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# EXPERIMENTAL ASPECTS FOR $CeO_2$ NANOPARTICLES SYNTHESIS AND CHARACTERIZATION

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## ABSTRACT

*In recent years, cerium oxide ($CeO_2$, or ceria) became a versatile nanostructured material because of its unique properties derived from the low dimensionality and high surface area. It was also extensively studied due to its practical performances in many scientific and industrial applications, such as fuel cells, luminescent materials, gas sensors, insulators, white LEDs, etc.*

*In this paper, the research focused on the synthesis and characterization of cerium oxide powder manufactured by the co-precipitation method, using inorganic cerium salt ($Ce(NO_3)_3$) and the precipitating agent (NaOH). In order to optimize the $CeO_2$ particles synthesis process, the parameters of the process were monitored to obtain the quantitative precipitate and to optimize the heat treatment. The precursors type and concentration used, reaction temperature and time, the pH of reaction medium and order of the precipitating agent addition are the main factors influencing the particle size and morphology of cerium oxide nanoparticles.*

*The physico-chemical properties of the cerium oxide nanoparticles were determined by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX). The FTIR spectrum of the $CeO_2$ particles calcinated at 550 °C, in normal atmosphere, exhibits a strong band at 482 $cm^{-1}$ corresponding to Ce-O stretching vibration. The XRD pattern confirmed the crystalline nature of the $CeO_2$ nanoparticles with a cubic structure and average crystallite size around 15 nm. Moreover, EDX analysis confirms the presence of the Ce and O atoms corresponding to the theoretical formula. The morphology and microstructure were studied using SEM analysis.*

KEYWORDS: cerium oxide, nanoparticles, synthesis, powders

## 1. Introduction

Cerium is a rare earth element, belonging to the lanthanide group, whose elements are arranged into an [Xe] $4f^15d^16s^2$ type electronic configuration, that can exist both free or in the oxide form [1-3]. Cerium oxide, also known as ceria or ceric oxide, is an excellent semiconductor material that has two valence states of $Ce^{3+}$ ($Ce_2O_3$) and $Ce^{4+}$ ($CeO_2$). It has the ability to switch very easily and reversibly between these oxidation states, with the possibility of rapidly forming, filling, and moving oxygen vacancies within the material [4–6].

From the two characteristic forms, $CeO_2$ is considered the most stable with a fluorite cubic structure, which contains eight coordinate cerium centers surrounded by a cube of eight oxide ions that are tetrahedrally coordinated into four cerium centers. Moreover, this material does not show any known crystallographic change from room temperature up to its melting point (2700 °C) [8, 9, 20].

According to the literature, cerium oxide has become an intensely studied material due to its

interesting features (size, morphology, specific surface area, dispersion state, oxygen storage capacity, oxygen deficiency and electronic conductivity) and its applicability in many areas of practical and modern technology, such as gas sensors, electrochemical devices, insulators, hybrid solar cells, protective products against sunlight exposure (for ultraviolet radiation absorption), ceramic biomaterials, polishing materials, white light emission, etc. [10–16].

Over the years, a considerable interest in enhancing the practical activity of cerium oxide is due to the excellent physical and chemical properties of $CeO_2$ nanoparticles, which are based on known and extensive synthesis methods. Thus, research has shown that many methods have been proposed to synthesize $CeO_2$ nanoparticles with promising control of properties, such as hydrothermal, mechanical processing, spray pyrolysis, sol-gel, solvothermal, thermal decomposition and precipitation methods [2, 8, 17, 18]. However, each of the applied methods is evidenced both by advantages and disadvantages for each particular process, the several disadvantages referring to the use of some toxic reagents and solvent, high reaction parameters and the necessity of requiring capping or / and stabilizing additives during the reaction [6, 19].

From the known chemical methods, co-precipitation synthesis is the most appropriate and simple method for obtaining oxide materials with a limited size distribution of particles and is widely applicable. It is considered a reliable method due to the advantages of a light synthesis condition. And because of certain concentration conditions and pH it can precipitate double salts, with complex stoichiometry. And also, by sintering the reactants with the monophasic amorphous structure, nanocrystalline powders with homogeneous chemical composition are obtained. In general, the physico-chemical characteristics of cerium oxide nanoparticles (size, morphology, type of intrinsic and / or extrinsic defect, crystal structure) largely depend on their synthesis procedures [7, 14, 19].

