

Scientific paper

Combustion Synthesis and Characterization of CeO₂ Nanopowder

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Abstract

Modified combustion procedure, named as polymer complex solution method (PCS), was used for synthesis of CeO₂ nanopowder. As fuel was employed polyethylene glycol (PEG) with average molecular weight 200. Post-synthesis thermal treatments were done at 800 °C for 2 hours. X-ray powder diffraction, electron microscopy (SEM and TEM), laser light scattering, infrared spectroscopy, UV-VIS diffuse reflectance spectroscopy and luminescence spectroscopy were used as characterization methods. The objectives were to investigate the structure and morphology of the synthesized powder, in particular the aggregation and particle size distribution, and its luminescence properties. Photoluminescent properties of CeO₂ nanopowder were determined from its emission and excitation spectra. In the excitation spectra two lines were present: one at 322 nm and other at 356 nm. Two lines were also visible in the emission spectra, one at 427 nm and other at 492 nm. Violet emission placed at 427 nm and excitation at 356 nm corresponded to ⁵D₁ → ⁴F₁ transition of cerium trivalent ion. A UV-VIS diffuse reflectance spectrum shows the absorption edge at 375 nm. The observed spectral blue shift revealed the presence of fine crystallites which escape XRD detection. The presented results demonstrate that this simple preparation technique provides well crystallized nanoparticles of CeO₂.

Keywords: Combustion synthesis, ceria, optical spectroscopy, nanopowder, luminescence.

1. Introduction

Cerium (IV) oxide (CeO₂, ceria) with a cubic fluorite-type structure¹ is thermally stable cerium source suitable for numerous commercial applications in metallurgy, glass and glass polishing, ceramics, catalysts, and phosphors.^{2,3} Cerium oxide is transparent to visible light but also has excellent ultraviolet radiation absorption properties, due to appropriate refractive index (2.1) and band-gap energy of 3.1 eV.² These characteristics make it ideal for use in broad-spectrum inorganic sunscreens for cosmetics, while Ce-doped glass, able to block out UV light, is utilized in the manufacturing of medical glassware and aerospace windows.² CeO₂ is considered to be the most efficient glass polishing agent for precision optical polishing.² It is also used in a variety of ceramics, including dental compositions⁴ and as a phase stabilizer in zirconia-based products.⁵

Common preparation methods for ceria powders are hydrothermal synthesis,⁶ precipitation,⁷ emulsion method,⁸ spray-pyrolysis,⁹ electrochemical¹⁰ and solid-state synthesis.¹¹ In recent years combustion synthesis (CS) has emerged as an important technique for the synthesis and processing of advanced ceramics, catalysts, composites, alloys, intermetallics and nanomaterials. In a typical reaction, the precursor mixture of water, metal nitrates, and fuel decomposes, dehydrates, and ruptures into a flame.¹² For the reaction, an organic fuel is utilized, typically urea (CH₄N₂O), carbonylhydrazide (CH₆N₄O), or glycine (C₂H₅NO₂). Recently, polyethylene glycol (PEG) has been successfully introduced as fuel to facilitate combustion reaction and moreover, to provide formation of homogenous spherical particles.¹³ PEG influences nucleation process of crystal by forming the nuclei, strongly absorbed and surrounded by PEG chains, in super-saturated solution. In this way particles with nearly spherical shape

are formed, due to equal strain forces from PEG chains, which play in all directions around the nuclei. In addition, the adsorption of PEG polymer on the particle surfaces can prevent particle-particle aggregation due to the steric hindrance effect.^{14,15} Saving energy is also an advantage of CS. All it takes to ignite a CS reaction is a brief heat pulse – once heat is applied to start the reaction, it runs on its own. These features and use of relatively simple equipment make CS an attractive method for the manufacture of technologically useful materials at lower cost compared to conventional processes.

In this research we have attempted a combustion method with PEG as synthesis route for CeO₂ nanopowder. Herein we document its basic properties as obtained from XRD, FTIR, SEM, TEM, DLS and luminescence spectroscopy experiments.

