wide band gap metal oxide semiconductor, tin oxide (SnO_2) due to its broad spectrum of applications. It is commonly used in transparent conducting electrodes and chemical sensors[1,2] production of batteries in conjunction with carbon based materials[3], photocatalysts either in pure state, doped with non-lanthanide[4], lanthanide ions (Ln)[5] or in combination with another oxide (for example SnO_2/TiO_2[4], or SnO_2/ZnO[5]) as well as photocatalysts with a post-illumination photocatalytic "memory"[6]. SnO_2 has the rutile-type tetragonal structure belonging to the P_{42}/mnm space group (lattice parameters a = b = 4.738 Å and c = 3.187 Å) with a band energy-gap situated between 3.5 and 3.8 eV according to both experimental results and theoretical calculations[9,10]. Band- gap engineering has been used as an effective way to tune the band structure and optoelectronic properties of this oxide[11]. For this purpose, SnO_2 has been synthetized by exploiting numerous approaches such as precipitation[12], photochemical growth at the air–water interface[9,10], thermal decomposition[13], sol-gel[14], surfactant-assisted solvothermal[10], hydrothermal synthesis[15,16] and sono-chemical method[17].

Doping of SnO_2 nanomaterials with metal cations proved to be a successful tool for tailoring their electrical, optical, and microstructural properties. The luminescence of pure SnO_2, observed in the UV and/or visible region (350–550 nm) is generally correlated with the presence of crystalline defects resulting from the various synthesis processes[18,19]. The literature agrees towards the oxygen vacancies as the most probable candidates for the recombination centers in the emission processes of SnO_2[18,19]. Of the various metal dopants of SnO_2, the aliovalent Ce^{3+}[18,19], Mn^{2+}[18,19] Co^{2+}[20], Ni^{2+}[21] or Cr^{3+}[22] revealed significant information on the relationships between doping, defects related luminescence, surface effects, changes in morphology and particle size.

[1]Department of Organic Chemistry, Biochemistry and Catalysis, University of Bucharest, 4-12 Regina Elisabeta Bvd, Bucharest, 030016, Romania. [2]National Institute for Laser, Plasma and Radiation Physics, P.O. Box MG-36, RO 76900, Bucharest-Magurele, Romania. [3]Department of Molecular Sciences, Biocenter, SLU, Box 7015, SE-75007, Uppsala, Sweden. Correspondence and requests for materials should be addressed to C.T. (email: carmen.tiseanu@inflpr.ro)

Dissemination of Results - 2017 Conferences

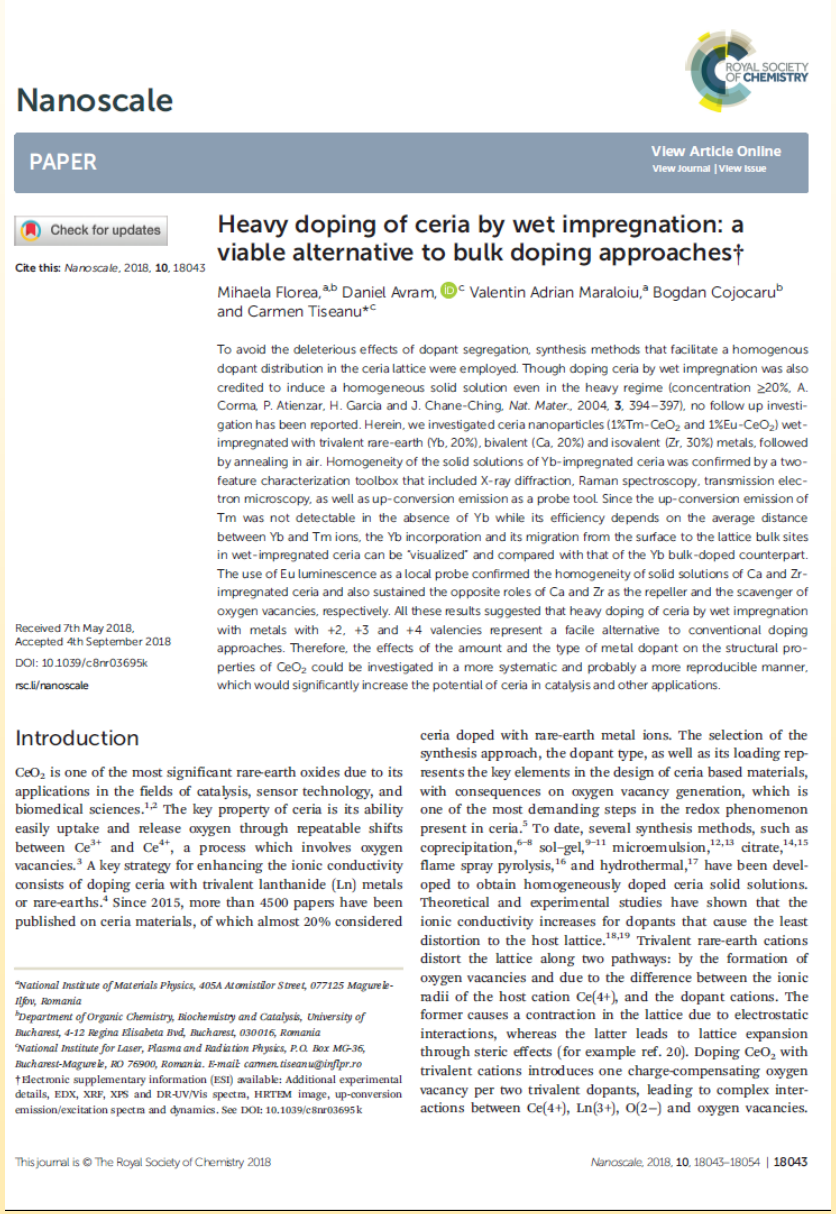
1. Daniel Avram, Bogdan Cojocaru, Mihaela Florea, Ion Tiseanu, Carmen Tiseanu “NIR optical and X-ray excitation of luminescence in Er doped oxide nanoparticles for spectral converters and theranostics” EUROMAT 2017, 17 – 22.09.2017, Thessaloniki, Greece
2. Daniel Avram, Bogdan Cojocaru, Ion Tiseanu, Mihaela Florea, Carmen Tiseanu “X-ray and Near-Infrared Excitation of Luminescence in Ln doped Nanoparticles for Bio-imaging Applications”, **SHIFT** 2017 (**S**pectral s**H**ap**I**ng **F**or biomedical and energy applica**T**ions), 12 – 17.11.2017, Costa Adeje, Spain (Awarded Poster prize (special mention) offered by J Mater Chem B, Royal Society of Chemistry , FI 4.5)

Dissemination of Results - 2018
Articles in ISI Journals

1. Mihaela Florea, Daniel Avram, Valentin Adrian Maraloiu, Bogdan Cojocaru & Carmen Tiseanu "Heavy doping ceria by wet impregnation: A viable alternative to bulk doping approaches" Nanoscale, **2018**, 10, 18043-18054

Acknowledgements

MF acknowledges Romanian National Authority for Scientific Research and Innovation (CNCS-UEFISCDI), project PN-III-P4-ID-PCE-2016-0692, contract 177/2017 for the partial financial support. CT and DA acknowledge the Ministry of Research and Innovation (Nucleus programme - contract 4N/2016) and the Romanian National Authority for Scientific Research and Innovation (CNCS-UEFISCDI), project PN-III-P4-ID-PCE-2016-0305, contract PCE 67/2017 for the financial support. Authors are grateful to Dr Cristi Mihailescu for help with XPS measurements.



