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# Nanosized ceria solid solutions obtained by different chemical routes

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Nanometric size ceria powder particles were obtained by applying modified glycine/nitrate, as well as self propagating room temperature methods. The powders were doped and co-doped with rare earth cations in the concentration range $0 \le x \le 0.25$. The results showed that by doping with one or more dopants simultaneously in the mentioned concentration range solid solutions with host ceria were formed. Differences in the properties of nanopowders obtained by the two methods were discussed. Defect model introducing anion vacancy radius was applied to calculate lattice parameters of single doped and co-doped ceria nanosized solid solutions.

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*Keywords:* Ceria solid solutions, Doping with rare-earth cations, XRD, EELS, Raman

## 1. Introduction

Nanocrystalline particles represent very important group of materials in novel technologies like production of components for SOFC. From this point of view, nanometric ceria based material is interesting as an electrolyte for SOFC since it exhibits high ionic conductivity at relatively low temperatures [1,2,3,4]. The addition of dopants in ceria is desirable and even many of them can be simultaneously incorporated in the crystal structure to improve electrical conductivity that

is very much dependent on the composition [5] and crystal structure parameters of ceria solid solutions [6,7]. It was reported that electrical conductivity of fluorite type ceria depended on the dopant ion size[6,7]. It was also shown[8] that electrical conductivity of co-doped ceria increased by 30% in comparison with single doped material. Besides, the properties of ceria including electrical conductivity are also dependent on the microstructure of the material [9] which is on the other hand, influenced also by starting powder properties that are, in turn, sensitive to powder production technique.

Since different synthesis routes produce different powder properties, in this paper single and multiple doped ceria were synthesized by applying SPRT [10] and MGNP [11] methods. In the case of the two applied methods, great difference, by an order of magnitude, in crystallite and particle sizes were observed. Bearing in mind that lattice parameter can be a useful tool for indication of electrical conductivity behavior, this constants for doped and co-doped ceria nanopowders were measured experimentally and in addition, calculated according to ion packaging model [12]. The differences in lattice parameters between the powders obtained by the two methods were observed and discussed. Besides, it turned out that the mentioned model can be applied for calculation of lattice parameters of multiple doped ceria solid solutions which was found earlier [13].

## 2. Experimental

Ceria doped and co-doped powders were synthesized by SPRT [10] and MGNP [11] methods. The following compositions were prepared: $CeO_2$, $Ce_{0.90}Y_{0.10}O_{2-\delta}$, $Ce_{0.85}Y_{0.15}O_{2-\delta}$, $Ce_{0.80}Y_{0.20}O_{2-\delta}$ y, $Ce_{0.75}Y_{0.25}O_{2-\delta}$, $Ce_{0.90}Gd_{0.10}O_{2-\delta}$, $Ce_{0.85}Gd_{0.15}O_{2-\delta}$ $Ce_{0.80}Gd_{0.20}O_{2-\delta}$, $Ce_{0.75}Gd_{0.25}O_{2-\delta}$, $Ce_{0.90}Sm_{0.10}O_{2-\delta}$, $Ce_{0.85}Sm_{0.15}O_{2-\delta}$, $Ce_{0.80}Sm_{0.20}O_{2-\delta}$, $Ce_{0.75}Sm_{0.25}O_{2-\delta}$, $Ce_{0.90}Nd_{0.10}O_{2-\delta}$, $Ce_{0.85}Nd_{0.15}O_{2-\delta}$, $Ce_{0.80}Nd_{0.20}O_{2-\delta}$, $Ce_{0.75}Nd_{0.25}O_{2-\delta}$, $Ce_{0.80}Y_{0.10}Nd_{0.10}O_{2-\delta}$, $Ce_{0.80}Yb_{0.10}Gd_{0.06}Sm_{0.04}O_{2-\delta}$ and $Ce_{0.80}Y_{0.05}Gd_{0.05}Sm_{0.05}Nd_{0.05}O_{2-\delta}$.

SPRT procedure is based on the self-propagating room temperature reaction between metal nitrates and sodium hydroxide. During SPRT synthesis hand-mixing of nitrates with NaOH was performed in alumina mortar for 5 – 7 min until the mixture got light brown. After being exposed to air for 3 h, the mixture was suspended in water. Rinsing out of $NaNO_3$ was performed in centrifuge – Centurion 1020D, at 3500 rpm for 10 min. This procedure was repeated three times with distilled water and twice with ethanol [10].