2. Experimental

Appropriate quantity of cerium-nitrate hexahydrate (Ce(NO₃)₃·6H₂O) was dissolved in deionised water. In obtained solution we added PEG, with average molecular weight 200, in 1:1 mass ratio to expected CeO₂ product. Formed metal-PEG solution is stirred at 80 °C, resulting in metal-PEG solid complex which is further fired at 800 °C in air. In order to decompose the residual PEG and nitrate ions obtained powder is annealed at 800 °C for 2h.

X-ray diffraction data were collected on a Philips PW 1050 diffractometer with Cu-Kα_{1,2} radiation (Ni filter) at the room temperature. Measurements were done in 2θ range of 10°–150° with scanning step width of 0.02° and 12 seconds per step. Crystal structure refinement has been done with Rietveld full profile method¹⁶ using the Koalariet computing program based on a fundamental parameters convolution approach to generate line profiles.¹⁷ This program is appropriate for processing the data obtained from the samples with dominant microstructure parameters.

FT-IR spectra are recorded in the wavenumber range of 4000–400 cm⁻¹ on a Nicolet spectrophotometer (Model 380, Thermo Nicolet Corporation, Madison, USA), with 4 cm⁻¹ resolution.

The morphology of the powder agglomerates were examined with electron microscopy. Scanning electron microscopy (SEM) observations were performed with a Cambridge 250MKIII. TEM images were taken on a Phillips CM100 microscope. SEM and TEM specimens were prepared with standard powder preparation technique.

Dynamic laser light scattering is measured on the “Light Scattering System BI-200SM, Brookhaven Instruments” device equipped with the BI-200SM goniometer, the BI-9000AT correlator, temperature controller, and the Coherent INOVA 70C argon-ion laser. DLS measurements are performed using 135 mW intense laser excita-

tion at 514.5 nm and at detection angle of 90°. Particle size distribution is calculated using the Brookhaven Instruments Particle sizing software.

Photoluminescent properties of studied material were determined by measuring its emission and excitation spectra using Perkin-Elmer Luminescent Spectrophotometer LS45. A Xenon discharge lamp was used for illumination while a gated red-sensitive R928 photomultiplier was used for detection. The system provided ±1.0 nm wavelength accuracy and ±0.5 nm wavelength reproducibility. Diffusion reflectance spectroscopy in ultraviolet and visible spectrum regions are obtained with Perkin-Elmer Lambda 35 Spectrometer equipped with an integrating sphere based diffuse reflectance accessory.

3. Results and Discussion

X-ray powder diffraction patterns were used for the structural analysis of the synthesized samples. The refinement results show that CeO₂ powder is well crystallized as single-phase ceria. The structure of CeO₂ has been refined in the 225th space group Fm3m (O_h⁵) in well-known fluorite-type structure (see Fig. 1a) with cations in special crystallographic position 4a [0, 0, 0] with local symmetry m3m and O²⁻ ions in special crystallographic positions 8c [1/4, 1/4, 1/4] with local symmetry $\bar{4}5m$. Since all fractional coordinates of CeO₂ were fixed only unit cell parameter, displacement, background and profile parameters were refined. The starting parameters in the least-square refinement were taken from the reference.¹⁸

The observed and calculated X-ray diffraction profiles are given in Fig. 1b, while main results of the final Rietveld refinements are presented in Table 1. In this fluorite-type structure a small number of structural parameters are variable, so the aim of the refinement was to determine microstructural parameters (crystal size and microstrains). In that purpose we utilized the Koalariet computing program, based on a fundamental parameters convolution approach to generate line profiles. In order to obtain least

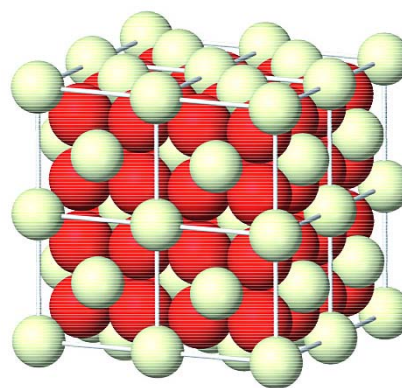


Figure 1a: Schematics of fluorite-type structure.