Nanoscale

PAPER

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Nanoscale*, 2018, **10**, 18043

Heavy doping of ceria by wet impregnation: a viable alternative to bulk doping approaches†

Mihaela Florea,[a,b] Daniel Avram,[c] Valentin Adrian Maraloiu,[a] Bogdan Cojocaru[b] and Carmen Tiseanu*[c]

To avoid the deleterious effects of dopant segregation, synthesis methods that facilitate a homogenous dopant distribution in the ceria lattice were employed. Though doping ceria by wet impregnation was also credited to induce a homogeneous solid solution even in the heavy regime (concentration ≥20%, A. Corma, P. Atienzar, H. Garcia and J. Chane-Ching, *Nat. Mater.*, 2004, **3**, 394–397), no follow up investigation has been reported. Herein, we investigated ceria nanoparticles (1%Tm-CeO_2 and 1%Eu-CeO_2) wet-impregnated with trivalent rare-earth (Yb, 20%), bivalent (Ca, 20%) and isovalent (Zr, 30%) metals, followed by annealing in air. Homogeneity of the solid solutions of Yb-impregnated ceria was confirmed by a two-feature characterization toolbox that included X-ray diffraction, Raman spectroscopy, transmission electron microscopy, as well as up-conversion emission as a probe tool. Since the up-conversion emission of Tm was not detectable in the absence of Yb while its efficiency depends on the average distance between Yb and Tm ions, the Yb incorporation and its migration from the surface to the lattice bulk sites in wet-impregnated ceria can be "visualized" and compared with that of the Yb bulk-doped counterpart. The use of Eu luminescence as a local probe confirmed the homogeneity of solid solutions of Ca and Zr-impregnated ceria and also sustained the opposite roles of Ca and Zr as the repeller and the scavenger of oxygen vacancies, respectively. All these results suggested that heavy doping of ceria by wet impregnation with metals with +2, +3 and +4 valencies represent a facile alternative to conventional doping approaches. Therefore, the effects of the amount and the type of metal dopant on the structural properties of CeO_2 could be investigated in a more systematic and probably a more reproducible manner, which would significantly increase the potential of ceria in catalysis and other applications.

Received 7th May 2018,
Accepted 4th September 2018

DOI: 10.1039/c8nr03695k

rsc.li/nanoscale

Introduction

CeO_2 is one of the most significant rare-earth oxides due to its applications in the fields of catalysis, sensor technology, and biomedical sciences.[1,2] The key property of ceria is its ability easily uptake and release oxygen through repeatable shifts between Ce^{3+} and Ce^{4+}, a process which involves oxygen vacancies.[3] A key strategy for enhancing the ionic conductivity consists of doping ceria with trivalent lanthanide (Ln) metals or rare-earths.[4] Since 2015, more than 4500 papers have been published on ceria materials, of which almost 20% considered ceria doped with rare-earth metal ions. The selection of the synthesis approach, the dopant type, as well as its loading represents the key elements in the design of ceria based materials, with consequences on oxygen vacancy generation, which is one of the most demanding steps in the redox phenomenon present in ceria.[5] To date, several synthesis methods, such as coprecipitation,[6–8] sol–gel,[9–11] microemulsion,[12,13] citrate,[14,15] flame spray pyrolysis,[16] and hydrothermal,[17] have been developed to obtain homogeneously doped ceria solid solutions. Theoretical and experimental studies have shown that the ionic conductivity increases for dopants that cause the least distortion to the host lattice.[18,19] Trivalent rare-earth cations distort the lattice along two pathways: by the formation of oxygen vacancies and due to the difference between the ionic radii of the host cation Ce(4+), and the dopant cations. The former causes a contraction in the lattice due to electrostatic interactions, whereas the latter leads to lattice expansion through steric effects (for example ref. 20). Doping CeO_2 with trivalent cations introduces one charge-compensating oxygen vacancy per two trivalent dopants, leading to complex interactions between Ce(4+), Ln(3+), O(2−) and oxygen vacancies.

[a]National Institute of Materials Physics, 405A Atomistilor Street, 077125 Magurele-Ilfov, Romania
[b]Department of Organic Chemistry, Biochemistry and Catalysis, University of Bucharest, 4-12 Regina Elisabeta Blvd, Bucharest, 030016, Romania
[c]National Institute for Laser, Plasma and Radiation Physics, P.O. Box MG-36, Bucharest-Magurele, RO 76900, Romania. E-mail: carmen.tiseanu@inflpr.ro

†Electronic supplementary information (ESI) available: Additional experimental details, EDX, XRF, XPS and DR-UV/Vis spectra, HRTEM image, up-conversion emission/excitation spectra and dynamics. See DOI: 10.1039/c8nr03695k

Dissemination of Results - 2018
Articles in ISI Journals

2. Claudiu Colbea, Daniel Avram, Bogdan Cojocaru, Raluca Negrea, Corneliu Ghica, Vadim G. Kessler, Gulaim A. Seisenbaeva, Vasile Parvulescu & Carmen Tiseanu "Full Tetragonal Phase Stabilization in ZrO_2 Nanoparticles Using Wet Impregnation: Interplay of Host Structure, Dopant Concentration and Sensitivity of Characterization Technique" Nanomaterials 2018, **8**(12), 988

Funding: C.C., D.A., B.C. and C.T. acknowledge the financial support from CNCS-UEFISCDI, project PN-III-P4-ID-PCE-2016-0305, contract PCE 67/2017. D.A. and C.T. acknowledge the financial support from the Romanian Ministry of Research and Innovation through the program NUCLEU, contract 4N/2016. R.N. and C.G. acknowledge the financial support from the Romanian Ministry of Research and Innovation through the Core Program PN18-11. G.A.S. and V.G.K. thank Swedish Research Council (Vetenskapsrådet) for support of the grant No. 2014-03938, Hybrid organic-inorganic 3D nanostructures as biomimetic nanoreactors and drug delivery vehicles.

nanomaterials MDPI

Article

Full Tetragonal Phase Stabilization in ZrO_2 Nanoparticles Using Wet Impregnation: Interplay of Host Structure, Dopant Concentration and Sensitivity of Characterization Technique

Claudiu Colbea [1], Daniel Avram [1], Bogdan Cojocaru [2], Raluca Negrea [3], Corneliu Ghica [3], Vadim G. Kessler [4], Gulaim A. Seisenbaeva [4], Vasile Parvulescu [2] and Carmen Tiseanu [1,*]

1 National Institute for Laser, Plasma and Radiation Physics, RO 76900 Bucharest-Magurele, Romania; claudiu.colbea@inflpr.ro (C.C.); radu.avram@inflpr.ro (D.A.)
2 Department of Chemistry, University of Bucharest, B-dul Regina Elisabeta, nr. 4-12, 030018 Bucharest, Romania; bogdan.cojocaru@chimie.unibuc.ro (B.C.); vasile.parvulescu@g.unibuc.ro (V.P.)
3 National Institute of Materials Physics, 405A Atomistilor Street, 077125 Magurele-Ilfov, Romania; raluca.damian@infim.ro (R.N.); cghica@infim.ro (C.G.)
4 Department of Molecular Sciences, Biocenter, SLU, Box 7015, SE-75007 Uppsala, Sweden; vadim.kessler@kemi.slu.se (V.G.K.); gulaim.seisenbaeva@slu.se (G.A.S.)
* Correspondence: carmen.tiseanu@inflpr.ro; Tel.: +40-21-457-44-89

Received: 2 November 2018; Accepted: 23 November 2018; Published: 28 November 2018 check for updates

Abstract: Here, we show that wet impregnation of ZrO_2 nanoparticles with 10% and 20% Eu oxide followed by thermal anneal in air above 500 °C produces full stabilization of the tetragonal phase of ZrO_2 without evidencing any phase separation. The bare ZrO_2 nanoparticles were obtained using three synthetic methods: oil in water microemulsion, rapid hydrothermal, and citrate complexation methods. The homogeneity of the solid solutions was assessed using X-ray diffraction, Raman spectroscopy, high resolution transmission electron microscopy, and advanced luminescence spectroscopy. Our findings show that wet impregnation, which is a recognized method for obtaining surface doped oxides, can be successfully used for obtaining doped oxides in the bulk with good homogeneity at the atomic scale. The limits of characterization technique in detecting minor phases and the roles of dopant concentration and host structure in formation of phase stabilized solid solutions are also analyzed and discussed.