The objective of this paper was to synthesize cerium oxide nanoparticles by co-precipitation chemical method, which is a very simple method, accessible and with a small amount and cheap raw materials, in order to obtain pure $CeO_2$ powder for various practical applications.

The physico-chemical properties of cerium oxide nanoparticles were determined by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX).

## 2. Experimental details for the $CeO_2$ powder synthesis and characterization

In our experiments, cerium (III) nitrate ($Ce(NO_3)_3$), sodium hydroxide (NaOH), deionized water ($H_2O$ DI), ethanol ($C_2H_5OH$) were used for the synthesis of cerium oxide nanoparticles. All chemicals were of reagent grade and used without further purification. In a typical synthesis, the cerium nitrate solution with 0.1M concentration was prepared and continuously stirred with a magnetic stirrer at 80 °C for 2 h. Then, the NaOH solution with a concentration of 1M was added dropwisely to the precursor solution and stirring was maintained for 3 hours at the same temperature, until a yellow precipitate was formed. The formed precipitate was left in repose for several minutes, after that it was filtered and washed alternatively with deionized water and ethanol for purification and removal of the secondary compounds.

After this step, the precipitate was further pre-sintered at 80 °C for 3 hours, these conditions being necessary for the complete conversion to $CeO_2$.

The sintering of the dried sample was carried out in a calcination furnace at a rate of 5 °C/min up to a temperature of 550 °C for 3 hours, in order to obtain a slightly light yellowish powder of $CeO_2$.

The structural characteristics for the sample in powder form were determined by Fourier Transform Infrared spectrometry (FTIR), in which IR spectra were recorded using a Bruker Tensor 27 spectrometer, in the wavenumber range of 4000-400 $cm^{-1}$ by averaging 64 scans with a resolution of 4 $cm^{-1}$ using the KBr pellet method.

The average crystallite size, crystalline phase and lattice parameters of the sample in powder form were analyzed by the X-ray diffraction (XRD) method using a 9 kW rotating anode SmartLab diffraction system (Rigaku Corporation, Japan) equipped with a $CuK\alpha_1$ tube and a multilayer mirror ($\lambda$ = 1.5406 A). The experimental profile was recorded in grazing incidence XRD (GIXRD) with the incidence angle equal to 0.25°, while the detector was performed in the 2θ range from 20° to 90°.

The elemental analysis of the sample was carried out using energy-dispersive X-ray spectroscopy (EDAX, Smart Insight AMETEK). In addition, energy dispersive X-Ray (EDX) spectroscopy is attached to the scanning electron microscopy technique.

The morphology and microstructure were studied using a Field Emission Scanning Electron Microscope (FE-SEM). The SEM image was taken using an FEI Nova NanoSEM 630, with ultra-high resolution at high and low voltage in high vacuum of

1.6 nm @ 1 kV. For increasing the SEM images quality, the sample in powder form was dispersed in ethanol, dripped onto the silicon wafer surface and then, a gold layer was vaporized onto the sample surface.

## 3. Results and discussions

### *3.1. FTIR analysis*

The FTIR spectrum of synthesized $CeO_2$ nanoparticles pre-sintered at 80 °C and calcined at 550 °C, in normal atmosphere, is presented in Figure 1.

The feature in FTIR spectrum of pre-sintered precipitate presents bands in the range of 4000 -1300 $cm^{-1}$ which can be attributed to nitrate species vibration from raw materials and hydroxyl from water absorption. After calcinations, the peaks from this region were significantly changed with the increase of the heat-treatment temperature. The spectrum of $CeO_2$ nanoparticles calcined at 550 °C, clearly showed three peaks centered at 3446, 1638 and below 700 $cm^{-1}$. The bands at 3446 $cm^{-1}$ and 1638 $cm^{-1}$ can be attributed to the stretching mode of O-H bonds from absorption during the processing step of FTIR analysis [8, 18].

The strong band centered at 491 $cm^{-1}$ can be assigned to the presence of C-O stretching vibration mode from $CeO_2$ molecules.