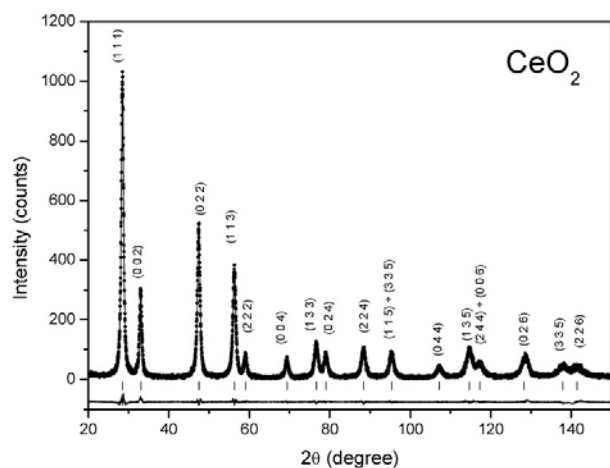


Figure 1b: The observed (crosses), calculated (solid line) and difference XRD patterns for CeO_2 nanopowder.

correlation between crystal size and microstrain peak broadening, a wide 2θ range was used (10° – 150°). Table 1 shows that obtained values for Ce^{4+} and O^{2-} isotropic temperature factors were as expected. Small value of microstrain parameter also implies structural perfection of synthesized sample. The value of crystallite size is found to be 15.2 nm (Table 1).

FT-IR spectra of (a) pure PEG, (b) Ce-PEG solid complex, (c) powder after firing and (d) after thermal

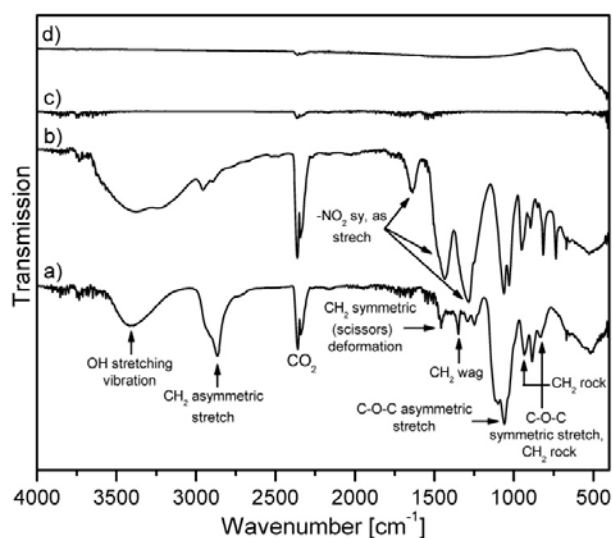


Figure 2: FT-IR spectra of (a) pure PEG, (b) Ce-PEG solid complex, (c) powder after firing and (d) after thermal treatment at 800°C (2h).

Table 1: The results of the Rietveld refinement procedure.

Lattice parameter [Å]	Cell volume [Å ³]	Mean crystallite size [nm]	Microstrain [%]	B (Ce^{4+}) [Å ²]	B (O^{2-}) [Å ²]	RB factor [%]
$a = 5.4126$ (1)	$V = 632.43$	15.2 (5)	0.025 (2)	0.35 (2)	0.65 (5)	8.7

