

PAPER • OPEN ACCESS

A comparative study of morphology and composition on oxide nanopowders elaborated by SPVD

To cite this article: E S Bârc *et al* 2015 *IOP Conf. Ser.: Mater. Sci. Eng.* **95** 012028

View the [article online](#) for updates and enhancements.

Related content

- [A COMPARATIVE STUDY OF MORPHOLOGY AND VELOCITY FIELD OF THE EMISSION NEBULAE S153, S207, S211, AND A71](#)
P. Pismis, I. Hasse and A. Quintero
- [Microwave assisted synthesis of copper oxide and its application in electrochemical sensing](#)
S Felix, R Bala Praveen Chakkravarthy and A Nirmala Grace
- [Spectral and lasing characteristics of 1% Ho:YAG ceramics under intracavity pumping](#)
S N Bagayev, V V Osipov, S M Vatrik et al.

A comparative study of morphology and composition on oxide nanopowders elaborated by SPVD

E S Bârcă¹, V Rizea¹, M Abrudeanu¹, A G Plaiasu¹, B Istrate² and C Munteanu²

¹University of Pitesti, Faculty of Mechanics and Technology, Department of Manufacturing and Industrial Management, 1st Tg din Vale Str, 110040, Arges, Romania

²"Gheorghe Asachi" Technical University of Iasi, Faculty of Mechanics, Materials Science Department, 43 Dimitrie Mangeron Str, 700050, Iasi, Romania

E-mail: eddward_82@yahoo.com

Abstract. The paper proposes a method of obtaining oxide nanopowders in a solar reactor using the solar energy (solar physical vapor deposition). The proposed method is a new method of obtaining nanopowders. Taking into consideration that the properties of the materials change once they get to nanodimensions it is desirable to obtain nanomaterials starting from base materials. Because of the properties that nanomaterials provide, the demand has grown in the last period of time. Also the last few years provided a various number of nanomaterials used in different fields of research. Among the materials that were obtained by SPVD there can be reminded the MoS₂, the MoS₂ doped with Zn, CeO₂ doped with Zr. The CeO₂ is used in applications such as catalysis, gas sensor, fuel cell as well as optical additives. All of the obtained nanopowders were analyzed and characterized by X-Ray diffraction (XRD) and by scanning electron microscopy (SEM) in order to acquire the information about the crystallography and morphology considering the reactions parameters that were used in obtaining the nanopowders. From the X-Ray diffraction can be concluded in the case of the CeO₂ that doping occurred. By controlling the reactions parameters the end result is different in terms of obtained morphology of the nanopowders. All of the above elaborated nanopowders can be deposited in the form of thin films by laser ablation method in order to obtain better properties of the base material.

1. Introduction

Because of the raised interest in nanomaterials different methods for obtaining nano scaled materials have been developed. This paper focuses on obtaining nanopowders by a different, less used method known as SPVD (solar physical vapor deposition) [1]. Obtaining techniques vary and can include chemical or physical vapor deposition, precipitation methods, sol-gel and hydrothermal methods [2-5]. By SPVD there have been obtained different nanopowders including pure ZnO and Bi₂O₃ doped ZnO with better electrical properties than other nanopowders obtained by the same method [6]. Also by the same process there have been obtained Al-doped ZnO nanopowders and it has been noticed that when the amount of Al is smaller the crystallite size is smaller [2].

When switching to nano-dimension materials properties change, making them more appropriate for use in many applications such as electronics, automotive, construction industries and chemical. The interest in materials with nano-dimensions is rapidly increasing because of the large scale of opportunities that are provided by the materials properties. One of the advantages in using the solar



furnaces is the fact that the used energy for the reaction is solar energy which has unlimited resources. The solar furnaces uses a solar beam concentrated by mirrors in order to melt down the target which is then vaporized and then reaches a cold support where it remains in order to be collected at the end of the process. In order to have the best end result, studies concerning the orientation of the mirrors of a solar furnace have been carried out by different researchers. Because it is hard to realize a mirror in the needed size, the solution is to use a large number of smaller mirrors that would direct the energy towards the target [7-8]. Manufacturing of different nanopowders by solar physical vapor deposition has shown the possibility of obtaining the desired nanoscale meanwhile controlling the composition and the morphology at the same time.