Keywords: ZrO_2; tetragonal phase stabilization; average structure; local symmetry; wet impregnation; luminescence

1. Introduction

Zirconium oxide (ZrO_2) is a well-established ceramic material where the physical and chemical properties depend strongly on the structural phase leading to a variety of applications [1,2]. Both tetragonal and cubic phases can be stabilized at ambient temperatures upon doping with trivalent ions such as Y^{3+} or lanthanides (Ln) [3,4]. Due to the facile doping of the Ln metals in ZrO_2 lattice, there are many reports that describe the potential applications of Ln doped ZrO_2 as dielectric film transistor [5], white light emitting diodes [6], catalysis [7,8], fuel cells [9], temperature sensor [10], oxygen sensor [11], dosimetry [12], photocatalyst [13], and bioimaging [14]. Among the Ln series, Eu is considered as an ideal dopant/stabilizer as the average structural properties of ZrO_2 can be correlated with the local scale properties around Eu. As such, Eu shows distinct changes in the emission/excitation spectra and excited state dynamics with changes in the local symmetry with fingerprint emissions characteristic

Dissemination of Results - 2018 Conferences

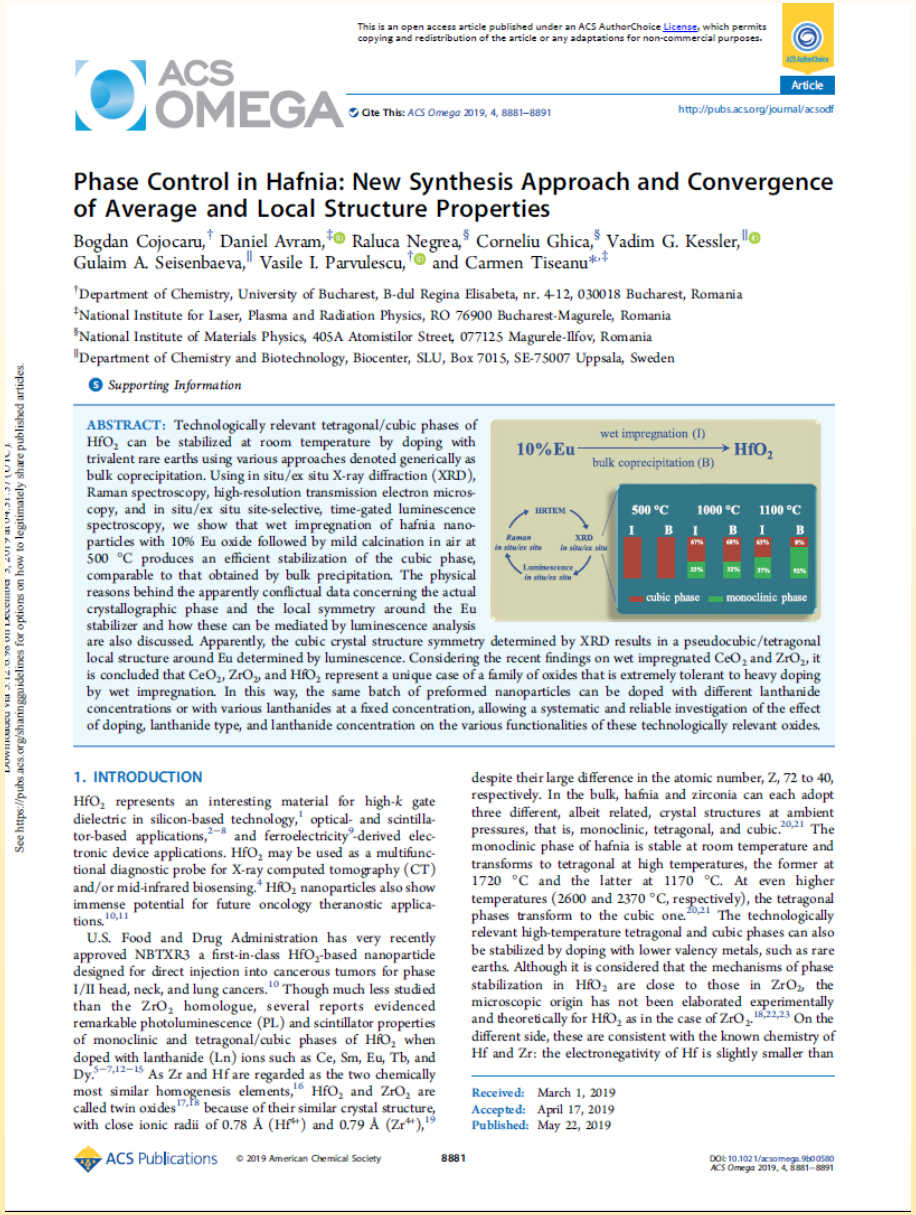
1. Claudiu Colbea, Alin Broasca, Mihaela Florea, Carmen Tiseanu “Tetragonal to monoclinic phase tuning of nano-zirconia doped erbium with lithium addition and its effect of 1500 nm upconversion properties”, IBWAP (18th International Balkan Workshop on Applied Physics and Materials Science), 10-13.07.2018, Constanta Romania.
2. Daniel Avram, Claudiu Colbea, Alin Broasca, Bogdan Cojocaru, Carmen Tiseanu “Remarkable enhan-cement of emission intensity of Eu-SnO_2 nanoparticles by Li addition” IBWAP (18th International Bal-kan Workshop on Applied Physics and Materials Science), 10-13.07.2018, Constanta Romania.
3. 3. Daniel Avram, Claudiu Colbea, Alin Broasca, Ion Tiseanu, Mihaela Florea, Carmen Tiseanu „Phase-tuning of Er dopde ZrO_2 and correleation with upconversion emission proprties” ICOM 2018 (The 5th International Conference on the Physics of Optical Materials and Devices), 27-31.08.2018, Igalo, Montenegro.

Dissemination of Results - 2019
Articles in ISI Journals

3. Claudiu Colbea, Daniel Avram, Bogdan Cojocaru, Raluca Negrea, Corneliu Ghica, Vadim G. Kessler, Gulaim A. Seisenbaeva, Vasile Parvulescu & Carmen Tiseanu "Phase Control in Hafnia: New Synthesis Approach and Convergence of Average and Local Structure Properties" ACS Omega 2019, 4, 5, 8881-8891

Funding

C.T. and D.A. acknowledge the financial support from CNCS-UEFISCDI, project PN-III-P4-ID-PCE-2016-0305, contract PCE 67/2017. R.N. and C.G. acknowledge the financial support from the Romanian Ministry of Research and Innovation through the Core Program PN19-03. V.G.K. and G.A.S. acknowledge the financial support from Swedish Research Council (VR), project 201403938 "Hybrid organic-inorganic 3D nanostructures".



