

UDK 546.655:54-165

Crystal Structure Analysis of Nd-Doped Ceria Solid Solutions

**B. Matović^{1*)}, J. Dukić¹, A. Devečerski¹, S. Bošković¹, M. Ninić¹,
Z. Dohčević - Mitrović²**

¹ Materials Science Laboratory, INN Vinča, 11001 Belgrade, Serbia,

² Center for Solid State Physics and New Materials, Institute of Physics, 11080 Belgrade, Serbia

Abstract:

This paper deals with Nd-doped ceria solid solutions: $Ce_{1-x}Nd_xO_{2-\delta}$ with "x" ranging from 0 to 0.25. Six different powders were synthesized by applying the method based on self-propagating room temperature reaction (SPRT) between metallic nitrates and sodium hydroxide. The method is known to assure very precise stoichiometry of the final product in comparison with a tailored composition. Rietveld refinement was employed to get structural information on the synthesized powder. An increase of Nd ion concentration increases the unit cell parameters and average bond distances. We have shown that all obtained powders were solid solutions with a fluorite-type crystal structure and all powder particles were of nanometric size (about 3 nm).

Keywords: Ceria, Solid solution, Structural refinement, XRD.

1. Introduction

Ceria based materials have excellent oxygen storage behavior. This behavior 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 [1, 2]. For comparable doping conditions, the overall oxygen ionic conductivity in doped ceria is approximately an order of magnitude greater than that of stabilized zirconia [3]. The larger ionic radius of Ce^{4+} (0.97 Å) than Zr^{4+} (0.72 Å), results in a much more open structure through which oxygen ions can easily migrate [4]. This allows ceria to be used as an electrolyte at moderate operating temperatures.

However, the mentioned properties are strongly dependent on the structural features. Therefore for the design of ceria based materials with high oxygen storage and transport capacity it is important to know how to increase the number of structural defects (oxygen vacancies) and to maintain at the same time 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 [5].

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 a

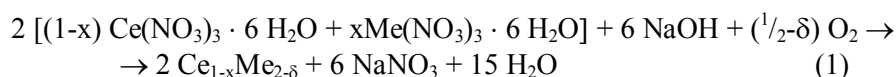
*) Corresponding author: mato@vin.bg.ac.yu

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 reaction (SPRT) [6]. This technique gives the possibility of producing very fine powders with very precise stoichiometry in accordance with the tailored compositions [7].

This paper describes in addition, characterization of a number of solid solutions of neodymium doped ceria by X-ray diffraction using Rietveld refinement in order to study the variation of the lattice parameter with Nd content and microstructure size-strain behavior.

2. Experimental

Solid solutions of neodymium doped ceria samples were synthesized by a SPRT method using nitrates of Ce and Nd (Aldrich, USA) and NaOH (p.a. Zorka, Serbia) as starting materials. The compositions of reacting mixtures were calculated according to the nominal composition of the final reaction product. Compositions of $Ce_{1-x}Nd_xO_{2-\delta}$ powders were synthesized with x ranging from 0 to 0.25. Preparation of $Ce_{1-x}Nd_xO_{2-\delta}$ powders was performed according to reaction:



The above reaction belongs to a group of double exchange reactions which proceeds at room temperature after the mixture of reactants was for a very short time, mechanically activated by hand mixing in mortar. The products were centrifuged in order to eliminate $NaNO_3$. After drying at 60°C in ambient atmosphere, the structure of the solid solutions was identified by means of X-ray powder diffraction (XRD) on a Siemens D-500 XRD diffractometer with $Cu_{K\alpha}$ radiation at room temperature. Data for structural refinement were taken in the 2θ range 20 – 100 °, with a step width of 0.025 ° and 5 s per step. The structure refinement was carried out on a Fullprof program which adopts the Rietveld calculation method. A pseudo-Voigt function was chosen as a profile function among profiles in the refinement program. Line-broadening analysis was performed using the Rietveld method in conjunction with the Warren-Averbach procedure in order to obtain the crystallite size and lattice microstrain parameters. In the present approach the grain size broadening was represented by a Lorentzian function, and microstrain broadening by a Gaussian function. The convolution of these functions is a Voigt function which is approximated by a modified Thompson-Cox-Hastings pseudo-Voigt function [8].

3. Results and discussion

The crystal structure of pure ceria is shown in Fig. 1. Ce occupies FCC lattice positions and O occupies all tetrahedral sites. Thus, around Ce^{4+} there are eight O^{2-} in the nearest neighbor shell, and 12 Ce^{4+} in the next nearest neighbor shell. After doping with Nd_2O_3 , for example, some oxygen sites change to vacancy sites and some Ce^{4+} are substituted by Nd^{3+} causing structure distortion. The most common way to clarify the structural change is X-ray Rietveld refinement. Rietveld refinement requires a structural model that has an approximation for the actual structure. The starting structural model for the cubic system was built up with crystallographic data reported by Kuemmerle and Heger [9].

