



Research article

Spectroscopic and structural properties of CeO₂ nanocrystals doped with La³⁺, Nd³⁺ and modified on their surface with Ag nanoparticlesMonika Michalska^{a,b,*}, Karol Lemański^c, Andrzej Sikora^d^a *Lukasiewicz Research Network - Institute of Microelectronics and Photonics, Al. Lotników 32/46, 02-668 Warsaw, Poland*^b *Department of Chemistry, Faculty of Materials Science and Technology, VSB-Technical University of Ostrava, 17. Listopadu 15/2172, 708 00 Ostrava-Poruba, Czech Republic*^c *Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okólna 2, 50-422 Wrocław, Poland*^d *Faculty of Microsystem Electronics and Photonics, Wrocław University of Science and Technology, Janiszewskiego 11/17, 50-372 Wrocław, Poland*

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ABSTRACT

The purpose of this work is to present our efforts focused on applications of chemical synthesis of nanocrystalline cerium dioxide (CeO₂) powders doped with La³⁺ ions and CeO₂:Nd³⁺ modified, on their surface, with Ag nanoparticles (NPs). The synthesized powders were examined by X-ray powder diffraction (XRD), absorption, emission spectroscopy, scanning electron (SEM) and atomic force microscopy (AFM). The relations between crystallographic properties and stability of CeO₂ compounds doped by La ions and surface-modified by Ag were studied. XRD patterns revealed that all studied samples are single-phase and crystallized in the cubic fluorite-type structure, in space group Fm-3m. The average crystallite sizes estimated by Rietveld method of series: La-doped CeO₂ were in the range of 7–14 nm, and CeO₂:1%Nd³⁺/n-Ag (n: 1- 5wt.%) were found to be in the range of 29–34 nm, respectively. The lattice parameter *a* for La-doped CeO₂ powders varying from 5.416 to 5.482 Å with increasing content of La³⁺ ions from 0 to 20wt.%, respectively. For series of CeO₂:Nd³⁺/n-Ag materials lattice parameter *a* was at the same level and in accordance with the standard value *a*₀ = 5.411 Å (ICDD - 43-1002). The SEM and AFM observations depicted the grainy structure of all obtained CeO₂-powder samples. The estimated grain size ranged from 50 to 500 nm. The diverse grain shapes and packing was remarked in the samples. According to our knowledge, the relationship between the structural, spectroscopic and morphological characteristics of CeO₂ samples was presented in this work for the first time.

1. Introduction

The most stable modification of cerium dioxide, CeO₂, crystallizes in the fluorite-type structure, space group Fm-3m [1]. The CeO₂ compounds, due to its unique properties, have been widely used in various applications, e.g.: supercapacitors [2, 3, 4], solid oxide fuel cells (SOFC) [5, 6, 7], solar cells [8, 9, 10], catalytic [11, 12, 13, 14], gas sensing [15, 16] and corrosion protection [17, 18].

By changing the grain size, especially for nanosized compounds, new properties can be obtained and, as a result, new applications can be found [19, 20]. As to CeO₂ nanoparticles, it was shown that a decrease in the size stays in relation to a significant increase in the cell parameter [21, 22, 23]. The ferromagnetism as well as the other magnetic properties of CeO₂ depends also on its particles size [24, 25]. It was shown in the literature, that La³⁺ considerably improves the catalytic activity of CeO₂

for soot oxidation by O₂ [26]. For La-doped NPs, it was found, that both the dopant (La³⁺) and Ce³⁺ were distributed homogeneously throughout the particles [27]. CeO₂ nanostructures are interesting materials, also due to their ability for strong UV radiation absorption and the potential excitation of the doped optically active ions by energy transfer. Surface modification of CeO₂ with Ag nanoparticles have positive effect in the photocatalysis experiments realized under visible light irradiation of the degradation of 4-nitrophenol and methylene blue than pristine CeO₂ material [28, 29].

A variety of approaches were developed to achieve at the same time a single-phase, ultrafine and homogenous CeO₂ materials in the form of powder or thin films, such as: solid-state synthesis [30], sol-gel [31, 32], precipitation [31, 32, 33, 34, 35, 36, 37], combustion [38, 39, 40], hydrothermal [41, 42, 43], solvothermal [44, 45], microemulsion [46, 47], electrochemical deposition [48] and so on.

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In this contribution, we present the structural, morphological and spectroscopic studies on CeO₂ nanocrystals doped with La³⁺ or Nd³⁺ ions, and modified CeO₂:Nd³⁺ on their surface with Ag metals. The correlation between the structural, morphological and spectroscopic properties of CeO₂ nanocrystals doped with Nd³⁺ ions and modified on their surface with silver metallic nanoparticles was examined for the first time. To the best of our knowledge, this is also the first case of the utilization of atomic force microscopy (AFM) to observe the difference between the nanocrystalline powders of CeO₂ with and without modified surface. In this work, the nanocrystalline CeO₂ powders doped with La³⁺ ions were prepared using a modified sol-gel process, and the surface-modified commercial CeO₂ particles with 1–5%wt.Ag were fabricated using the low-temperature chemical synthesis. The structural features were examined by X-ray powder diffraction, absorption, emission spectroscopy, scanning electron and atomic force microscopy. As the result, the structural, morphological and spectroscopy studies performed in this work were carried out to assess the readiness in terms of the verification of the usefulness of CeO₂ nanocrystalline powders as a potential material for application in UV light detection, which transfer energy (in the UV region) to the doped rare earth ions.