The glycine nitrate process, a self-combustion method for powder synthesis, uses amino acetic acid (glycine) as a fuel and metal nitrate of the composition to be synthesized, as an oxidant. We however, use the modified method [11] that gives the possibility of controlling the strong exothermicity of the reaction, and therefore the possibility of producing very fine, very clean, nanometric powders in a very short time, with the yield of 98-99%. This process is especially convenient in preparing complex compositions with homogeneously distributed dopants, since the process started from the liquid phase.

Synthesized single doped and co-doped powders with two to four cations were characterized by XRD, Raman spectroscopy that was done at room temperature in the 300-700 $cm^{-1}$ spectral range, and TEM and EELS analyses by using ZEISS EM 912 Omega.

## 3. Results and discussion

In our previus papers [10,11] detail in the preparation methods, MGNP and SPRT, were explained, and also advantages and disadvantages of the methods are named. It should be however, outlined, that both methods are time effective, need inexpensive equipment, and enable preparation of very clean powders with precise composition. In this paper we concentrate on the differences in powder properties obtained by the two methods

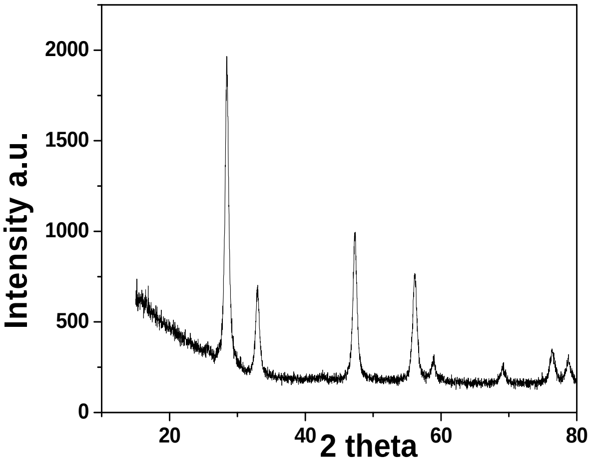

*Fig. 1 XRD of* $Ce_{0.8}Y_{0.05}Gd_{0.05}Sm_{0.05}Nd_{0.05}O_{2-\delta}$ *obtained by MNGP method.*

The ashes obtained by MGNP method after the reaction (that illustrates formation of single doped solid solution), had come to an end undergone calcination procedure with the intention to burn out possible organic remains

$$4C_2H_5NO_2+2\{(1-x)Ce(NO_3)_3.6H_2O\}+ 2\{xMe(NO_3)_3.6H_2O\}+2O_2\rightarrow 2\,Ce_{1-x}Me_xO_{2-y}+22\,H_2O\uparrow+5\,N_2\uparrow+8\,CO_2\uparrow \quad (1)$$

from the powders. The calcination was performed at 600°C, 4 h with all the synthesized powders. XRD of all the calcined compositions showed that the single phase solid solutions of ceria were obtained in the concentration range that was investigated. Multiply doped ceria solid solution can also be obtained by MGNP that is as mentioned especially suitable for complex compositions. The XRD pattern of the single phase solid solution doped simultaneously with Y, Gd, Sm and Nd is shown in Fig.1. Lattice parameter vs. dopants concentration for Y,Gd,Sm and Nd obeyed Vegards law[10,13] as is illustrated in Fig.2 for Sm doped ceria.

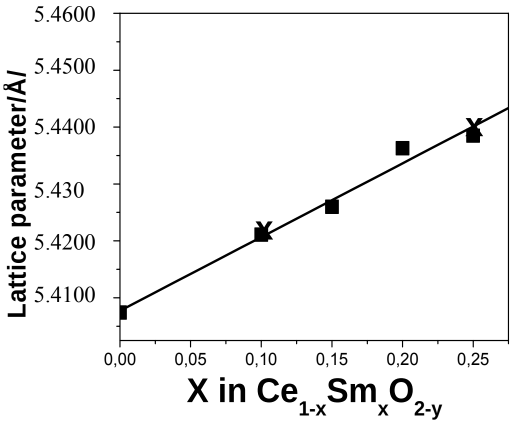

*Fig. 2. Measured (■)and calculated (x) lattice parameter vs. dopant's concentration.*

By self propagating room temperature synthesis, single phase solid solutions were obtained, according to reaction (2) for single

$$2[(1-x)Ce(NO_3)_3.6H_2O + xMe(NO_3)_3.6H_2O]+ 6\,NaOH + (½-y)\,O_2 \rightarrow 2\,Ce_{1-x}Me_xO_{2-y} + 6\,NaNO_3 + 15\,H_2O \quad (2)$$

