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# Cerium Oxide Based Nanometric Powders: Synthesis and Characterization

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*Abstract:*

*Nanometric powders of solid solutions of cerium oxide were obtained by a modified glycine nitrate procedure. Solid solutions of the host compound $CeO_2$ with one or more dopants in the lattice were synthesized. Rare earth cations (Re = Yb, Gd and Sm) were added to ceria in total concentration of x = 0.2 that was kept constant. The criterion in doping was to keep the value of lattice parameter of ceria unchanged. The lattice parameters were calculated by using the model that takes into account the existence of oxygen vacancies in the structure.*

***Keywords:*** *Ceria, Fluorite structure, Modified glycine-nitrate procedure.*

## 1. Introduction

Solid ionic conductors with the fluorite structure have been extensively studied due to their applications as oxygen sensors, oxygen pumps, and as solid electrolytes in solid oxide fuel cell (SOFC) systems. Rare earth-doped ceria solid electrolytes are of great interest especially for the application in intermediate temperature SOFC [1,2]. Several properties of these solid solutions, such as ionic conductivity and phase stability, are dependent among others also on physical and chemical characteristics of the synthesized materials.

In oxygen-ion conductors, doping with lower valency cations creates a definite concentration of anion vacancies for charge compensation whereby, generally, the ionic conductivity increases. In addition, the unit cell undergoes contraction or expansion depending upon the size of the dopant cation. This variation of the unit cell size with the dopant size obeys Vegard's law if solid solution is formed.

The addition of dopants into ceria lattice is desirable, since it is known that electrical conductivity increases with doping. The electrical conductivity of SOFC electrolyte is affected by ionic radii of dopants [3]. The conductivity is higher if the mismatch in ionic sizes of host and dopant cations is as low as possible [4].

In this paper the synthesis of ceria based nanopowders co-doped with three dopant cations was performed. The intention was to synthesize co-doped powder, keeping the lattice parameter unchanged in respect to pure ceria as much as possible. For that reason we

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introduced small (Yb), as well as large cations (Sm, Gd), into the $CeO_2$ lattice simultaneously. Single doped ceria solid solutions were prepared, as well, for comparison.


## 2. Experimental

Nanometric powders of solid solutions of cerium oxide were obtained by modified glycine/nitrate procedure (MGNP) [5]. Rare earth cations (Re = Yb, Gd, and Sm) were used as dopants with total concentration of x = 0.2. Starting chemicals used for the synthesis of nanopowders were amino acetic acid-glycine (Fluka), cerium acetate and metal nitrates (Ce, Yb, Gd and Sm) produced by Aldrich. Glycine and acetates were used in as received form, whereas nitrates were used in the form of water solutions. The concentrations of nitrates solutions used for experimental work are shown in Tab. I.


**Tab. I.** Concentrations of nitrate solutions

| No | Sample | Concentration [mg/ml] |
|----|--------|------------------------|
| 1 | $Ce(NO_3)_3 \cdot xH_2O$ | $83.5 \pm 0.8$; $105 \pm 1$ |
| 2 | $Yb(NO_3)_3 \cdot xH_2O$ | $68.0 \pm 0.7$ |
| 3 | $Gd(NO_3)_3 \cdot xH_2O$ | $80.2 \pm 0.8$; $14.4 \pm 0.2$ |
| 4 | $Sm(NO_3)_3 \cdot xH_2O$ | $106 \pm 1$; $13.4 \pm 0.1$ |


Concentrations of nitrate solutions were determined by the ICP-OES method. The following wavelengths were appropriate; Ce-448,691 nm; Sm-356,827 nm; Gd-335,862 nm; Yb-328,937 nm. The amounts of chemicals were weighed according to previously calculated composition of the solid solution. To determine the amount of nitrates, the data from Table. I were used.

The glycine nitrate method [5,6] is based on the exothermicity of the redox reaction between the fuel–glycine and oxidizer-nitrate. The procedure needs to be performed in three stages, which are as follows: dissolution of metal nitrates and glycine in water, autoignition of solution at about 180°C, that afterwards undergoes the selfsustaining combustion giving ash as a product, and finally calcination of ash to burn out organic components producing a clean homogeneous oxide powder of the required stoichiometry. The results showed that ceria based nanopowders with a very precise stoichiometry can be produced in a very energy- and time- effective way.

Synthesis was carried out in a glass beaker in which all reactants dissolved in distilled water were added according to the previously calculated composition of the final powder.

