

Doped ceria - LaMeO₃ (Me=Mn, Fe, Co) nanocomposites: synthesis via mechanochemical activation route and properties

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ABSTRACT

Nanocomposite oxide materials Ln-Me-O were prepared by mechanical treatment of the mixture of industrial raw material – mixed lanthanide oxide (LnO_x, Ln=Ce+La+Pr+Nd+Sm) and 3d oxide (MeO_x, Me=Fe,Co,Mn) followed by calcination in the range of 900-1100 °C. Materials were investigated with XRD, TEM, BET, IR, Raman and H₂ TPR. Two phases (fluorite and perovskite) were detected by X-ray analysis, while TEM revealed formation of particles composed of fluorite and perovskite nanodomains (50-100 nm). As prepared Ln-Me-O nanocomposites demonstrate a high lattice oxygen mobility and reactivity exceeding that of individual phases, being rather insensitive to samples calcination temperature.

INTRODUCTION

Synthesis of inexpensive mixed ionic - electronic conducting materials stable under contact with air, air +methane or even methane feeds is a very important task for design of cathodes and anodes of IT SOFC and bipolar plates [1-3]. Nanocomposites comprised of fluorite-like oxides (ionic conductors) and perovskites (electronic conductors) appear to be a promising option. A low cost of these materials required for the practical application can be ensured by using industrially available inexpensive mixed oxides of lanthanides LnO_x (Ln=Ce(51%)+La(26%)+Pr(5%)+Nd(12.8%)+Sm(1%)) and an efficient preparation technique - mechanochemical treatment (MC) of their mixture with simple transition metal oxides in high power planetary ball mills followed by annealing [4-5]. As compared with traditional ceramic approach, this method allows to accelerate synthesis and increase the products dispersion.

This work aims at developing approaches to mechanochemical synthesis of such nanocomposites by MC method and studies of their structural properties as well as the lattice oxygen mobility and reactivity.

EXPERIMENTAL

Samples Ln-Me-O were prepared from the mixture of LnO_x (Ln=Ce+La+Nd+Pr+Sm) and 3d oxides MeO_x (Me=Fe, Mn, Co) taken in the stoichiometric ratio La:Me = 1:1. After its MC treatment in the high power planetary ball mill APF-5 for 3 minutes (the weight ratio of milling balls and the oxide powder was equal to 7.5:1,

acceleration achieved in the drums of the mills $\sim 40g$), powders were calcined in air at 900° , 1000° , 1100° C for 6 hours.

XRD patterns were obtained with an URD-6 diffractometer (Germany) using Cu K_{α} monochromatic radiation ($\lambda=1.5418 \text{ \AA}$). The 2θ scanning region was $5-90^{\circ}$.

TEM micrographs were obtained with a JEM-2010 instrument (lattice resolution 1.4 \AA) and acceleration voltage 200 kV . Local elemental analysis was performed with EDX method on Energy-dispersive X-ray Phoenix Spectrometer equipped with Si(Li) detector with energy resolution not worse than 130 eV .

IR and Raman spectroscopy data were obtained with a BOMEM MB-102 spectrometer, the rate of survey was 21 scan/min .

Samples stoichiometry was analyzed by using differential dissolution (DD) method. Samples ($5-10 \text{ mg}$) were dissolved in the stream of electrolyte (flow rate 5 ml/min) with acidity and temperature increasing in a programmed mode. The chemical analysis of dissolved elements was carried out with inductively coupled plasma spectrometry (a BAIRD spectrometer).

Temperature-programmed reduction of samples by H_2 (H_2 TPR) was used to characterize the lattice oxygen reactivity and mobility. These studies were performed with $0.25-0.5 \text{ mm}$ fraction of a sample (25 mg) in a flow installation equipped with a thermal conductivity detector. Samples were pre-treated in O_2 for 0.5 h at 500° C and cooled to a room temperature with subsequent temperature ramp at $10^{\circ}/\text{min}$ up to 900° C. The reducing gas was $10\% H_2$ in Ar at $40 \text{ cm}^3/\text{min}$ flow rate.

BET specific surface area (S_{sp}) was determined from Ar thermal desorption data.

RESULTS AND DISCUSSION

1. Microstructure, phase and chemical composition of nanocomposites

According to XRD (Fig. 1), all prepared samples consist of two phases: CeO_2^* with the fluorite-like and $LnMeO_3$ ($Me=Mn, Fe, Co$) with the perovskite-like structures. For both phases, the X-ray particle size was $\sim 100 \text{ nm}$. As judged by the lattice parameter of CeO_2^* in the composite (Table 1) as compared with the initial LnO_x and pure CeO_2 [JCPDS 43-1002], already after calcinations at 900° C, La is extracted from the LnO_x to form the perovskite structure [6]. A smaller cell parameter of the fluorite phase in the case of Ln-Co-O system (5.460 \AA) as compared with that for Ln-Mn-O (5.482 \AA) and Ln-Fe-O (5.481 \AA) systems suggests the higher ability of cobalt to extract La (along with other big Ln^{3+} cations) from CeO_2^* structure with formation of the perovskite phase.