ACS OMEGA

Article

Cite This: ACS Omega 2019, 4, 8881−8891

http://pubs.acs.org/journal/acsodf

Phase Control in Hafnia: New Synthesis Approach and Convergence of Average and Local Structure Properties

Bogdan Cojocaru,[†] Daniel Avram,[‡] Raluca Negrea,[§] Corneliu Ghica,[§] Vadim G. Kessler,[∥] Gulaim A. Seisenbaeva,[∥] Vasile I. Parvulescu,[†] and Carmen Tiseanu*[,‡]

[†]Department of Chemistry, University of Bucharest, B-dul Regina Elisabeta, nr. 4-12, 030018 Bucharest, Romania

[‡]National Institute for Laser, Plasma and Radiation Physics, RO 76900 Bucharest-Magurele, Romania

[§]National Institute of Materials Physics, 405A Atomistilor Street, 077125 Magurele-Ilfov, Romania

[∥]Department of Chemistry and Biotechnology, Biocenter, SLU, Box 7015, SE-75007 Uppsala, Sweden

Supporting Information

ABSTRACT: Technologically relevant tetragonal/cubic phases of HfO_2 can be stabilized at room temperature by doping with trivalent rare earths using various approaches denoted generically as bulk coprecipitation. Using in situ/ex situ X-ray diffraction (XRD), Raman spectroscopy, high-resolution transmission electron microscopy, and in situ/ex situ site-selective, time-gated luminescence spectroscopy, we show that wet impregnation of hafnia nanoparticles with 10% Eu oxide followed by mild calcination in air at 500 °C produces an efficient stabilization of the cubic phase, comparable to that obtained by bulk precipitation. The physical reasons behind the apparently conflictual data concerning the actual crystallographic phase and the local symmetry around the Eu stabilizer and how these can be mediated by luminescence analysis are also discussed. Apparently, the cubic crystal structure symmetry determined by XRD results in a pseudocubic/tetragonal local structure around Eu determined by luminescence. Considering the recent findings on wet impregnated CeO_2 and ZrO_2, it is concluded that CeO_2, ZrO_2, and HfO_2 represent a unique case of a family of oxides that is extremely tolerant to heavy doping by wet impregnation. In this way, the same batch of preformed nanoparticles can be doped with different lanthanide concentrations or with various lanthanides at a fixed concentration, allowing a systematic and reliable investigation of the effect of doping, lanthanide type, and lanthanide concentration on the various functionalities of these technologically relevant oxides.

1. INTRODUCTION

HfO_2 represents an interesting material for high-k gate dielectric in silicon-based technology,[1] optical- and scintillator-based applications,[2−8] and ferroelectricity[9]-derived electronic device applications. HfO_2 may be used as a multifunctional diagnostic probe for X-ray computed tomography (CT) and/or mid-infrared biosensing.[4] HfO_2 nanoparticles also show immense potential for future oncology theranostic applications.[10,11]

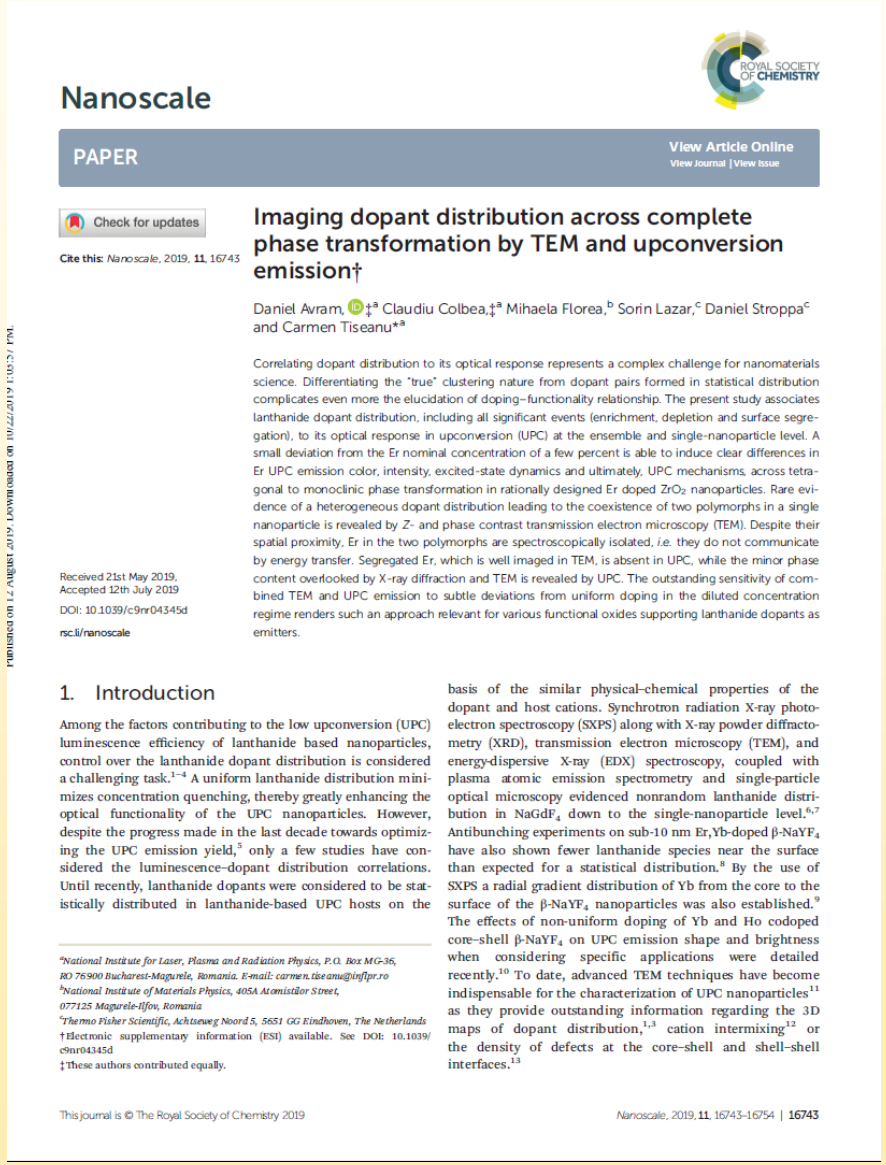
U.S. Food and Drug Administration has very recently approved NBTXR3 a first-in-class HfO_2-based nanoparticle designed for direct injection into cancerous tumors for phase I/II head, neck, and lung cancers.[10] Though much less studied than the ZrO_2 homologue, several reports evidenced remarkable photoluminescence (PL) and scintillator properties of monoclinic and tetragonal/cubic phases of HfO_2 when doped with lanthanide (Ln) ions such as Ce, Sm, Eu, Tb, and Dy.[5−7,12−15] As Zr and Hf are regarded as the two chemically most similar homogenesis elements,[16] HfO_2 and ZrO_2 are called twin oxides[17,18] because of their similar crystal structure, with close ionic radii of 0.78 Å (Hf^{4+}) and 0.79 Å (Zr^{4+}),[19] despite their large difference in the atomic number, Z, 72 to 40, respectively. In the bulk, hafnia and zirconia can each adopt three different, albeit related, crystal structures at ambient pressures, that is, monoclinic, tetragonal, and cubic.[20,21] The monoclinic phase of hafnia is stable at room temperature and transforms to tetragonal at high temperatures, the former at 1720 °C and the latter at 1170 °C. At even higher temperatures (2600 and 2370 °C, respectively), the tetragonal phases transform to the cubic one.[20,21] The technologically relevant high-temperature tetragonal and cubic phases can also be stabilized by doping with lower valency metals, such as rare earths. Although it is considered that the mechanisms of phase stabilization in HfO_2 are close to those in ZrO_2, the microscopic origin has not been elaborated experimentally and theoretically for HfO_2 as in the case of ZrO_2.[18,22,23] On the different side, these are consistent with the known chemistry of Hf and Zr: the electronegativity of Hf is slightly smaller than