The elaboration of the nanopowders has been performed in France, Font-Romeu in one of the solar furnace, named Heliotron. The "heliotron" solar furnace is one of the 12 furnaces built in Odeillo-Font Romeu and is made out of mobile plane mirrors which capture the sun light and reflects its radiation toward a parabolic concentrator. The parabolic mirrors focus on a reactor containing a glass flask in which the reaction occurs using solar energy. Inside the glass flask the reaction can take place under an inert gas, the atmosphere being controlled. The advantage of the method is that nano-sized crystals are obtained, the disadvantage being the fact that it needs perfect weather conditions and that it takes several hours to complete the reaction. Due to the properties they have, Al doped ZnO and pure ZnO have been elaborated by this technique. As applications can be reminded the gas sensors, electrodes and piezoelectric devices [9-10].

The paper aims to obtain CeO₂ and ZrO₂ doped CeO₂ nano-powders starting from micro scaled powders. Choosing these powders was made according with the applications they have as fuel cell, gas sensors, free radical scavenger and optical additives [11]. The CeO₂ can also be used to deposit thin films due to the properties and applications the thin layer would have in corrosion prevention, photocatalysis, electrochemical cells, microelectronics, optical devices, thermal coatings and biomaterials. These applications become possible due to the transition to nanoscale. For better results in the chosen application close inspection for surface defects such as oxygen vacancies needs to be carried out. Using the tetravalent Zr as the doping agent for CeO₂ increases the oxygen storage capacity and using the trivalent Zr increases CeO₂ conductivity. Another factor that influences the layers thickness is considered to be the interaction that the Ce atoms have with the substrate [12-13]

2. Experimental procedure

Pure and Zr doped CeO₂ powders with a general formula of (CeO₂)_x(ZrO₂)_y were prepared by solar physical vapor deposition (SPVD). In this formula x/y represents the molar ratio of the two powders. The paper presents 2 compositions: Ce_{0.95}Zr_{0.05}O_{2-x} and Ce_{0.75}Zr_{0.25}O_{2-x} obtained by this method.

The SPVD process consists in a material being melted under concentrated solar beam inside a solar reactor. As the name suggests, the power source is the energy from the sun. The process took place in Odeillo-Font Romeu in France in one of the 12 solar furnaces. The solar furnace consists of a plane mirror field named "heliostat" and a parabolic mirror, or concentrator as it can be seen in (figure 1a). The plane mirror captures the sun radiation and directs it to the parabolic concentrator. At the focus of the parabolic concentrator is placed the solar reactor "heliotron" which is composed out of a glass balloon inside which the controlled atmosphere can be maintained. The used target is the powder that we want to obtain in nanoscale, that prior to the process has been prepared in a press of 14.7 to 19.6 kN in order to obtain the initial pills. The pressure inside the balloon depends on the material and on the atmosphere. While the reaction takes place vapor of materials are condensed either on a cold metallic support or on a ceramic filter attached to the glass balloon as presented in (figure 1b). The "heliotron" associates both processes, the collecting on the metallic support and on the filter which increases the quantity of the obtained powder and decreases the condensation process on the balloon walls. The gas flux is regulated as to be in the desired parameters, being higher at low pressures

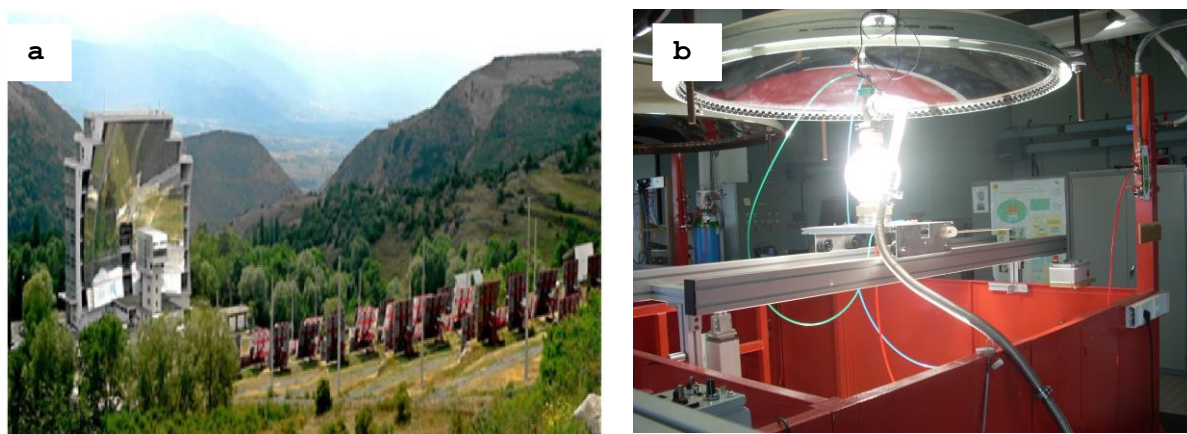


Figure 1. (a) Solar furnace in PROMES Laboratory France, Font-Romeu, Odeillo , (b) 2kW solar concentrator with "heliotron" reactor during reaction.

