Synthesis and characterization of (Ba,Yb) doped ceria nanopowders

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Abstract

Nanometric size (Ba, Yb) doped ceria powders with fluorite-type structure were obtained by applying self-propagating room temperature methods. Tailored composition was: $Ce_{0.95-x}Ba_{0.05}Yb_xO_{2-\delta}$ with fixed amount of Ba − 0.05 and varying Yb content "x" from 0.05 to 0.2. Powder properties such as crystallite and particle size and lattice parameters have been studied. Röntgen diffraction analyses (XRD) were used to characterize the samples at room temperature. Also, high temperature treatment (up to 1550°C) was used to follow stability of solid solutions. The mean diameters of the nanocrystals are determined from the full width at half maxima (FWHM) of the XRD peaks. It was found that average diameter of crystallites is less than 3 nm. Williamson-Hall plots were used to separate the effect of the size and strain in the nanocrystals.

I. Introduction

Ceria (CeO_2) is very important material for many fascinating reasons. The capability of ceria to change oxidation state in relatively easy way, affects the local structure and functionality of ceria [1]. Ceria is also of great importance for its function as a solid-oxide electrolyte for electrochemical devices as well as oxygen storage capacity component in three-way heterogeneous catalysis [2]. This behaviour results from the balance between reduced and oxidized states of ions, i.e. Ce^{+3} and Ce^{+4} and from increased oxygen transport capacity. Thus, ceria is very promising material for use as an electrolyte in solid oxide fuel cell (SOFC) applications [3,4]. For comparable doping levels, the overall oxygen ionic conductivity in doped ceria is approximately an order of magnitude greater than that of stabilized zirconia [5]. The larger ionic radius of Ce^{4+} (0.97 Å) than Zr^{4+} (0.72 Å), results in much more open structure through which oxygen ions can easily migrate [6]. This allows ceria to be used as an electrolyte at moderate operating temperatures.

However, mentioned properties are strongly dependent on the structural features. Therefore for the design of ceria-based materials with high oxygen storage and trans-

port capacity, it is important to know how to increase the number of structural defects (oxygen vacancies) and at the same time to maintain a fluorite-type crystal structure. There are two possibilities to obtain ceria-based oxide as an oxygen storage component, either by promotion of Ce^{4+} reduction into Ce^{3+} or to chemically dope ceria with other transition or rare-earth elements [7,8].
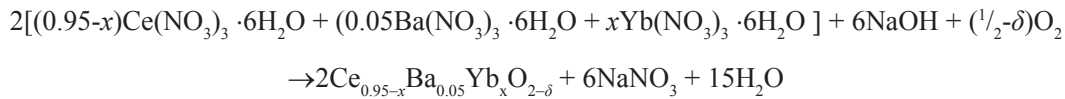
The key factor in the design of modified ceria is the choice of dopant elements, as well as their introduced amounts. In addition, the preparation method of the powder has also very strong influence on the homogeneity and stability of the solid solutions. In this work the powders were prepared by the self-propagating room temperature (SPRT) reaction [9,10].

This paper describes characterization of a number of solid solutions of (Ba, Yb) doped ceria by X-ray diffraction using the Rietveld refinement in order to study the variation of the lattice parameter with dopant content and microstructure size-strain behaviour.

II. Experimental

The solid solution of Ba and Yb doped ceria samples were synthesized by the SPRT method using nitrates of Ce, Ba and Yb (Aldrich, USA) and NaOH (p.a. Zorka, Serbia) as starting materials. The compositions of reacting mixtures were calculated according to nominal com-

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$$2[(0.95\text{-}x)Ce(NO_3)_3 \cdot 6H_2O + (0.05Ba(NO_3)_3 \cdot 6H_2O + xYb(NO_3)_3 \cdot 6H_2O] + 6NaOH + (^1/_2\text{-}\delta)O_2$$

$$\rightarrow 2Ce_{0.95-x}Ba_{0.05}Yb_xO_{2-\delta} + 6NaNO_3 + 15H_2O$$

position of the final reaction product. Compositions of $Ce_{0.95-x}Ba_{0.05}Yb_xO_{2-\delta}$ powders were synthesized with x ranging from 0.05 to 0.2. Preparation of $Ce_{0.95-x}Ba_{0.05}Yb_xO_{2-\delta}$ powders was performed according to the reaction:

