Short communication

Self-propagating room temperature synthesis of nanopowders for solid oxide fuel cells (SOFC)

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Abstract

Ceria based solid solutions are promising ceramic electrolytes for SOFC which will be able to function at intermediate temperatures. In accordance with common trends to decrease the production and operating costs of new generation of SOFC materials the reaction based on metathetical pathway is described, whereby solid solution powders of rare earth doped ceria in the nanoscale range were obtained at room temperature. By simple hand mixing of reactants the reaction was enhanced, propagating afterwards by itself. Nanometric ceria powders doped with Y or Nd, as well as co doped with both cations were synthesized. Composition of $Ce_{1-x}Me_xO_{2-y}$ ranged from $x = 0$–0.25. The reaction course is described in detail and the properties of the obtained powders are presented.
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1. Introduction

Fuel cell technology belongs to the key technologies of the 21st century. It is hoped that the operation of mobile phones, laptops, cars driven by hydrogen, housings heating, electricity, etc. [1] will be based on hydrogen energy. For that reason, highly efficient fuel cells are needed. At the time being the solid oxide fuel cells (SOFC) attract interest as a potentially reliable, durable, and inexpensive technology for generating electricity from hydrogen and hydrocarbon fuels. The research in the field of SOFC is concentrated nowadays on the development of the new generation of cell component materials to allow operation at intermediate temperatures (500–700 °C), as well as on the development of the low cost technologies for their production.

It is known that the sintering temperature decreases when nanosized powders are used. On the other hand, the conductivity in the nanocrystalline grain boundary regions is greater than for larger grains [2]. In this respect it is important, as a first step, to develop powders of high quality with particle size in the nanometric range. There are plenty of methods that are described in the literature offering such a possibility but the chance for a large scale production will be given to the least expensive one, allowing at the same time preparation of high quality nanoscale powders. A very promising method to produce a single-phase and highly pure nanosized powder with a precise stoichiometry would enable reproducibility of powder quality and ensure high yield of powder in a short time. One of the method, to our opinion cost and time effective, is the self propagating room temperature synthesis (SPRT). Many of such reactions need to be performed at elevated temperatures to start propagating, than the reactions develop by themselves, and terminate extremely fast. According to literature data [3] synthesis of pure ceria was performed by

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self-propagating method at room temperature. However, ceria solid solutions have not been obtained by this method so far.

In this paper we discuss the results on studying the self-propagating reaction at room temperature, and present the properties of the synthesized doped ceria nanopowders. Solid solutions of ceria containing Y^{3+} and Nd^{3+} cations, as well as, co-doped with both cations were prepared.
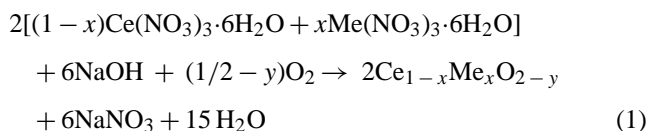
2. Experimental work

Starting reactants used in the experiments were cerium nitrate (Merck), yttrium nitrate (Alfa Aesar), neodymium nitrate (John Mathey) and sodium hydroxide. All used nitrates were in the form of hexahydrates. Amounts of nitrates and NaOH were calculated according to the nominal composition of the solid solutions: CeO_2, $Ce_{0.90}Y_{0.10}O_{2-y}$, $Ce_{0.85}Y_{0.15}O_{2-y}$, $Ce_{0.80}Y_{0.20}O_{2-y}$, $Ce_{0.75}Y_{0.25}O_{2-y}$, $Ce_{0.90}Nd_{0.10}O_{2-y}$, $Ce_{0.85}Nd_{0.15}O_{2-y}$, $Ce_{0.80}Nd_{0.20}O_{2-y}$, $Ce_{0.75}Nd_{0.25}O_{2-y}$, $Ce_{0.80}Y_{0.10}Nd_{0.10}O_{2-y}$. The chemicals were not milled. Hand-mixing 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 of $NaNO_3$ was performed in centrifuge – Megafuge 1.0, Heraeus, at 3200 rpm for 10 min. This procedure was performed three times with distilled water and twice with ethanol. After drying, powder was analysed by applying X-ray diffraction (XRD, Siemens D-5000), scanning electron microscopy (SEM, Zeiss DSM 982 Gemini), Raman spectroscopy (Jobin-Ivon monochromator), and specific surface area measurement (BET). Chemical analysis of dopants concentration was carried out by titration to check the difference between nominal and true compositions of solid solution powders. To follow the reaction path, differential thermal analysis (DTA) and thermogravimetry (TG, Netzsch STA 409) were performed in air atmosphere, at a heating and cooling rates of $5\,°C\,min^{-1}$.