Received: March 1, 2019
Accepted: April 17, 2019
Published: May 22, 2019

DOI: 10.1021/acsomega.9b00580
ACS Omega 2019, 4, 8881−8891

Dissemination of Results - 2019
Articles in ISI Journals

4. Daniel Avram, Claudiu Colbea, Mihaela Florea, Sorin Lazar, Daniel Stroppa & Carmen Tiseanu “Imaging dopant distribution across complete phase transformation by TEM and upconversion emission” Nanoscale, 2019, 11, 16743-16754



Nanoscale

PAPER

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Nanoscale*, 2019, **11**, 16743

Imaging dopant distribution across complete phase transformation by TEM and upconversion emission†

Daniel Avram, ‡[a] Claudiu Colbea,‡[a] Mihaela Florea,[b] Sorin Lazar,[c] Daniel Stroppa[c] and Carmen Tiseanu*[a]

Correlating dopant distribution to its optical response represents a complex challenge for nanomaterials science. Differentiating the “true” clustering nature from dopant pairs formed in statistical distribution complicates even more the elucidation of doping–functionality relationship. The present study associates lanthanide dopant distribution, including all significant events (enrichment, depletion and surface segregation), to its optical response in upconversion (UPC) at the ensemble and single-nanoparticle level. A small deviation from the Er nominal concentration of a few percent is able to induce clear differences in Er UPC emission color, intensity, excited-state dynamics and ultimately, UPC mechanisms, across tetragonal to monoclinic phase transformation in rationally designed Er doped ZrO_2 nanoparticles. Rare evidence of a heterogeneous dopant distribution leading to the coexistence of two polymorphs in a single nanoparticle is revealed by *Z*- and phase contrast transmission electron microscopy (TEM). Despite their spatial proximity, Er in the two polymorphs are spectroscopically isolated, *i.e.* they do not communicate by energy transfer. Segregated Er, which is well imaged in TEM, is absent in UPC, while the minor phase content overlooked by X-ray diffraction and TEM is revealed by UPC. The outstanding sensitivity of combined TEM and UPC emission to subtle deviations from uniform doping in the diluted concentration regime renders such an approach relevant for various functional oxides supporting lanthanide dopants as emitters.

Received 21st May 2019,
Accepted 12th July 2019

DOI: 10.1039/c9nr04345d

rsc.li/nanoscale

1. Introduction

Among the factors contributing to the low upconversion (UPC) luminescence efficiency of lanthanide based nanoparticles, control over the lanthanide dopant distribution is considered a challenging task.[1–4] A uniform lanthanide distribution minimizes concentration quenching, thereby greatly enhancing the optical functionality of the UPC nanoparticles. However, despite the progress made in the last decade towards optimizing the UPC emission yield,[5] only a few studies have considered the luminescence–dopant distribution correlations. Until recently, lanthanide dopants were considered to be statistically distributed in lanthanide-based UPC hosts on the basis of the similar physical–chemical properties of the dopant and host cations. Synchrotron radiation X-ray photoelectron spectroscopy (SXPS) along with X-ray powder diffractometry (XRD), transmission electron microscopy (TEM), and energy-dispersive X-ray (EDX) spectroscopy, coupled with plasma atomic emission spectrometry and single-particle optical microscopy evidenced nonrandom lanthanide distribution in $NaGdF_4$ down to the single-nanoparticle level.[6,7] Antibunching experiments on sub-10 nm Er,Yb-doped β-$NaYF_4$ have also shown fewer lanthanide species near the surface than expected for a statistical distribution.[8] By the use of SXPS a radial gradient distribution of Yb from the core to the surface of the β-$NaYF_4$ nanoparticles was also established.[9] The effects of non-uniform doping of Yb and Ho codoped core–shell β-$NaYF_4$ on UPC emission shape and brightness when considering specific applications were detailed recently.[10] To date, advanced TEM techniques have become indispensable for the characterization of UPC nanoparticles[11] as they provide outstanding information regarding the 3D maps of dopant distribution,[1,3] cation intermixing[12] or the density of defects at the core–shell and shell–shell interfaces.[13]

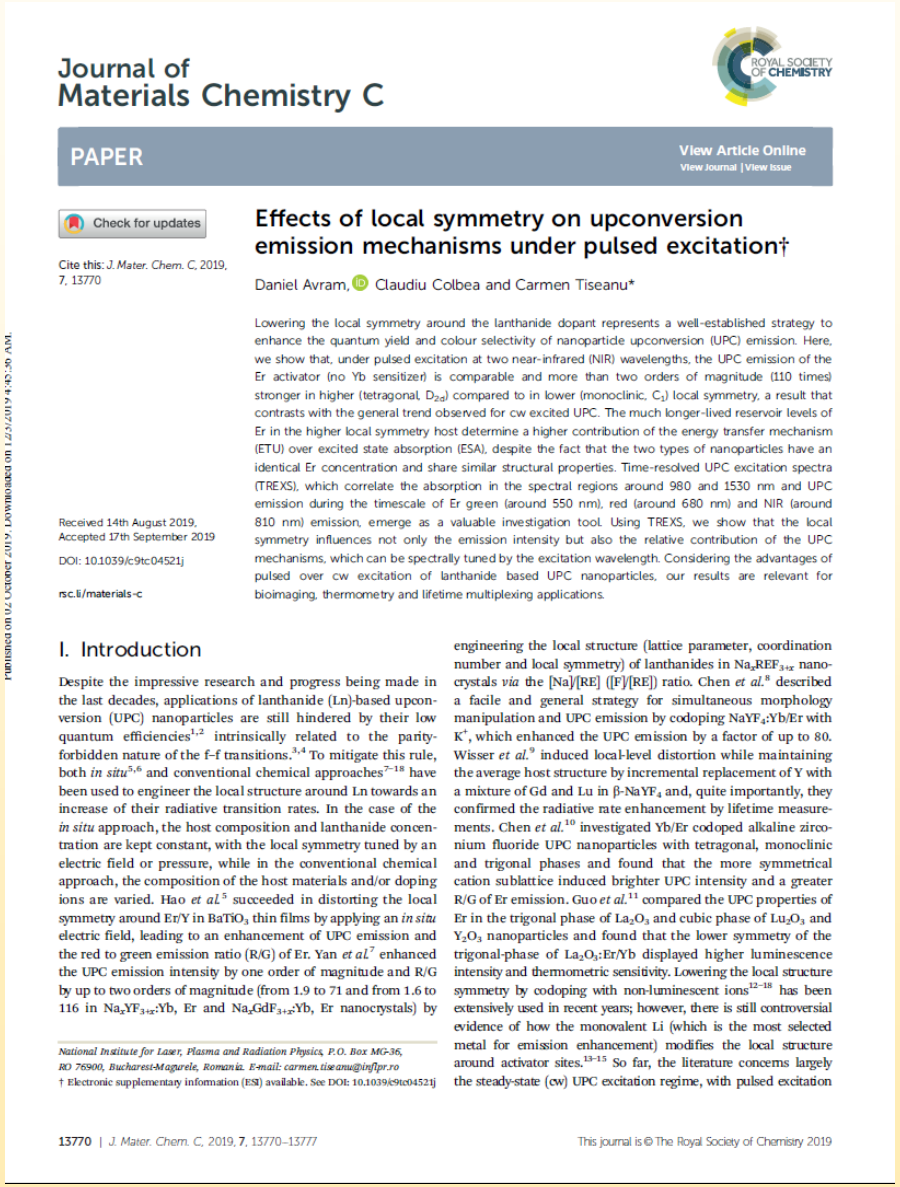
[a]National Institute for Laser, Plasma and Radiation Physics, P.O. Box MG-36, RO 76900 Bucharest-Magurele, Romania. E-mail: carmen.tiseanu@inflpr.ro
[b]National Institute of Materials Physics, 405A Atomistilor Street, 077125 Magurele-Ilfov, Romania
[c]Thermo Fisher Scientific, Achtseweg Noord 5, 5651 GG Eindhoven, The Netherlands
†Electronic supplementary information (ESI) available. See DOI: 10.1039/c9nr04345d
‡These authors contributed equally.

