



# Lattice thermal expansion and solubility limits of neodymium-doped ceria



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## ABSTRACT

$\text{Nd}_x\text{Ce}_{1-x}\text{O}_{2-0.5x}$  ( $x=0-1.0$ ) powders were prepared by reverse coprecipitation-calcination method and characterized by XRD. The crystal structure of product powders transformed from single fluorite structure to the complex of fluorite and C-type cubic structure, and finally to trigonal structure with the increase of  $x$ -value. An empirical equation simulating the lattice parameter of neodymium doped ceria was established based on the experimental data. The lattice parameters of the fluorite structure solid solutions increased with extensive adoption of  $\text{Nd}^{3+}$ , and the heating temperature going up. The average thermal expansion coefficients of neodymium doped ceria with fluorite structure are higher than  $13.5 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$  from room temperature to  $1200 \text{ } ^\circ\text{C}$ .

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## 1. Introduction

The oxygen ionic conductivity and diffusivity of  $\text{CeO}_2$  will be significantly improved by aliovalent rare earth ions ( $\text{Ln}^{3+}$ ) doping due to the creation of oxygen vacancies in the anion sub-lattice as charge compensating defects [1–4]. The catalytic performances of the solid solutions, such as the activity, selectivity and thermal stability of catalysts will be improved [5–8]. Fluorite-type ceria-based solid solution materials have attracted much attention due to their wide variety of applications in solid oxide fuel cells, gas sensors, oxygen separation membranes, and catalysts and catalytic support in automotive exhaust systems [9–13].

In the above-mentioned applications, the materials usually consist of several parts. For example, the solid oxide fuel cells are composed of an anode, a cathode, a solid electrolyte and interconnector. The composition materials at the interface need nearly the same thermal expansion coefficients, in case of mismatch among them during heating and cooling cycles. Therefore, thermal properties of doped ceria are very important for its application. Many studies focusing on the thermal expansion of the doped ceria have been reported, but a systematic study on the lattice thermal expansion of neodymium doped ceria is seldom reported [14–19].

In the present work, effects of neodymia on the solubility limits

and lattice thermal expansion of the neodymium-doped ceria were investigated, lattice parameters of neodymium-doped ceria at different temperature were measured and the lattice thermal expansion properties were discussed as well.

## 2. Experimental

### 2.1. Sample preparation

In this study, neodymium oxide ( $\text{Nd}_2\text{O}_3$ ) and cerium nitrate hexahydrate ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ) were chosen as starting materials.  $\text{Nd}_x\text{Ce}_{1-x}\text{O}_{2-0.5x}$  were prepared by reverse coprecipitation-calcination method. Neodymium oxide and cerium nitrate hexahydrate were first dissolved in hydrogen nitrate and distilled water respectively, these solutions were then mixed in appropriate proportions and stirred for 30 min for preparation of  $\text{Nd}_x\text{Ce}_{1-x}\text{O}_{2-0.5x}$  ( $x=0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0$ ) ceramic powders. The precursor solution was slowly added to ammonia solution and stirred continuously with pH 10 or so to obtain gel-like precipitates. And then the product was centrifugated and washed with distilled water, finally washed by absolute ethyl alcohol twice. The precursor powders were obtained by oven-drying the precipitates at  $105 \text{ } ^\circ\text{C}$  for 12 h, and then calcined at  $1300 \text{ } ^\circ\text{C}$  for 3 h.

### 2.2. X-ray diffraction

X-ray diffraction (XRD) data collection was performed with a

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Philips X'Pert PRO diffraction with Ni filtered Cu K $\alpha$  radiation ( $\lambda=0.15418$  nm). For the solubility study, the XRD patterns of samples were recorded from  $2\theta=10\text{--}120^\circ$  at room temperature. For lattice thermal expansion studies, the XRD patterns of samples were recorded from  $2\theta=15\text{--}90^\circ$ , in the temperature range of 25–1200 °C on a Philips X'Pert PRO unit equipped with Anton Paar HTK attachment with Pt sample holder at the vacuum(6.3 Pa). The temperature was controlled by a PID-type temperature controller unit during the XRD measurements. The samples were heated at the rate of 10 °C /min and equilibrated for 2 min at each temperature before measuring. The lattice parameters were refined by a least squares method [20].