2. Experimental

2.1. Synthesis of CeO₂ doped with La³⁺ ions

High pure cerium (III) nitrate hexahydrate (Ce(NO₃)₃ · 6H₂O from Sigma-Aldrich, 99.99%), lanthanum (III) nitrate hexahydrate (La(NO₃)₃ · 6H₂O from Sigma-Aldrich, 99.99%), citric acid monohydrate (C₆H₈O₇ · H₂O, pure p.a., 99.5% from Avantor Performance Materials Poland S.A), acetic acid (C₂H₄O₂ from CHEMPUR, 99.5%) were utilized to obtain CeO₂ nanocrystalline powders doped with 5, 10 and 20% wt. of La ions. The nominal Ce:La molar composition ratios were 1.95:0.05, 0.9:0.1 and 0.8:0.2.

Stoichiometric amounts of cerium and lanthanum nitrates were separately turned from solid to liquid phases in deionized water under continuous magnetic stirring. Then, the cerium and lanthanum water salt solutions were mixed together and, followingly citric and acetic acids were slowly dropped into the solutions. The excess water was evaporated very slowly from the properly prepared solutions until gels were formed. The gel precursors created in the preceding process were air-dried at 150 °C for a few hours. The pre-dried powders so-called xerogels were calcined in a one-stage process between 300 °C and 500 °C for the few hours in an air atmosphere.

2.2. Synthesis of CeO₂ modified with Ag NPs and Nd³⁺ ions

To synthesize the CeO₂/n-Ag composites, silver nitrate (AgNO₃, pure, Avantor Performance Materials Poland S.A) was first dissolved in ethanol (96%, Avantor Performance Materials Poland S.A) solution. Then, the cerium (IV) oxide (CeO₂, ≥99.0%, ca. 1% of impurities of Nd³⁺ ions, Aldrich) powder was introduced into to the silver nitrate solution to obtain a suspension (AgNO₃–EtOH–H₂O–CeO₂) under continuous magnetic stirring process. Appropriate weight ratio: 0.01, 0.02, 0.03, 0.04 and 0.05 of Ag and CeO₂ was used. To obtain a homogeneously dispersed suspension, the resulting mixture was magnetically stirred for several hours. Lately, to remove excess alcohol and water from the suspension the conditions of air-dried at 150 °C for a few hours was utilized. In order to obtain a fine powders, the so-obtained composites in an agate mortar were grounded [49, 50, 51, 52, 53].

2.3. Measurements

XRD analysis was utilized as a pivotal technique to recognize the crystalline phase of the prepared powders. The XRD patterns were acquired in angle range from 10° to 60° (2θ angle) using a Siemens D-500 X-ray powder diffractometer equipped with a Cu K_α radiation source, emitting λ = 1.542 Å. The phase analysis as well as the structural

parameters refinement performed using Rietveld method were acquired using a PDF4+2019 database.

The absorption spectra were recorded using a Cary 5000 spectrophotometer. The emission spectra were acquired using a Hamamatsu spectrometer. As an excitation source, the fourth harmonic (266 nm) of Q-switched Nd:YAG pulsed laser was used.

The morphology as well as the particle size of the products were observed and measured using scanning electron microscopy (SEM, Cross Beam Auriga, Carl Zeiss).

The atomic force microscopy measurements were performed using a Dimension 3000 system from Digital Instruments Company. The Tapping Mode was enabled, and the scanning process was carried out at ambient conditions (temperature: 25 °C, relative humidity: 35%). The device was equipped with a 100 μm × 100 μm scanner, which was calibrated using a typical silicon grid provided by NT-MDT. The probes used in the measurements were provided by Nanosensor company. Pointprobes type was utilized, having the parameters as follows: nominal tip radius r_{tip} = 10 nm, resonance frequency range f_{res} = 306–353 kHz, and spring constant k = 43–68 N m⁻¹. The data processing was performed using the SPIP software providing by Image Metrology company [54]. Next to standard 2D surface images, the Sobel transform was provided, as it reveals subtle morphological details. This image processing tool was successfully used in many previous works [55, 56, 57, 58, 59, 60].

3. Results and discussion

3.1. XRD measurements results

The crystal cubic fluorite-type of space group Fm-3m structure of the CeO₂ compound is presented in Figure 1. One can notice, that each cerium (IV) ion (Ce⁴⁺) is coordinated by eight oxygen (O²⁻) ions.