Acknowledgements

DA, CC and CT acknowledge CNCS-UEFISCDI through project PN-III-P4-ID-PCE-2016-0305, contract PCE 67/2017 for the financial support. MF acknowledges the Romanian Ministry of Research and Innovation through the Core Program PN18-110201 and project PN-III-P4-ID-PCE-2016-0692 for the partial financial support.

Dissemination of Results – 2019
Articles in ISI Journals

5. Daniel Avram, Claudiu Colbea & Carmen Tiseanu "Effects of local symmetry on upconversion emission mechanisms under pulsed excitation" J. Mater. Chem. C, 2019,7, 13770-13777



Journal of Materials Chemistry C

PAPER

View Article Online
View Journal | View Issue

Check for updates

Cite this: J. Mater. Chem. C, 2019, 7, 13770

Effects of local symmetry on upconversion emission mechanisms under pulsed excitation†

Daniel Avram, Claudiu Colbea and Carmen Tiseanu*

Lowering the local symmetry around the lanthanide dopant represents a well-established strategy to enhance the quantum yield and colour selectivity of nanoparticle upconversion (UPC) emission. Here, we show that, under pulsed excitation at two near-infrared (NIR) wavelengths, the UPC emission of the Er activator (no Yb sensitizer) is comparable and more than two orders of magnitude (110 times) stronger in higher (tetragonal, D_{2d}) compared to in lower (monoclinic, C_1) local symmetry, a result that contrasts with the general trend observed for cw excited UPC. The much longer-lived reservoir levels of Er in the higher local symmetry host determine a higher contribution of the energy transfer mechanism (ETU) over excited state absorption (ESA), despite the fact that the two types of nanoparticles have an identical Er concentration and share similar structural properties. Time-resolved UPC excitation spectra (TREXS), which correlate the absorption in the spectral regions around 980 and 1530 nm and UPC emission during the timescale of Er green (around 550 nm), red (around 680 nm) and NIR (around 810 nm) emission, emerge as a valuable investigation tool. Using TREXS, we show that the local symmetry influences not only the emission intensity but also the relative contribution of the UPC mechanisms, which can be spectrally tuned by the excitation wavelength. Considering the advantages of pulsed over cw excitation of lanthanide based UPC nanoparticles, our results are relevant for bioimaging, thermometry and lifetime multiplexing applications.

Received 14th August 2019,
Accepted 17th September 2019

DOI: 10.1039/c9tc04521j

rsc.li/materials-c

I. Introduction

Despite the impressive research and progress being made in the last decades, applications of lanthanide (Ln)-based upconversion (UPC) nanoparticles are still hindered by their low quantum efficiencies[1,2] intrinsically related to the parity-forbidden nature of the f–f transitions.[3,4] To mitigate this rule, both *in situ*[5,6] and conventional chemical approaches[7–18] have been used to engineer the local structure around Ln towards an increase of their radiative transition rates. In the case of the *in situ* approach, the host composition and lanthanide concentration are kept constant, with the local symmetry tuned by an electric field or pressure, while in the conventional chemical approach, the composition of the host materials and/or doping ions are varied. Hao *et al.*[5] succeeded in distorting the local symmetry around Er/Y in $BaTiO_3$ thin films by applying an *in situ* electric field, leading to an enhancement of UPC emission and the red to green emission ratio (R/G) of Er. Yan *et al.*[7] enhanced the UPC emission intensity by one order of magnitude and R/G by up to two orders of magnitude (from 1.9 to 71 and from 1.6 to 116 in Na_xYF_{3+x}:Yb, Er and Na_xGdF_{3+x}:Yb, Er nanocrystals) by engineering the local structure (lattice parameter, coordination number and local symmetry) of lanthanides in Na_xREF_{3+x} nanocrystals *via* the [Na]/[RE] ([F]/[RE]) ratio. Chen *et al.*[8] described a facile and general strategy for simultaneous morphology manipulation and UPC emission by codoping $NaYF_4$:Yb/Er with K^+, which enhanced the UPC emission by a factor of up to 80. Wisser *et al.*[9] induced local-level distortion while maintaining the average host structure by incremental replacement of Y with a mixture of Gd and Lu in β-$NaYF_4$ and, quite importantly, they confirmed the radiative rate enhancement by lifetime measurements. Chen *et al.*[10] investigated Yb/Er codoped alkaline zirconium fluoride UPC nanoparticles with tetragonal, monoclinic and trigonal phases and found that the more symmetrical cation sublattice induced brighter UPC intensity and a greater R/G of Er emission. Guo *et al.*[11] compared the UPC properties of Er in the trigonal phase of La_2O_3 and cubic phase of Lu_2O_3 and Y_2O_3 nanoparticles and found that the lower symmetry of the trigonal-phase of La_2O_3:Er/Yb displayed higher luminescence intensity and thermometric sensitivity. Lowering the local structure symmetry by codoping with non-luminescent ions[12–18] has been extensively used in recent years; however, there is still controversial evidence of how the monovalent Li (which is the most selected metal for emission enhancement) modifies the local structure around activator sites.[13–15] So far, the literature concerns largely the steady-state (cw) UPC excitation regime, with pulsed excitation

National Institute for Laser, Plasma and Radiation Physics, P.O. Box MG-36, RO 76900, Bucharest-Magurele, Romania. E-mail: carmen.tiseanu@inflpr.ro

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c9tc04521j

Acknowledgements

CT, CC and DA acknowledge the Romanian National Authority for Scientific Research and Innovation (CNCS-UEFISCDI) through project PN-III-P4-ID-PCE-2016-0305, contract PCE 67/2017 for financial support. The authors thank Dr Mihaela Florea for help in the synthesis of Er-ZrO_2 nanoparticles. The authors acknowledge CETAL for supplying the near infrared spectroscopic acquisition system used in the NIR emission decay measurements.