treatment at 800°C (2h) are shown in Fig. 2. The spectrum of Ce-PEG solid complex (Fig. 2, spectrum b) shows that vibrational line of ether group placed around 1100 cm^{-1} ,¹⁹ typical for PEG, shifts to the direction of lower wavenumber. This could be due to the coordination of the oxygen from C–O with Ce, probably on the surface of ceria nanocrystals.²⁰ Three broad lines placed in the region around 1300 – 1650 cm^{-1} , can be attributed to the stretching, symmetric and asymmetric vibrations of nitrate complexes.¹⁹ Peak at around 2900 cm^{-1} , due to asymmetric stretching vibrations of the $-\text{CH}_2$ group²¹ can be observed in both spectra of pure PEG and Ce-PEG solid complex (Fig. 2, spectra a and b). In both spectra a wide peak at about 3400 cm^{-1} of the $-\text{OH}$ vibration bend of PEG and H_2O is present.¹⁹ FTIR spectra of powders obtained after firing (Fig. 2, spectrum c) and additional thermal treatment at 800°C (Fig. 2, spectrum d) shows that all lines attributed to the impurities of nitrate ions, water and carbon disappear. More details on FTIR of CeO_2 can be found elsewhere.^{22–24} These results indicate that PEG is very good organic fuel for our method of synthesis as there is

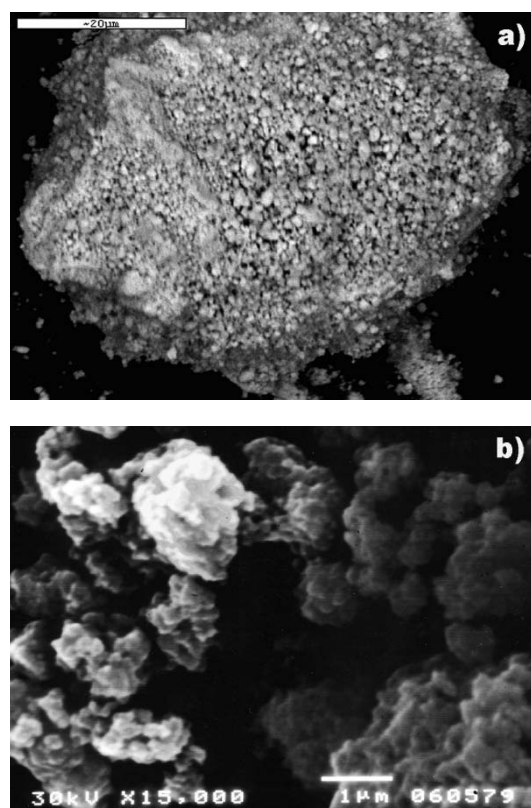


Figure 3: Typical SEM images of CeO_2 sample after annealing at 800°C for 2h, taken at a) low magnification (2000 \times , scale bar 20 μm); b) high magnification (15000 \times , scale bar 1 μm).

no traces of PEG even very short ignition time has been applied (only 10 minutes).

SEM observations of ceria sample show agglomerates ranging from few microns to a few tens of microns with highly porous morphology, which is common feature for the materials produced with combustion synthesis (see Fig. 3, image a). Observations at higher magnification show the presence of highly agglomerated sub-micron particles with irregularly spherical or elliptical morphology (Fig. 3, image b). Further observations at TEM suggest fractal organization of the material: particles observed with SEM are made up of smaller particles with estimated size ranges from 3 to 10 nm (Fig. 4).

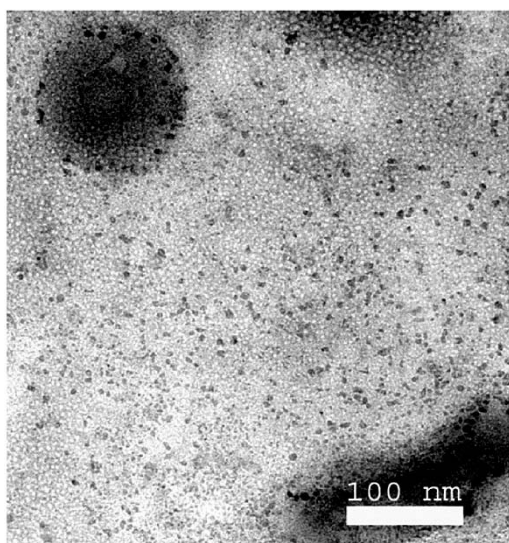


Figure 4: TEM image taken from one region containing CeO₂ nanoparticles.