According to X-ray diffraction analysis, the obtained powders are single phase, independent of dopant concentration in the range investigated. The best fit between calculated and observed X-ray diffraction pattern is shown in Fig. 2 and Fig. 3(a-d). Peaks related to

isolated Nd phases or the spurious phases are not observed. All solid solution powders exhibit the fluorite crystal structure. The dissolution of Nd_2O_3 in a cubic fluorite lattice causes shifting of ceria peaks toward lower angles indicating the existence of a solid solution (Fig. 4). This behavior coincides with changes of lattice constant, a_o (Tab. I). Namely, replacement of smaller Ce^{4+} ions with larger Nd^{3+} ions (the ionic radii of Ce^{4+} and Nd^{3+} are 0.97 and 1.1053 Å [10]) leads to the cubic ceria lattice expansion [11].

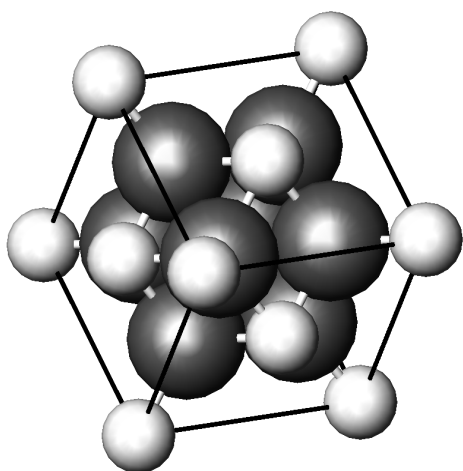


Fig. 1 Crystal structure of pure ceria. White (gray) spheres denote Ce (O) ions.

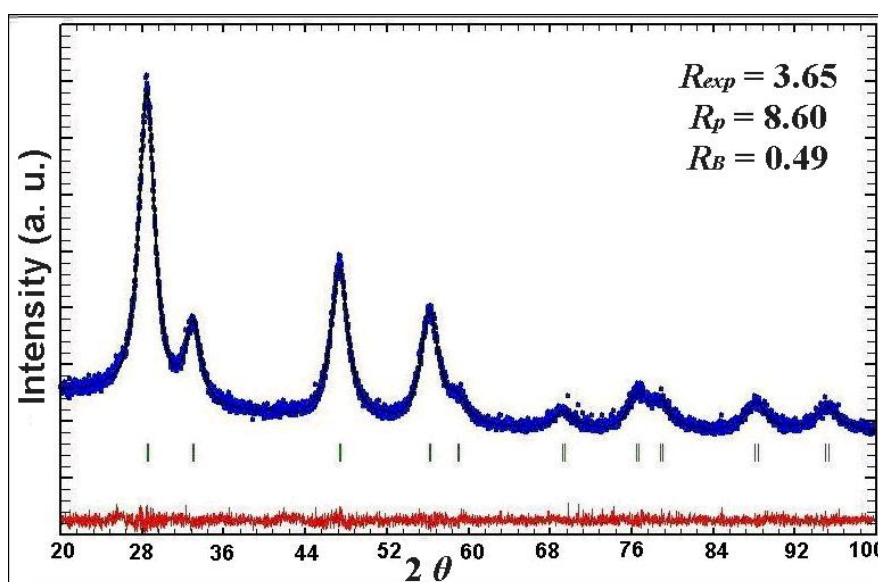


Fig. 2 The structural refinement patterns of pure CeO_2 using X-ray powder diffraction data based on the cubic phase. A difference (observed - calculated) plot is shown beneath. Tick marks above the difference data indicate the reflection position.

The change of lattice constant, a_o , is also followed by average $\langle\text{Ce-O}\rangle$ bond distance change (Tab. I). The $\langle\text{Ce-O}\rangle$ bond distance in undoped CeO_2 is 2.3483 Å, whereas in doped samples the bond distance increases with dopant concentration increase. In addition, all obtained powders show that crystallite sizes are in nanometric range, about 3 nm.