The above reaction belongs to a group of double exchange reactions, which proceeds at room temperature after the mixture of reactants was mechanically activated by hand mixing in mortar for very short time. The products were centifuged in order to eliminate $NaNO_3$. After draying at 60°C in ambient atmosphere, the structures of the solid solutions were identified by means of powder X-ray diffraction (XRD) on Siemens D-5000 XRD diffractometer with CuKα radiation at room temperature. Data for structural refinement were taken afterwords in the angular range of $2\theta = 20-120°$. Before

the measurements the angular correction has been done by high quality Si standard. Williamson-Hall plots were used to separate the effect of the size and strain in the nanocrystals, using the equation:

$$\beta_{Total} \cdot \cos\theta = 0.9\lambda/D + 4\Delta d/d \cdot \sin\theta$$

where β_{Total} is the full width half maximum of the XRD peak, λ is the incident x-ray wave length, θ is the diffraction angle, D is crystallite size and Δd is the difference of the d spacing corresponding to a typical peak. By plotting $\beta_{Total} \cdot \cos\theta$ versus $\sin\theta$ it is possible to obtain D from the intercept and $\Delta d/d$ from the slope.

The phase stability of the solid solution powders was examined on heavily doped ceria (with 20 % of Yb) after pressing and annealing at 1550°C for 4 h.
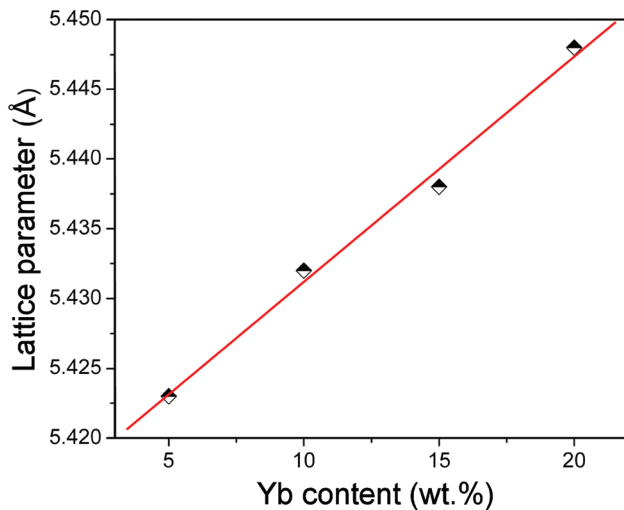
III. Results and discussion

Typical x-ray diffraction patterns for the solid solutions of (Ba, Yb) doped ceria with different dopant concentration are shown in Fig. 1. According to X-ray diffraction analysis, the obtained powders are single phase, independent of dopant concentration in the range investigated. Peaks related to isolated Ba and/or Yb - phases are not observed and all of solid solution powders exhibit the fluorite crystal structure. This high solubility may be attributed to nanometric nature of powders. XRD analysis reveals that all peaks for each sample were significantly broadened indicating small crystallite size or/and strain. Moreover, it exhibits very diffuse diffraction lines, in such way that some atomic planes are impossible to notice (hkl: 200, 222, 400, 331, 420).

Calculation of cell parameters (Fig. 2) on the basis of X-ray results, shows the linear dependence of unit cell parameter on the portion of Yb^{+3} ions, x, in at.%. According to Shannon's compilation [11], the ionic radii of Ce^{+4}, Ba^{2+} and Yb^{+3} for CN 8 (coordination number of ions) are 0.97, 1.42 and 0.985 Å, respectively. Thus, doping with much bigger Ba^{2+} ion will increase the lattice parameter of ceria. In addition, rising of the content of slightly bigger sized Yb^{+3} ions will keep on increasing cell lattice. Also, lattice parameter (a_o) of doped ceria versus fix amount of Ba^{2+} and various Yb^{3+} content, obeys Vegard's law (Fig. 2). The crystallite size, calculated on the basis of XRD data, for all powders lay below 3 nm (Table 1).

The Williamson-Hall plot for the obtained solid solutions obtained is shown in Fig. 3. The presence of slopes on the $\beta \cdot \cos\theta$ axis indicates the internal strain of nanocrystals. An increasing value of the slopes for the different additive concentration exhibits a clear contribution of strain effect. The strain is present along crystalline boundaries due to lattice mismatch. With increasing amount of Yb^{3+} ion, strain increases (Table 1).

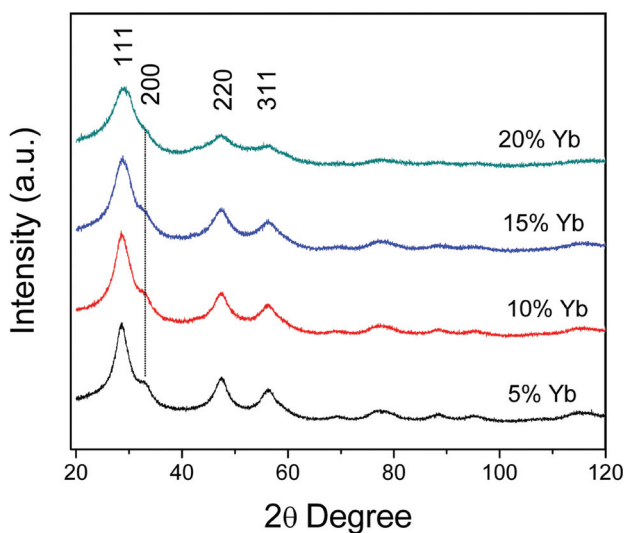**Figure 1 X-ray diffraction patterns of $Ce_{0.95-x}Ba_{0.05}Yb_xO_{2-\delta}$ powders**