The collected XRD patterns of the pristine and La-doped CeO₂ powders are presented in Figure 2 (A, B). The XRD analysis indicates that all synthesized La-doped CeO₂ powders (Figure 2) are single-phase and they crystallized in the cubic fluorite-type structure, space group Fm-3m, and no other phases are observed in the diffraction patterns. All diffraction peaks are indexed to the cubic structure of cerium (IV) oxide (ICDD - 43-1002) [61,62]. The XRD patterns of the La-doped CeO₂ powders present 5 characteristic peaks for CuK_α radiation (λ = 1.542 Å), which correspond to the crystal planes of (111), (200), (220), (311) and (222), as given in Figure 2. The average crystallite sizes of La-doped CeO₂ estimated by Rietveld method were in the range of 7–14 nm. The cell parameter in La-doped CeO₂ powders increases with the doping concentration of La ions. This relation is correlated with the ionic size of the La-ions (dopant). It also means that the doping of La-ions affects the crystal structure of pristine CeO₂ (see Table 1). To understand the doping on La ions into CeO₂ host structure we decided to closer look at the

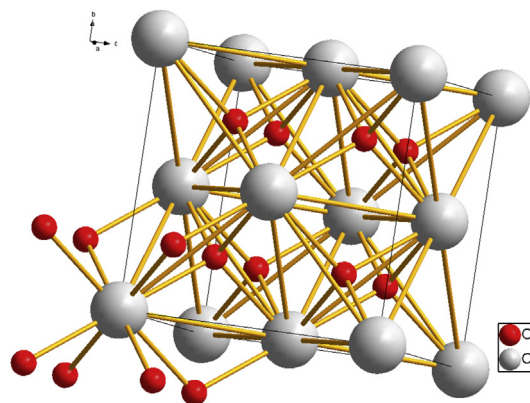


Figure 1. Visualization of the crystal CeO₂ structure with the cubic space group of Fm-3m (225), (ICDD - 43-1002).

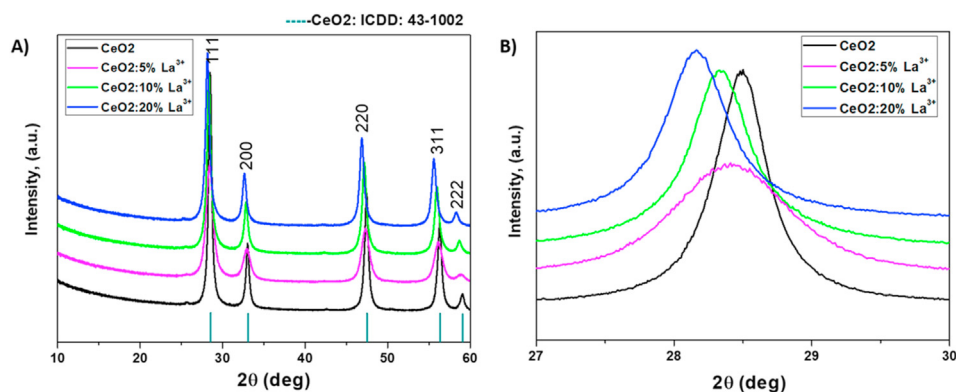


Figure 2. Full-angle (2θ : 10–60°) XRD experimental diffraction patterns of pristine CeO₂ and La-doped samples (2θ : 10–60°) with reference lines of matching CeO₂ phase from a database (A), and narrow angular range (2θ : 27–30°) for (111) diffraction lines (B).

Table 1. Crystallite sizes and cell parameters of pristine and n-La doped CeO₂, as acquired from XRD measurements.

Material	Average crystallite size (XRD), nm	Lattice parameter a , Å	Cell volume, Å ³
A) pristine	14	5.4163 (2)	158.90 (1)
B) doped 5% wt. La	7	5.4324 (2)	160.32 (1)
C) doped 10% wt. La	10	5.4506 (2)	161.93 (1)
D) doped 20% wt. La	10	5.4823 (2)	164.78 (1)

changes that could take place in the narrow angular range from 27 to 30° (2θ) at the (111) crystal planes. The slight shift towards lower values of 2θ from 28.5 to 28.2° (2θ) for pristine CeO₂, and CeO₂:10%La³⁺ was observed (Figure 2B). This appearance has been confirmed in other works [63, 64, 65, 66, 67]. It could be assumed according to other researchers and studies, that this phenomenon is connected to estimated i) very small crystallite sizes of synthesized materials by modified sol-gel method what is connected to use to the synthesis conditions, like i.e.: temperature, time, atmosphere, complexing agents, pH, etc., ii) created during synthesis oxygen vacancies and the stacking defects in ceria as well as, iii) structural defects, which originating the stress within the crystal lattice and influencing on the minor shift observed on the XRD peaks at (111) diffraction lines towards lower angles [63, 64, 65, 66, 67].

The XRD patterns of pure and silver-decorated CeO₂:1%wt. Nd³⁺ powders are presented in Figure 3 (A, B). For each sample (see Figure 3A), all peaks are attributed to cerium (IV) oxide structure (ICDD - 43-1002), confirming that the decoration surface of pristine CeO₂ does not lead to any phase segregation. No significant change during performing structural analysis in the Ag content was noticed. The average crystallite sizes of CeO₂ achieved by the Rietveld method, were in the

range from 29 to 34 nm. In the result, due to the very low peak intensity caused by the low silver weight content, it was not possible to estimate from the XRD data the crystallite size of Ag nanoparticles. Similar to previous set of ceria-samples, narrow angular range from 27 to 30° (2θ) at the (111) crystal planes, was studied (Figure 3B). The shift effect to lower angles was very small and ranged from 28.6 to 28.5° (2θ) for commercial CeO₂, and surface modified with 5%Ag, respectively (Figure 3B). This observation showing and comparing the results of pristine CeO₂ prepared by modified sol-gel method, and commercial CeO₂ material. The estimated lattice parameters and cell volumes for both mentioned samples is almost the same. It is clearly shown, that formation of nanostructures causes the creation of oxygen vacancies, defects and other structural strains [63, 64, 65, 66, 67].