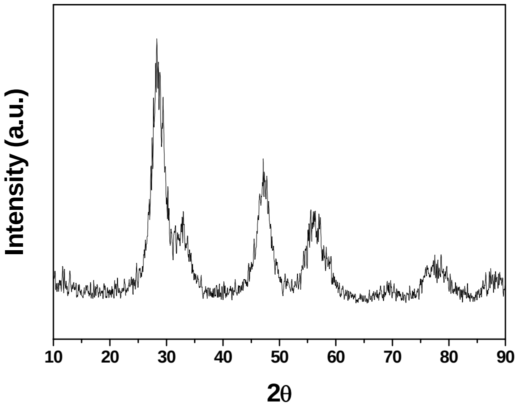

*Fig. 3. XRD of* $Ce_{0.8}Y_{0.05}Gd_{0.05}Sm_{0.05}Nd_{0.05}O_{2-\delta}$ *obtained by SPRT method.*

doped ceria. However, by this method also multiple doped $Ce_{0.8}Y_{0.05}Gd_{0.05}Sm_{0.05}Nd_{0.05}O_{2-\delta}$ ceria solid solutions were prepared. XRD pattern of this composition is illustrated in Fig.3. It indicates that single phase powder was obtained. By EELS analysis all the dopants were detected in fourfold doped sample synthesized at room temperature (Fig.4).

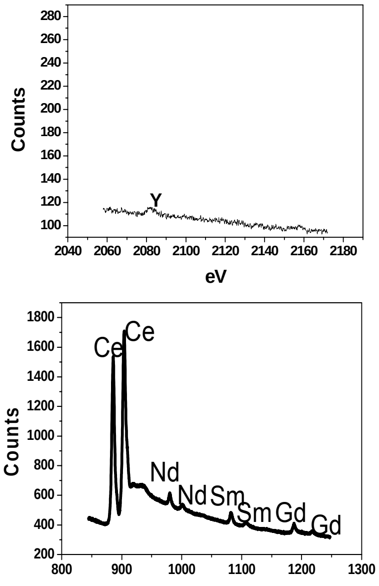

*Fig. 4. EELS of fourfold doped sample.*

In addition, Raman spectroscopy was performed to prove that single phase solid solution was formed. In Fig.5 Raman spectrum typical for doped ceria was obtained [14,15,16]. Beside basic mode at 453 cm$^{-1}$ typical for ceria two additional modes can be seen at 545 and 601 cm$^{-1}$, that were observed earlier[15,16]. These modes are attributed to the presence of additional O$^{2-}$ vacancies introduced into ceria lattice by substitution of Ce$^{4+}$ ions with Re$^{3+}$ ions in order to keep charge neutrality[14,15], as well as to intrinsic oxygen vacancies in ceria[16], respectively.

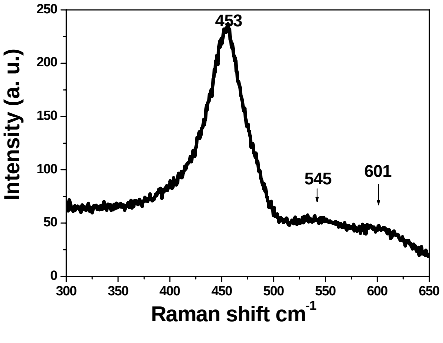

*Fig. 5. Raman spectrum of doped ceria* $Ce_{0.8}Y_{0.05}Gd_{0.05}Sm_{0.05}Nd_{0.05}O_{2-\delta}$ *obtained by SPRT method .*

Since modes typical for doped ceria appeared, while no additional modes that correspond to free single oxides used as dopants were observed, the data in Fig. 5 were interpreted [10,14,15] as the proof that single phase ceria solid solution containing four dopants, was prepared at room temperature.