Size distribution of CeO₂ particles was evaluated using dynamic light scattering (DLS) and resulting histogram is presented in Fig. 5. Sample was prepared by

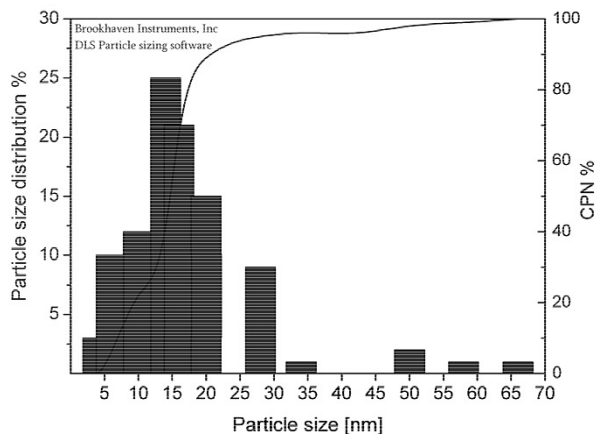


Figure 5: Size distribution of synthesized CeO₂ particles obtained using dynamic light scattering method.

dispersing powder in deionised water (0.1 mM). The pH of the dispersion was adjusted by addition of 1M HCl and set to 6. Sample was magnetically stirred for 24 h and then exposed to ultrasound for 60 min. Obtained suspension is left to stand 24 h prior to any measurements. CeO₂ particles exhibited size distribution ranging from 4 nm to 20 nm, with majority of particles around 14 nm. Agglomerates of bigger size are detected in a region from 50–70 nm.

Room temperature luminescence excitation and emission spectra of CeO₂ nanopowder are presented in Fig. 6. The broad violet emission centered near 427 nm and excitation peak at 356 nm correspond to the 5d¹ → 4f¹ transition for Ce³⁺ ions. This electric-dipole transition between the 4f ground state and the 5d excited state of Ce³⁺ is parity allowed and has large oscillator strength.

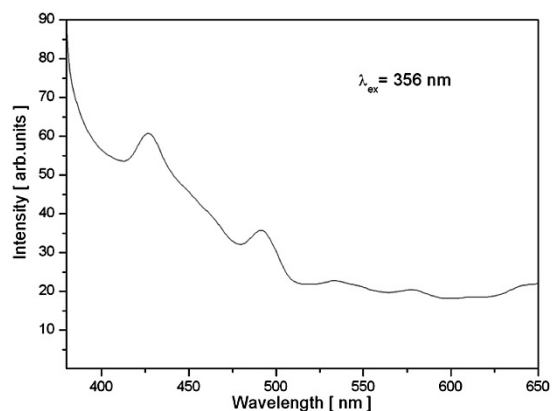
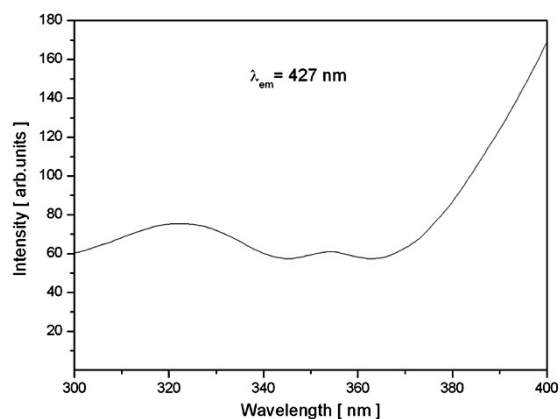


Figure 6: Emission and excitation spectra of CeO₂ nanopowder.

The violet emission can be rarely observed due to self-absorption and charge transfer between Ce ions.²⁵ However, when particles are very small, the efficiencies of these processes are greatly reduced and this emission phenomenon may be detected.

A UV-VIS diffuse reflectance spectrum of CeO₂ is shown in Fig. 7. The absorption edge is found at 375 nm.

