Structure and phase stability of nanocrystalline $\text{Ce}_{1-x}\text{Ln}_x\text{O}_{2-x/2-\delta}$ (Ln = Yb, Lu) in oxidizing and reducing atmosphere

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Abstract The structure and phase evolution of nanocrystalline $\text{Ce}_{1-x}\text{Ln}_x\text{O}_{2-x/2-\delta}$ (Ln = Yb, Lu, $x = 0 - 1$) oxides upon heating in H_2 was studied for the first time. Up to 950 °C the samples were single-phase, with structure changing smoothly with x from fluorite type (F) to bixbyite type (C). For the Lu-doped samples heated at 1100 °C in the air and H_2 , phase separation into coexisting F- and C-type structures was observed for $\sim 0.40 < x < \sim 0.70$ and $\sim 0.25 < x < \sim 0.70$, respectively. It was found also that addition of Lu^{3+} and Yb^{3+} strongly hinders the crystallite growth of ceria during heat treatment at 800 and 950 °C in both atmospheres. Valency of Ce and Yb in $\text{Ce}_{0.1}\text{Lu}_{0.9}\text{O}_{1.55-\delta}$ and $\text{Ce}_{0.95}\text{Yb}_{0.05}\text{O}_{1.975-\delta}$ samples heated at 1100 °C was studied by XANES and magnetic measurements. In the former Ce was dominated by Ce^{4+} , with small contribution of Ce^{3+} after heating in H_2 . In the latter, Yb existed exclusively as $3+$ in both O_2 and H_2 .

Keywords Nanocrystalline ceria based oxide · $\text{CeO}_2\text{--Lu}_2\text{O}_3$ · $\text{CeO}_2\text{--Yb}_2\text{O}_3$ · Crystallite growth · Hydrogen · TEM · XANES · EBSD · Magnetic susceptibility

Introduction

The structure stability of ceria-based mixed oxides ($\text{Ce}_{1-x}\text{Ln}_x\text{O}_{2-x/2-\delta}$, $x = \text{Ln}/(\text{Ce} + \text{Ln})$) containing lanthanide ions is an important issue because possible phase separation at high temperatures often limits potential applications of such systems. Existing data are, however, scarce and obtained mostly for samples prepared by solid-state reaction between polycrystalline oxides at high temperature (~ 1400 °C) in an oxidizing atmosphere. Phase separation in ceria doped with heavy lanthanides-ions (Er^{3+} , Yb^{3+} and Lu^{3+}) but only for $x = 0.5$ was reported by Chavan et al. 2005. More complete data exist for similar $\text{CeO}_2\text{--Y}_2\text{O}_3$ system (Wallenberg et al. 1989; Longo and Podda 1981), where phase separation into two phases—Ce-rich oxide and Y-rich oxide—was observed over a wide composition range. The range of two phase region was strongly dependent on the heating temperature (Longo and Podda 1981).

For $\text{CeO}_2\text{--Lu}_2\text{O}_3$ (Yb_2O_3) mixed oxide system, two structure types (F-type and C-type) are expected. CeO_2 has a fluorite structure (F-type) described in $Fm\bar{3}m$ (225) space group and may exist over a wide range of oxygen deficiency as $\text{CeO}_{2-\delta}$ ($0 < \delta < 0.5$) or more

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precisely as $\text{Ce}_{1-z}\text{Ce}_z^{\text{IV}}\text{Ce}_z^{\text{III}}\text{O}_{2-z/2}$ (Adachi and Imanaka 1998). Ln_2O_3 has a bixbyite structure (C-type) described in *Ia-3* (206) space group. Cation arrays in both structures are very similar and a unit cell of C-type structure can be build from eight F-type unit cells with simultaneous removing 25% oxygen ions (Wallenberg et al. 1989; Ou et al. 2006). In ceria-based mixed oxides, apart from above-mentioned F, and C- structures intermediate structures may be formed due to oxygen vacancy ordering. The vacancies can be arranged to form a superstructure (Ou et al. 2006) or a modulated (commensurately) F-type $\text{Ce}_{1-x}\text{Ln}_x\text{O}_{2-x/2-\delta}$ structure (Wallenberg et al. 1989).

Catalytic activity of ceria-based systems is due to their ability to partially change oxidation state from Ce^{4+} to Ce^{3+} during reaction ($\text{Ce}^{\text{IV}}\text{O}_2$ to $\text{Ce}_{1-z}^{\text{IV}}\text{Ce}_z^{\text{III}}\text{O}_{2-z/2}$) (Aneggi et al. 2006). This process can be modified by partial substitution of Ce^{+4} with Ln^{+3} , which facilitates a bulk reduction of ceria (Rossignol et al. 2003; Sasikala et al. 2001). The improved reducibility is due to creation of extrinsic oxygen vacancies in the lattice, which enhances the oxygen anion mobility (Sasikala et al. 2001).