Dissemination of Results - 2019 Conferences

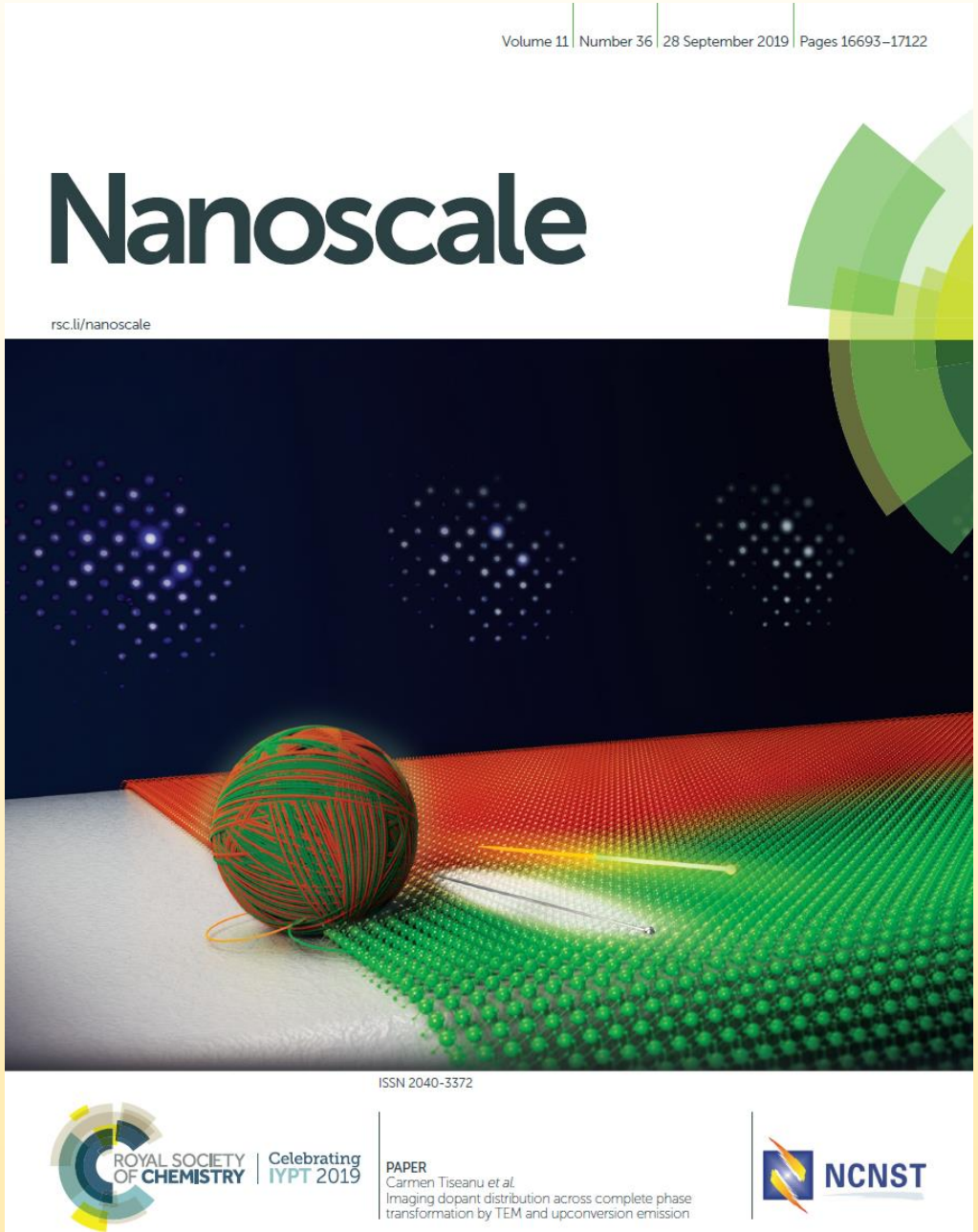
1. C. Colbea, D. Avram, M. Florea, C. Tiseanu "Can wet impregnation be a viable alternative to bulk doping?" 47th IUPAC World Chemistry Congress, 5-12 July 2019, Paris, France
2. C. Colbea, D. Avram, M. Florea, C. Tiseanu "Bulk doping versus wet impregnation: nanoparticle preparation of doped metal oxides" IBWAP (19th International Balkan Workshop on Applied Physics and Materials Science), 16-19.07.2018, Constanta, Romania
3. D. Avram, C. Colbea, M. Florea and C. Tiseanu "The effects of local symmetry on the upconversion emission intensity, color and dynamics under ns pulsed excitation" 8th International Workshops on Photoluminescence of Rare-Earth: Photonic Materials and Applications (PRE'19), 4-6.09.2019, Nice, France (Awarded 2nd Prize for Poster presentation)
4. D. Avram, C. Colbea, F. Baiasu, M. Florea and C. Tiseanu "Emission enhancement mechanisms in lanthanide based materials by Li, Mo and Mn codoping" International Conference on Excited States of Transitions Ele-ments (ESTE), 8-13.09.2019, Kudowa Zdrój, Poland

Outstanding results

Authors: Daniel Avram, Claudiu Colbea, Mihaela Florea, Sorin Lazar, Daniel Stroppa & Carmen Tiseanu

Article Title: Imaging dopant distribution across complete phase transformation by TEM and upconversion emission

Article presented on Front Cover of Nanoscale, 2019,11 (36)



Outstanding results

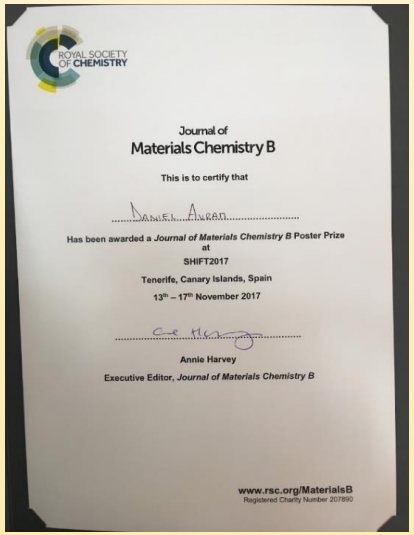
Authors: Daniel Avram, Claudiu Colbea & Carmen Tiseanu

Article Title: Effects of local symmetry on upconversion emission mechanisms under pulsed excitation

Article presented on Front Cover of J. Mater. Chem. C, 2019,7 (44)

Outstanding results

D. Avram, B. Cojocaru, I. Tiseanu, M. Florea, C. Tiseanu "X-ray and Near-Infrared Excitation of Luminescence in Ln doped Nanoparticles for Bio-imaging Applications", SHIFT 2017 (**S**pectral s**H**ap**I**ng For biomedical and energy applica**T**ions), 12 – 17.11.2017, Costa de Adeje, Spain. (Poster presentation) (Awarded Poster prize (special mention) offered by J Mater Chem B, Royal Society of Chemistry , FI 4.5)