The unit cell parameters and the volumes of all obtained CeO₂ doped with La-ions and modified with Ag NPs calculated from the XRD data are coherent with the typical values ($a_0 = 5.411$ Å, $V_0 = 158.46$ Å³) of the ICDD PDF card. The calculated crystallite sizes, cell parameters and cell volumes for all powders are presented in Table 1 and Table 2. It should be also pointed here that the nanocrystalline CeO₂ material synthesized by modified sol-gel method has smaller average crystallite size and does not have any impurities in comparison with commercial CeO₂ contaminated with Nd³⁺ ions.

3.2. Absorption and emission spectra

The absorption spectra of pure CeO₂ and La³⁺-doped CeO₂ nanocrystals are similar to each other (Figure 4).

The broad absorption bands are observed from the ultraviolet (UV) up to the blue region, at about 450 nm. From around 500 nm to the near-infrared (NiR) range, the absorption does not occur, so the spectra are

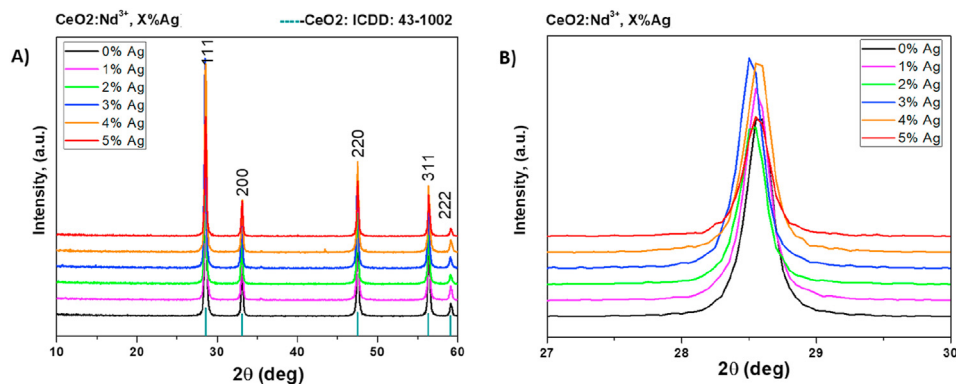
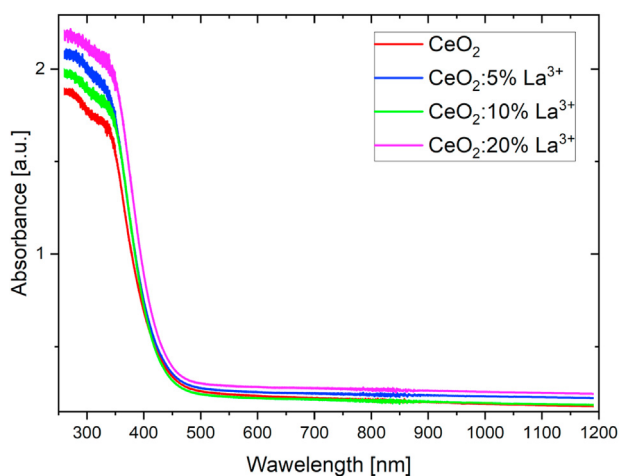
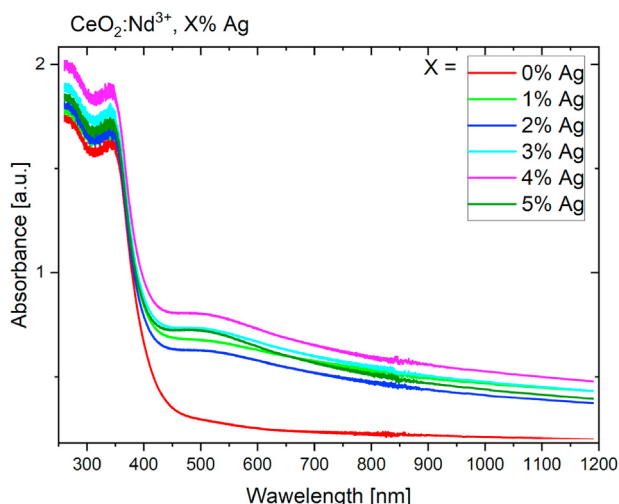
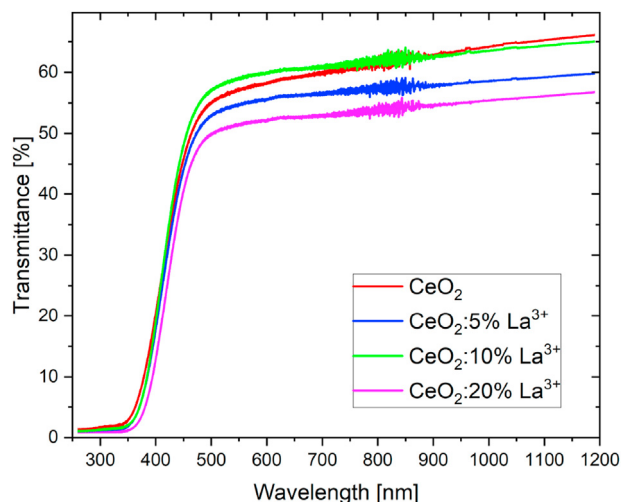