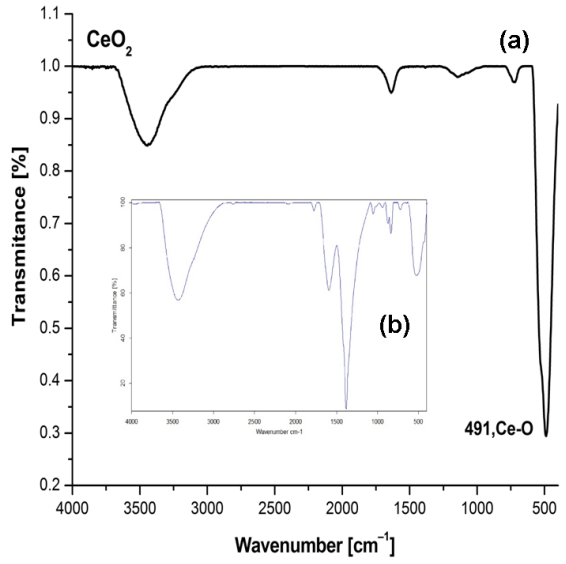


***Fig. 1.*** *FTIR spectrum of the $CeO_2$ powder: a) pre-sintered at 80 °C, b) sintered at 550 °C*

### *3.2. XRD analysis*

The XRD pattern of the $CeO_2$ nanoparticles was carried out by X-ray diffraction in the range of 2θ between 20° to 90° as shown in Figure 2.

XRD was also used to check the purity and crystallinity of $CeO_2$ nanoparticles, and to estimate the average crystalline size.

The sample exhibits typical peaks corresponding to the $CeO_2$ crystalline planes with Miller indices of (111), (200), (220), (311), (222), (400), (331), (420), (422) for a series of characteristic peaks located at 2θ = 28.3°, 33.1°, 47.4°, 56.3°, 59.0°, 69.3°, 76.6°, 79.0°, 88.3°, respectively [9, 14]. All the diffraction peaks of the sample were indexed to the cerianite (Ce) symmetric structure with cubic structure (lattice parameters are a = b = c = 5.4154 Å), belonging to Fm-3m space group no. 225 [DB no. 00-900-9008]. No peak of other crystalline impurities (i.e: $Ce_2O_3$) was detected, thus indicating the high purity and good crystallinity of the cerium oxide sample.

Using the full width at half maximum (FWHMs) of the diffraction peaks, the average size of the crystallites was estimated through Debye Scherrer's formula:

$$D = K\lambda/(\beta \cos \theta)$$

where: $D$ is the crystallite size; $K$ is the shape coefficient (0.94), $\lambda$ is the radiation wavelength (1.54 A), $\beta$ is the line broadening at half the maximum intensity (FWHM) in radians, and $\theta$ is the Bragg diffraction angle obtained from $2\theta$ value corresponding to the maximum intensity peak (in radians).

Based on this formula, the average crystallite size of the $CeO_2$ powder sample was found to be around 11.5 nm.

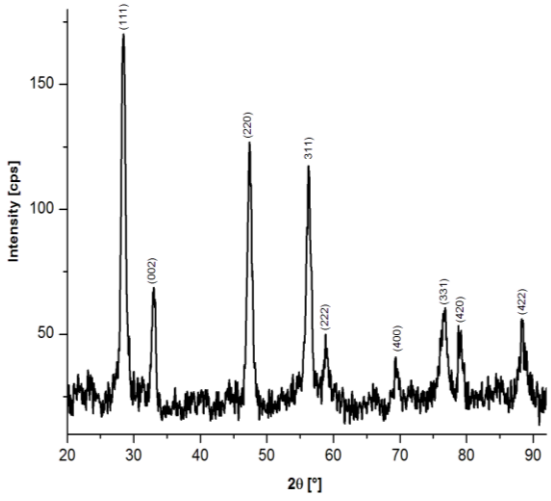


***Fig. 2.*** *XRD pattern of the $CeO_2$ powder*

### 3.3. EDX analysis

In order to achieve a qualitative study, EDX analysis was performed as presented in Figure 3.

EDX provided information on the elemental analysis or chemical characterization of the powder sample, which further confirmed that the synthesized $CeO_2$ was pure and consisted in Ce and O. In the energy-dispersive X-ray spectrum (Figure 3), we can see peaks that correspond to the atoms of oxygen (O(K) at 0.53 keV) and cerium (Ce(L) at 4.84 keV and Ce(M) at 0.88 keV).