Important characteristic of nano-sized ceria for practical applications is particle size and structure stability at high temperatures. Additives such as lanthanide Ln^{3+} ions are known to hinder strongly crystallite growth of ceria during heating in oxidizing atmosphere. The inhibiting effect is explained by additive segregation at the ceria grain boundaries (Luo et al. 2006; Małecka et al. 2007).

In this work, the structure and texture properties of nanocrystalline $\text{Ce}_{1-x}\text{Lu}_x\text{O}_{2-x/2-\delta}$ and $\text{Ce}_{1-x}\text{Yb}_x\text{O}_{2-x/2-\delta}$ were studied over the whole composition range ($0 < x < 1$) at various temperatures (up to 1100 °C) and atmospheres (O_2 and H_2). Samples subjected to various treatments were thoroughly characterized by powder X-ray Diffraction (XRD) and Transmission Electron Microscopy (TEM). Additionally, selected samples were characterized by Electron Backscatter Diffraction (EBSD), X-ray absorption spectroscopy (XAS), and magnetic susceptibility measurements.

Materials and methods

Nanoparticles of mixed $\text{Ce}_{1-x}\text{Lu}_x\text{O}_{2-x/2-\delta}$ and $\text{Ce}_{1-x}\text{Yb}_x\text{O}_{2-x/2-\delta}$ oxides were prepared by precipitation using the water-in-oil (W/O) microemulsion

technique described previously (Małecka et al. 2007; Małecka and Kępiński 2007). The powder samples were dried and then preheated in oxygen flow at 500 °C for 3 h, before calcining in oxygen or hydrogen at 800 or 950 °C for 3 h, or in static air or hydrogen at 1100 °C for 45 h and 3 h, respectively.

True Ln-content in $\text{Ce}_{1-x}\text{Ln}_x\text{O}_{2-x/2-\delta}$ samples ($\text{Ln} = \text{Lu}, \text{Yb}$), measured with Energy Dispersive Spectroscopy (EDAX PV 9800 spectrometer), appeared to agree within ± 0.02 with nominal content corresponding to $x = 0.05\text{--}0.90$.

Morphology and microstructure of the oxides were investigated by TEM and EBSD. Analysis of TEM images, acquired with Philips CM-20 SuperTwin operating at 200 kV and providing 0.25 nm resolution, was made with ImageJ program (Rasband 1997). The EBSD patterns were acquired using the Nordlys S detector mounted on a Zeiss Supra 55 VP FEG-SEM. Analysis of EBSD patterns, including phase identification and generation of orientation maps was performed with Channel5 System (Oxford Instruments HKL A/S). The phase composition and lattice parameters were determined by XRD (STOE, monochromatized $\text{CuK}_{\alpha 1}$ radiation) with WinPLOTR program (Roisnel and Rodriguez-Carvajal 2000) used for display and analysis. Mean crystallite size and average maximum strain were calculated from XRD patterns with the profile fitting routine of the WinPLOTR software (Roisnel and Rodriguez-Carvajal 2000). Instrumental resolution function was calculated from XRD data recorded for Si standard sample.

Valence of additive and host lanthanide ions was determined using XAS (X-ray absorption spectroscopy) and magnetic susceptibility measurements. XAS near the Ce L3 edge was performed at different temperatures between 4 K and 300 K at the EXAFS beamline A1 of the Hamburg Synchrotron laboratory (Hasylab at Desy). Absorption spectra near the Yb L3 edge were collected at EXAFS beamline E4 at Hasylab. Magnetic measurements were carried out in the temperature range 1.71–400 K and in external magnetic fields up to 5 T using a commercial SQUID magnetometer (Quantum Design MPMS-5 type).

Results and discussion

As-synthesized $\text{Ce}_{1-x}\text{Ln}_x\text{O}_{2-x/2-\delta}$ ($\text{Ln} = \text{Yb}, \text{Lu}$; $0 < x < 1$) contains small (~ 4 nm) crystalline

particles with narrow size distribution, similar to that observed in other ceria-based oxides (Małacka et al. 2007; Małacka et al. 2008b). Chemical formula with undetermined “ δ ” factor was used, instead of stoichiometric $\text{Ce}_{1-x}\text{Lu}_x\text{O}_{2-x/2}$, because a fraction of Ce ions at the surface of particles may exist as Ce^{+3} even in non-reducing conditions (Kimmel et al. 2006). The $\text{Ce}^{3+}/\text{Ce}^{4+}$ ratio may be close to 1 for very small particles (<2 nm), but decreases to ~ 0.01 for larger ones (>15 nm) (Bae et al. 2004). The latter estimation may not be valid for the samples heated in hydrogen where bulk reduction of Ce (Rossignol et al. 2003; Kępiński et al. 1995) as well as Ln-ions (e.g., Yb (Kaczmarek et al. 2005)) can occur.

