



## The influence of short thermal treatment on structure, morphology and optical properties of Er and Pr doped ceria pigments: Comparative study

Dragana Mićović<sup>1</sup>, Maja C. Pagnacco<sup>2</sup>, Predrag Banković<sup>2</sup>, Jelena Maletaškić<sup>3</sup>, Branko Matović<sup>3</sup>, Veljko R. Djokić<sup>4</sup>, Marija Stojmenović<sup>3,\*</sup>

<sup>1</sup>Faculty of Physical Chemistry, University of Belgrade, Studentski trg 12, 11000 Belgrade, Serbia

<sup>2</sup>Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Department of Catalysis and Chemical Engineering, Njegoševa 12, 11000 Belgrade, Serbia

<sup>3</sup>Vinča Institute of Nuclear Sciences, University of Belgrade, P. O. Box 522, Belgrade, Serbia

<sup>4</sup>Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia

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### Abstract

Potential non-toxic pink and red ceramic pigments based on  $CeO_2$  were successfully synthesized by self-propagating room temperature method and thermally treated at 600, 900 and 1200 °C for 15 min. The structure, morphology and optical properties, as well as thermal stability of  $Ce_{1-x}Er_xO_{2-\delta}$  and  $Ce_{1-x}Pr_xO_{2-\delta}$  ( $x = 0.05$ ) were examined. Single-phase composition of all obtained  $CeO_2$  pigments was confirmed using XRPD method and Raman spectroscopy and it was not dependent on temperature. The mechanism of structural behaviour was thoroughly examined using Raman and FTIR spectroscopy. Nanometric dimensions of the crystallites of all pigments were confirmed using XRPD, TEM and FE-SEM analysis. Colour properties were dependent on the temperature treatment, and their position in the chromaticity diagram was studied using UV/VIS spectrophotometry. Colour efficiency measurements were supplemented by colorimetric analysis. It is proved that all samples are thermally stable in the investigated temperature range (up to 1200 °C), and their potential application as environmentally friendly pigments of desired colour is confirmed.

**Keywords:**  $CeO_2$ , Er and Pr doping, structure, optical properties, colour, pigments

### I. Introduction

Recently, almost all fields of science have been dedicated to solving different problems in order to protect the environment. One of the fields of science that deals with this problem is the field of development of new non-toxic environmentally pure inorganic pigments. Today, inorganic pigments are frequently used for the colouration of many materials in the industry including the production of plastics, ceramics, inks, rubbers, paints and glasses [1,2]. Traditional pigments, such as matrix of lead oxide ( $Pb_3O_4$ ) and tin oxide ( $SnO_2$ ), are used in large extents [3]. Iron oxide ( $Fe_2O_3$ ) encapsulated in zircon ( $ZrSiO_4$ ) matrix, which gives pale red or pink colours [3], and  $Cd(S_xS_{1-x})-ZrSiO_4$  as red-orange

pigment [4], are also widely used. However, the application of the  $Cd(S_xS_{1-x})-ZrSiO_4$  system at temperatures above 900 °C is very toxic and unstable [4]. Although some inorganic pigments containing elements such as Pb, Sn, Fe, Cr, Se, Cd, Hg, Sb have shown excellent properties, their application is strictly controlled and regulated by legislation and regulations adopted by governments in many countries due to their high toxicity (not only for the environment but also for human health) [5–7].

Lately, many attempts have been made in order to eliminate the application of above mentioned toxic and unstable pigments [8–11]. With a few exceptions, majority of ceramic pigments is based on inorganic oxides. Researches have been increasingly focused on the development of new nanosized ceramic pigments, in particular based on cerium(IV)-oxide ( $CeO_2$ ), with

\*Corresponding author: tel: +381 11 340 8860, e-mail: [mpusevac@vin.bg.ac.rs](mailto:mpusevac@vin.bg.ac.rs)

the goal of spreading the range of applications of ceramic pigments [12–15]. Thanks to their high thermal resistance, chemical stability (low corrosion) and very good optical and colouristic properties, ceramic pigments based on CeO<sub>2</sub> are increasingly used nowadays [6,7,9,10,12,13,16]. They attract particular attention because of ability to filter ultraviolet (UV) radiation and protection capabilities from the effects of solar light (UV, VIS and IR light) when applied in the form of coloured coating [13,14].

In order to enable development of environmentally non-harmful ceramic pigments based on CeO<sub>2</sub>, many problems have to be solved starting with those related to powder synthesis. The syntheses of ceramic pigments are each time more focused on obtaining CeO<sub>2</sub> pigments in the form of fine nanosized particles with high surface area, because these features influence colour intensities [12,17,18]. Namely, the properties of the obtained pigments can be controlled by the incorporation of another element into the CeO<sub>2</sub> lattice using different processes of synthesis and modification [12,19–23]. The colouring mechanism is based on the charge transfer transition from O<sub>2p</sub> to Ce<sub>4f</sub> within the CeO<sub>2</sub> band structure, which can be modified by the introduction of an additional electronic level between the anionic O<sub>2p</sub> valence band and the cationic Ce<sub>4f</sub> conduction band [7]. The process of ceria (CeO<sub>2</sub>) doping with different ions (Ru<sup>3+/4+</sup>, Yb<sup>3+</sup>, Er<sup>3+</sup>, Y<sup>3+</sup>, Gd<sup>3+</sup>, Sm<sup>3+</sup>, Dy<sup>3+</sup>, Nd<sup>3+</sup>, Pr<sup>3+/4+</sup>) by using the self-propagating reaction at room temperature (SPRT method) has proven to be a very easy and unique way to obtain pigments with stable structure, morphology and optical properties [12,23–27]. The SPRT procedure, which is one of the most promising because of several advantages over conventional methods [12,23–27], is based on the self-propagating room temperature reaction between metal nitrates and sodium hydroxide, whereby the required equipment is extremely simple and inexpensive. The reaction is spontaneous, whereas the stoichiometry of the final product precisely matches the tailored composition.

Because of the above mentioned advantages, CeO<sub>2</sub> doped with Er<sup>3+</sup> and Pr<sup>3+</sup> (Ce<sub>1-x</sub>Er<sub>x</sub>O<sub>2-δ</sub> and Ce<sub>1-x</sub>Pr<sub>x</sub>O<sub>2-δ</sub>;  $x = 0.05$ ), as new potential environmentally friendly non-toxic ceramic pink and red pigments, were synthesized using the SPRT method [12,18,24,26]. The parameter  $\delta$  denotes oxygen deficiency, i.e. departure from stoichiometry, both because of the introduction of dopant cations ( $x$ ), and because of intrinsic non-stoichiometry. In our previous research [12], various shades of pink colour were obtained for Er<sup>3+</sup> doped CeO<sub>2</sub> (Ce<sub>1-x</sub>Er<sub>x</sub>O<sub>2-δ</sub>;  $x = 0.05–0.20$ ) at room temperature (25 °C) and after thermal treatment at 600, 900 and 1200 °C for 4 h in an air.

In this work, structure, morphology and optical properties of Ce<sub>1-x</sub>Er<sub>x</sub>O<sub>2-δ</sub> and Ce<sub>1-x</sub>Pr<sub>x</sub>O<sub>2-δ</sub> ( $x = 0.05$ ) at room temperature (25 °C), and after thermal treatment at 600, 900 and 1200 °C for 15 min in air, were compared. Thermal treatment lasted only for 15 min because the

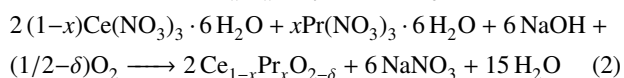
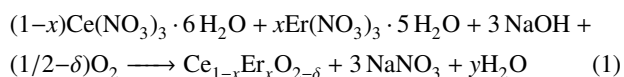
ceramic pigment (Ce<sub>1-x</sub>Pr<sub>x</sub>O<sub>2-δ</sub>;  $x = 0.05$ ) very quickly reached different hues of red colour at 600, 900 and 1200 °C. In addition, praseodymium (Pr<sup>3+</sup>) was selected as a very suitable candidate for obtaining ceramic pigments with a range of shades of red colour [18], because of its lower valence state, comparing with ceria, and good incorporation in its crystal lattice. Furthermore, Pr<sup>3+</sup> doped CeO<sub>2</sub> has still been unused up to now as a ceramic pigment for colouring of different oxides and glass for the application in industrial production [28,29]. Here presented research was focused on the development of a novel class of potential environmentally friendly non-toxic pigments based on CeO<sub>2</sub> with different shades of pink and red colour, aiming to expand the range of ceramic pigments application in the industry.