The glycine /nitrate procedure based on self-combustion of the glycine and nitrate mixture can be described via following reaction:

$$4NH_2CH_2COOH + 2 \cdot 0.8Ce(NO_3)_3 \cdot 6H_2O + 2 \cdot 0.2Re(NO_3)_3 \cdot 6H_2O + 2O_2 \rightarrow 2Ce_{0.8}Re_{0.2}O_2 + 22\ H_2O + 5N_2\uparrow + 8CO_2\uparrow,$$

which spontaneously occurs at about 180°C. The obtained powders were thereafter calcined for 4 hours at 600°C to burn up the organic remainders.

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Synthesized powders were characterized by XRD (Philips X'Pert MPD), TEM and EELS analyses (ZEISS EM 912 Omega). Also the specific surface area was measured by Brunauer-Emmet-Teller (BET) method on Micromeritics FlowSorb II 2300.

## 3. Results and Discussion

The addition of dopants into ceria lattice is desirable, and even many of them, as we found out, may be simultaneously incorporated into the host lattice [5] by applying the used method. The electrical conductivity of SOFC electrolyte is affected by ionic radii of dopants [3]. The conductivity is higher if the mismatch in ionic sizes of host and dopant cations is as low as possible [4]. On the other hand, it was shown that the activation energy for co-doped samples was lower, whereas the electrical conductivity was by 30% higher, as compared to best single doped samples with the same vacancy concentration [3,4].That is why we made the attempt to synthesize ceria solid solution with three dopants while keeping lattice parameter close as much as possible to pure ceria.

Recently proposed equation [7] for determining lattice parameters of substances with fluorite structure, based on the ion-packing model is:

$$a = 4/\sqrt{3} \; [ \; xr_M + (1-x) \, r_{Ce} + (1- 0.25)r_O + 0.25xr_{V\ddot{o}} \; ] \bullet 0.9971 \qquad (1)$$

where *a* is the lattice parameter, $r_M$, $r_{Ce}$, $r_O$ and $r_{V\ddot{o}}$ are the radii of the dopant cation, radius of cerium ion (0.97 Å), oxygen ion (1.38 Å) and oxygen vacancy radius (1.164 Å), respectively; *x* is the dopant molar fraction. The correction factor, 0.9971, accounts for the observed difference in the experimental value and the value calculated from the ionic radii for the lattice parameter of pure ceria. Lattice parameter of pure ceria is 5.411 Å. Ionic radii [8] of $Yb^{3+}$, $Gd^{3+}$ and $Sm^{3+}$ are, 0.985 Å, 1.053 Å and 1.079 Å, respectively. This model was applied for the calculation of the fraction of the constituting ions that will give the composition with lattice parameter close to pure ceria. This was done prior to experimental work. Experimentally obtained powders according to the previously calculated composition were characterized by XRD, TEM, EELS and specific surface area measurements.

XRD patterns of all calcined powders show (Fig.1) that we obtained single phase solid solutions of doped ceria and co-doped ceria. It was identified that all synthesized doped ceria powders exhibited a cubic fluorite structure, the same as pure ceria.
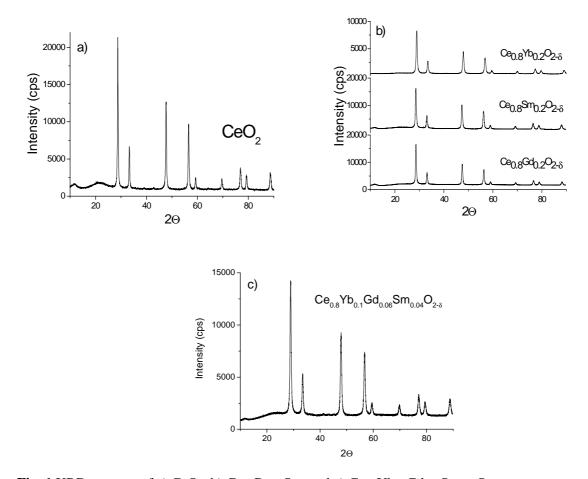
From XRD data crystallite size, microstrain, as well as lattice parameters were determined. The average crystallite size and mean lattice distortion of $CeO_2$ were obtained on the basis of the full width at half maximum intensity (FWHM) of the (111), (200), (220) and (311) peaks of $CeO_2$, measured after the separation of the Kα-doublet by Diffrac$^{plus}$ software. Calculation of the crystallite size and lattice distortion was performed applying Williamson-Hall method and Cauchy expression [9]:

$$\beta \cdot cos\theta = K \cdot \lambda / D + 4 \cdot \varepsilon \cdot sin\theta$$

in which the total peak broadening (*β*) is the sum of peak broadening due to crystallite size (*D*) and broadening due to lattice distortion (*ε*). Elimination of the instrumental broadening was done using an empirical formula: $\beta = B - b^2 / B$, where *B* represents the measured peak width, whereas *b* is the instrumental width obtained from a Si standard. It is obvious, from Tab. II that the crystallite size decreases with doping, compared to pure ceria.