ROYAL SOCIETY OF CHEMISTRY

Journal of Materials Chemistry B

This is to certify that

Has been awarded a *Journal of Materials Chemistry B* Poster Prize at SHIFT2017

Tenerife, Canary Islands, Spain

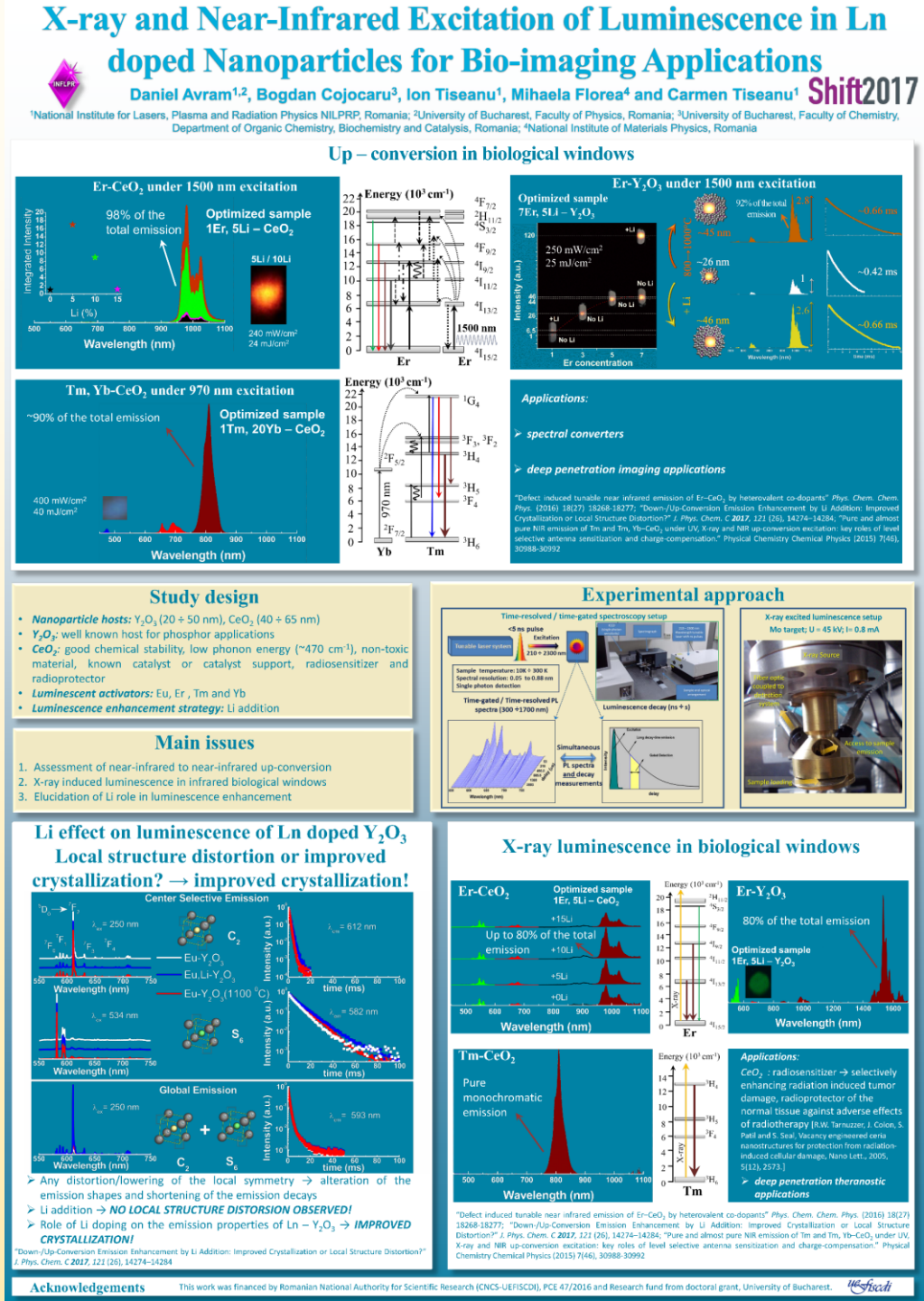
13th – 17th November 2017

Annie Harvey

Executive Editor, *Journal of Materials Chemistry B*

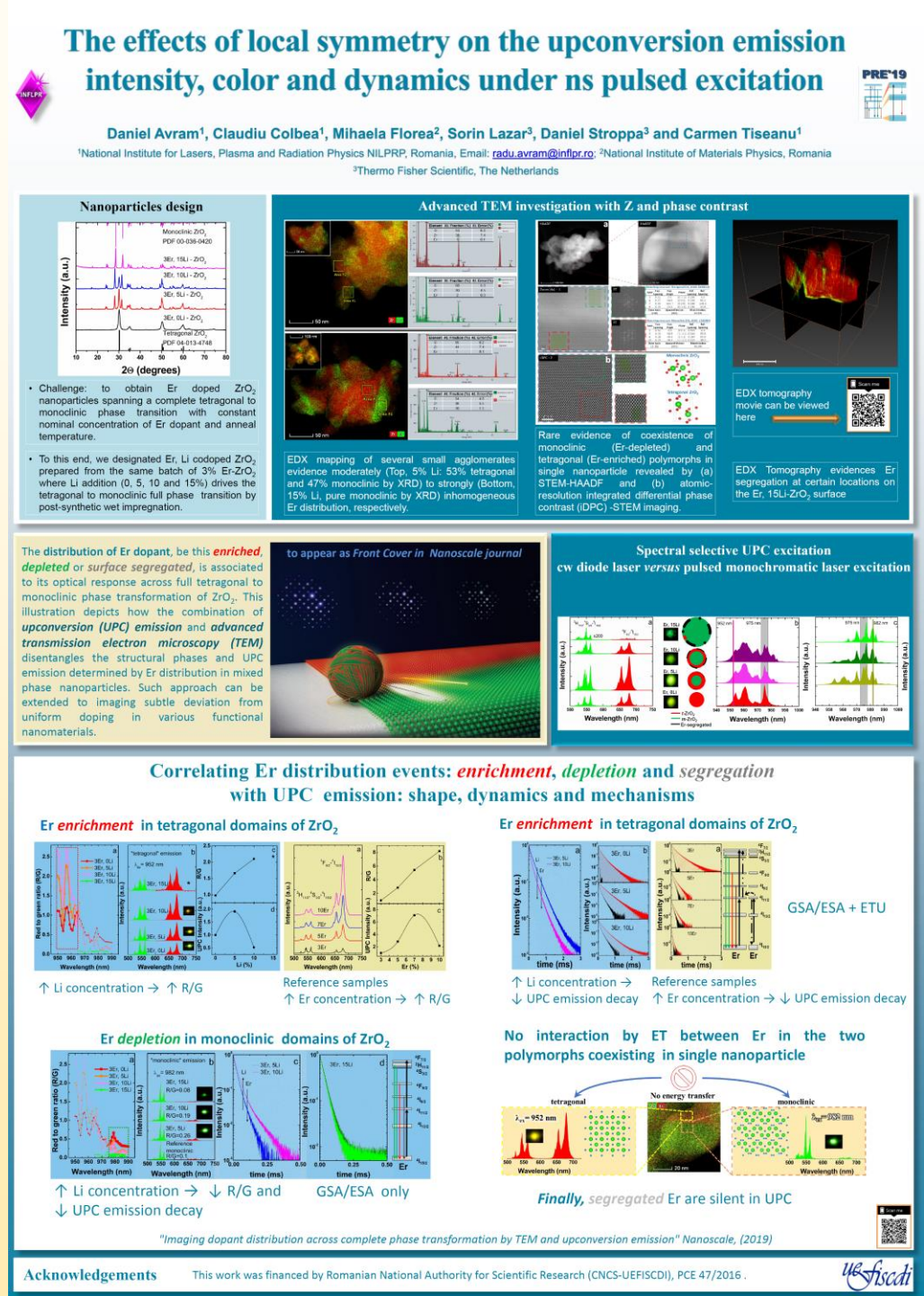
www.rsc.org/MaterialsB

Registered Charity Number 207890



Outstanding results

D. Avram, C. Colbea, M. Florea and C. Tiseanu "The effects of local symmetry on the upconversion emission intensity, color and dynamics under ns pulsed excitation" 8th International Workshops on Photoluminescence of Rare-Earth: Photonic Materials and Applications (PRE'19), 4-6.09.2019, Nice, France (Awarded 2nd Prize for Poster presentation)



Outstanding results

Mentorship of exceptional young researchers

Due to the accumulated experience within the project framework, Claudiu Colbea, a Msc student within the team project won a PhD scholarship to prestigious ETH School (Swiss Federal Institute of Technology in Zurich), Zurich within „Scientific Center for Optical and Electron Microscopy” (https://scopem.ethz.ch/) research group.