Figure 3. Full-angle range (2θ : 10–60°) XRD experimental diffraction patterns of commercial CeO₂:1%wt. Nd³⁺ with X%Ag with reference lines of matching CeO₂ phase from database (A), and narrow angular range (2θ : 27–30°) for (111) diffraction lines (B).

Table 2. Crystallite sizes and cell parameters of commercial and n-Ag modified CeO₂, as enumerated from XRD measurements.

Material	Average crystallite size (XRD), nm	Lattice parameter <i>a</i> , Å	Cell volume, Å ³
A) pristine	29	5.414 (1)	158.71 (5)
B) 1% n-Ag	34	5.412 (1)	158.54 (6)
C) 2% n-Ag	31	5.411 (1)	158.44 (4)
D) 3% n-Ag	31	5.411 (1)	158.46 (6)
E) 4% n-Ag	31	5.412 (1)	158.51 (4)
F) 5% n-Ag	30	5.412 (1)	158.49 (7)

flat. The CeO₂ UV absorption bands are characteristic for this material. The similar absorption spectra were earlier reported for CeO₂ [28-29, 68-70]. Strong ultraviolet absorption capability of cerium oxide is related to the charge transfer from O²⁻ to Ce⁴⁺ ions. For commercial CeO₂ powders surface modified with Ag NPs and containing 1% of Nd³⁺ ions, the absorption spectra possess similar, but more clearly separated bands in the UV range (with the separation at about 310 nm). The absorption of Ag metallic nanoparticles is observed in the broad region over 450–600 nm. This band does not occur for the commercial CeO₂ powder and is more raised for the samples with a higher amount of Ag NPs (from 3% Ag, see Figure 5).

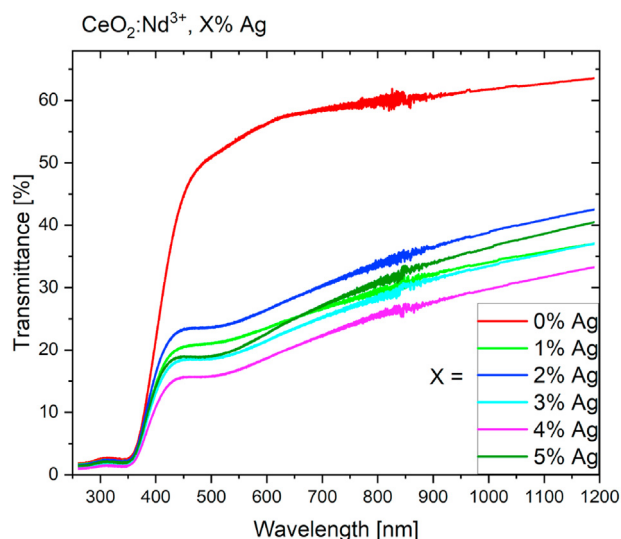
**Figure 4.** The absorption spectra of pure CeO₂ and La³⁺-doped CeO₂ nanocrystals.**Figure 5.** The absorption spectra of CeO₂:1% Nd³⁺, Ag nanocrystals.**Figure 6.** The transmittance spectra of CeO₂ nanocrystals doped with the La³⁺ ions.

The Ag absorption is very sensitive to the local structure environment and related absorption band may appear in different spectral regions, from UV to NiR range [71]. Further luminescence analysis shows that the commercial CeO₂ (with 1% of impurities) is contaminated by some amount of Nd³⁺ ions. The content of Nd³⁺ was too small to be observed in the absorption spectra and XRD patterns.

The transmittance spectra (Figures 6 and 7) were obtained by the mathematical conversion of the measured absorbance, by using the equation: $A = -\log_{10} T$, where *A* is the absorbance and *T* is the transmittance. As seen in Figure 6, for the CeO₂ doped with La³⁺ ions, there are no significant differences for different doping levels. The transmission in the visible region is about 50–60%. For the CeO₂ nanocrystals surface modified with silver NPs, the optical transmission is significantly lower than that in the commercial CeO₂ sample and reaches up to about 30%. In this compound, Ag nanoparticles possess a higher ability to absorb light than La³⁺ ions.

The energy band gap for each CeO₂ sample was determined by using the Kubelka-Munk method [72], basing on Eq. (1):

$$F(R) = \frac{(1 - R)^2}{2R} \quad (1)$$

**Figure 7.** The transmittance spectra of CeO₂:1% Nd³⁺, Ag nanocrystals.

where R is the reflectance and $F(R)$ is proportional to the extinction coefficient. After multiplying the $F(R)$ function by $h\nu$ and using coefficient n , associated with electronic transition type (in this case $n = 2$, for an indirect allowed transition), Eq. (2) is obtain:

$$(F(R) \cdot h\nu)^n \quad (2)$$

By plotting this equation as a function of the energy in eV, the band gap energy (E_g) can be received (see Figure 8).