In this study, optical properties of solid solutions based on CeO<sub>2</sub>, after very short thermal treatment in air, were investigated in order to replace toxic red pigments in a potential application in industrial production.

## II. Experimental section

### 2.1. Materials and methods

Starting reactants used in the experiments were cerium nitrate hexahydrate (Ce(NO<sub>3</sub>)<sub>3</sub> · 6 H<sub>2</sub>O; Aldrich, USA), erbium nitrate pentahydrate (Er(NO<sub>3</sub>)<sub>3</sub> · 5 H<sub>2</sub>O; Aldrich, USA), praseodymium nitrate hexahydrate (Pr(NO<sub>3</sub>)<sub>3</sub> · 6 H<sub>2</sub>O; John Mathey) and sodium hydroxide (NaOH, Vetprom-Chemicals). The desired compositions of the solid solutions were calculated from the ion-packing model equation [30]. The concentrations of the starting reactants were calculated in accordance with the chemical formula of the final products (Ce<sub>0.95</sub>Er<sub>0.05</sub>O<sub>2-δ</sub> and Ce<sub>0.95</sub>Pr<sub>0.05</sub>O<sub>2-δ</sub>) [24,26], which were derived from the reactions (1) and (2):



The starting chemicals were hand mixed [18,26] in alumina mortar for 15 min and then exposed to air for 3 h, which provided required energy for total termination of reaction according to the equation (1). For the removal of NaNO<sub>3</sub> the entire mixture was dispersed in water, and rinsing was performed in a Centurion 102 D centrifuge at 3000 rpm for 10 min. The procedure was performed three times with distilled water and twice with ethanol. The absence of NaNO<sub>3</sub> was confirmed by the titration analysis of the powder on Na using EDTA as the titrant. After drying at 100 °C for 24 h, the powders were thermally treated at 600, 900 and 1200 °C for 15 min in ambient atmosphere.

### 2.2. Characterization

All powders were characterized at room temperature by X-ray powder diffraction (XRPD) using an Ultima

IV Rigaku diffractometer, equipped with Cu  $K_{\alpha 1,2}$  radiation, using a generator voltage of 40.0 kV and a generator current of 40.0 mA. The  $2\theta$  range of  $20\text{--}80^\circ$  was used for all powders in a continuous scan mode with the scanning step size of  $0.02^\circ$  and the scan rate of  $2^\circ/\text{min}$ . Phase analysis was performed using the PDXL2 software (version 2.0.3.0), with reference to the patterns of the International Centre for Diffraction Data database (ICDD), version 2012. XRPD method was also used to evaluate the crystallite size ( $D_{XRPD}$ ) and lattice parameter ( $a_{XRPD}$ ) as a function of temperature. Assuming that line broadening ( $\beta = \beta' + \beta''$ ) is the sum of the contributions attributed to the crystalline size ( $D_{XRPD}$ ) and microstrain ( $e_{XRPD}$ ), which can be written as  $\beta' = 1/(D_{XRPD} \cdot \cos \theta)$  and  $\beta'' = 4e_{XRPD} \cdot \tan \theta$ , the crystallite size and microstrain can be determined from the linear relationship between  $\beta \cos \theta$  and  $4 \sin \theta$ , where  $\theta$  is the Bragg diffraction angle, and microstrain is  $e_{XRPD} = \Delta d/d$  ( $\Delta d$  is the displacement of the lattice) [31]. Before measurement, the angular correction was done using high quality Si standard. Lattice parameters were refined from the data using the least square procedure. Standard deviation was about 1%.

Raman spectra were collected in the spectral range from  $300\text{--}700\text{ cm}^{-1}$  using a DXR Raman microscope (Thermo Scientific, USA) equipped with a diode pumped solid state high-brightness laser (532 nm), an Olympus optical microscope and a CCD detector. Laser power was kept constant at 1 mW. The analysis of the scattered light was carried out using a spectrograph with grating of 900 lines/mm.

Transmission electron microscopy (TEM) analysis of investigated samples was carried by using JEOL JEM-2100 at 200 kV.

Microstructure and morphology of the investigated samples were observed using the field emission-scanning electron microscopy (FE-SEM) analysis (TESCAN Vega TS5130MM). The samples were pre-coated with a several-nanometre thick layer of gold before observation. A Fine Coat JFC-1100 ION SPUTTER Company JEOL device was used for the coating procedure.

Particle size distribution was determined from the obtained TEM and FE-SEM micrographs, immediately after they had been taken, using the Digital Micrograph software. Approximately 40 particles from each micrograph were chosen for the measurements. The diameter of the particles was measured manually, on screen and the result was recalculated into particle sizes using the Digital micrograph software. The mean value was taken as the relevant particle size of the powder.

The EDS analysis was carried out at the invasive electron energy of 30 keV by means of a QX 2000S device by Oxford Microanalysis Group. The maximum resolution was 0.4 nm.

Fourier transform infrared (FTIR) spectra of the samples were collected before and after the heat treatment at different temperatures by using a Perkin Elmer Spectrum Two FTIR spectrometer in the transmission mode. Pressed KBr pellets (technique 1 : 100) were recorded in the range from  $450$  to  $4000\text{ cm}^{-1}$  with the resolution of  $4\text{ cm}^{-1}$ .

Optical properties were analysed by using a diffuse reflectance (DR) Thermo Electron Nicolet Evolution 500 spectrophotometer. Labsphere USRS-99-010 was used as the reflectance standard. The spectra were registered in the wavelength range from 350 to 800 nm and corresponding diffuse reflectance curves were recorded. Scan speed, step recording and bandwidth were  $240\text{ nm}/\text{min}$ ,  $1\text{ nm}$  and  $4\text{ nm}$ , respectively.

The analysis of colour characteristics of all samples was performed according to the CIE  $L^*a^*b^*$  (1976) standard, using illuminant C spectral energy distribution. In this system,  $L^*$  is the colour lightness ( $L^* = 0$  for black and  $L^* = 100$  for white),  $a^*$  is the green (-)/red (+) axis, and  $b^*$  is the blue (-)/yellow (+) axis, and their values were calculated according to the CIE  $L^*a^*b^*$  standard.

### III. Results and discussion

The X-ray diffraction patterns of all obtained doped ceria powders ( $\text{Ce}_{1-x}\text{Er}_x\text{O}_{2-\delta}$  and  $\text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta}$ ;  $x = 0.05$ ) are shown in Fig. 1. Regardless of the dopant type or

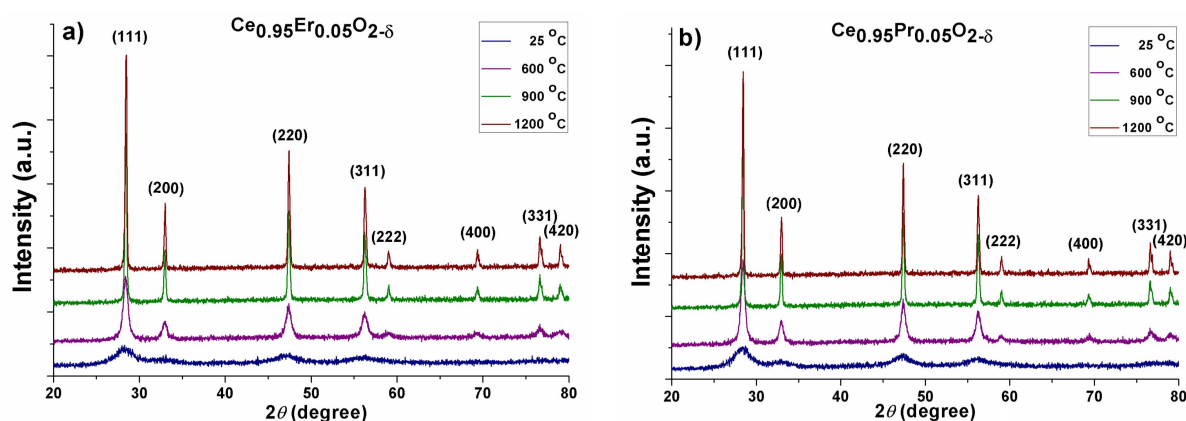


Figure 1. XRPD patterns of: a)  $\text{Ce}_{0.95}\text{Er}_{0.05}\text{O}_{2-\delta}$  and b)  $\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$  powders, thermally treated in air for 15 min at different temperatures