One of the advantages of this method is that there is obtained a direct synthesis of nanopowders. The disadvantage consists in the long period of time necessary in order to complete the process of about 1 to 2 hours in perfect sunny conditions.

All the powders involved in the process were characterized both by X-Ray Diffraction with the X'Pert Pro Mrd diffractometer and by scanning electron microscopy with the Quanta 200 3D electronic microscope.

The X-Ray diffractions were carried out in the 10° - 90° 2θ interval, each taken step having the a value of $0.013^{\circ}(2\theta)$. The link between the diffraction angle θ and the wavelength is given by Bragg's relation:

$n \cdot \lambda = 2 \cdot d \cdot \sin\theta$, where :

n - positive integer

λ - wavelength of the rays

d - the spacing between layers of atoms

θ - the angle between the incident rays and the analyzed surface

The diffractometer works according to Debye-Scherrer principle's, data being transmitted and interpreted by a computer with a dedicated software for this equipment , X'Pert Data Collector, X'Pert High Score Plus and X'Pert Data Viewer, results being presented as diffractions. The diffractometer has an X Ray tube with an Cu α anode, $\lambda=1.54 \text{ \AA}$, to which a 45kV tension has been applied at an intensity of 40mA. The used radiation was Cu α 1 with a wavelength of 1.54060 \AA and Cu α 2 with a wavelength of 1.54443 \AA .

All SEM analysis were carried out in High Vacuum module, at working pressure between 50 - 60 Pa, using the LFD (Large Field Detector). The accelerating voltage of the scanning electron microscope was of 20kV. All of the XRD and SEM analysis were carried out at "Gh. Asachi" Technical University of Iasi, Romania.

3. Results and discussion

The XRD pattern of the base CeO₂ powder is presented (in figure 2.a) and shows the position of the peaks, information about the crystallographic parameters and confirms the system it crystallizes in, cubic with $5.4037 \times 5.4037 \times 5.4037$ cell. Also the XRD provides information about the Miller indices and about the FWHM values (in figure 2.b). We see in figure 3 and in figure 4 the XRD pattern for the Ce_{0.95}Zr_{0.05}O_{2-x} and Ce_{0.75}Zr_{0.25}O_{2-x} powders. As can be seen some differences appear when the doping occurs, especially for the nanopowder with a higher quantity of dopant, Ce_{0.75}Zr_{0.25}O_{2-x}.

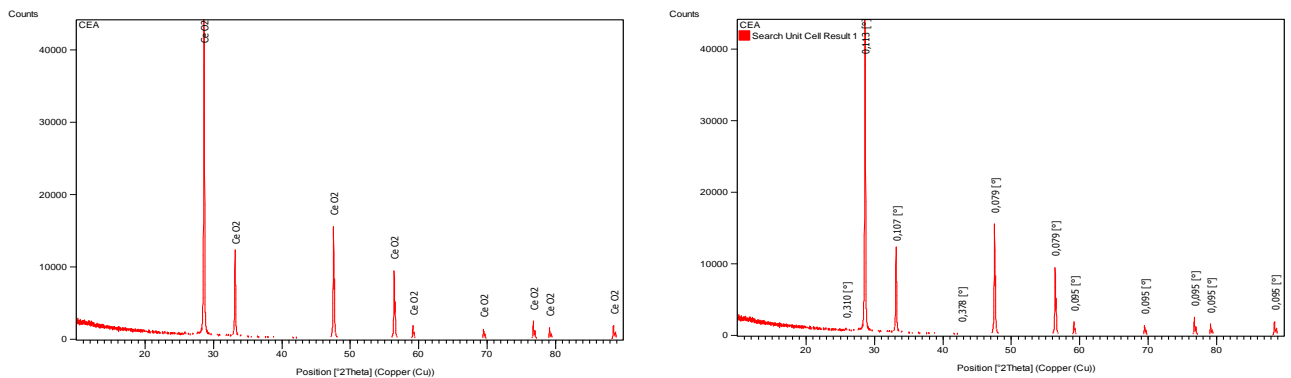


Figure 2. (a) XRD pattern of the CeO₂ powder, (b) FWHM for the CeO₂ powder.