Thermal evolution of the microstructure of $\text{Ce}_{1-x}\text{Lu}_x\text{O}_{2-x/2-\delta}$ samples heated up to 1100 °C in oxidizing atmosphere was described in our previous paper (Małacka et al. 2008a).

XRD, TEM, and EBSD

XRD patterns of the samples heated at 800 °C and 950 °C in O_2 or H_2 for 3 h were similar and revealed a continuous transformation of the structure from fluorite (*Fmm*) (F-type) to bixbyite (*Ia-3*) (C-type). Figure 1A shows as an example XRD patterns of $\text{Ce}_{1-x}\text{Lu}_x\text{O}_{2-x/2-\delta}$ heated in H_2 at 950 °C. F–C phase change, monitored as appearance of a weak (112) peak characteristic for C-type structure at $2\theta \sim 20^\circ$, occurred in this samples at $x = \sim 0.5$, i.e., at lower Lu content than in oxygen ($x = \sim 0.6$) (Małacka et al. 2008a). This shift is due to lowered stability of highly doped fluorite lattice under reducing conditions (see below). For $\text{Ce}_{1-x}\text{Yb}_x\text{O}_{2-x/2-\delta}$, F–C transformation occurred at $x = \sim 0.5$ in both atmospheres. The XRD patterns of pure CeO_2 , Lu_2O_3 , and Yb_2O_3 fitted well the reference data: ICDD PDF Nr. 00-034-0394, 00-012-0728 and 04-001-2438, respectively. Addition of Lu and Yb decreased the cell parameter of parent cubic CeO_2 over the whole x range (for bixbyite type structure half of the cell parameter was taken), as expected from the effective ionic radii ($\text{Ce}^{4+} = 0.0870$ nm, $\text{Lu}^{3+} = 0.0861$ nm, $\text{Yb}^{3+} = 0.0868$ nm,—for coordination VI (Shannon 1976)) (Fig. 1B, C) and the fact that oxygen vacancies were formed in the ceria lattice upon $\text{Ce}^{4+}\text{—Ln}^{+3}$ substitution (one vacancy for two ions substituted). The formation of oxygen vacancies is necessary to ensure the electrical neutrality of the oxide. Hong and

Virkar (1995), introduced a concept of an oxide vacancy radius, and the estimated oxygen vacancy radius was 0.1164 nm for trivalent, rare-earth oxide doped ceria, significantly less than the radius of O^{2-} ion (0.1400 nm Shannon 1976). For both dopants, deviations from Vegard’s rule were observed. In $\text{Ce}_{1-x}\text{Lu}_x\text{O}_{2-x/2-\delta}$, the change of cell parameter with Lu content is slow and linear for $x < \sim 0.35$, but then the slope becomes steeper. This observation agrees well with dependence of the cell parameter on composition reported by Kimmel et al. 2006 at similar temperature and time of heating (900 °C/3 h) for Y-doped ceria. The authors assigned the deviations from linearity to coalescence of oxygen vacancies, which grows up with increasing dopant content (Bae et al. 2004). For $x > \sim 0.5$, where C-type structure occurs, the slope is higher again because bixbyite structure is less prone to doping with aliovalent ions. $\text{Lu}^{3+} \rightarrow \text{Ce}^{4+}$ substitution requires introduction of large O^{2-} ion into interstitial position, causing the lattice expansion. For $\text{Ce}_{1-x}\text{Yb}_x\text{O}_{2-x/2-\delta}$, only one inflection point at $x \sim 0.5$ was observed in both atmospheres (Fig. 1C). The change in the slope of the plots is correlated with the F $\rightarrow$ C transformation of the structure.