**Table 1. Lattice parameters obtained by ion-packing model ( $a_{ipm}$ ), lattice parameter ( $a_{XRPD}$ ), crystallite size ( $D_{XRPD}$ ) and microstrain ( $e_{XRPD}$ ) obtained by XRPD analysis, and particle size obtained by TEM and FE-SEM of investigated samples at different temperatures**

Sample	$a_{ipm,Er^{3+}}$ [Å]	$a_{ipm,Pr^{3+}}$ [Å]	$a_{ipm,Pr^{4+}}$ [Å]	$a_{XRPD}$ [Å]	$D_{XRPD}$ [nm]	$e_{XRPD}$ [%]	Particle size [nm]
25 °C							
Ce <sub>0.95</sub> Er <sub>0.05</sub> O <sub>2-δ</sub> [24]	5.4091	-	-	5.4023	3.72	0.87	3.5*
Ce <sub>0.95</sub> Pr <sub>0.05</sub> O <sub>2-δ</sub>	-	5.4231	5.4040	5.4410	2.39	1.07	2.3*
600 °C							
Ce <sub>0.95</sub> Er <sub>0.05</sub> O <sub>2-δ</sub>	5.4091	-	-	5.3996	12.68	0.35	12.2*
Ce <sub>0.95</sub> Pr <sub>0.05</sub> O <sub>2-δ</sub>	-	5.4231	5.4040	5.4181	10.66	0.87	10.1*
900 °C							
Ce <sub>0.95</sub> Er <sub>0.05</sub> O <sub>2-δ</sub>	5.4091	-	-	5.3895	32.23	0.11	32.0**
Ce <sub>0.95</sub> Pr <sub>0.05</sub> O <sub>2-δ</sub>	-	5.4231	5.4040	5.4120	29.63	0.12	27.9**
1200 °C							
Ce <sub>0.95</sub> Er <sub>0.05</sub> O <sub>2-δ</sub>	5.4091	-	-	5.3854	36.81	0.08	37.9**
Ce <sub>0.95</sub> Pr <sub>0.05</sub> O <sub>2-δ</sub>	-	5.4231	5.4040	5.4103	35.06	0.07	34.5**

\* TEM, \*\* FE-SEM

heat treatment temperature, all obtained solid solutions exhibited the single-phase fluorite crystal structure with  $Fm\bar{3}m$  space group [18]. High solubility of the dopants in the obtained solid solutions and retaining of the fluorite crystalline structure can be attributed to their nanometric dimensions. The structure information was taken from the American Mineralogist Crystal Data Structure Base (AMCDSB). The reflections for the as-prepared powders, that had not been thermally treated, were significantly broadened (Fig. 1), indicating small crystallite size ( $D_{XRPD}$ ) and/or microstrain ( $e_{XRPD}$ ) (Table 1). Because of very low crystallinity, the XRPD patterns exhibited very diffuse diffraction lines, in such a way that some XRD peaks are not visible (i.e. 222, 400, 331, 420). However, after the thermal treatment, the powders were depicted by XRPD diagrams with sharper diffraction lines, which is in line with the increase of crystallite sizes  $D_{XRPD}$  (Table 1).

The results of lattice parameters ( $a_{XRPD}$ ), crystallite size ( $D_{XRPD}$ ) and microstrain ( $e_{XRPD}$ ) of the Ce<sub>0.95</sub>Pr<sub>0.05</sub>O<sub>2-δ</sub> and Ce<sub>0.95</sub>Er<sub>0.05</sub>O<sub>2-δ</sub> powders are shown in Table 1. It was found that the crystallite size of the doped ceria powders increases with the increase of temperature from 25–1200 °C. This is in a good agreement with the lattice parameter values, which decreased with increasing thermal treatment temperature decreased, and approached the value of the standard pure ceria crystal lattice [23], as well as the theoretical values obtained by ion-packing model ( $a_{ipm}$ ) (Table 1). Namely, according to Shannon's compilation [32], the ionic radii of Ce<sup>4+</sup>, Ce<sup>3+</sup>, Er<sup>3+</sup>, Pr<sup>3+</sup> and Pr<sup>4+</sup> are 0.970, 1.143, 1.004, 1.126 and 0.960 Å, respectively, for eight-fold coordination. Additionally, it is known that CeO<sub>2</sub> crystal lattice contains Ce<sup>4+</sup> and Ce<sup>3+</sup> ions per core-shell model [33, 34]. It was found that most of Ce<sup>3+</sup> is located at the surface [33,34]. All above mentioned indicates that doping process can lead to the substitution of Ce<sup>4+</sup> and Ce<sup>3+</sup> ions with Er<sup>3+</sup> and Pr<sup>3+</sup> ions (confirmed by Raman spectroscopy results presented further in the text).

Besides, it is also known that praseodymium ions can easily change the oxidation state (Pr<sup>3+</sup> ↔ Pr<sup>4+</sup>) [35,36]. Since the ionic radius of Er<sup>3+</sup> is smaller than the ionic radius of Ce<sup>3+</sup> and larger than the ionic radius of Ce<sup>4+</sup>, the doping process can lead to the dilation of the lattice and the reduction of the lattice parameter values in comparison with the pure CeO<sub>2</sub> [23]. With increasing temperature, the lattice parameter value of the CeO<sub>2</sub> doped with Er<sup>3+</sup> ions further decreased. Such behaviour can be explained by the loss of oxygen vacancies because of the influence of high temperature. Namely, theoretical calculations predict that oxygen vacancies tend to migrate from the nanoparticle's interior to the surface [24,37]. According to our results it seems that the migration of oxygen vacancies was intensified when the samples were exposed to higher temperatures. In the case of Er<sup>3+</sup> doped ceria subjected to the high temperature heat treatment (900 and 1200 °C), oxygen vacancies probably migrated from CeO<sub>2</sub> nanoparticles' interior to the surface, and furthermore, left the sample surface thus leading to lattice stabilization. This assumption can be supported by the obtained Raman spectra (Fig. 2a), where the Raman intensity of "vacancies mode" decreased as the consequence of the heat treatment. On the other hand, the lattice of the ceria doped with praseodymium ions exhibited expansion, which can be explained in terms of higher oxygen vacancy concentration because of possible presence of Ce<sup>3+</sup>, Pr<sup>3+</sup> and Pr<sup>4+</sup> ions. Besides, the lattice parameter of the CeO<sub>2</sub> doped with Pr<sup>3+/4+</sup> ions gradually decreased with increasing temperature, although Raman spectroscopy confirmed increased Raman intensity of "vacancies mode". The reason for this behaviour would have to be the change of the oxidation state of Pr<sup>3+</sup> in Pr<sup>4+</sup> (0.960 Å), with similar ionic radius as Ce<sup>4+</sup> ion (0.970 Å), which explains the decrease in lattice parameter with the formation of a new oxygen vacancy (confirmed by Raman spectroscopy; Fig. 2b). Additionally, all treated samples exhibited strong influence of temperature on the microstrain, where with in-