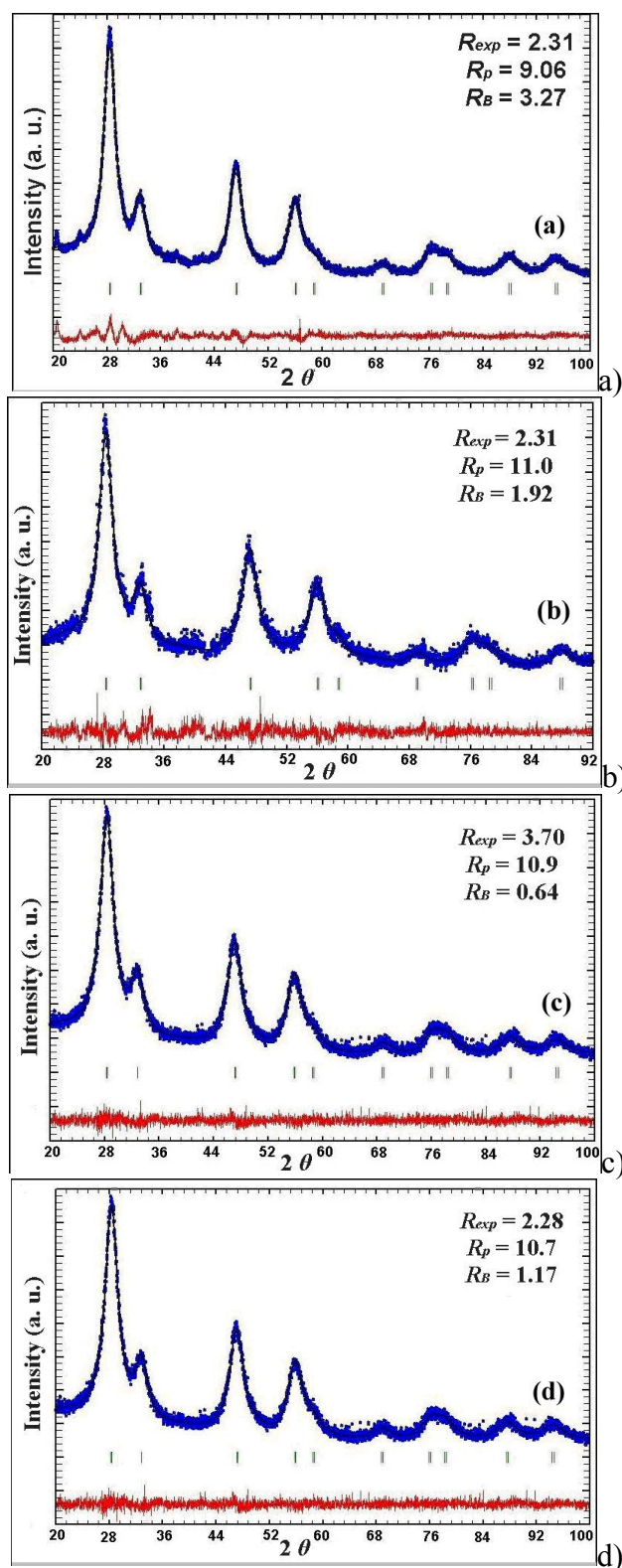


Fig. 3 The structural refinement patterns of (a) $\text{Ce}_{0.9}\text{Nd}_{0.1}\text{O}_{2-\delta}$, (b) $\text{Ce}_{0.85}\text{Nd}_{0.15}\text{O}_{2-\delta}$ (c) $\text{Ce}_{0.8}\text{Nd}_{0.2}\text{O}_{2-\delta}$ and (d) $\text{Ce}_{0.75}\text{Nd}_{0.25}\text{O}_{2-\delta}$ samples using X-ray powder diffraction data based on the cubic phase. A difference (observed - calculated) plot is shown beneath. Tick marks above the difference data indicate the reflection position.

The results obtained for the Ce ion occupation factor show that there is very good agreement between experimental and calculated values. For the $\text{Ce}_{0.75}\text{Nd}_{0.25}\text{O}_{2-\delta}$ solid solution, there is a 4% of discrepancy. It can be attributed to changes in the anion vacancy radius or to a decrease in the cation coordination number [12] which influences the correctness of the fit that might be responsible for the observed deviation.

Tab. I Crystallographic data and the results of Rietveld refinement for $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-\delta}$ nanopowders.