3. Results and discussion

3.1. Reaction development

SPRT procedure is based on the self-propagating room temperature reaction [3] between metal nitrates and sodium hydroxide, and in the case of the doped ceria solid solution the reaction can be written as follows:

$$2[(1-x)Ce(NO_3)_3 \cdot 6H_2O + xMe(NO_3)_3 \cdot 6H_2O]$$
$$+ 6NaOH + (1/2 - y)O_2 \rightarrow 2Ce_{1-x}Me_xO_{2-y}$$
$$+ 6NaNO_3 + 15H_2O \tag{1}$$

During heating of the reacting mixture (Fig. 1) a sharp peak is observed on DTA curve showing that the reaction is strongly exothermic. At peak point (about $50\,°C$) of this exothermic
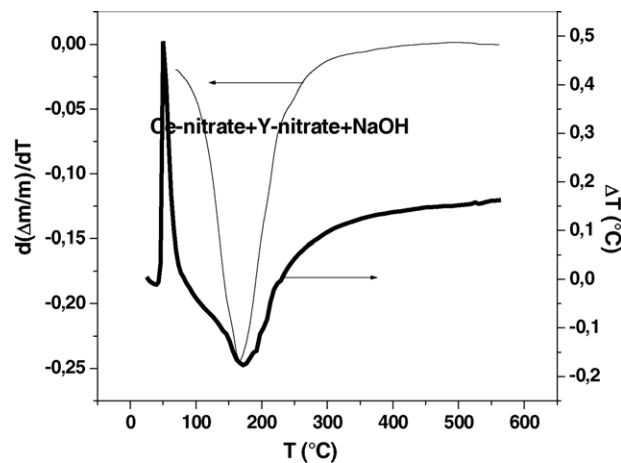

Fig. 1. DTA and DTG patterns of $Ce(NO_3)_3 \cdot 6H_2O$–$Y(NO_3)_3 \cdot 6H_2O$–NaOH mixture.

effect, the rate of weight loss start to increase. The maximum rate at $160\,°C$ (Fig. 1) coincides with the termination of heat release from the mixture. This indicates that the reaction is initiated by the rapid, strong heat release, developing easily afterwards. Weight loss terminates at $300\,°C$, where cerium nitrate hexahydrate was completely converted into ceria after a gradual loss of crystalline water (Fig. 2). As soon as the weight loss process had started, it is supposed, that the formation of the solid solution, $Ce_{0.9}Y_{0.1}O_{2-y}$ starts simultaneously due to a very rapid reaction. However, formation of solid solution is not a direct process. Judging by the stepwise decomposition of cerium nitrate hexahydrate (Fig. 2) it can be assumed that the reaction between nitrates and sodium hydroxide proceeds via intermediate reaction steps. However, these reaction steps develop in the reacting mixture under heating conditions very fast one after another and for that reason cannot be observed separately in Fig. 1.