Figure 2. Lattice parameter (a_o) of doped ceria as a function of Yb content in samples ($Ce_{0.95-x}Ba_{0.05}Yb_xO_{2-\delta}$)

Table 1. Unit cell parameters, crystallite size and lattice strain of $Ce_{0.95-x}Ba_{0.05}Yb_xO_{2-\delta}$

$Ce_{0.95-x}Ba_{0.05}Yb_xO_{2-\delta}$				
Content of Yb, x [at.%]	5	10	15	20
Lattice paremeter, a_0 [Å]	5.423(4)	5.432(4)	5.438(4)	5.443(4)
Crystallite size, D [nm]	2.85	2.83	2.81	2.80
Lattice strain, ε	$2.78 \cdot 10^{-3}$	$2.79 \cdot 10^{-3}$	$3.33 \cdot 10^{-3}$	$3.36 \cdot 10^{-3}$
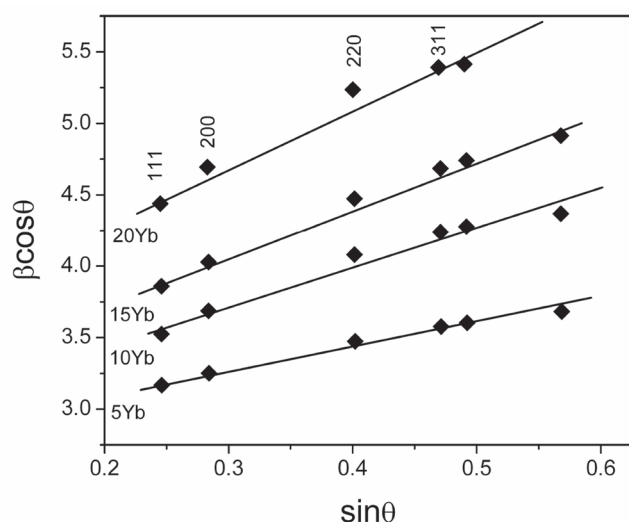
Figure 3. Williamson-Hall plot of the $Ce_{0.95-x}Ba_{0.05}Yb_xO_{2-\delta}$ powders with different Yb^{3+} content

Figure 4. XRD pattern of $Ce_{0.75}Ba_{0.05}Yb_{0.20}O_{2-\delta}$ sample heat-treated at 1550°C for 4 h

High temperature annealing of the $Ce_{0.75}Ba_{0.05}Yb_{0.2}O_{2-\delta}$ shows fluorite structure. Peaks related to isolated secondary phases are not observed (Fig. 4). In spite of being heavily doped (Ba, 5% and Yb, 20%), the solid solution is stable at high temperature.
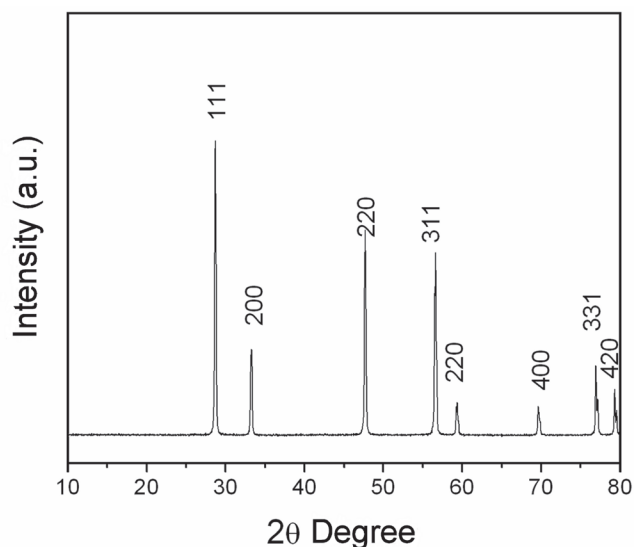
IV. Conclusions

New nanostructured $Ce_{0.95-x}Ba_{0.05}Yb_xO_{2-\delta}$ ($x=0.05-0.2$) oxides have been synthesized by self-propagating room temperature method. It was found that the particle size lies in the nanometric range, less than 3 nm. Variation of lattice parameter with increasing Yb content obeys the Vegard's law. The phase stability of solid solutions at high temperature is confirmed by heat treatment at 1550°C for 4 h.

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