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**Tab. II** Crystallite size, lattice strain and lattice parameters in pure and doped ceria powders

| Composition | Crystallite size [nm] | Microstrain (E10000) | Lattice parameter-calculated [Å] | Lattice parameter-experimental [Å] |
|---|---|---|---|---|
| $CeO_2$ | 32.5 | 9.9 | 5.4114 | 5.397(3) |
| $Ce_{0.8}Yb_{0.1}Gd_{0.06}Sm_{0.04}O_{2-\delta}$ | 18.5 | 7.6 | 5.4114 | 5.393(4) |
| $Ce_{0.8}Yb_{0.2}O_{2-\delta}$ | 17.1 | 7.7 | 5.3934 | 5.374(4) |
| $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ | 22.5 | 8.1 | 5.4247 | 5.416(3) |
| $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ | 20.0 | 7.8 | 5.4367 | 5.426(3) |



**Fig. 1** XRD patterns of a) $CeO_2$, b) $Ce_{0.8}Re_{0.2}O_{2-\delta}$ and c) $Ce_{0.8}Yb_{0.1}Gd_{0.06}Sm_{0.04}O_{2-\delta}$ (Re= Yb,Sm,Gd).

The lattice parameter of cerium oxides with the fluorite structure was refined by the WINCELL program. It is also obvious that lattice parameter value of co-doped sample does not differ very much in comparison with the value of pure $CeO_2$. This is the proof that calculated and experimental data were in very good agreement.
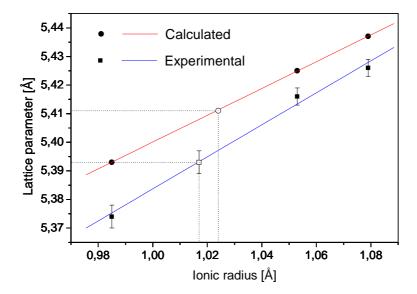
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**Fig. 2** Lattice parameter of $Ce_{0.8}Re_{0.2}O_{2-\delta}$ as a function of ionic radius of dopant cation (Re = $Yb^{3+}$, $Gd^{3+}$ and $Sm^{3+}$).

Calculated and measured lattice parameters are shown in Fig. 2. which represents the lattice parameter of single doped ceria as a function of the ionic radius of the dopant cation ($Yb^{3+}$, $Gd^{3+}$ and $Sm^{3+}$). The lattice parameter increases linearly with increasing dopants radii. Calculated and experimentally obtained values for the average ionic radius of dopants in complex composition $Ce_{0.8}Yb_{0.1}Gd_{0.06}Sm_{0.04}O_{2-\delta}$ are respectively, 1.024 Å and 1.017 Å, as seen from Fig.2, which are very close. It is therefore, important to outline that the values of lattice parameters of pure ceria and of the co-doped sample, both calculated and measured after synthesis, are also in very good agreement (Tab.II). This result shows that it is possible to reliably predict the composition of the ceria solid solution, and experimentally synthesize the very same composition using MGNP method.
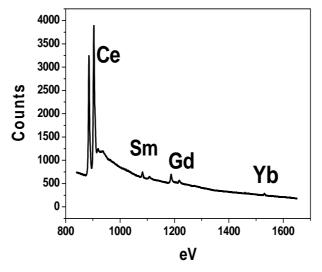


**Fig. 3** EELS spectrum of $Ce_{0.8}Yb_{0.1}Gd_{0.06}Sm_{0.04}O_{2-\delta}$.

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The composition of the co-doped powder was checked by EELS and analytical methods, as well. The electron energy loss spectroscopy, (Fig. 3) proved the presence of Sm, Gd, and Yb in the $Ce_{0.8}Yb_{0.1}Gd_{0.06}Sm_{0.04}O_{2-\delta}$ solid solution.

Quantitative results on the concentration of these dopants were determined by the ICP-OES method. The results are given in Tab. III.