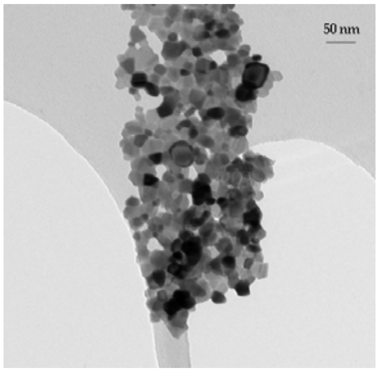

*Fig. 6. TEM image of the composition* $Ce_{0.80}Yb_{0.10}Gd_{0.06}Sm_{0.04}O_{2-\delta}$ *obtained by MGNP method.*

In Fig 6, TEM micrograph of MGNP produced powder $Ce_{0.80}Yb_{0.10}Gd_{0.06}Sm_{0.04}O_{2-\delta}$ with average particle size cca.16 nm is given as an example, while TEM image of sample with $Ce_{0.8}Y_{0.05}Gd_{0.05}Sm_{0.05}Nd_{0.05}O_{2-\delta}$ composition obtained by SPRT method is shown in Fig 7. Mean particle size of this powder is clearly around 5 nm, close to crystallite size (Tab.1).

Powders obtained by both methods are nanometric in size, that was proved by TEM analyses (Figs 6 and 7). However, diffraction lines of SPRT powder (Fig.3) are more diffuse compared to MGNP powders (Fig.1), indicating even smaller crystallite size. This parameter was calculated for both types of powders from XRD data and the values are given in Tab.1 The results show indeed, that crystallite size of SPRT powders is an order of magnitude lower compared to MGNP produced powders. In addition, the results from Figs. 6 and 7, as well as from Table 1 indicate that both powders seem to be monodisperse.

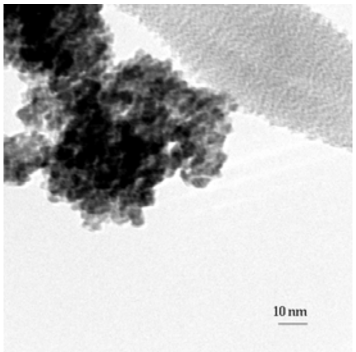

*Fig. 7. TEM of* $Ce_{0.8}Y_{0.05}Gd_{0.05}Sm_{0.05}Nd_{0.05}O_{2-\delta}$ *(SPRT).*

Specific surface areas (Tab.2) of our samples obtained by the two mentioned methods are considerably different. Specific surface area of SPRT obtained powders is about three times higher, compared to powders obtained by MGNP method that could be expected bearing in mind much smaller particle size of the first series of powders.

*Table 1. Crystallite size of the powders obtained by SPRT and MGNP procedures.*

| Composition | Crystallite size/nm/ MGNP | Crystallite size/nm/ SPRT |
|---|---|---|
| $\mathrm{CeO_2}$ | 17 | 4.2 |
| $\mathrm{Ce}_{0.9}\mathrm{Y}_{0.1}\mathrm{O}_{2-\delta}$ | 10 | 4.3 |
| $\mathrm{Ce}_{0.85}\mathrm{Y}_{0.15}\mathrm{O}_{2-\delta}$ | 15 | 4.2 |
| $\mathrm{Ce}_{0.8}\mathrm{Y}_{0.2}\mathrm{O}_{2-\delta}$ | 17 | 5.0 |
| $\mathrm{Ce}_{0.75}\mathrm{Y}_{0.25}\mathrm{O}_{2-y}$ | 16 | - |
| $\mathrm{Ce}_{0.9}\mathrm{Gd}_{0.1}\mathrm{O}_{2-\delta}$ | 16 | - |
| $\mathrm{Ce}_{0.85}\mathrm{Gd}_{0.15}\mathrm{O}_{2-\delta}$ | 18 | - |
| $\mathrm{Ce}_{0.8}\mathrm{Gd}_{0.2}\mathrm{O}_{2-\delta}$ | 15 | - |
| $\mathrm{Ce}_{0.75}\mathrm{Gd}_{0.25}\mathrm{O}_{2-\delta}$ | 20 | - |
| $\mathrm{Ce}_{0.9}\mathrm{Sm}_{0.1}\mathrm{O}_{2\,\delta}$ | 14 | - |
| $\mathrm{Ce}_{0.85}\mathrm{Sm}_{0.1}\mathrm{O}_{2-\delta}$ | 15 | - |
| $\mathrm{Ce}_{0.8}\mathrm{Sm}_{0.2}\mathrm{O}_{2-\delta}$ | 17 | - |
| $\mathrm{Ce}_{0.75}\mathrm{Sm}_{0.25}\mathrm{O}_{2-\delta}$ | 19 | - |
| $\mathrm{Ce}_{0.9}\mathrm{Nd}_{0.1}\mathrm{O}_{2-\delta}$ | 14 | 4.4 |
| $\mathrm{Ce}_{0.85}\mathrm{Nd}_{0.15}\mathrm{O}_{2-\delta}$ | 16 | 4.4 |
| $\mathrm{Ce}_{0.8}\mathrm{Nd}_{0.2}\mathrm{O}_{2-\delta}$ | 15 | 4.2 |
| $\mathrm{Ce}_{0.75}\mathrm{Nd}_{0.25}\mathrm{O}_{2-\delta}$ | 15 | 4.1 |
| $\mathrm{Ce}_{0.80}\mathrm{Y}_{0.10}\mathrm{Nd}_{0.1}\mathrm{O}_{2-\delta}$ | - | 4.5 |
| $\mathrm{Ce}_{0.8}\mathrm{Y}_{0.05}\mathrm{Nd}_{0.05}\mathrm{Sm}_{0.05}\mathrm{Gd}_{0.05}\mathrm{O}_{2-\delta}$ | 13 | 3.9 |