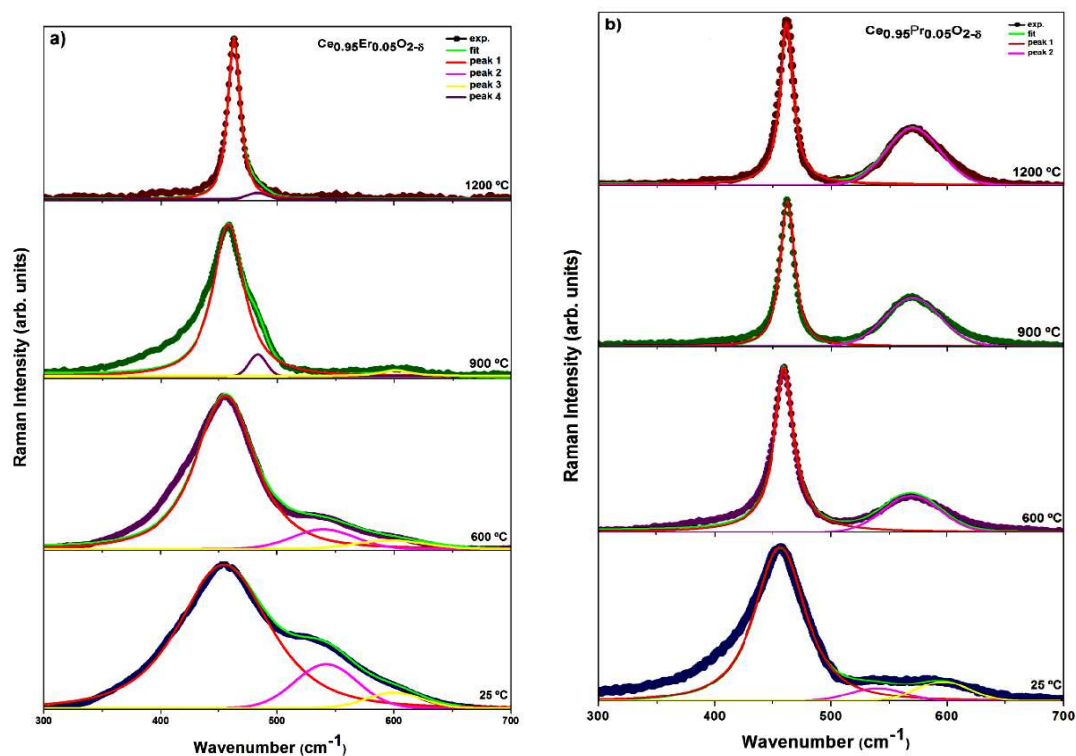


Figure 2. De-convoluted Raman spectra of: a)  $\text{Ce}_{0.95}\text{Er}_{0.05}\text{O}_{2-\delta}$  and b)  $\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$  at different temperatures

creased temperature the values of the crystallite sizes increases together with lowering the microstrain (Table 1). According to our findings, the decrease of microstrain can lead to lattice stabilization, which was achieved by two completely different processes. Thus, in the case of the samples containing  $\text{Er}^{3+}$  that lacks in the oxidized form of erbium ( $\text{Er}^{4+}$ ) lattice stabilization (reflected in decreasing microstrain and lattice parameter) was achieved by oxygen vacancies leaving the sample surface. On the other hand, with the samples containing praseodymium ions, the change in the oxidation state (from  $\text{Pr}^{3+}$  to  $\text{Pr}^{4+}$ ) that has similar ionic radius and the same oxidation state as  $\text{Ce}^{4+}$  ions, leads to the decreased microstrain and lattice parameter values and general lattice stabilization.

The identification of the Raman spectrum of the materials based on  $\text{CeO}_2$  allowed the information about their potential behaviour and applications. Especially, based on Raman signature for oxygen vacancies in the above mentioned materials, the mechanism of their behaviour under the influence of temperature can be defined. The Raman spectra of the as-prepared  $\text{Ce}_{0.95}\text{Er}_{0.05}\text{O}_{2-\delta}$  and  $\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$  powders (25 °C) and those thermally treated in air for 15 min at different temperatures (600, 900 and 1200 °C) are presented in Fig. 2. It is well documented that the main feature in the Raman spectrum of the pure and stoichiometric  $\text{CeO}_2$  with fluorite structure is a single allowed Raman mode of the first order ( $F_{2g}$  symmetry), positioned at the wavenumber of  $465\text{ cm}^{-1}$  [23]. This mode occurs as a result of the symmetric breathing mode of O atoms

around each cation ( $\text{CeO}_8$ , the lattice vibration). In the present work, the obtained nanopowders at room temperature (25 °C; Fig. 2) exhibited shifting of this mode to lower energies ( $457$  and  $450\text{ cm}^{-1}$ ) with increased line width and expressed asymmetry at the lower energy side. These changes in Raman peak profile [18,23] may be due to the nanosized effects such as phonon confinement, inhomogeneous strain and non-stoichiometry. After thermal treatment in air during 15 min at different temperatures (600, 900 and 1200 °C), the Raman mode was shifted to higher frequencies both for  $\text{Ce}_{0.95}\text{Er}_{0.05}\text{O}_{2-\delta}$  ( $460$ ,  $462$  and  $463\text{ cm}^{-1}$ , respectively), and for the  $\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$  ( $456$ ,  $459$  and  $463\text{ cm}^{-1}$ , respectively), with the reduction of line width (Table 2) and the appearance of symmetry. All these characteristics of the Raman peak profile showed that thermal treatment led to grain growth and the formation of better ordered structures, which was confirmed by XRPD (Fig. 1; Table 1), TEM (Figs. 3a and 3b) and FE-SEM analyses (Figs. 3c and 3d).

In addition to the mentioned Raman mode of the first order, the Raman spectra of the powders based on  $\text{CeO}_2$  showed the presence of additional second order modes positioned at about  $550$  and  $600\text{ cm}^{-1}$  [12,23], and defined as Raman signature for oxygen vacancies. The modes positioned at about  $550$  and  $600\text{ cm}^{-1}$  are assigned to intrinsic and extrinsic oxygen vacancies, generated in  $\text{CeO}_2$  lattice with reduction in particle size and doping process, respectively [12,23]. Namely, with particle size decreasing the overall free surface of the powder increases, enabling easier release of oxygen from



the lattice, thus leaving a vacancy and two electrons localized on a cerium atom. This process causes the formation of  $\text{Ce}^{3+}$  ions (lowering of  $\text{Ce}^{4+}$  valence, which is due to electroneutrality demands) and the emergence of the Raman mode at around  $600\text{ cm}^{-1}$  (Fig. 2) [23]. On the other hand, for the doped nanopowders additional Raman mode at around  $550\text{ cm}^{-1}$  was attributed to oxygen vacancies introduced into the ceria lattice when  $\text{Ce}^{4+}$  ions were replaced with cations of lower valence state [12,23] (in this case oxidation numbers were 3+). At  $25\text{ }^\circ\text{C}$  the occurrence of the mode originating from the oxygen vacancies can be explained by the substitution of two  $\text{Ce}^{4+}$  ions with two dopant ions ( $\text{Er}^{3+}$  or  $\text{Pr}^{3+}$ ), when one oxygen vacancy is introduced into the ceria lattice in order to maintain the electrical neutrality [24,26]. However, with increasing heat treatment temperature, the mentioned mode for the  $\text{Ce}_{0.95}\text{Er}_{0.05}\text{O}_{2-\delta}$  was slowly disappearing [12], while for the  $\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$  these modes merged into one at about  $570\text{ cm}^{-1}$ , whose intensity increased with increasing temperature [18,24]. This behaviour of the mode originating from the oxygen vacancies introduced into the ceria lattice can be explained by two different mechanisms for the two dopants:

1. With increasing temperature, the Raman intensity of “vacancies mode” related to the  $\text{Er}^{3+}$  doped  $\text{CeO}_2$  decreases (Fig. 2a), which can be due to the intensified migration of oxygen vacancies towards the surface of the sample and their loss under the influence of temperature. The loss of oxygen vacancies due to the influence of temperature was in agreement with theoretical calculations which also predict their migration from the nanoparticles’ interior to the surface [24,37]. Thus, under the influence of increased temperature, the migration of oxygen vacancies was intensified, followed by their leaving of the sample surface at higher temperatures. The higher temperature, the more eased leaving of sample surface was. This mechanism was supported by the recorded Raman spectra (Figs. 2a and 3), where it is clear that Raman intensity of “vacancies mode” de-

creases with increasing temperature of the heat treatment.