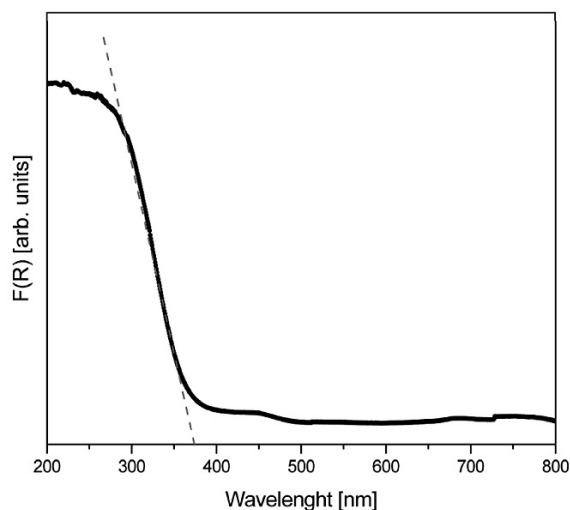


Figure 7: Diffuse reflectance spectra of CeO₂ nanopowder.

The wavelength corresponding to the absorption edge of a semi-conductive powder such as ceria can be successfully used to find the presence of nanocrystallites, which escape XRD detection.²⁶ An UV absorption edge at about 400 nm (3.1 eV) occurs for bulk CeO₂ caused by Ce⁴⁺ ← O²⁻ charge transfer.^{27,28} Several studies have shown^{28–30} that decreasing the size of semi-conducting micro-crystallites entails a blue shift of the absorbance edge of the interband transition. According to Bensalem et al.²⁷ an absorbance occurring at ≤ 375 nm may imply the presence of finer crystallites which escape XRD detection. In addition, significant absorbance below 250 nm indicates Ce³⁺ ← O²⁻ charge transfer and presence of lattice defects creating Ce³⁺. This is the reason for observed Ce³⁺ luminescence presented in Fig. 6.

4. Conclusions

Presented investigation gives a preliminary picture of CeO₂ nanocrystalline sample obtained by polymer complex solution method. The combination of XRD, SEM and TEM data drives to the conclusion that CeO₂ sample have polycrystalline porous structure made up of well crystallized particles in 4 to 20 nm range. From UV-VIS diffuse reflectance spectrum of CeO₂ the absorption edge at 375 nm is found. This spectral blue shift from 400 nm (bulk CeO₂) indicates electronic confinement which is characteristic of nano-scaled semiconductors. The CeO₂ nanopowder exhibits violet emission from 5d¹ → 4f¹ electronic transitions in Ce³⁺ ions that are created by lattice defects.

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5. References

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Povzetek

Sintezo nano delcev CeO₂ smo izvedli z modificirano metodo zgorevalne sinteze, znano kot metoda raztopine kompleksnih polimerov. Pri tem smo kot gorivo uporabili polietilenglikol s povprečno molekulkso maso 200. Po sintezi smo vzorce žarili dve uri pri 800 °C. Za njihovo karakterizacijo smo uporabili metode rentgenske difrakcije, elektronske mikroskopije (SEM in TEM), sipanja laserske svetlobe, spektroskopije IR, UV-VIS difuzne refleksijske spektroskopije in luminiscenčne spektroskopije. Namen karakterizacije je bil ugotoviti strukturo in morfologijo sintetiziranih prahov ter predvsem agregacijo in razporeditev velikosti delcev in njihove luminiscenčne lastnosti. Fotoluminiscenčne lastnosti nano delcev CeO₂ smo določevali za emisijske in vzbujevalne spektre in pri slednjih ugotovili dve značilni spektralni črti pri 322 nm in 356 nm. V emisijskem spektru pa smo zaznali spektralni črti pri 427 nm in 492 nm. Emisija violečne svetlobe (427 nm) pri vzbujanju s 356 nm ustreza ⁵D₁ → ⁴F₁ prehodom v trivalentnem cerijevem ionu. UV-VIS difuzni refleksijski spektri so pokazali absorpcijski rob pri 375 nm. Opaženi spektralni modri premik je potrdil prisotnost drobnih kristaliziranih delcev, ki jih z rentgensko difrakcijo nismo zaznali. Predstavljeni rezultati potrjujejo, da opisana metoda daje ustrezno kristalizirane nano delce CeO₂.