Mean crystallite size and average maximum strain for the mixed oxides were calculated from XRD patterns with the profile fitting procedure (Roisnel and Rodriguez-Carvajal 2000). Results obtained for $\text{Ce}_{1-x}\text{Lu}_x\text{O}_{2-x/2-\delta}$ and $\text{Ce}_{1-x}\text{Yb}_x\text{O}_{2-x/2-\delta}$ heated at 950 °C in O_2 and H_2 are presented in Fig. 2A and B, respectively. Figure 2 also contains volume weighted mean crystallite sizes ($\sum n_i d_i^4 / \sum n_i d_i^3$) calculated for the same samples from TEM images. The volume weighted mean was used instead of simple arithmetic mean to make it comparable with the mean crystallite sizes calculated from XRD data (Matyi et al. 1987). It appears that there is qualitative agreement between both sets of mean crystallite size data, indicating that there is no additional broadening XRD reflections due to contingent phase separation. For both mixed oxides strong dependence of crystallite size on Ln content (x) was found, which to some extent was affected by the heating atmosphere. In O_2 even small Ln addition ($x \leq 0.1$) caused very strong inhibiting effect on crystallite growth, which saturated for $x > 0.3$. In samples heated in H_2 , the mean crystallite sizes were bigger for small dopings but then became smaller for $x > 0.3$. The behavior

Fig. 1 XRD patterns for $\text{Ce}_{1-x}\text{Lu}_x\text{O}_{2-x/2-\delta}$ (A) and cell parameters for $\text{Ce}_{1-x}\text{Lu}_x\text{O}_{2-x/2-\delta}$ (B) and $\text{Ce}_{1-x}\text{Yb}_x\text{O}_{2-x/2-\delta}$ (C) heated at 950 °C for 3 h in (○) O_2 and (●) H_2 . Data marked as (○) for $\text{Ce}_{1-x}\text{Lu}_x\text{O}_{2-x/2-\delta}$ are taken from Małecka et al. 2008a

observed in Fig. 2 agrees well with literature data for similar $\text{CeO}_2\text{--Ln}_2\text{O}_3$ systems heated in oxidizing atmosphere (Luo et al. 2006; Małecka et al. 2007). The possible explanation of the strong inhibiting effect of Ln addition on the crystallite growth could be segregation of the dopant ions at the surface of ceria crystallites reported for La (Belliere et al. 2006)

and Pr (Luo et al. 2006) doped ceria. Data on crystallite growth in ceria-based nanocrystalline oxides heated in a reducing atmosphere are scarce. For $\text{Ce}_{1-x}\text{Zr}_x\text{O}_{2-\delta}$ strong inhibiting effect of Zr on ceria sintering, similar to that in oxygen was reported (Zhang et al. 2006).

Observed relation between the mean crystallite size and Ln content correlated well with the data describing the average maximum strain (Fig. 2). For Ln content $x < 0.3$, the strain was bigger in the samples heated in O_2 than in H_2 but for higher x the opposite was true. Higher strain in low doped samples heated in O_2 may be related to the presence of thicker segregated layer enriched in Ln^{3+} ions. Further steep increase of strain with Ln content in the samples heated in H_2 is caused by creation of additional oxygen vacancies due to $\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$ reduction. At $x \cong 0.5$ the transformation to C-type structure stops this process. It is seen, however, that for very high Ln content (Ln_2O_3 doped with Ce) the strain increases very steeply with doping. It indicates that C-type bixbyite lattice is much less prone to doping with aliovalent ions than fluorite lattice.

Extensive crystal growth was observed for all samples heated at 1100 °C in reducing and oxidizing atmosphere, irrespective of additive content. Due to limitations of experimental methods applied, we could not precisely quantify differences in crystallite size. Estimations by XRD performed for selected samples (where no phase separation occurred) confirmed the tendency seen in Fig. 2 that Lu or Yb addition decreases the mean crystallite size. Moreover, for high Ln dopant content mean crystallite size after treatment in H_2 was smaller than after treatment in air. This observation has been confirmed by EBSD (see below).

Phase separation was observed in $\text{Ce}_{1-x}\text{Lu}_x\text{O}_{2-x/2-\delta}$ heated at 1100 °C for 3 h in H_2 (Fig. 3A). As in oxygen (Małecka et al. 2008a), two main phases, F-type and C-type, and additionally a third $\text{C}^\#$ -type phase with bixbyite structure were observed (Fig. 3B). Reducing atmosphere promotes however the phase separation. It is seen clearly in the inset to Fig. 3A, which compares the XRD diagrams of the $\text{Ce}_{0.6}\text{Lu}_{0.4}\text{O}_{1.8-\delta}$ sample heated in H_2 and in O_2 . The multi-phase region observed in a range $0.17 < x < 0.7$ in the samples treated in H_2 atmosphere is broader than that in oxidizing one ($0.35 < x < 0.7$). The reason could be reduction of Ce^{4+} to Ce^{3+} in the mixed oxide,

Fig. 2 Mean crystallite size and average maximum strain calculated from XRD patterns and mean crystallite size measured from TEM for (A) $\text{Ce}_{1-x}\text{Lu}_x\text{O}_{2-x/2-\delta}$ and (B)