In the next figure (figure 3) we observe the Ce_{0.95}Zr_{0.05}O_{2-x} were the doping occurred, being visible that the peaks are slightly different and less higher compared to the analyzed base powder. The system it crystallizes is cubic, with 5.3890x5.3890x5.3890 cell.

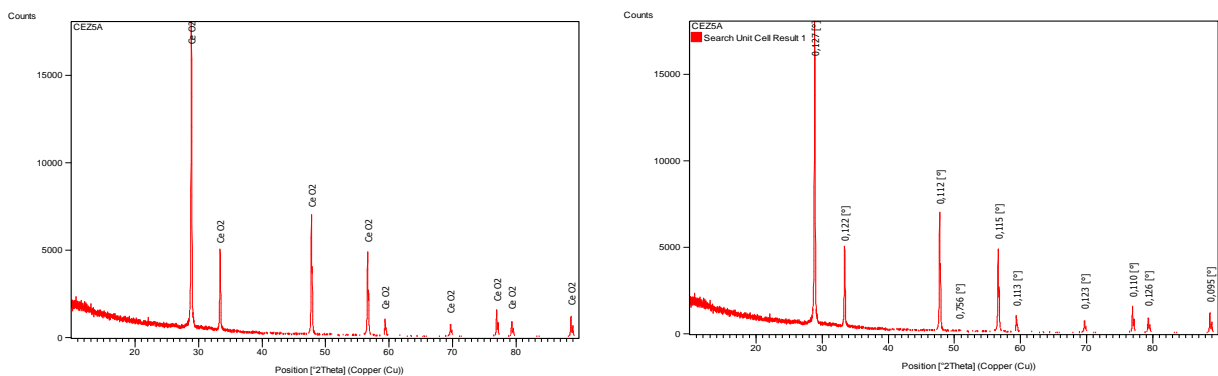


Figure 3. (a) XRD pattern for the Ce_{0.95}Zr_{0.05}O_{2-x}, (b) FWHM for the Ce_{0.95}Zr_{0.05}O_{2-x} powder.

The more notable difference can be seen in Figure 4 for the Ce_{0.75}Zr_{0.25}O_{2-x} where the presence of some peaks of Zr appears, the system it crystallizes in is cubic, with 5.4100x5.4100x5.4100 cell.

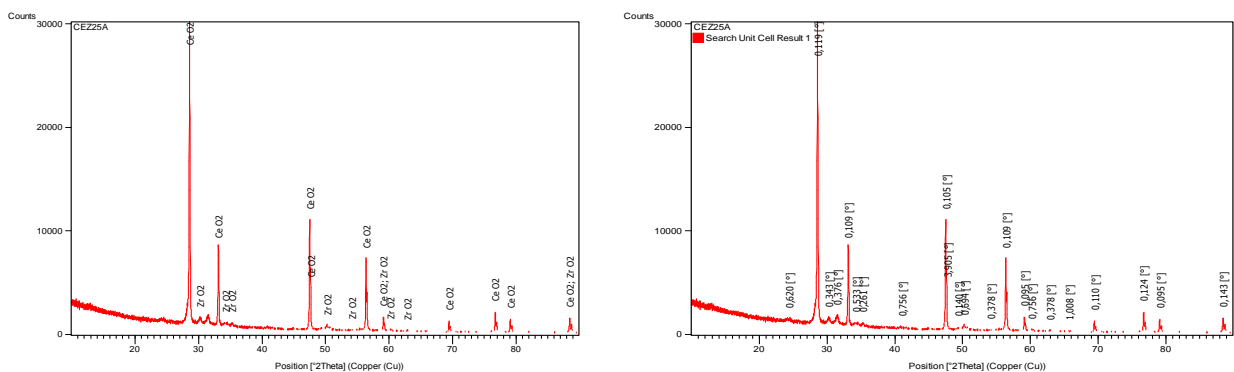


Figure 4. (a) XRD pattern for the Ce_{0.75}Zr_{0.25}O_{2-x}, (b) FWHM for the Ce_{0.75}Zr_{0.25}O_{2-x} powder.