*Table 2 Specific surface area of ceria solid solutions obtained by different chemical routes.*

| Composition | Specific surface area/m$^2$/g MGNP | Specific surface area/m/g SPRT |
|---|---|---|
| $\mathrm{CeO_2}$ | 34.85 | 106.9 |
| $\mathrm{Ce}_{0.90}\mathrm{Y}_{0.10}\mathrm{O}_{2-\delta}$ | 37.69 | 103.2 |
| $\mathrm{Ce}_{0.85}\mathrm{Y}_{0.15}\mathrm{O}_{2-\delta}$ | 36.76 | 137.1 |
| $\mathrm{Ce}_{0.80}\mathrm{Y}_{0.20}\mathrm{O}_{2-\delta}$ | 40.21 | 109.7 |
| $\mathrm{Ce}_{0.75}\mathrm{Y}_{0.25}\mathrm{O}_{2-\delta}$ | 40.64 | 109.7 |
| $\mathrm{Ce}_{0.90}\mathrm{Gd}_{0.10}\mathrm{O}_{2-\delta}$ | 40.10 | - |
| $\mathrm{Ce}_{0.85}\mathrm{Gd}_{0.15}\mathrm{O}_{2-\delta}$ | 33.55 | - |
| $\mathrm{Ce}_{0.80}\mathrm{Gd}_{0.20}\mathrm{O}_{2-\delta}$ | 35.94 | - |
| $\mathrm{Ce}_{0.75}\mathrm{Gd}_{0.25}\mathrm{O}_{2-\delta}$ | 29.71 | - |
| $\mathrm{Ce}_{0.90}\mathrm{Sm}_{0.10}\mathrm{O}_{2-\delta}$ | 43.16 | - |
| $\mathrm{Ce}_{0.85}\mathrm{Sm}_{0.15}\mathrm{O}_{2-\delta}$ | 40.98 | - |
| $\mathrm{Ce}_{0.80}\mathrm{Sm}_{0.20}\mathrm{O}_{2-\delta}$ | 35.48 | - |
| $\mathrm{Ce}_{0.75}\mathrm{Sm}_{0.25}\mathrm{O}_{2-\delta}$ | 31.79 | - |
| $\mathrm{Ce}_{0.90}\mathrm{Nd}_{0.10}\mathrm{O}_{2-\delta}$ | 43.33 | 118.4 |
| $\mathrm{Ce}_{0.85}\mathrm{Nd}_{0.15}\mathrm{O}_{2-\delta}$ | 40.86 | 137.6 |
| $\mathrm{Ce}_{0.80}\mathrm{Nd}_{0.20}\mathrm{O}_{2-\delta}$ | 35.60 | 141.5 |
| $\mathrm{Ce}_{0.75}\mathrm{Nd}_{0.25}\mathrm{O}_{2-\delta}$ | 41.37 | 110.0 |
| $\mathrm{Ce}_{0.80}\mathrm{Y}_{0.10}\mathrm{Nd}_{0.10}\mathrm{O}_{2-\delta}$ | - | 110.0 |
| $\mathrm{Ce}_{0.80}\mathrm{Y}_{0.05}\mathrm{Nd}_{0.05}\mathrm{Gd}_{0.05}\mathrm{Sm}_{0.05}\mathrm{O}_{2-\delta}$ | 40.68 | 90.0 |
| $\mathrm{Ce}_{0.80}\mathrm{Yb}_{0.10}\mathrm{Gd}_{0.o6}\mathrm{Sm}_{0.04}\mathrm{O}_{2-\delta}$ | 26.60 | - |

Lattice parameters of single doped solid solutions $\mathrm{Ce}_{1-x}\mathrm{Re}_x\mathrm{O}_{2-\delta}$, at x=0.2 for both type of powders was measured as a function of dopants ionic radii at constant x and presented in Fig.8.