$\text{Ce}_{1-x}\text{Yb}_x\text{O}_{2-x/2-\delta}$ heated at 950 °C for 3 h in (○) O_2 and (●) H_2 . Data marked as (○) for $\text{Ce}_{1-x}\text{Lu}_x\text{O}_{2-x/2-\delta}$ are taken from Malecka et al. 2008a

which generates additional oxygen vacancies and destabilizes fluorite structure. Contrary to what occurred in oxygen, the intensity of the XRD reflections of the intermediate $\text{C}^\#$ phase increased with increasing heat treatment time at 1100 °C. Besides above-mentioned phases, perovskite-type CeLuO_3 (Ito et al. 2001) was also found in hydrogen for narrow composition range $0.4 < x < 0.5$. Analysis of

the variation of the lattice parameter with Lu content indicates that at 1100 °C up to 17 mol% Lu dissolves in CeO_2 and the solubility of Ce in $\text{LuO}_{1.5}$ is 20 mol%. The solubility limit of Lu in CeO_2 is narrower than 35 mol% observed in air at the same temperature (Malecka et al. 2008a). To our knowledge, there is no information in literature about structure stability of Lu-doped ceria in hydrogen.

Fig. 3 XRD patterns for $\text{Ce}_{1-x}\text{Lu}_x\text{O}_{2-x/2-\delta}$ (A) and cell parameters for $\text{Ce}_{1-x}\text{Lu}_x\text{O}_{2-x/2-\delta}$ (B) and $\text{Ce}_{1-x}\text{Yb}_x\text{O}_{2-x/2-\delta}$ (C) heated at 1100 °C in (○) O_2 and (●) H_2 . Data marked as (○) for $\text{Ce}_{1-x}\text{Lu}_x\text{O}_{2-x/2-\delta}$ are taken from Malecka et al. 2008a. Diagrams illustrating phase change with composition are included

Weak ~ 0.76 nm fringes were observed in HRTEM images (or more clearly in corresponding FFT patterns) and SAED patterns of $\text{Ce}_{0.5}\text{Lu}_{0.5}\text{O}_{1.75-\delta}$ heated at 1100 °C for 3 h in hydrogen (Fig. 4). Similar

effect was found for samples heated in the air (Malecka et al. 2008a). The fringes could be assigned to superstructure $\frac{1}{4}\{220\}$ reflections occurring due to doubling of the fluorite cell as a result of oxygen vacancy ordering (Ou et al. 2006), or due to modulation (commensurate) of F-type structure with a periodicity of $2a_F$ reported for $\text{CeO}_2\text{--Y}_2\text{O}_3$ system (Wallenberg et al. 1989). We think that the second explanation is more plausible because of the character of SAED patterns, where sharp, strong Bragg reflections due to F-type structure are observed together with sharp, low intensity satellite reflections. Particles exhibiting superstructure reflections belong to the $\text{C}^\#$ phase identified in XRD patterns (Fig. 4). We think that true structure model of the $\text{C}^\#$ phase may involve complex oxygen vacancy ordering, similar to that proposed by Ou et al. (2008).

Recently, it has been shown that exposure of CeO_2 to intense electron beam in TEM causes partial reduction of Ce^{4+} to Ce^{3+} (Garvie and Buseck 1999) with formation and ordering of oxygen vacancies which results in superstructure reflections in SAED pattern (Akita et al. 2006). To exclude the possible effect of electron beam on observation of superstructure reflections in our study of $\text{Ce}_{1-x}\text{Ln}_x\text{O}_{2-x/2-\delta}$ samples, a blank experiment was performed. Figure 5 shows SAED patterns of CeO_2 crystallite taken after various exposure times to electron beam under normal working conditions. It appears that very weak additional satellite reflections became visible only after 30 min exposure while 60 min exposure time was necessary to produce well-developed superstructure reflections. Since the exposure time necessary for focussing and taking image is several minutes, we may exclude the possibility of decisive role of electron beam and/or vacuum conditions on superstructure formation in our samples. The much weaker beam effects in our case as compared with Akita et al. (2006) may be due to lower acceleration voltage used (200 kV instead of 300 kV) and smaller beam intensity (LaB₆ gun instead of FEG).