2. With increasing temperature, the Raman “vacancies modes” related to the praseodymium doped  $\text{CeO}_2$  appeared originating from the presence of  $\text{Ce}^{3+}$  ions. They underwent merging in one mode at about  $570\text{ cm}^{-1}$ , whose intensity increased with increasing temperature (Fig. 2b). This can be due to the presence of  $\text{Ce}^{3+}$  and  $\text{Pr}^{3+}$ , but also  $\text{Pr}^{4+}$  ions ( $0.960\text{ \AA}$ ) in  $\text{CeO}_2$  structure, whose ionic radii are similar to that of  $\text{Ce}^{4+}$ . Namely, the praseodymium ions can easily change the oxidation state ( $\text{Pr}^{3+} \leftrightarrow \text{Pr}^{4+}$ ) [24,36], which allows the stabilization of the crystal lattice, formation of a new oxygen vacancy and increase of the Raman intensity of “vacancies mode” (Figs. 2b and 3).

Thus, according to the literature [18,23,24] and here presented results (Figs. 2 and 3), the intensity of peaks at  $550$  and  $600\text{ cm}^{-1}$  is dependent on the number of vacancies. Their absence or presence may indicate the mechanisms of vacancy behaviour with increasing tempera-

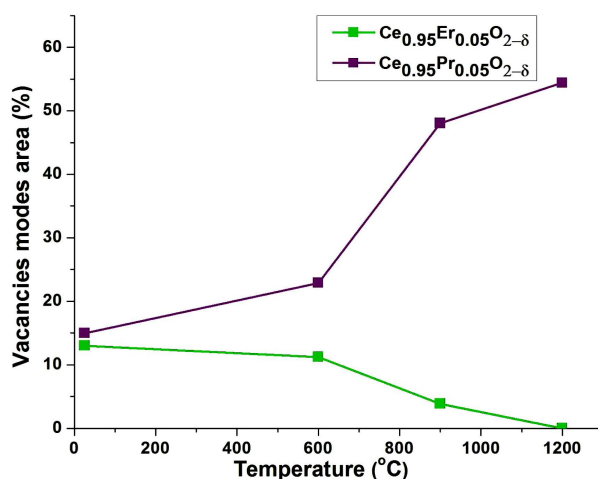


Figure 3. Vacancies modes area as a result of Raman peak’s area sum at  $550$  and  $600\text{ cm}^{-1}$  illustrating two different mechanisms of vacancy behaviour with increasing temperatures

Table 2. Results of the de-convolution of Raman spectra of the  $\text{Ce}_{0.95}\text{Er}_{0.05}\text{O}_{2-\delta}$  and  $\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$  powders, at room temperature ( $25\text{ }^\circ\text{C}$ ) and those thermally treated at different temperatures ( $600$ ,  $900$  and  $1200\text{ }^\circ\text{C}$ ), in air for 15 min

Sample	Area [%]				
	Peak 1 ( $465\text{ cm}^{-1}$ )	FWHM ( $465\text{ cm}^{-1}$ )	Peak 2 ( $550\text{ cm}^{-1}$ )	Peak 3 ( $600\text{ cm}^{-1}$ )	Peak 4 ( $480\text{ cm}^{-1}$ )
25 °C					
$\text{Ce}_{0.95}\text{Er}_{0.05}\text{O}_{2-\delta}$	86.95	60.05	7.47	5.57	-
$\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$	85.03	42.14	5.87	9.10	-
600 °C					
$\text{Ce}_{0.95}\text{Er}_{0.05}\text{O}_{2-\delta}$	88.74	53.21	6.59	4.67	-
$\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$	77.10	15.77		22.90	-
900 °C					
$\text{Ce}_{0.95}\text{Er}_{0.05}\text{O}_{2-\delta}$	90.82	31.98	-	3.87	5.31
$\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$	51.96	11.87		48.04	-
1200 °C					
$\text{Ce}_{0.95}\text{Er}_{0.05}\text{O}_{2-\delta}$	95.36	12.88	-	-	4.64
$\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$	45.58	11.85		54.42	-

tures, and improvement of properties for potential applications [12,25–27]. It is evident from Fig. 3 that the total vacancies content for the  $\text{Er}_3^+$  doped  $\text{CeO}_2$  decreased, while it increased in the case of  $\text{Pr}^{3+/4+}$  doped  $\text{CeO}_2$ .

Additional mode positioned at about  $480\text{ cm}^{-1}$ , which occurs in the case of the  $\text{Ce}_{0.95}\text{Er}_{0.05}\text{O}_{2-\delta}$  thermally treated at the temperature at  $900^\circ\text{C}$  and above, can be a result of the surface mode appearing in the case of very small crystallites like  $\text{CeO}_{2-x}$  [37]. The appearance of this infrared active mode in the Raman spectra can be explained by the lack of long-range order in small crystallites and by the relaxation of the selection rules as a consequence of the defective structure. With further increase of temperature, the intensity of the mentioned mode decreases (Fig. 2a), which confirmed the formation of ordered  $\text{CeO}_2$  structures. The occurrence of this mode is in correlation with the FTIR results, and according to our knowledge, its presence in both Raman and FTIR spectra of the doped  $\text{CeO}_2$  nanocrystals is first reported here (discussed below).

The TEM images of the as-prepared  $\text{Ce}_{0.95}\text{Er}_{0.05}\text{O}_{2-\delta}$  and  $\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$  nanopowders at  $25^\circ\text{C}$  and those thermally treated at  $600^\circ\text{C}$  for 15 min in air, are presented in Figs. 4a and 4b. In all the images the presence of the agglomerates and formed aggregates can be seen, which results from the natural tendency of crystallites to agglomerate [12,23,26]. The first reason for this is energetically more stable configuration of the agglomerated form, while the second reason is the possibility of the crystallite growth. The additional information on the morphology and microstructure of the  $\text{Ce}_{0.95}\text{Er}_{0.05}\text{O}_{2-\delta}$  and  $\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$  nanopowders thermally treated at  $900$  and  $1200^\circ\text{C}$  for 15 min in air were

obtained by using FE-SEM technique (Figs. 5a and 5b). These two powders show homogeneous structure and grain growth upon thermal treatment can be traced, indicating good thermodynamical stability. It is noteworthy that the mean particle size calculated from TEM (Fig. 4) and FE-SEM images (Fig. 5) shows increase with increasing heat treatment temperature for both doped  $\text{CeO}_2$  powders (Table 1). The results obtained from the TEM images indicate that the mean particle size was below  $4\text{ nm}$  and that it differed at most by  $1\text{ nm}$  from those obtained by XRPD. Besides, the results indicate that the average grain size measured from the FE-SEM images was smaller than  $40\text{ nm}$  and it differed at most by  $2\text{ nm}$  from those obtained by XRPD. This confirms the consistence of the TEM and FE-SEM results with the results obtained by XRPD.

Corresponding EDS spectra of the  $\text{Ce}_{0.95}\text{Er}_{0.05}\text{O}_{2-\delta}$  and  $\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$  nanopowders thermally treated at  $1200^\circ\text{C}$  in air for 15 min (Fig. 6), and mean values of the  $\text{Ce}^{3+/4+}/\text{Er}^{3+}$  and  $\text{Ce}^{3+/4+}/\text{Pr}^{3+/4+}$  chemical ratios confirmed that  $\text{Er}^{3+}$  and  $\text{Pr}^{3+/4+}$  ions in the concentrations of 5% ( $\text{Ce}^{3+/4+}/\text{Er}^{3+} = 95.23/4.77$ ,  $\text{Ce}^{3+/4+}/\text{Pr}^{3+/4+} = 95.11/4.89$ ) are successfully incorporated into the host matrix.