Since low temperatures are needed for the reaction to start and come to an end, it is to expect that by mechanical activation this reaction will be easily enhanced. That is why we tried simple hand-mixing of reactants. Indeed, by introducing mechanical energy into the system, instead of the
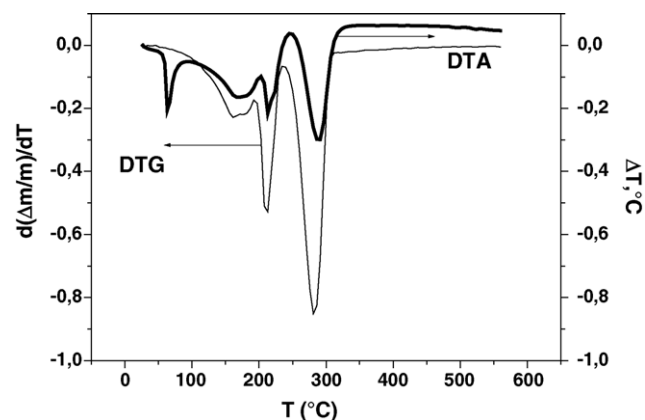
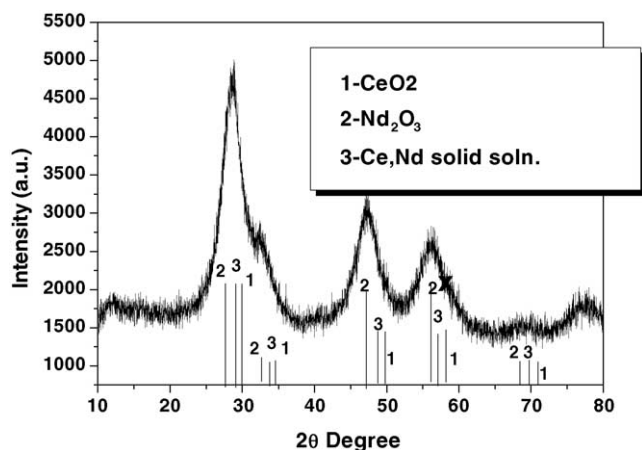

Fig. 2. DTA and DTG patterns of $Ce(NO_3)_3 \cdot 6H_2O$.

Fig. 3. X-ray pattern of $Ce_{0.90}Nd_{0.10}O_{2-y}$ "as prepared" powder.

Fig. 5. Water milled Ce and Y nitrates with NaOH in planetary ball mill.

thermal one, the reaction proceeds at room temperature in air and could be observed by the naked eye. The first step of the reaction is the release of crystalline water from nitrates [4] (loosely bound two molecules [5]), which is expected according to Fig. 2 at about 50 °C. The release of water enables easier the hand homogenization of reactants. With further mixing, the rest of crystalline water is released which is also confirmed by the results given in Fig. 2. Exposition to air of the homogenized mixture is necessary to bring the reaction to the end as described by Eq. (1). As an example X-ray pattern of "as prepared" $Ce_{0.90}Nd_{0.10}O_{2-y}$ is shown in Fig. 3. From X-ray profile, it can be concluded that the obtained powder is very fine and poorly crystallized at the same time.

It is interesting to note that the reaction also proceeded with a non-homogenized mixture. Namely, the reactants $Ce(NO_3)_3 \cdot 6H_2O$ and NaOH, were brought into contact without mixing and allowed for 24 h to react. XRD pattern of this sample (Fig. 4) revealed the presence of final reaction products, CeO_2 and $NaNO_3$, besides intermediate products like
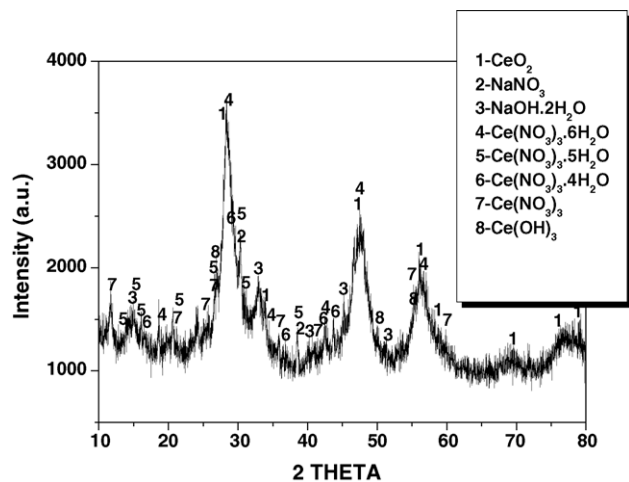