**Tab. III** Rare earth cation content in nominal composition $Ce_{0.8}Yb_{0.1}Gd_{0.06}Sm_{0.04}O_{2-\delta}$

| Element | Content [wt.%] |
|---------|----------------|
| Ce | $61.1 \pm 0.70$ |
| Sm | $3.74 \pm 0.12$ |
| Gd | $4.63 \pm 0.05$ |
| Yb | $9.91 \pm 0.01$ |
| O | $19.9 \pm 0.20$ |

From these data we calculated the true composition of our co-doped solid solution as $Ce_{0.8}Yb_{0.105}Gd_{0.05}Sm_{0.045}O_{2-\delta}$ which is very close to the nominal composition.

Comparing this formula with the tailored one, $Ce_{0.8}Yb_{0.1}Gd_{0.06}Sm_{0.04}O_{2-\delta}$ one can see that the desired composition was experimentally prepared with good precision, applying the MGNP procedure.
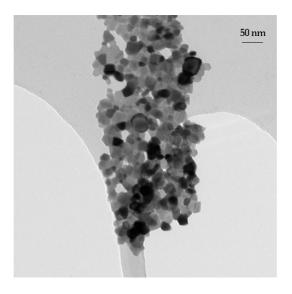


**Fig. 4** TEM micrograph of $Ce_{0.8}Yb_{0.105}Gd_{0.05}Sm_{0.045}O_{2-\delta}$.

Specific surface area values of the powders are summarized in Table IV. While the crystallite size decreased with doping (Table II), the specific surface area shows an increasing trend, starting with pure $CeO_2$ as was found earlier [5].

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Tab. IV Specific surface area of ceria solid solutions

| No | Composition | Specific Surface Area [$m^2$/g] |
|----|-------------|-------------------------------|
| 1 | $CeO_2$ | 34.50 |
| 2 | $Ce_{0.8}Yb_{0.105}Gd_{0.05}Sm_{0.045}O_{2-\delta}$ | 56.50 |
| 3 | $Ce_{0.8}Yb_{0.2}O_{2-\delta}$ | 40.21 |
| 4 | $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ | 35.94 |
| 5 | $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ | 35.48 |

From the TEM micrograph of a triple doped sample we determined that the average particle size is approximately 15-20 nm, a value very close to the crystallite size that goes along with the high specific surface area. These data indicate that the agglomeration degree may be quite low. From Tables III and IV one can see that the crystallite size andecific surface increases with decreasing dopant ionic radius. Further work is needed to really prove this observation.

## 4. Conclusion

The results have shown that the nominal composition obtained by calculation according to the ion packaging model can be prepared with a very good precision by applying the MGNP procedure. This was proved through very close values of average ionic radii, both calculated and measured ones, as well as by similar values of the measured lattice parameter. Nanometric powders of ceria solid solutions with x = 0.2 were obtained as single phase materials. The same goes for co-doped composition $Ce_{0.8}Yb_{0.105}Gd_{0.05}Sm_{0.045}O_{2-\delta}$ that was synthesized during this work.

## Acknowledgements

## 5. References

1. B.C.H.Steele, Solid State Ionics, 129 (2000) 95.
2. M. Mogensen, N. M. Sammes, G. A. Tompsett, Solid State Ionics, 129 (2000) 63.
3. J. van Herle, D. Senevirante, A.J. McEvoy, J.Eur. Ceram. Soc., 19 (1999) 837.
4. D. J. Kim, J.Am.Ceram.Soc., 72 (1989) 1415.
5. S. B.Bošković, B. Z. Matovic, M. D. Vlajić, V. D. Kristić, Ceramics International, 33 (2007) 89.
6. R.D. Purohit, B. P. Sharma, K. T. Pillai, A. K. Tyagi, Mat. Res. Bull. 36 (2001) 2711.
7. S. J. Hong, A. V. Virkar, J. Am. Ceram. Soc., 78 (1995), 433.
8. R.D.Shannon, Acta Cryst., A32 (1976) 751.

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9.  B. Lönnberg, J. Mat. Sci., 29 (1994) 3224.

***Садржај:*** *Нанометарски прахови чврстих раствора церијум диоксида, добијени су модификованом методом глицин/нитрат (MGNP). Синтетизовани су прахови чврстих раствора са једним или више допаната. Као допанти су коришћени јони ретких земаља (Yb, Gd и Sm) у константној концентрацији x = 0.2, чија је комбинација изабрана тако да се основни параметар решетке церијум диоксида не мења, упркос присуству допаната. У складу с тим, номинални састави вишеструко допираних чврстих раствора израчунати су на основу претходно добијених вредности параметара решетке према моделу који узима у обзир постојање кисеоничних ваканција.*

***Кључне речи:*** *Церијум диоксид, флуоритна структура, модификована глицин/нитрат метода.*