### 3. Results and discussion

#### 3.1. Crystal structure

The XRD patterns of the  $\text{Nd}_x\text{Ce}_{1-x}\text{O}_{2-0.5x}$  products were shown in Fig. 1. The results show that:

- (1) When  $0 \leq x \leq 0.4$ ,  $\text{Nd}_x\text{Ce}_{1-x}\text{O}_{2-0.5x}$  products have fluorite type structure (space group Fm-3m (225)), which consist with the X-ray diffraction data of  $\text{CeO}_2$ (PDF 89-8436) [21]. The X-ray diffraction peaks shifted gradually to lower angles with increase of  $x$ -value, which means that  $d_{hkl}$  and the lattice parameter increased with extensive adoption of  $\text{Nd}^{3+}$ . In a perfect fluorite structure, the coordination numbers (CN) of rare-earth ions and oxygen ions were 8 and 4 respectively. Even though the octahedral packing of oxygen ions with respect to cerium ions did not yield the ideal ionic radii ratio, ( $r_{\text{Ce}^{4+}}/r_{\text{O}^{2-}}=0.097/0.138 \approx 0.703 < \text{ideal ratio}=0.732$ ), it is known that the fluorite structure is stable and can dissolve a high concentration of an aliovalent dopant [3].
- (2) As  $x$ -value reached to 0.5, a series weak peaks mismatched with the  $\text{CeO}_2$  and well matched with C-type cubic  $\text{Nd}_2\text{O}_3$  (space group Ia-3(206), PDF 65-3184) [22] were observed. The C-type cubic structure (space group Ia-3) of rare earth oxide was characterized by the presence of typical peaks different with fluorite structure at  $2\theta \approx 19.7^\circ(2\ 1\ 1)$ ,  $34.5^\circ(4\ 1\ 1)$ ,  $38.3^\circ(3\ 3\ 2)$ ,  $41.8^\circ(1\ 3\ 4)$  (using Cu K $\alpha$  as radiation source). These peaks could help us to distinguish the fluorite and C-type structures. Goswami et al. [23] investigated the structure and lattice parameters of Nd-doped ceria synthesized by solid state reaction. In their research,  $\text{Nd}_x\text{Ce}_{1-x}\text{O}_{2-0.5x}$  have fluorite

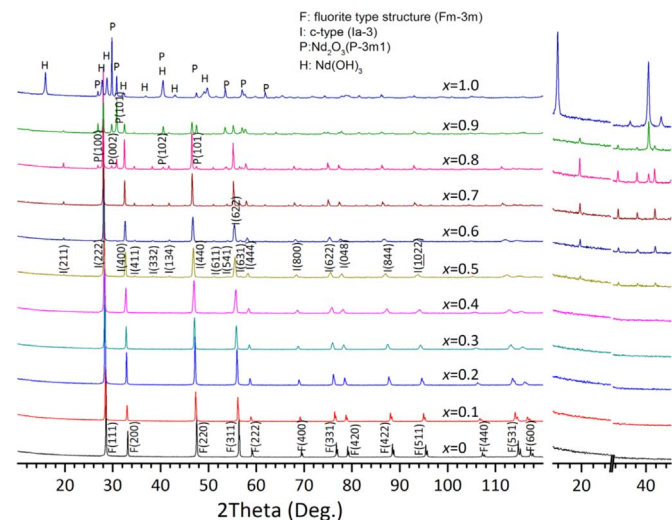


Fig. 1. The XRD patterns of the  $\text{Nd}_x\text{Ce}_{1-x}\text{O}_{2-0.5x}$  products.