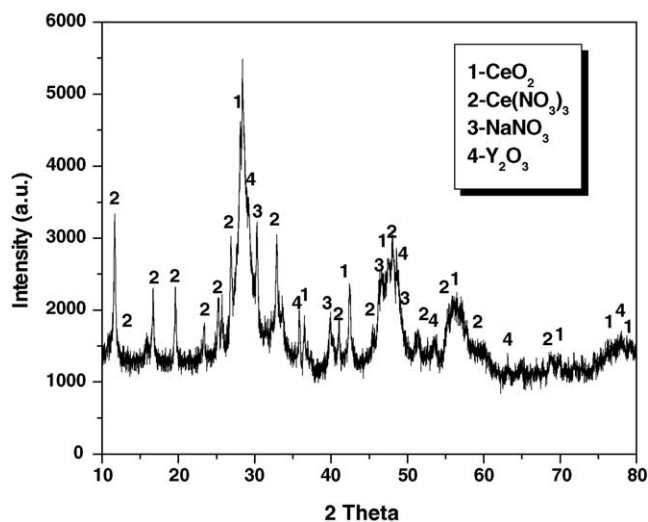Fig. 4. . X-ray pattern of non homogenized $Ce(NO_3)_3 \cdot 6H_2O$ and NaOH mixture after drying.

Ce-nitrates with less crystalline water. These results are in accordance with the DTA/TG shown in Fig. 2. It comes out that water is gradually released from nitrates being converted from hexahydrate into anhydrous Ce-nitrate as mentioned before. In the case of reacting mixture, these intermediate steps cannot be observed, due to very high reaction rate (Fig. 1). At room temperature, however, the mentioned reaction steps (Fig. 2) can be detected. It is assumed that $Ce(NO_3)_3$ directly reacts with NaOH in the presence of released water producing oxide powder and $NaNO_3$. These results indicate that under given experimental conditions, the reaction does not need any source of energy to start propagating. Thus by hand-mixing small quantity of mechanical energy was introduced into the system enhancing the reaction.

The milling of the reacting mixture in a planetary ball mill, in the presence of added water, proved the importance of close contacts between particles.

In this case, according to XRD data (Fig. 5), the reaction did not terminate under the same experimental conditions. The diffraction lines of ceria, yttria, (most probably of ceria solid solution, too), $Ce(NO_3)_3$ and $NaNO_3$ were detected. From these results it is obvious that and important condition to be fulfilled in order to speed up the development of the reaction is to keep close contact between the reacting particles. This condition is typical for the solid-state reactions. On the basis of these results the reaction course may be described as follows: as a first step, loosely bound two molecules of crystalline water [5] are released during mixing of reacting particles, followed by the release of the rest of water molecules. The total amount of the released water is low, thus creating conditions for the very close contact of reacting particles during mixing that enhances the reaction. Anhydrous Ce-nitrate and NaOH are most probably dissolved in the released water creating conditions for double cation exchange (Eq. (1)). The role of water, therefore, could be understood as to help reactants to get dissolved, enabling the double exchange of
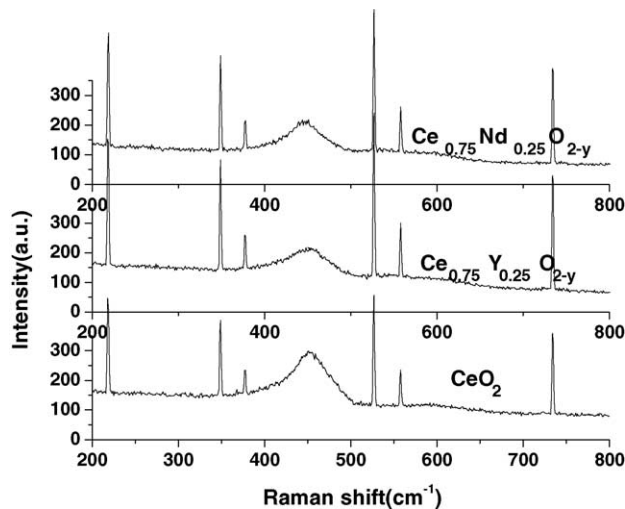
Fig. 6. Raman spectra of pure ceria and ceria doped with Y and Nd.

Fig. 7. SEM micrograph of $Ce_{0.90}Y_{0.10}O_2$.

cations in Eq. (1) to take place, and keeping close contact between reacting particles.

If we accept that the reaction studied is a solid state one, than the mechanical energy causes the breaking up of the chemical bonds of the reactants whereby the reaction product is formed in "statu nascendi". This is assisted in the presence of water, whereby we assume, that the mobility of ions during reaction may be increased in a very limited period of time. On the other hand, it is difficult to accept that the growth of formed reaction product nuclei would be remarkable at room temperature since diffusion is very slow and most likely restricted to recombination of chemical bonds [3]. In accordance with this assumption, we expect very small particles size, because high concentration of new phase nuclei are also formed during hand mixing.