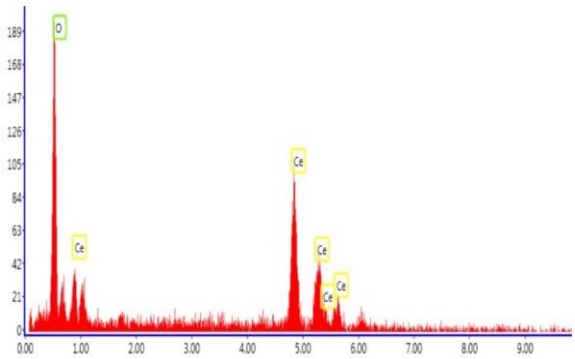


***Fig. 3.*** *EDX spectrum of the $CeO_2$ powder*

This analysis also reveals the weight and atomic percentage of each component present in the synthesized sample as shown in Table 1. The quantitative analysis was based on the use of atomic percentages for calculating the molecular formula of the cerium oxide sample. The final composition was calculated and corresponds to the theoretical $Ce_{1.017}O_{1.983}$ formula, suggesting a good crystallinity of the material, being very close to that of the desired material [10].

***Table 1.*** *Weight and atomic percentage of the elements present in the $CeO_2$ powder from EDX data*

| Element | Wt% | At% |
|---|---|---|
| OK | 18.2 | 66.08 |
| CeL | 81.8 | 33.92 |

### 3.4. Surface morphology

The surface morphology and size details of the $CeO_2$ nanoparticles were studied through the SEM image in Figure 4.

The SEM image displays the existence of crystalline particles with the sizes in the range of 15 to 30 nm. Spherical shapes of $CeO_2$ nanoparticles and a slightly tendency for agglomeration were confirmed. A homogeneous distribution of spherically synthesized $CeO_2$ nanoparticles was observed. This result is consistent with the crystallite size calculation by Scherrer formula from the XRD analysis.

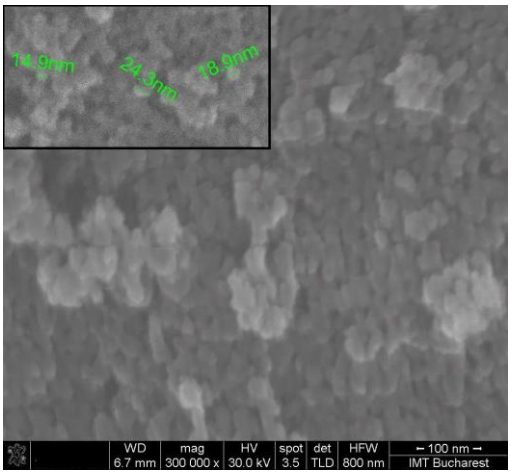


***Fig. 4.*** *SEM micrograph of the $CeO_2$ powder*

## 4. Conclusion

$CeO_2$ nanoparticles were synthesized by the chemical precipitation method and the parameters and optimal synthetic conditions were established.

The influence of process conditions on the structural and morphological properties of synthesized particles has been investigated.

The FTIR spectrum indicated a strong band at 491 $cm^{-1}$ due to the presence of Ce-O stretching vibration mode of $CeO_2$.

The results obtained from XRD and SEM confirm the crystalline nature of the synthesized sample and the nanoscale size of the crystallite (particle).

XRD pattern shows the formation of the fluorite type structure, with cubic symmetry characteristic for ceria, without other crystalline impurities. The average crystallite size of $CeO_2$ powder was calculated around 11.5 nm.

EDX spectrum indicates that the particle is composed only of Ce and O and it confirms the theoretical formula and the purity of the sample.

SEM image displays the existence of crystalline particles with the sizes in the range of 15 to 30 nm, but also spherical shapes of the particles with clumped distribution.

The co-precipitation method was preferred in cerium oxide nanoparticle synthesis because by optimizing the reaction conditions and calcination temperature, lower crystallite (particle) size was obtained. Moreover, the desired properties of $CeO_2$ nanoparticles make it a promising material in order to develop applications in the environmental field. The

particles thus obtained have demonstrated their usefulness and were subsequently used for the synthesis of ion-doped garnet phosphorus and cerium-doped aluminum phosphate, for optoelectronics ("*Influence of Sintering Temperature on the Structure of the Yttrium Based Phosphor Nanoparticles*" – the paper presented to SCDS-UDJG 2017 and awarded the First price), as well as for the development of applications within the TEHNOSPEC project –No. PN1632/2016.

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