For all the CeO₂ powders SEM analysis have been carried out. All of the results are presented in the next 3 figures (figure 5, figure 6 and figure 7). As can be seen after the SPVD process the dimension of the particle size has smaller values. For both obtained nanopowders Ce_{0.95}Zr_{0.05}O_{2-x} and Ce_{0.75}Zr_{0.25}O_{2-x} the particle size is between 38 and 75nm which proves the fact that the transition to

nanoscale occurred along with the doping of the powders. In the nanopowders we can observe agglomeration of grains with spherical morphology.

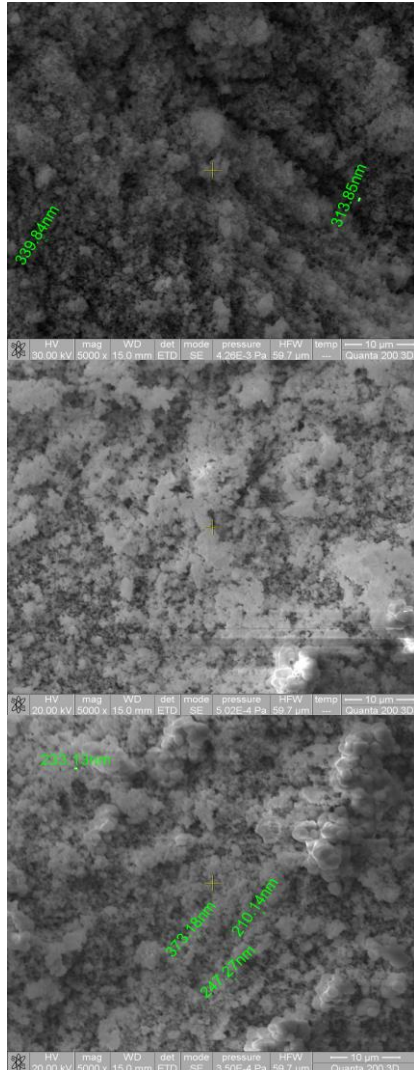


Figure 5. (a) CeO_2 powder (b) CeO_2 after SPVD process.

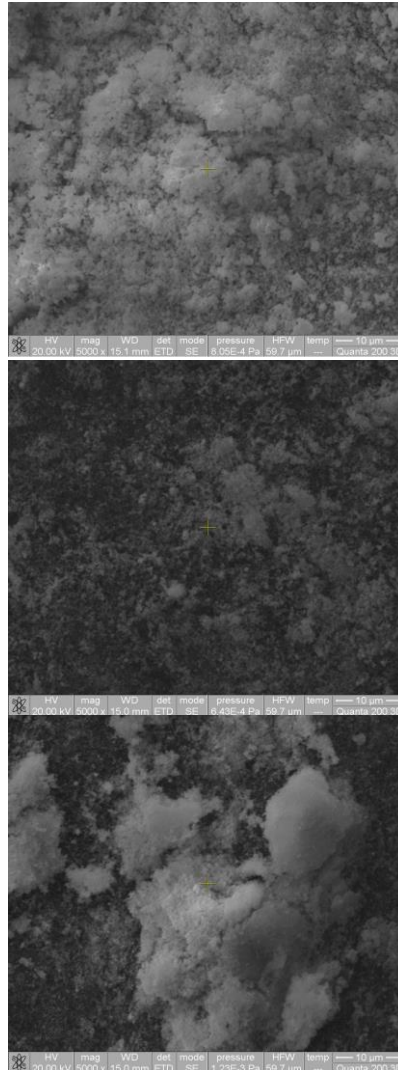


Figure 6. (a) $\text{Ce}_{0.95}\text{Zr}_{0.05}\text{O}_{2-x}$ powder (b) $\text{Ce}_{0.95}\text{Zr}_{0.05}\text{O}_{2-x}$ after SPVD process.

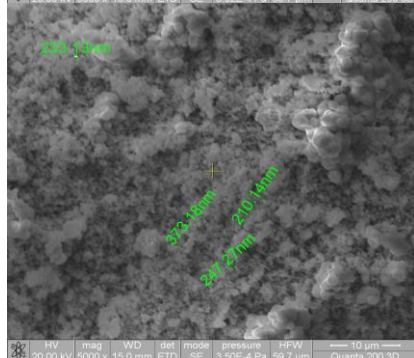


Figure 7. (a) $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_{2-x}$ powder (b) $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_{2-x}$ after SPVD process.