In Fig. 7, FTIR spectra of the as-prepared  $\text{Ce}_{0.95}\text{Er}_{0.05}\text{O}_{2-\delta}$  and  $\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$  powders ( $25^\circ\text{C}$ ) and those thermally treated at different temperatures ( $600$ ,  $900$  and  $1200^\circ\text{C}$ ) in air for 15 min are presented. Both spectra show a large absorption band located at around  $480\text{ cm}^{-1}$ . This band can be attributed to the Ce–O stretching vibration [12,38,39] and corresponds to the  $\text{F}_{1u}$  IR active mode of the  $\text{CeO}_2$  fluorite structure. Additionally, the mode positioned at about

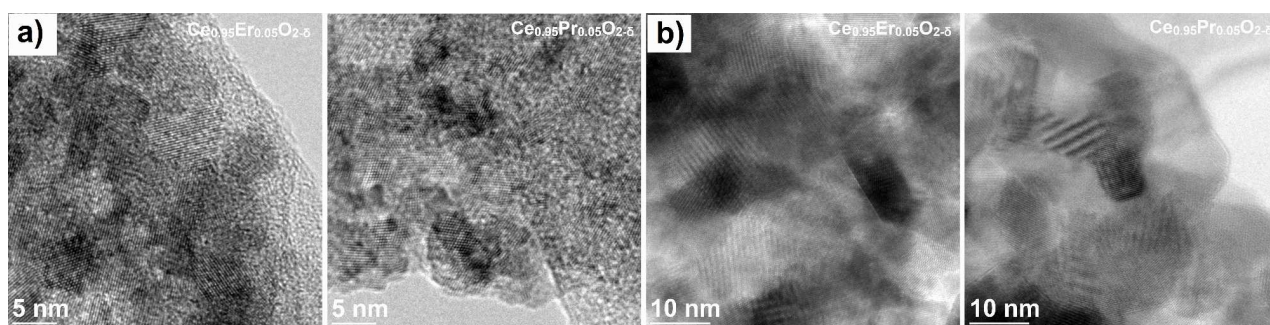


Figure 4. TEM images of investigated samples: a) as-prepared and b) thermally treated at  $600^\circ\text{C}$

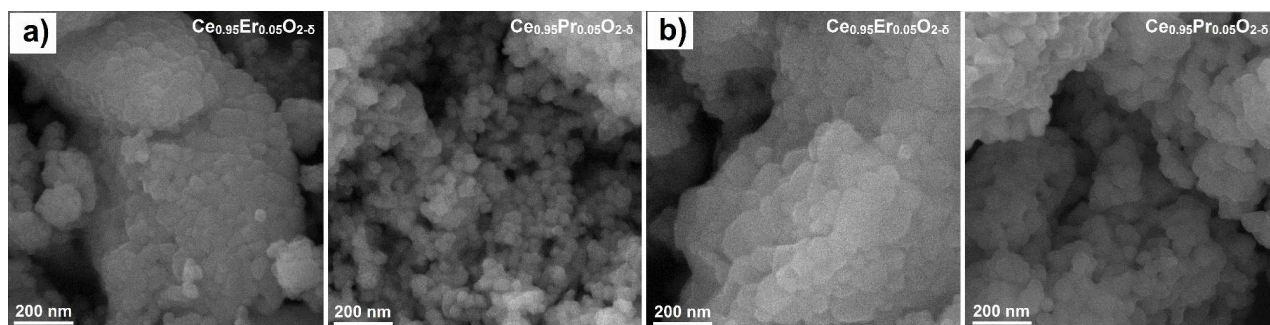


Figure 5. FE-SEM images of investigated samples thermally treated at: a)  $900^\circ\text{C}$  and b)  $1200^\circ\text{C}$

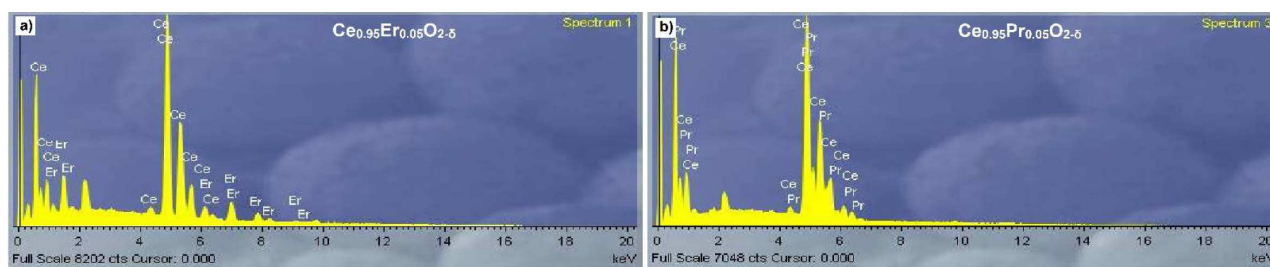


Figure 6. EDS spectra of: a)  $\text{Ce}_{0.95}\text{Er}_{0.05}\text{O}_{2-\delta}$  and b)  $\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$  samples thermally treated at  $1200\text{ }^\circ\text{C}$

$480\text{ cm}^{-1}$  was observed in Raman spectrum of the sample  $\text{Ce}_{0.95}\text{Er}_{0.05}\text{O}_{2-\delta}$  and can be ascribed to a surface mode appearing in very small crystallites such as  $\text{CeO}_{2-x}$  whose energy lies between the infrared active TO and LO phonons of  $\text{CeO}_2$  [37]. As already mentioned, the appearance of this IR active mode in the Raman spectra can be explained by the lack of long-range order in small crystallites and by the relaxation of the selection rules as a consequence of defective structure. Furthermore, the bands located at around  $720$ ,  $840$ , and  $1060\text{ cm}^{-1}$  can be attributed to the  $\text{CO}_2$  asymmetric stretching vibration,  $\text{CO}_3^{2-}$  bending vibration, and C–O stretching vibration, respectively [40]. These bands arise as the consequence of the reaction of atmospheric  $\text{CO}_2$  with water and sodium hydroxide during the synthesis process, which leads to the adsorption of atmospheric  $\text{CO}_2$  on the cations [21] and formation of “carbonate-like” species on the particle surfaces [38]. The bands at around  $1360$  and  $1520\text{ cm}^{-1}$  can be attributed to the vibrations of carbonate species [38,40]. The attenuation of the bands after heat treatment indicates that the carbonate species were thermally decomposed. The band located at around  $1640\text{ cm}^{-1}$  is attributed to the H–O–H bending vibration [21] and indicates the presence of water. Both groups’ spectra contain a large band with the maximum located at around  $3400\text{ cm}^{-1}$ , which can be attributed to the O–H stretching vibration [12]. It confirms the presence of moisture and structural water in the sample before its exposure to heat treatment. Since the band is attenuated in the spectrum collected after heat treatment at  $1200\text{ }^\circ\text{C}$  during 15 min in air, it can be concluded that some moisture was absorbed after calcination.

The temperature influence on the optical properties of the  $\text{Ce}_{0.95}\text{Er}_{0.05}\text{O}_{2-\delta}$  and  $\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$ , particularly the reflectance and band gap energy, was examined using DR UV-VIS spectrometry. Both samples have showed absorption maximum (complementary reflectance minimum) at around  $380\text{ nm}$ , which is attributed to the charge transfer of  $\text{O}_{2p} \rightarrow \text{Ce}_{4f}$  [41]. The reflectance curves for  $\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$  samples showed slow growth with increasing wavelength, reaching reflectance maximum at around  $650\text{ nm}$  (red region). On the other hand, the reflectance curves for the  $\text{Ce}_{0.95}\text{Er}_{0.05}\text{O}_{2-\delta}$  samples showed a sudden increase in reflectance with increasing wavelength and plateau was reached at around  $450\text{ nm}$  (blue region). In addition, the diffuse reflectance spectra of the  $\text{Ce}_{0.95}\text{Er}_{0.05}\text{O}_{2-\delta}$  and  $\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$  showed the absorption difference between the as-prepared ( $25\text{ }^\circ\text{C}$ ) and thermally treated ( $600$ ,  $900$  and  $1200\text{ }^\circ\text{C}$ ) samples (Fig. 8), respectively. For the  $\text{Ce}_{0.95}\text{Er}_{0.05}\text{O}_{2-\delta}$  and  $\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$  samples that were not thermally treated, intensive reflectance occurred along the full range of electromagnetic spectrum. It is evident from Fig. 8 that increasing heat treatment temperature resulted in increasing absorption (decreasing of reflectance plateau), especially for the samples treated at  $1200\text{ }^\circ\text{C}$ . The intensive absorption peaks at  $490$ ,  $520$ ,  $546$ ,  $652$  and  $677\text{ nm}$  were found on  $\text{Ce}_{0.95}\text{Er}_{0.05}\text{O}_{2-\delta}$  reflectance plateau. Due to the increasing absorption at these wavelengths with increasing  $\text{Er}^{3+}$  content in ceria lattice, these peaks are assigned to erbium ion transitions [12]. Since dopant  $\text{Er}^{3+}$  ions replace  $\text{Ce}^{4+}$  ions, they appear as new light absorbing species. The corresponding absorption bands and transition energies are presented in Fig. 9. According to our findings, the absorption peaks at  $490$ ,