No F–C phase separation was observed for $\text{Ce}_{1-x}\text{Yb}_x\text{O}_{2-x/2-\delta}$ heated at 1100 °C in air and in hydrogen (Fig. 3C). This is an important difference relative to what occurred for Lu-doped ceria, where extensive phase separation occurred in both atmospheres at 1100 °C. However, as in case of Lu-doped ceria, the F-type structure modulation with a periodicity of $2a_F$ was observed in SAED and HRTEM

Fig. 4 SAED image with reflection map for $\text{Ce}_{0.5}\text{Lu}_{0.5}\text{O}_{1.75-\delta}$ heated at 1100 °C for 3 h in H_2

Fig. 5 SAED images of pure ceria (A) before and after (B) 10 min, (C) 30 min, and (D) 60 min exposure to electron beam irradiation in TEM

images for samples heated at 1100 °C in both atmospheres. Presented results for $\text{Ce}_{1-x}\text{Yb}_x\text{O}_{2-x/2-\delta}$ heated in oxidizing atmosphere contradict those presented in Chavan and Tyagi (2005), Mandal et al. (2007), and Bevan and Summerville (1979) where phase separation into coexisting F-type and C-type phases over wide composition range $0.5 < x < 0.9$ was reported. We think that the apparent difference is due to method of the sample preparation and temperatures (>1400 °C) used in Mandal et al. (2007), and Bevan and Summerville (1979). No data are available in literature on high temperature phase stability of $\text{Ce}_{1-x}\text{Yb}_x\text{O}_{2-x/2-\delta}$ in reducing

atmosphere, but formation of the perovskite-type CeYbO_3 was reported (Ito et al. 2001). The conditions necessary for CeYbO_3 growth were much more severe than for CeLuO_3 (Ito et al. 2001), which explains why the former compound was not detected in our samples.

Differences in structure stability of $\text{Ce}_{1-x}\text{Yb}_x\text{O}_{2-x/2-\delta}$ and $\text{Ce}_{1-x}\text{Lu}_x\text{O}_{2-x/2-\delta}$ at high temperatures are clearly shown by the EBSD results (see maps in Figs. 6 and 7). Figure 6 shows an EBSD orientation map obtained for $\text{Ce}_{0.5}\text{Yb}_{0.5}\text{O}_{1.75-\delta}$ heated at 1100 °C for 45 h in air. The sample contains crystallites exhibiting fluorite type structure with mean size of 100 nm with a random distribution of orientations. Because the spatial resolution was ~ 25 nm all the grains from the map shown in Fig. 6 with an equivalent diameter smaller than 75 nm were not taken into account when the average grain size was calculated. This explains why the average grain size obtained from the EBSD data is significantly bigger than that estimated from XRD (32 nm).

EBSD analysis done on the $\text{Ce}_{0.5}\text{Yb}_{0.5}\text{O}_{1.75-\delta}$ sample heated at 1100 °C for 3 h in H_2 showed a similar microstructure but with finer crystallites compared with the sample treated in air for 45 h. Because the crystallite mean size was only slightly higher than the interaction volume (i.e., spatial resolution of EBSD) no reliable data could be acquired for calculating the mean grain size. XRD estimated this value as 13 nm.

Totally different picture emerges for the $\text{Ce}_{0.5}\text{Lu}_{0.5}\text{O}_{1.75-\delta}$ sample heated at 1100 °C for 3 h in H_2 (Fig. 7). In addition to relatively small crystallites with fluorite structure and average size of

Fig. 6 Orientation map (A) and the corresponding pole figures (B) obtained from $\text{Ce}_{0.5}\text{Yb}_{0.5}\text{O}_{1.75-\delta}$ heated at 1100 °C for 45 in air

470 nm, there are very large, micrometer size crystallites of second phase identified as orthorhombic, perovskite type CeLuO_3 . This corresponds well with XRD results presented above, but raises a question on the possible reason of such drastic differences between Lu, and Yb-doped samples.

In most $\text{Ce}_{1-x}\text{Ln}_x\text{O}_{2-x/2-\delta}$ systems ($\text{Ln} = \text{Nd}$ (Nitani et al. 2004; Chavan et al. 2005), Sm (Nitani et al. 2004), Yb (Mandal et al. 2007), Tm (Mandal et al. 2007)) reported in literature high temperature (>1200 °C) annealing in oxidizing atmosphere caused phase separation for x values close to 0.5 (Longo and Podda 1981; Nitani et al. 2004), though no phase separation was observed for Eu- (Mandal et al. 2006) or Gd-doped ceria (Grover and Tyagi 2004) even at very high temperatures (1400 °C). For $\text{CeO}_2\text{--Ln}_2\text{O}_3$ systems, where Ln is a heavy lanthanide (Dy, Tm, Yb) the tendency to phase separation in oxidizing atmosphere increases with decreasing radii of Ln^{3+} ion (Mandal et al. 2007; Bevan and Summerville 1979). The reason is decreasing lattice

Fig. 7 Orientation map from the $\text{Ce}_{0.5}\text{Lu}_{0.5}\text{O}_{1.75-\delta}$ sample heated at 1100 °C for 3 h in H_2 (A) and the pole figures corresponding to the phase with the fluorite structure (B)

parameter of C-type Ln_2O_3 oxide leaving less free space for additional, interstitial O^{2-} ions that must be incorporated due to $\text{Ln}^{3+} \rightarrow \text{Ce}^{4+}$ substitution. This also explains why we observed phase separation in $\text{Ce}_{1-x}\text{Lu}_x\text{O}_{2-x/2-\delta}$ already at 1100 °C.