4. Conclusions

All of the solar physical vapor depositions were carried out in a 2kW solar furnace which includes a "heliostat", a concentrator and a solar reactor "heliotron". The solar reactor is positioned in the direct beam of the parabolic mirror thus making the reaction possible. The materials were prepared in the shape of pills in one press in order for the reaction to take place. The nanopowders were synthesized through SPVD from the initial powders with the following composition $\text{Ce}_{0.95}\text{Zr}_{0.05}\text{O}_{2-x}$ and $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_{2-x}$. After the SPVD, $\text{Ce}_{0.95}\text{Zr}_{0.05}\text{O}_{2-x}$ and $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_{2-x}$ nanopowders were obtained with a particle size is between 38 and 75nm which proves the fact that the transition to nanoscale occurred along with the doping of the powders. The obtained nanopowders will be used to obtain the targets in order to deposit them as thin films through laser ablation. The study will continue with the analysis of the thin films deposited taking into consideration all the applications that the CeO_2 can be used in, such as corrosion prevention, optical devices, thermal coatings and biomaterials.

Acknowledgements

This work of Bârcă Eduard Sebastian was supported by the strategic grant POSDRU/159/1.5/S/138963 - PERFORM, co-financed by the European Social Fund – Investing in People, within the Sectoral Operational Programme Human Resources Development 2007-2013.

All authors are indebted to SFERA Grant Agreement no. 228296, 7th EU program which has provided opportunities to collaborate with researchers from France working with the Odeillo solar facilities on close fields.

References

- [1] Guogang T, Jianrong S et al. 2012 Synthesis and characterization of flower like MoS₂ nanostructures through CTAB-assisted hydro thermal process, journal homepage: www.elsevier.com/locate/matlet *Materials Letters* **86** pp 9–12
- [2] Kouam J, Ait-Ahcene T, Plaiasu A G et al 2008 Characterization and properties of ZnO based nanopowders prepared by solar physical vapor deposition (SPVD), www.elsevier.com/locate/solener *Solar Energy* **82** pp 226–238
- [3] Townshend A and Jackwerth E 1989 Precipitation of major constituents for trace preconcentration: potential and problems *Pure & App Chem* **61(9)** pp 1643-1656
- [4] Hench L L and West J K 1990 The sol-gel process *Chemical Reviews* **90(1)** pp 33–72
- [5] Byrappa K, Masahiro Y 2001 *Handbook of Hydrothermal Technology* (Norwich New York: Noyes Publications) Chapter 2: History of Hydrothermal Technology
- [6] Ait Ahcene T, Monty C, Kouam J, Thorel A, Petot-Ervas G and Djemel A 2007 Preparation by solar physical vapor deposition (SPVD) and nanostructural study of pure and Bi doped ZnO nanopowders, www.elsevier.com/locate/jeurceramsoc, *Journal of the European Ceramic Society* **27** pp 3413–3424
- [7] Jafrancesco D, Sansoni P, Francini F, Contento G, Cancro C, Privato C, Graditi G, Ferruzzi D, Mercatelli L, Sani E and Fontani D 2014 Mirrors array for a solar furnace: Optical analysis and simulation results, journal homepage: www.elsevier.com/locate/renene *Renewable Energy* **63** pp 263-271
- [8] Plaiasu A G, Abrudeanu M, Dicu M M and Monty C Elaboration and nanostructural study of pure and Al doped ZnO nanopowders *Journal of Optoelectronics and Advanced Materials* **16(9-10)** pp 1116-1120
- [9] Plaiasu A G and Anghel D C 2010 Application of functional analysis to establish the process of nanostructured oxide film deposition *Proceedings of the International Conference ModTech* pp 459-462
- [10] Soren S, Besso M and Purnendu P A rapid microwave initiated polyol synthesis of cerium oxide nanoparticle using different cerium precursors, journal homepage: www.elsevier.com/locate/ceramint *Ceramics International* available online www.sciencedirect.com
- [11] Castano C E, Matthew J O’Keefe and William G Fahrenheitz 2015 Cerium-based oxide coatings, journal homepage: www.elsevier.com/locate/cossm *Current Opinion in Solid State and Materials Science* **19** pp 69–76
- [12] Parvulescu V I and Tiseanu C 2015 Local structure in CeO₂ and CeO₂–ZrO₂ nanoparticles probed by Eu luminescence, journal homepage: www.elsevier.com/locate/cattod *Catalysis Today* article in press
- [13] Vorokhta M, Matolínová I, Dubau M, Haviar S, Khalakhan I, Ševčíková K, Mori T, Yoshikawa H and Matolín V 2014 HAXPES study of CeOx thin film–silicon oxide interface *Applied Surface Science* **303** pp 46–53