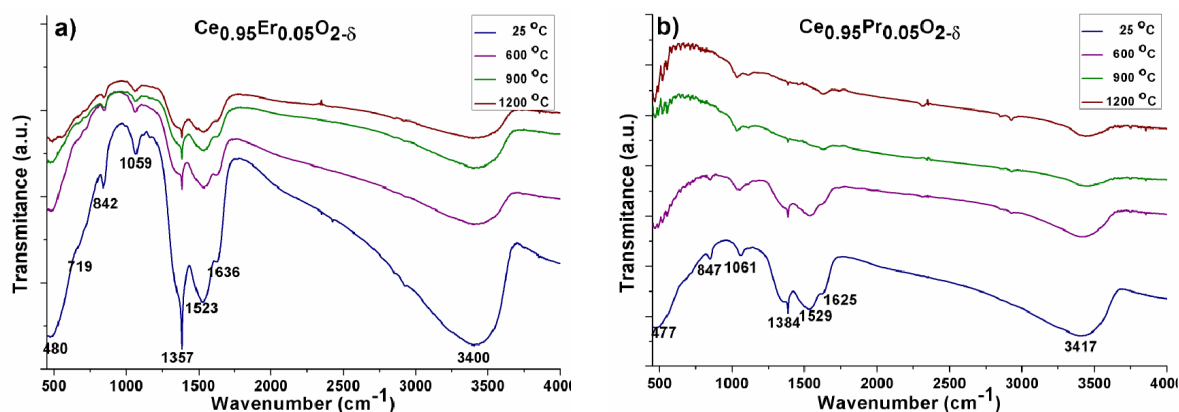


Figure 7. FTIR spectra of: a)  $\text{Ce}_{0.95}\text{Er}_{0.05}\text{O}_{2-\delta}$  and b)  $\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$  powders, thermally treated at different temperatures



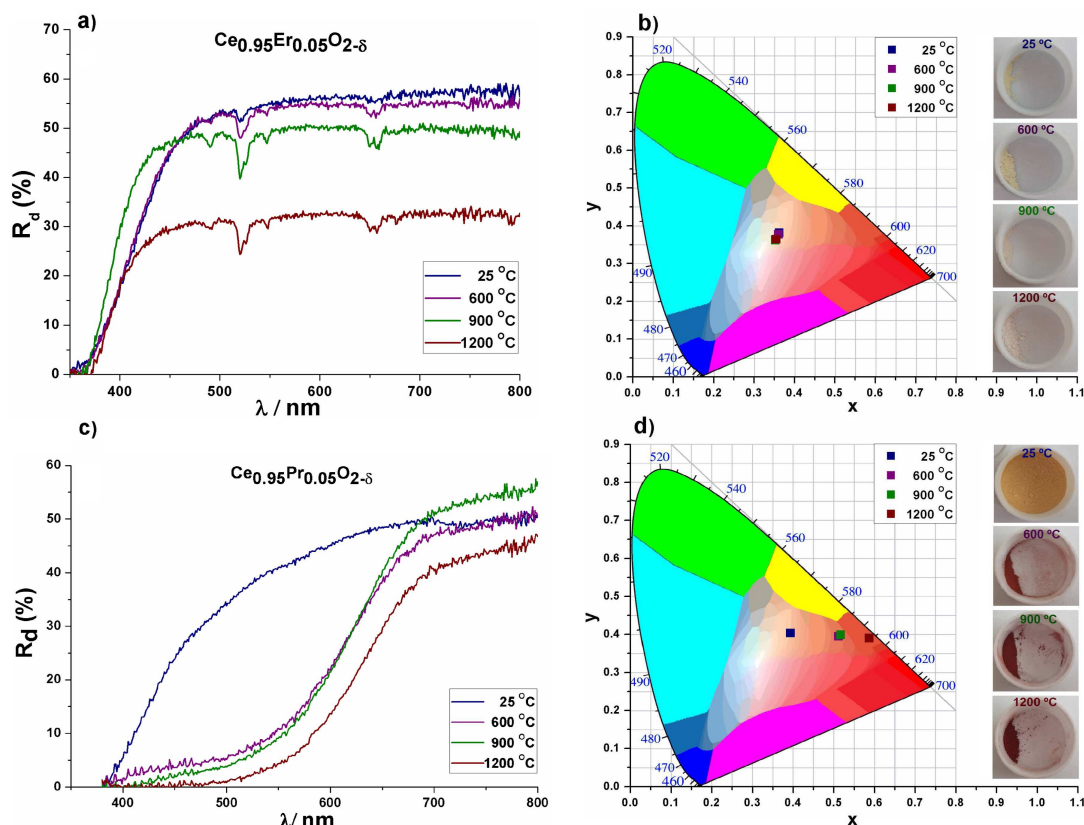


Figure 8. The DR UV-VIS spectra (a and c) and chromatic diagram (b and d) of the  $Ce_{0.95}Er_{0.05}O_{2-\delta}$  and  $Ce_{0.95}Pr_{0.05}O_{2-\delta}$  powders, thermally treated at different temperatures in air for 15 min

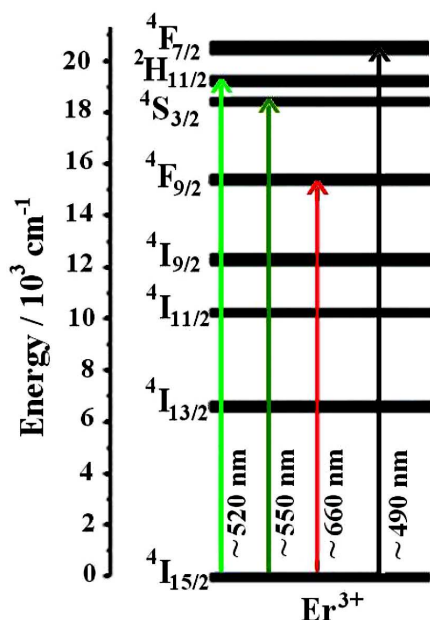


Figure 9. Scheme of the energy levels and energy transitions of  $Ce_{0.95}Er_{0.05}O_{2-\delta}$

520, 550 and 660 nm are assigned to following energy transitions  $^4I_{15/2} \rightarrow ^4F_{7/2}$ ,  $^4I_{15/2} \rightarrow ^2H_{11/2}$ ,  $^4I_{15/2} \rightarrow ^4S_{3/2}$  and  $^4I_{15/2} \rightarrow ^4F_{9/2}$  [15,41].

Beside differences in the reflectance plateau  $R$  [%], the temperature influence on the visible light absorption is evidenced as the shift of the reflectance curves to-

wards larger wavelengths and it had much greater impact on the  $Ce_{0.95}Pr_{0.05}O_{2-\delta}$  samples. The low energy shift signifies partial reduction of cerium to its trivalent state [42,43]. The reduction process ( $Ce^{4+} \rightarrow Ce^{3+}$ ) for the applied experimental conditions occurred in the praseodymium doped  $CeO_2$  samples rather than with erbium ions. This finding indicates that the  $Ce^{4+} \rightarrow Ce^{3+}$  reduction process has important role in the lattice stabilization. Additionally, the band gap energies ( $E_g$ ) of the  $Ce_{0.95}Er_{0.05}O_{2-\delta}$  and  $Ce_{0.95}Pr_{0.05}O_{2-\delta}$  samples treated at different temperatures 25, 600, 900 and 1200 °C were found (Table 3.). The band gap energy calculations were performed on the basis of the Tauc plot [44], and the Kubelka-Munk function [45]. The  $E_g$  values were determined by the extrapolation of the linear part of the  $[F(R) \times E]^2$  versus energy  $E$  curves, where  $F(R)$  is Kubelka-Munk function  $F(R) = (1 - R)^2 / (2R)$ , and  $R$  is reflectance.