3.2. Powder properties

From the results in Fig. 3 we can assume that the solid solution was formed at room temperature. It can also be seen
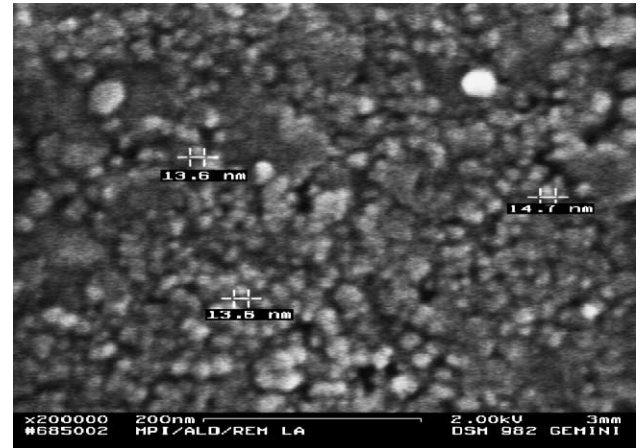
that the diffraction lines of ceria solid solution are broad. If we position the diffraction lines of yttria and neodymia in the same diagram we observe that they lay inside the broad diffraction peaks of solid solution. It turned out from these data that the above made assumption should be proved. Therefore, Raman spectroscopy was performed [6], in order to get information on the basis of which one can tell whether we are dealing with the simple mechanical mixture of two oxides or with their solid solution. In Fig. 6 Raman spectra are presented for pure as well as for doped ceria. Evident red shift and asymmetrical broadening of the main Raman mode can be ascribed to the confinement effects. This shift is larger for the Nd doped samples than for Y doped samples (due to the difference in ionic size). Because of the absence of the Raman modes of the dopant oxides, we concluded that the analyzed powders are not a simple mechanical mixture of ceria and rare earth oxides, but their solid solution of nanometric particle size.
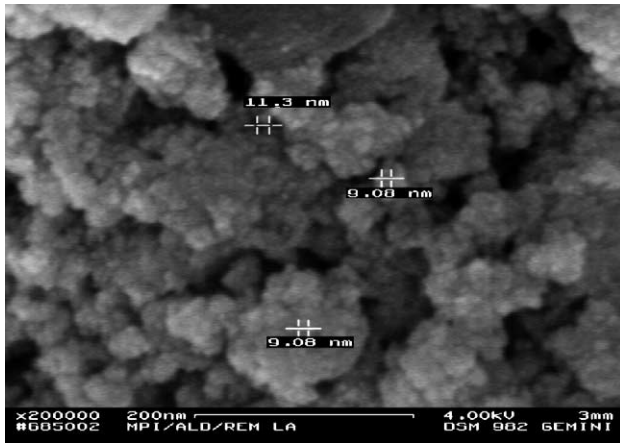
Crystallites size of as-prepared and heat-treated powders obtained by XRD are given in Table 1. Using SEM micrographs (Figs. 7 and 8) particle size is measured and also included in Table 1. SEM analysis proved that both

Table 1
Crystallites size, particles size and specific surface area of "as prepared" powders

Composition	Crystallite size (nm)		Particle size (nm)	Surf ace area ($m^2\,g^{-1}$)
	X-ray		SEM	
	a	b	a	b
CeO_2	4.2	26.7	16	106.9
$Ce_{0.90}Y_{0.10}O_2$	4.3	21.0	14	103.2
$Ce_{0.85}Y_{0.15}O_2$	4.2	20.1		137.1
$Ce_{0.80}Y_{0.20}O_2$	5.0	18.8		109.7
$Ce_{0.75}Y_{0.25}O_2$	5.6	17.9		94.0
$Ce_{0.90}Nd_{0.10}O_2$	4.4	17.0		118.4
$Ce_{0.85}Nd_{0.15}O_2$	4.4	14.8		137.6
$Ce_{0.80}Nd_{0.20}O_2$	4.2		10	141.5
$Ce_{0.75}Nd_{0.25}O_2$	4.1	13.3		99.6
$Ce_{0.80}Y_{0.10}Nd_{0.10}O_2$	4.5	15.4	12	110.0

a – As prepared powders, b – heat-treated in air, at 600 °C for 4 h.