Much less is known on the phase stability of lanthanide-doped ceria in reducing atmosphere. Wang et al. (2004) studied interaction of nanocrystalline, fluorite type $\text{Ce}_{1-x}\text{Tb}_x\text{O}_y$ ($x \leq 0.5$) with hydrogen during heating up to 900 °C using in situ XRD. For $x = 0.33$ and 0.5, the authors observed phase separation with formation of bixbyite type Tb_2O_3 . The process has been accounted for with the change of oxidation state of lanthanides ions from $\text{Ce}^{4+}/\text{Tb}^{4+}$ to $\text{Ce}^{3+}/\text{Tb}^{3+}$.

Valency of lanthanide ions in Lu- and Yb-doped ceria

In $\text{Ce}_{1-x}\text{Ln}_x\text{O}_{2-x/2-\delta}$ samples heated at high temperatures, especially in hydrogen there is uncertainty concerning the valency of minority (dopant) lanthanide ions. Lu is not expected to appear in the valency other than 3+, but for Ce and Yb reduction from Ce^{4+} to Ce^{3+} and from Yb^{3+} to Yb^{2+} may occur.

To get some insight into this, we performed XAS (X-ray absorption) and magnetic measurements for selected samples: $\text{Ce}_{0.1}\text{Lu}_{0.9}\text{O}_{1.55-\delta}$ and $\text{Ce}_{0.95}\text{Y}_{0.05}\text{O}_{1.975-\delta}$ heated at 1100 °C in air or in hydrogen.

In $\text{Ce}_{0.1}\text{Lu}_{0.9}\text{O}_{1.55-\delta}$ heated in air XANES spectra collected at various temperatures from 5 to 283 K were practically identical with that of CeO_2 standard (Fig. 8) indicating the absence of any significant amount of Ce^{3+} ions. As displayed in Fig. 9, the sample is diamagnetic at room and elevated temperatures with the molar magnetic susceptibility of about -3.8×10^{-4} emu/mol per Ce atom. A small upturn of the susceptibility observed at low temperatures arises likely due to the presence of very small amount of paramagnetic Ce^{3+} ions at the surface of nanocrystalline particles. This presumption is supported by the shape of the field variation of the magnetization taken at $T = 1.71$ K (see the inset to Fig. 9) being characteristic of weak diamagnets contaminated by minute amounts of paramagnetic impurities. Heating of $\text{Ce}_{0.1}\text{Lu}_{0.9}\text{O}_{1.55-\delta}$ in hydrogen at 1100 °C caused partial reduction of Ce^{4+} into Ce^{3+} . XANES spectra collected at various temperatures (Fig. 10) clearly show a shift of the absorption edge toward lower energies indicating the presence of Ce^{3+} . Figure 11 presents results of magnetic measurements for this sample, revealing a distinctly different behavior from that of the specimen treated in air. In contrast to the latter, the sample treated in hydrogen is paramagnetic at room temperature and shows a strong temperature dependence of the magnetic susceptibility. In the entire temperature range studied,

Fig. 8 XANES spectra of $\text{Ce}_{0.1}\text{Lu}_{0.9}\text{O}_{1.55-\delta}$ heated in air at the cerium L_{III} edge at various temperatures. Spectra of CeO_2 and CePO_4 standards are also shown

Fig. 9 Temperature dependence of the molar magnetic susceptibility of $\text{Ce}_{0.1}\text{Lu}_{0.9}\text{O}_{1.55-\delta}$ heated in air. Little hump near 60 K signals freezing of residual oxygen in the sample chamber. Inset: field variation of the magnetization measured at 1.71 K with increasing (full symbols) and decreasing (open symbols) magnetic field

the $\chi(T)$ curve can be well approximated by the formula $\chi(T) = \chi_{\text{TIP}} + \frac{C}{T}$, where the first term represents temperature independent paramagnetism due to Ce^{4+} ions and the second one accounts for the presence of Ce^{3+} ions. Least squares fit of this expression to the experimental data yielded $\chi_{\text{TIP}} = 1.78 \times 10^{-4}$ emu/mol_{Ce} and the parameter $C = 0.0943$ (K emu)/mol_{Ce}. Assuming that the Curie term results only from stable trivalent Ce atoms, one may estimate the content of such atoms to be about 12% of all the Ce atoms present in the sample studied. In line with this finding, the Curie paramagnetism of Ce^{3+}