Band gap width decreased with increasing heat treatment temperatures for both  $Ce_{0.95}Er_{0.05}O_{2-\delta}$  and  $Ce_{0.95}Pr_{0.05}O_{2-\delta}$  samples (Table 3). The greatest band gap values are determined for the  $Ce_{0.95}Er_{0.05}O_{2-\delta}$  (3.25 eV) and  $Ce_{0.95}Pr_{0.05}O_{2-\delta}$  (3.05 eV) samples that were not thermally treated. Because of slightly smaller band gap energy value for the praseodymium than for the as-prepared erbium doped sample (25 °C), it can be concluded that  $Pr^{3+/4+}$  ion incorporation in  $CeO_2$  enhanced lattice stabilization to a greater extent, comparing to  $Er^{3+}$  ion. The samples treated at 600 °C exhibited

**Table 3.** Calculated band gap energy,  $E_g$  [eV], and colour coordinates ( $L^*a^*b^*$ ) for the  $\text{Ce}_{0.95}\text{Er}_{0.05}\text{O}_{2-\delta}$  and  $\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$  powders, thermally treated at different temperatures, in air for 15 min

Sample	Band gap $E_g$ [eV]	Colour measurement		
		$L^*$	$a^*$	$b^*$
25 °C				
$\text{Ce}_{0.95}\text{Er}_{0.05}\text{O}_{2-\delta}$ [15]	3.25	78.880	-1.560	10.683
$\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$	3.05	70.351	1.548	22.616
600 °C				
$\text{Ce}_{0.95}\text{Er}_{0.05}\text{O}_{2-\delta}$	3.22	78.144	-1.268	9.103
$\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$	2.30	45.031	27.288	35.832
900 °C				
$\text{Ce}_{0.95}\text{Er}_{0.05}\text{O}_{2-\delta}$	3.20	75.127	1.572	2.319
$\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$	2.27	43.491	30.892	44.19
1200 °C				
$\text{Ce}_{0.95}\text{Er}_{0.05}\text{O}_{2-\delta}$	3.17	62.663	1.281	2.944
$\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$	2.13	33.633	34.299	49.291

greater band gap reduction (the greatest band gap energy drop) in comparison with the as-prepared samples. Low energy shift of the  $\text{Er}^{3+}$  doped samples insignificantly varies with the increase of heat treatment temperatures. The observed energy drop was significant for the  $\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$  samples. It is related to oxygen vacancies (detected with Raman spectroscopy, Table 2), as well as the  $\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$  reduction process. The latter results in the increase of  $\text{Ce}^{3+}$  concentration that can cause energy shift to a lower level [43].

Regarding the colour of samples, it is well-known that the colour of absorbed light includes the band gap energy, but also all colours of higher energy (shorter wavelength), because electrons can be excited from the valence band to a range of energies in the conduction band. Thus, we can easily calculate absorbed light ( $\lambda < 1240.8/E_g$ ) using  $E_g = hc/\lambda$ , where  $h$  is Planck's constant and  $c$  is the speed of light in vacuum. Therefore, wide band gaps obtained for  $\text{Ce}_{0.95}\text{Er}_{0.05}\text{O}_{2-\delta}$  at different temperatures (from 25 to 1200 °C) correspond to 382, 385, 388 and 391 nm, respectively and thus shades from yellow toward light pink appeared. Otherwise, band gaps obtained for  $\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$  at different temperatures (from 25 to 1200 °C) correspond to 407, 539.5, 547 and 583 nm, respectively. The  $\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$  at 25 °C has a band gap of 3.05 eV and thus absorbs light with  $\lambda < 407$  nm and appears yellow, while  $\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$  at 600 and 900 °C with  $\lambda < 539.5$  nm,  $\lambda < 547$  nm appear reddish-orange (the colours of light reflected) because it absorbs green, blue and violet light. The  $\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$  at 1200 °C absorbs light with  $\lambda < 583$  nm and appears a darker shade of reddish-orange because it besides green, blue and violet light absorbs and yellow light. Additionally, it can be concluded that abundance of defects related to oxygen vacancies as well as the  $\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$  reduction process, resulted in the narrowed band gap and enhanced optical absorption in  $\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$  at elevated temperatures.

Based on certain changes of band gap width and colour characteristics of the  $\text{Ce}_{0.95}\text{Er}_{0.05}\text{O}_{2-\delta}$  and  $\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$  samples (Figs. 8a and 8c), the values of

chromatic coordinates for both groups of compounds at room temperature (25 °C), and heat treated at 600, 900 and 1200 °C for 15 min in air are illustrated in chromatic diagrams (Figs. 8b and 8d). The calculated values of the band gap for both  $\text{Ce}_{0.95}\text{Er}_{0.05}\text{O}_{2-\delta}$  and  $\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$  samples are presented in Table 3. From the corresponding  $L^*a^*b^*$  coordinates (Table 3), it is obvious that colour changes are very intensive for the heat treated  $\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$  sample. On the other hand, changes of the colour characteristics of the  $\text{Ce}_{0.95}\text{Er}_{0.05}\text{O}_{2-\delta}$  are somewhat lower in intensity (Table 3). At the same time, increasing contribution of the coordinates  $a^*$  and  $b^*$  was in compliance with the progressive decrease of luminosity ( $L^*$ ), especially for the  $\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$  sample (from 70.351 to 33.633). Therefore, the colour shifted with increasing temperature from yellow toward light pink hue (increasing  $a^*$ ) and became more saturated (decreasing  $L^*$ ) for the  $\text{Ce}_{0.95}\text{Er}_{0.05}\text{O}_{2-\delta}$  sample. For the  $\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$  sample the colour shifted from yellow to dark-red hue. Successful incorporation of  $\text{Er}^{3+}$  as well as  $\text{Pr}^{3+/4+}$  ions in the lattice of  $\text{CeO}_2$  is thus confirmed. The most pink and red hues (the highest values of coordinates  $a^*$ ) are achieved for the pigments thermally treated at the highest temperature (1200 °C). Thus, according to Figs. 8b and 8d, and their corresponding insets (visual appearance), the colour and intensity of the pigments was dependent on the composition (dopant ion type) and heat treatment temperature, and the colour of the pigments could vary from white-pink to dark-red hue.

#### IV. Conclusions

Nanostructured non-toxic  $\text{Ce}_{0.95}\text{Er}_{0.05}\text{O}_{2-\delta}$  and  $\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$  oxides, as pink and red colour compounds, were successfully synthesized by low cost self-propagating room temperature method. All cerium oxide powders before (at 25 °C) and after heat treatment (treated at 600, 900 and 1200 °C during 15 min in air) had crystal structure of the fluorite type with  $Fm\bar{3}m$  space group, which confirmed the structural

and thermal stability of the obtained solid solutions. Particle sizes remained within the nanometric range along with temperature increase from 25–1200 °C for all obtained pigments. The absence of oxygen vacancies in the structure of the obtained pigments, examined by Raman spectroscopy, may indicate their future potential applications. Furthermore, the colour changes depended on the composition (dopant ion type) and the heat treatment temperature. Increased temperature resulted in colour variation from yellow to light-pink hue for  $\text{Ce}_{0.95}\text{Er}_{0.05}\text{O}_{2-\delta}$ , and from yellow to dark-red hue for  $\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$ . Another consequence of the increase of heat treatment temperature was the increase of crystallite size and light absorption, where the edge of absorption of visible light shifted toward lower energies.

The structure, morphology and optical properties of nanometric  $\text{Ce}_{0.95}\text{Er}_{0.05}\text{O}_{2-\delta}$  and  $\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$  synthesized in this work, suggest that these compounds may be interesting to be used as pigments for a wide area of applications such as in cosmetics, ceramics, plastics, paints, coatings and glass enamels. Thus, further investigation related to the testing stability of this nanometric  $\text{Ce}_{0.95}\text{Er}_{0.05}\text{O}_{2-\delta}$  and  $\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_{2-\delta}$  compounds in real samples, such as ceramics or glass, should be done. Anyhow, the results obtained in this work will pave the way for the potential alternative to the toxic pink and red pigments widely used.

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