The calculations were done for ten samples of CeO_2 (with or without dopants, or surface modification) and, as an example, the plotting for the CeO_2 surface modified with Ag NPs is given in Figure 8. The results were the same for all investigated samples; the energy band gaps were equal to about 3.4 eV (Figure 8). The obtained result is within the range of band gap values reported for CeO_2 in the literature (3.0–3.6 eV) [73].

The emission spectra are characteristic of the Nd^{3+} ions. The excitation was at 266 nm, so the host lattice of CeO_2 transfers energy to the Nd^{3+} ions. The most intensive emission peak is observed at 901 nm, which corresponds to the energy of 11099 cm^{-1} and represents the ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition [74, 75, 76]. The emission from the transition ${}^4F_{3/2} \rightarrow {}^4F_{11/2}$ is also observed, as well as the weak emission from the ${}^4F_{5/2} + {}^2H_{11/2}$ multiplets (see Figure 9).

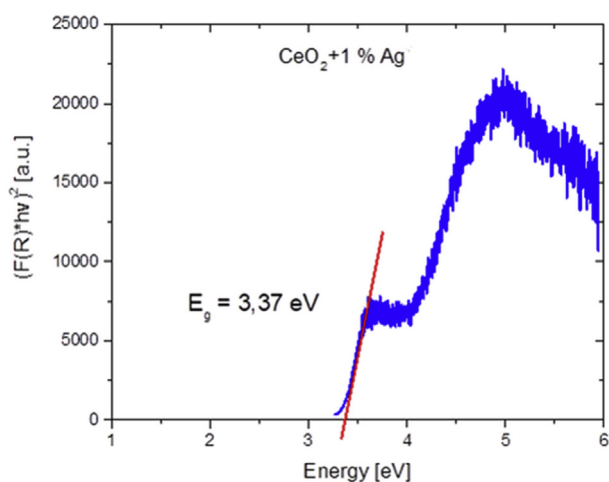


Figure 8. Graphical visualization of the Kubelka-Munk formula with estimation of the energy bandgap for the investigated cerium (IV) oxide.

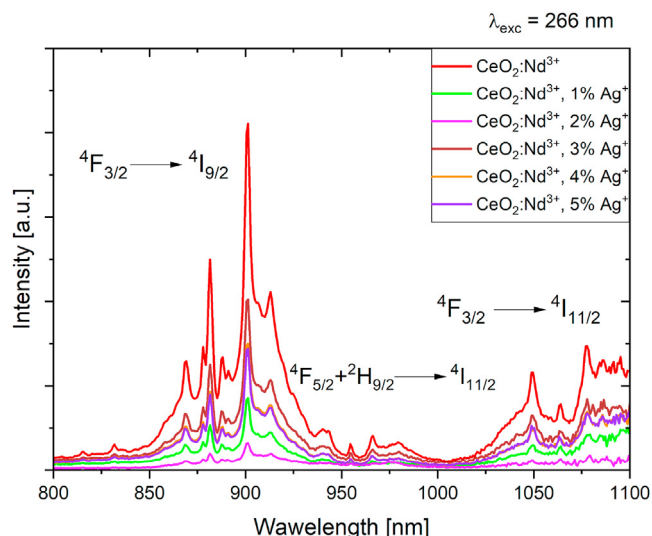


Figure 9. Near Infrared emission spectra of the $\text{CeO}_2: \text{Nd}^{3+}$, Ag nanocrystals.

The most intensive emission possesses the sample without Ag. This phenomenon may be due to the luminescence quenching mechanisms, which occur in this case when Nd^{3+} ions non-radiatively transfer their energy to the silver nanoparticles.

3.3. Morphological properties

The SEM pictures of all obtained powders are depicted in Figure 10. All powders show agglomerates, consisting of smaller grains (10–50 nm) - series of CeO_2 doped with La^{3+} ions, and of 50 nm to few micrometer-sized grains - series of CeO_2 with Ag NPs and Nd^{3+} ions.