Fig. 10 XANES spectra of $\text{Ce}_{0.1}\text{Lu}_{0.9}\text{O}_{1.55-\delta}$ heated in hydrogen and at the cerium L_{III} edge at various temperatures

Fig. 11 Temperature dependence of the molar magnetic susceptibility of $\text{Ce}_{0.1}\text{Lu}_{0.9}\text{O}_{1.55-\delta}$ heated in hydrogen. Solid line represents the modified Curie law fit. Inset: field variation of the magnetization measured at 1.71 K with increasing (full symbols) and decreasing (open symbols) magnetic field

ions dominates the low-temperature behavior of the magnetization of the $\text{Ce}_{0.1}\text{Lu}_{0.9}\text{O}_{1.55-\delta}$ sample heated in hydrogen, as manifested by curved character of the field variation $\sigma(B)$ (cf. the inset to Fig. 11).

These results answer the interesting question about the valency of Ce as dopant into bixbyite structure of Lu_2O_3 . There are two possible scenarios. In the first, Ce as $3+$ ion just replaces Lu^{3+} in the lattice, whereas in the second Ce^{4+} substitutes for Lu^{3+} and additionally one O^{2-} ion per two such events enters the lattice. In the former case, the strong lattice distortion is inevitable due to large differences in effective ion radii (Ce^{3+} : 0.101 nm and Lu^{3+} : 0.0861 nm). In the latter case, the difference in cation radii is smaller (Ce^{4+} = 0.0870 nm and Lu^{3+} : 0.0861 nm), but large oxygen anion must occupy interstitial site. The most probable one is 16c site in $Ia-3$ (206) space group of Lu_2O_3 (Ou et al. 2008). It appears that the latter possibility is realized.

For the $\text{Ce}_{0.95}\text{Yb}_{0.05}\text{O}_{1.975-\delta}$ sample, the valency of Yb was studied by measurements of Yb L3 absorption edge. Figure 12 shows XANES spectra of the sample heated in air and in hydrogen. Comparison with the spectrum of Yb_2O_3 standard suggests that ytterbium exists as Yb^{3+} with no evidence of Yb^{2+} . This result agrees with observed decrease of the lattice parameter of CeO_2 with Yb doping (Fig. 1C and 3C) since Ce^{4+} ions (0.0870 nm) are replaced with smaller Yb^{3+} (0.0868 nm); ionic radius of

Fig. 12 XANES spectra of $\text{Ce}_{0.95}\text{Yb}_{0.05}\text{O}_{1.975-\delta}$ heated in air and in hydrogen at the ytterbium L_{III} edge at various temperatures. Spectra of Yb_2O_3 standards are also shown

Yb^{2+} : 0.102 nm is bigger than that of Ce^{4+} (Shannon 1976).

Conclusions

Nano-sized (4–5 nm) particles of $\text{Ce}_{1-x}\text{Ln}_x\text{O}_{2-x/2-\delta}$ ($\text{Ln} = \text{Yb}, \text{Lu}$) in range $0 < x < 1$ were synthesized using a W/O microemulsion method. All mixed oxides were single-phase materials up to temperature of 950 °C. Phase separation was observed for Ce – Lu mixed oxide heated in air and hydrogen at 1100 °C for the composition range $0.40 < x < 0.70$ and $0.25 < x < 0.70$, respectively. Two main F- and C-type saturated solid solutions with additional intermediate $\text{C}^\#$ -type phase coexisted in the samples. No phase separation was observed for Yb-doped ceria even after heating at 1100 °C in air or in hydrogen. Fluorite-type (commensurately) modulated structure with a periodicity of $2a_{\text{F}}$ was observed at intermediate Lu-ions concentrations for all samples.

Strong dependence of mean crystallite size in Lu, and Yb-doped ceria on Ln content (x) and some dependence on atmosphere was found. Very strong inhibiting effect of dopant on crystallite growth occurred for small Ln content ($x < 0.2$) and saturated for $x > 0.3$. In H_2 , inhibiting effect of Ln addition is less pronounced for small, but slightly more efficient for high Ln contents ($x > 0.3$) than in oxidizing atmosphere.

Valency of Ce in $\text{Ce}_{0.1}\text{Lu}_{0.9}\text{O}_{1.55-\delta}$ samples heated at 1100 °C in oxidizing atmosphere was exclusively 4+, whereas in H_2 small contribution ($\sim 10\%$) of 3+ was also present. In $\text{Ce}_{0.95}\text{Yb}_{0.05}\text{O}_{1.975-\delta}$ Yb existed exclusively as 3+ in both O_2 and H_2 .

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