Sample	a_0 (Å)	Ce–O (Å)	Occupation factor (%)	Crystallite size (Å)
CeO_2	5.423(3)	2.3483	100	32.91(2)
$\text{Ce}_{0.9}\text{Nd}_{0.1}\text{O}_{2-\delta}$	5.434(3)	2.3531	90	39.45(1)
$\text{Ce}_{0.85}\text{Nd}_{0.15}\text{O}_{2-\delta}$	5.4413(6)	2.3561	85.1	28.17(2)
$\text{Ce}_{0.8}\text{Nd}_{0.2}\text{O}_{2-\delta}$	5.4518(5)	2.3607	81.2	26.89(1)
$\text{Ce}_{0.75}\text{Nd}_{0.25}\text{O}_{2-\delta}$	5.4531(3)	2.3613	71.2	30.63(1)

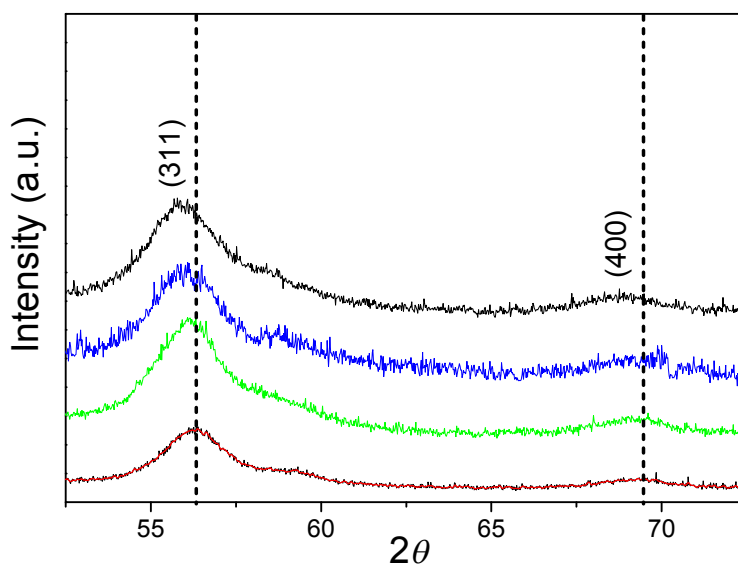


Fig. 4 Part of X-ray diffraction patterns of $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-\delta}$ nanopowders. Shifting of the peaks toward lower angles with increasing dopant concentration is clearly visible.

4. Conclusions

Nd-doped ceria solid solutions ($\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-\delta}$) with "x" ranging from 0 to 0.25 were prepared by the self-propagating room temperature reaction. The Rietveld refinement showed that the obtained powders exhibit a precise stoichiometry compared to the tailored composition. It was found that the crystallite size lies in the nanometric range (3 nm). The calculated and measured lattice parameters and average bond distances increase with higher dopant concentration.

Acknowledgement

This paper has been financially supported by the Ministry of Science of the Republic of Serbia, as a part of project No. 142003.

References

1. H. Inaba, H. Tagawa, Solid State Ionics, 83 (1996) 1.
2. N. Q. Minh, J. Am.Ceram.Soc., 76 (1993) 563.
3. B.C.H. Steele, Solid State Ionics, 129 (2000) 95.
4. S. M. Haile, Acta Materialia, 51 (2003) 5981.
5. M. Mogenson, N. M. Sammes, G. A. Tompsett, Solid State Ionics, 129 (2000) 63.
6. H. Yu, F. Li, X. Ye, X. Xin, Y. Hue, J.Am.Ceram.Soc., 83 (2000) 964.
7. Z. D. Dohčević-Mitrović, M. J. Šćepanović, M. U. Grujić-Brojčin, Z. V. Popović, S. B. Bošković, B. Z. Matović, M. V. Zinkevich, F. Aldinger, Solid State Comm., 137 (2006) 387.
8. R. A. Young, in: "IUCr Monographs on Crystallography", Oxford, UK 1996, Vol.5, p.132-166.
9. E. A. Kuemmerle, G. Heger, J.Solid State Chem., 147 (1999) 485.
10. A. Shannon, Acta Crystallogr., A32 (1976) 751.
11. B. Matović, S. Bošković, Lj. Živković, M. Vlajić, V. Krstić, Mater.Sci.Forum, 494 (2005) 175.
12. M. Yashima, N. Ishizawa, M. Yoshimura, J.Am.Ceram.Soc., 75 (1992) 1541.

Садржај: У овом раду разматрани су чврсти раствори церијум оксида допираног са Nd, $Ce_{1-x}Nd_xO_2$, (x од 0 до 0,25). Шест различитих прахова синтетизовано је применом методе која се заснива на самопропагирајућој реакцији на собној температури (SPRT) између металних нитрита и натријум-хидроксида. Метод је познат по томе што обезбеђује веома прецизну стехиометрију коначних продуката предвиђене композиције. Ритвалдова метода утачњавања употребљена је да би се добиле структурне информације о синтетизованим праховима. Повећање концентрације Nd јона доводи до повећања параметра јединичне ћелије и средњег растојања веза. Показали смо да су сви добијени прахови чврсти раствори флуоритне структуре и да су честице прахова нанометарских величина (око 3 nm).

Кључне речи: Церијум, чврсти раствор, структурно утачњавање, XRD.