The AFM results are presented as a set of images in Figure 11. It should be emphasized that the number of AFM measurements was performed for each sample to provide representative results. The grainy structure is clearly noticeable for all samples. The typical grain size varies in the range of 50–500 nm. Despite the fact that normally grainy materials tend to agglomerate, some specific grains ordering can be observed. In the 2A – $\text{CeO}_2 + 5\% \text{La}^{3+}$ sample, they are created as a high-density pack, locally showing complete fill, as the almost flat surface is created. In the 2B – $\text{CeO}_2 + 1\% \text{Ag}$ sample, the high aspect ratio structures (some microns in length and hundreds of nanometers in diameter) can be seen. For many samples, the amount of grains becomes bigger while their size decreases (tens of nanometers). In the sample 4B – $\text{CeO}_2 + 3\% \text{Ag}$, a large particle with flat surface covered with agglomerates of particles and single particles was found. It appears that they cover large grains of micrometer diameter, or create such large agglomerates. Except for 2B – $\text{CeO}_2 + 1\% \text{Ag}$ and 4B – $\text{CeO}_2 + 3\% \text{Ag}$ samples, no specific structure orientation was noticed. It is noted that the steep structures were not imaged properly, and, as it is typical for AFM scans, the side of the scanning tip influence was revealed (sample 3A – $\text{CeO}_2 + 10\% \text{La}^{3+}$). One can also notice that, while the metal content increases, the materials become more bulky, with smaller spaces and voids. The shape of grains is much better fit to each other in 3D space also in terms of shape. This feature is more visible in the case of silver than lanthanum addition. Simultaneously, the filling factor increase is related to the grain shapes. More square-like features instead of round ones makes the space filling more effective and easy. Those particular properties may have an impact on both mechanical and electrical properties, while it eliminates the content of weak bonds between the particles as well as poor electrical conductivity and capacitance-based charge transport. The developed metallic grains covering with optimal shapes determines also the optical properties, causing increased radiation absorption.

4. Conclusions

In this work, the nanocrystalline CeO_2 powders doped with La^{3+} ions were prepared using the modified sol-gel process. Also, the commercial CeO_2 particles surface-modified with 1–5% wt. Ag NPs and co-doped with Nd^{3+} ions were synthesized using the low-temperature chemical synthesis. The synthesized samples were phase-pure and they have the cubic CeO_2 -type crystal structure in space group Fm-3m. The average crystallite size estimated by the Rietveld method were in the range of 7–14 nm (La-doped CeO_2) and 29–34 nm ($\text{CeO}_2: 1\% \text{Nd}^{3+} / n\text{-Ag}$ (n : 1–5wt.%)) for the modified sol-gel and low-temperature chemical syntheses, respectively. The SEM and AFM studies revealed the grainy structure of all obtained powder samples. The grain size varied in the range of 50–500 nm. The diverse grain shapes and packing was observed in the samples. The main light absorption of pure and doped CeO_2 lies in the near-ultraviolet area, due to the strong charge transfer from O^{2-} to Ce^{4+} ions. The investigated samples may find future applications, e.g., for UV light detection and as materials with efficient transfer energy (in the UV region) to the doped rare earth ions.