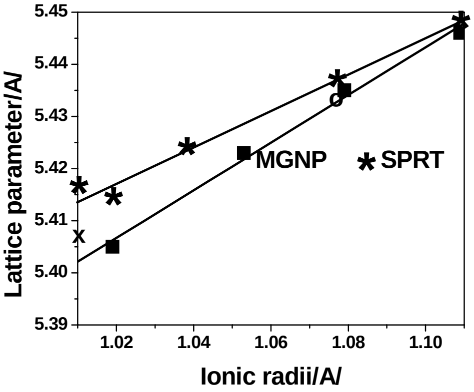

*Fig. 8. Lattice parameter vs. ionic radii of dopants (Y,Gd,Sm,Nd) for MGNP and SPRT prepared $Ce_{1-x}Re_xO_{2-\delta}$, at x=0.2.*

Linear dependence can be observed for lattice parameter change with increasing dopants radii. For powders with particle size smaller than 5 nm(SPRT), lattice parameters are larger as compared to MGNP powders which contained particles of about 16 -20nm in size( Figs 6 and 7). These results are in agreement with literature data paying attention to this anomaly of relatively strong increase of lattice parameter of ceria with decreasing particle size below 10nm[17,18,19]. This anomaly is ascribed to an increased $\mathrm{Ce}^{3+}$ concentration[17,18,19]. The data for pure ceria obtained by the two methods are introduced in the diagram at ordinate.

Since the radius mismatch between the host and dopant cations should be as low as possible, to achieve high electrical conductivity [6,7], lattice parameter measurement may be taken as a good indication. Lattice parameters can be also calculated and we showed earlier that measured and calculated values agreed very well for single doped ceria (Fig.2). Calculation of lattice parameters was done according to ion packaging model [12]:

$$a = 4/\sqrt{3} \ast [x r_M{}^{3+} + (1-x)\, r_{Ce}{}^{4+} + (1-0.25x)\, r_O{}^{2-} + 0.25 x r_{Vo}] \ast 0.9971 \qquad (3)$$

taking into account the anion vacancy radius. This model was developed for single doped solid solutions whereby ionic radii were used from the Shannon's compilation [20].

To calculate lattice parameter of co-doped solid solution, we applied the same model, whereby average ionic radius was introduced instead of individual radii of all of dopants present in the lattice. The average ionic radius was obtained graphically from experimentally measured lattice parameters with constant concentration of dopants (x=0.20) as shown in Fig 8. From this diagram for the measured value of lattice parameter 5.434 Å of $Ce_{0.8}Y_{0.05}Gd_{0.05}Sm_{0.05}Nd_{0.05}O_{2-\delta}$ we obtained the average ionic radius of 1.078 Å (marked as **o** in Fig.8). Taking the value of 1.078 Å as $r_M$ for the fixed value of x we obtained lattice parameter value of 5.436Å that is in very good agreement with the measured lattice parameter of co-doped sample.

The described differences in powder properties originate from the methods applied for powder production. While MGNP powders were obtained after calcinations at 600°C, SPRT powders were obtained at room temperature. Under these conditions it is difficult to expect the particles to grow since diffusivity is very low at room temperature. As a consequence, particle and crystallite sizes are smaller, while specific surface area and lattice parameters are increased for SPRT powders. It is interesting to note that with SPRT powders agglomeration degree is not high, and that these powders can easily flow, which is good indication for further powder processing that will be the next stage of our study.

It may be born in mind that calculation of lattice parameters, that gave very good agreement with the measured values [10,11,12,13] and that is definitely time saving procedure may be useful as fast preliminary indication of electrical conductvitiy of SOFC electrolytes.

## 4. Conclusions

Ceria solid solution of were obtained by two different chemical routes. Consequently different powder properties were observed. MGNP powders needed to be calcined at 600°C, SPRT powders were obtained at room temperature. Under room temperature the particles did not grow since diffusivity is very low. As a consequence, particle and crystallite sizes are smaller, while specific surface area and lattice parameters are increased for SPRT powders. It is interesting to note that with SPRT powders agglomeration degree is not high, and that these powder can easily flow. The calculated and measured values of lattice parameters agree very well. It was shown that ion packaging model can be applied for calculation of lattice parameters of multiple doped ceria.

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