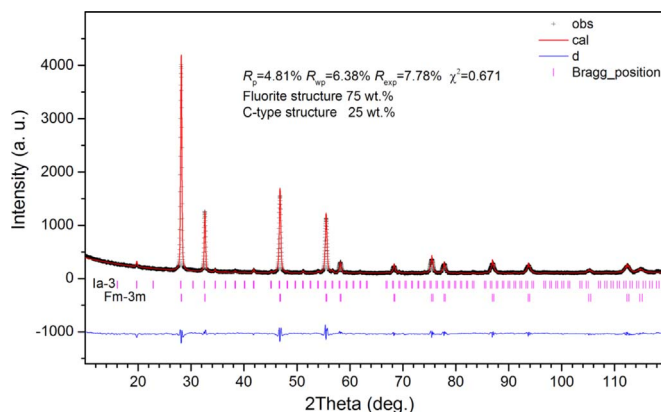
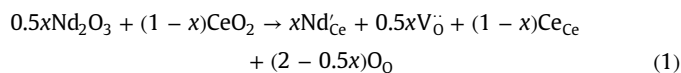


Fig. 2. The Rietveld refinement of X-ray powder diffraction pattern of the  $\text{Nd}_{0.5}\text{Ce}_{0.5}\text{O}_{1.75}$  sample.

- type structure when  $0 \leq x \leq 0.5$ ; when  $0.5 < x \leq 0.675$ , the fluorite type structure transformed to C-type cubic structure, both are accompanied with increase of lattice parameters when  $x$ -value increasing. Comparing the XRD patterns of  $\text{CeO}_2$  (PDF 89-8436) with  $\text{Nd}_2\text{O}_3$  (PDF 65-3184), it is obvious that the  $d_{(hkl)}$  of  $\text{CeO}_2$  equaled the  $d_{(HKL)}$  of  $\text{Nd}_2\text{O}_3$ , while  $H=2h$ ,  $K=2k$  and  $L=2l$ . In fact, it is difficult to determine whether fluorite type structure solid solutions were presented if the sample contained the C-type solid solutions. To exactly identify the phase composition, the Rietveld refinement of X-ray powder diffraction pattern was performed using FULLPROF program [24,25]. The refined results of  $\text{Nd}_{0.5}\text{Ce}_{0.5}\text{O}_{1.75}$  sample was shown in Fig. 2. The results demonstrated that the sample contained both fluorite type structure phase and C-type structure phase. The content of fluorite type structure phase is about 75 wt%. With the increasing of  $x$ -value, the content of fluorite type structure phase is decreased. The content of fluorite type structure phase is about 64 wt% with  $x$ -value increasing to 0.6, and 54 wt% with  $x$ -value increasing to 0.7 respectively.
- (3) As  $x$ -value increased to 0.8, a new phase was observed. The typical peaks at  $2\theta \approx 26.9^\circ(1\ 0\ 0)$ ,  $29.8^\circ(0\ 0\ 2)$ ,  $30.8^\circ(1\ 0\ 1)$  were consistent with trigonal  $\text{Nd}_2\text{O}_3$  (space group P-3m1(164), PDF 75-2255) [26]. The content of trigonal phase increased with  $x$ -value increasing. Both the C-type structure phase and fluorite structure phase were not observed when  $x$ -value up to 1.0.

#### 3.2. Lattice parameters

It is known that the following defect reaction predominate over the formation of a solid solution, when neodymium oxides were introduced in ceria:



The reaction implied that when  $0.5x$  moles of  $\text{Nd}_2\text{O}_3$  were added,  $\text{Ce}^{4+}$  sites were filled with  $x$  moles of dopant cations  $\text{Nd}^{3+}$  and the left host cations  $\text{Ce}^{4+}$  were  $1-x$  moles,  $\text{O}^{2-}$  sites were occupied by  $0.5x$  moles of oxygen vacancies and  $2-0.5x$  moles of host anions  $\text{O}^{2-}$ .

The theoretical lattice parameters of the rare earth-doped ceria with fluorite structure was given by the Eq. (2) reported by Hong et al. [3].

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