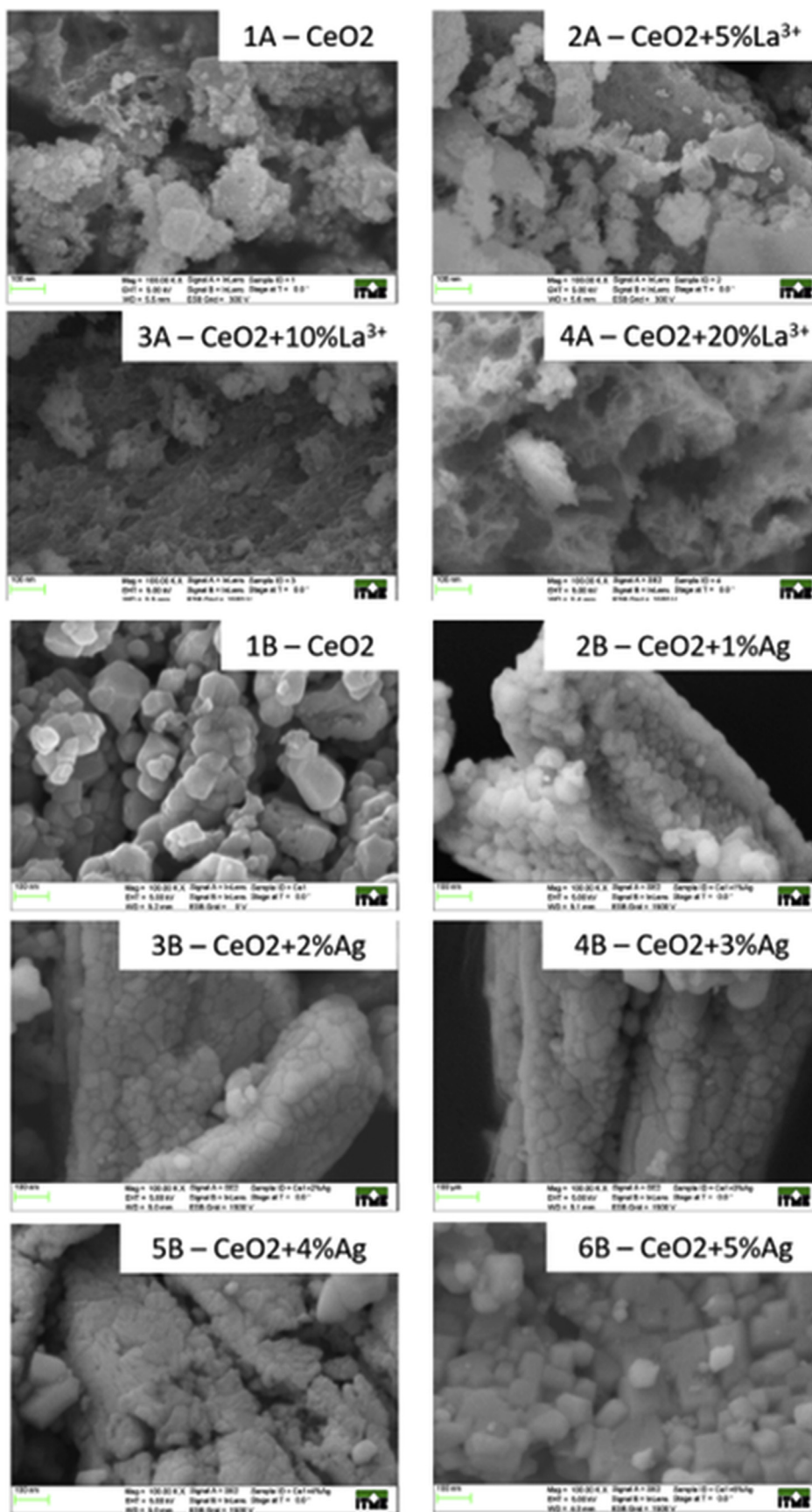


Figure 10. The SEM images of all obtained CeO₂ powders.

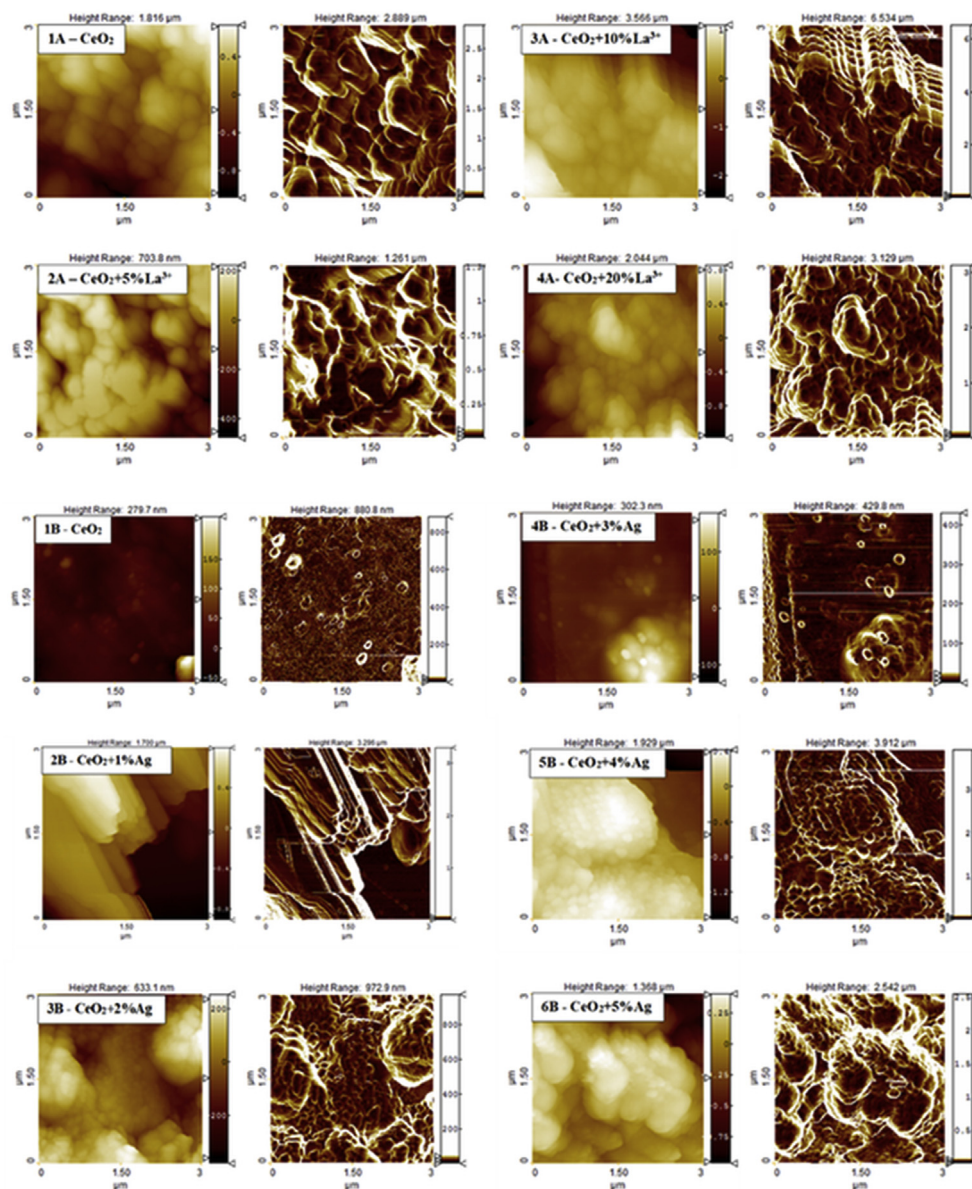


Figure 11. AFM images of all investigated samples. Left hand side – topography, right hand side – Sobel transform.

Declarations

Author contribution statement

Monika Michalska: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Karol Lemański, Andrzej Sikora: Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Data availability statement

Data will be made available on request.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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