Fig. 8. SEM micrograph of $Ce_{0.80}Nd_{0.20}O_2$.

Table 2
Lattice parameters of single and co-doped ceria

Composition	Lattice parameter (Å)
$Ce_{0.80}Y_{0.20}O_{2-y}$	5.397
$Ce_{0.80}Y_{0.10}Nd_{0.10}O_{2-y}$	5.406
$Ce_{0.80}Nd_{0.20}O_{2-y}$	5.436

Table 3
Chemical analysis of ceria doped samples

Desired composition	Concentration of Me (wt.%)	Na (wt.%)	True composition
$Ce_{0.90}Y_{0.10}O_{2-y}$	5.05 ± 0.10	0.05	$Ce_{0.904}Y_{0.096}O_{2-y}$
$Ce_{0.90}Nd_{0.10}O_{2-y}$	7.08 ± 0.07	0.07	$Ce_{0.914}Nd_{0.086}O_{2-y}$
$Ce_{0.75}Nd_{0.25}O_{2-y}$	17.6 ± 0.4	0.005	$Ce_{0.78}Nd_{0.22}O_{2-y}$
$Ce_{0.80}Y_{0.10}$	$Y = 4.45 \pm 0.09$	0.008	$Ce_{0.828}Y_{0.085}$
$Nd_{0.10}O_{2-y}$	$Nd = 7.38 \pm 0.14$		$Nd_{0.087}O_{2-y}$

$Ce_{0.90}Y_{0.10}O_{2-y}$ and $Ce_{0.80}Nd_{0.20}O_{2-y}$ powders consisted of nanoparticles of about 14 and 10 nm, respectively. The results show that very fine powders were obtained.

As we expected particle size is very small 10–14 nm, and crystallites size of powders lied between 4 and 6 nm. Accordingly, the specific surface areas are very high and among the highest published for this sort of powders (Table 1). It seems that with increasing dopant concentration the specific surface area of powders passes through maximum and attains the lowest value with highest dopants concentration both with Y and Nd. This effect needs a further study.

Lattice parameters of synthesized powders were calculated and presented as a function of dopants concentrations (Fig. 9) for powders heat-treated in air, at 600 °C for 4 h. Depending on ionic radii for Y^{3+} (0.893 Å) and Nd^{3+} (0.995 Å) in respect to Ce^{4+} (0.920 Å) lattice parameter increases or decreases with increasing concentration of dopant cations. For both series of solid solutions Vegard's law is obeyed.

Moreover, lattice parameter value of co-doped solid solution $Ce_{0.8}Y_{0.1}Nd_{0.1}O_{2-y}$ fits very well between the values of $Ce_{0.8}Y_{0.2}O_{2-y}$ and $Ce_{0.8}Nd_{0.2}O_{2-y}$ (Table 2).

As mentioned before, chemical analysis was performed to check the difference between the tailored and true compositions. The obtained results (Table 3) prove that the nominal composition can be achieved with a good precision, which is also seen from lattice parameters values in Fig. 9. In addition, if the rinsing of the powders is being performed with two more cycles in water than described in the experimental part, sodium content can be decreased by one order of magnitude.

4. Conclusion

By simple mixing of chemicals the reaction between cerium nitrate hexahydrate and sodium hydroxide was enhanced. Important condition for the development of the reaction is to enable close contact between reacting particles. The reaction proceeds via several intermediate stages due to the stepwise release of crystalline water from nitrate. The reaction steps, however, develop very fast and cannot be observed in the reacting mixture. On the basis of Rahman spectroscopy studies it was shown that the solid solutions of $Ce_{1-x}Me_xO_{2-y}$ with one and two dopants can be synthesized by SPRT. It should be emphsized that:

- the reaction starting at room temperature, is much less energy consuming in comparison with other methods of powder preparation,
- single phase nanopowders are obtained in a very short time near the room temperature,
- chemical composition can be controlled with a good precision.
- calcination step is not needed,
- simplicity of equipment is advantageousand cannot be neglected.

Fig. 9. Lattice parameter of $Ce_{1-x}M_xO_{2-y}$ solid solution vs. concentration of the dopants.

Acknowledgements

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