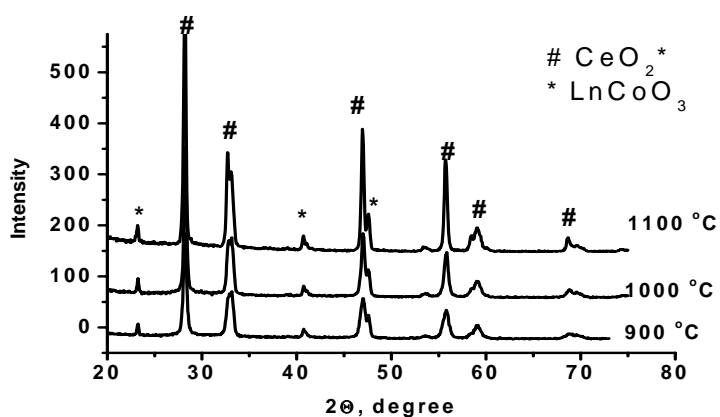


Figure 1. XRD patterns of Ln-Co-O composites versus calcination temperature

Table 1. CeO_2^* and LaCoO_3 pseudocubic cell parameters in Ln-Co-O system versus calcination temperature

Ln-Co-O calcination temperature, °C	CeO_2^*	LaCoO_3
900	5.460(1)	3.830
1000	5.464(3)	3.832
1100	5.470(2)	3.821
For comparison: CeO_2 [ICDD 43-1002]	5.411	-
LnO_x [4]	5.518(1)	-
LaCoO_3 [ICSD 28921]	-	3.820

For both phases present in studied systems, their lattice parameters depend only weakly upon the temperature of calcination. Some difference of these results with the reference data (Table 1) suggests doping of both phases with Pr, Sm, Nd cations.

Differential dissolution (DD) method allows analyzing the phase composition and estimating stoichiometry of phases including amorphous ones and those present as admixtures [7]. The perovskite phase dissolves in rather soft conditions (in HCl solutions), while dissolution of the fluorite phase requires a higher acidity (solutions of HF) and temperature and dissolves partly. Typical dissolution curves (concentration of a cation versus time) are shown in Fig. 2.

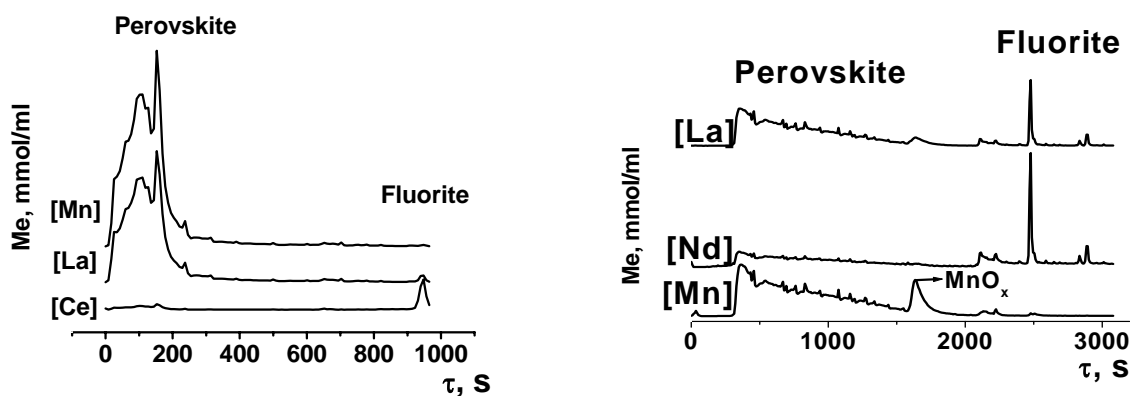


Figure 2. Typical dissolution curves for Ln-Mn-O system calcined at 1100 °C.

Differential dissolution revealed formation of two main phases (perovskite and fluorite) in samples. In the case of Ln-Mn-O system, there is an admixture of a mixed oxide phase containing some amount of Ln cations. The phase composition does not depend upon the calcination temperature. Phases stoichiometry for samples calcined at 1100 C is presented in the Table 2. All perovskites are doped with Nd and Ce cations, while fluorites contain an admixture of 3d, La and Nd cations.

For all samples, IR and Raman spectroscopy data confirm the presence of two phases with perovskite- and fluorite-like structures as well. Perovskite peaks were detected after subtraction of LnO_x spectrum from the spectra on composites. Irrespective of the calcination temperature, bands corresponding to the perovskite phases were observed. Thus, for Ln-Fe-O system, bands at 560, 407, 376 cm^{-1} (IR) and at 447 cm^{-1} (Raman) correspond to LaFeO_3 and

CeO₂ phases, respectively; for Ln-Mn-O system, IR bands are observed at 608 and 395 cm⁻¹ (LaMnO₃ phase), while for Ln-Co-O system IR bands at 600, 560, 420, 342 cm⁻¹ correspond to LaCoO₃ phase.

Table 2. Chemical composition of Ln-Me-O (Me-Mn, Fe, Co) samples calcined at 1100 °C by the differential dissolution data.

Composition of detected phases	Samples		
	Ln-Mn-O*	Ln-Fe-O	Ln-Co-O
Perovskite	La _{0.7} Ce _{0.1} Nd _{0.3} MnO ₃	La _{0.59} Ce _{0.07} Nd _{0.3} FeO ₃	La _{0.6} Ce _{0.09} Nd _{0.3} MnO ₃
Fluorite**	CeO ₂ , Ce _{0.95} La _{0.03} Mn _{0.02} O ₂	Ce _{0.92} La _{0.07} Fe _{0.01} O ₂	Ce _{0.95} La _{0.03} Co _{0.03} O ₂

* Admixture of MnO_x was detected

** Stoichiometry of dissolved fluorite phase

According to TEM data (Fig. 3) the average particle size is ~ 450 nm. Particles are comprised of stacked domains with perovskite and fluorite structures with typical sizes in the range of 50-100 nm. According to EDX analysis, the chemical composition of fluorite domains corresponds to Ce_{0.72}La_{0.18}Co_{0.1}O_{2-δ} which confirms DD data about incorporation of La and transition metal cations into fluorite structure.

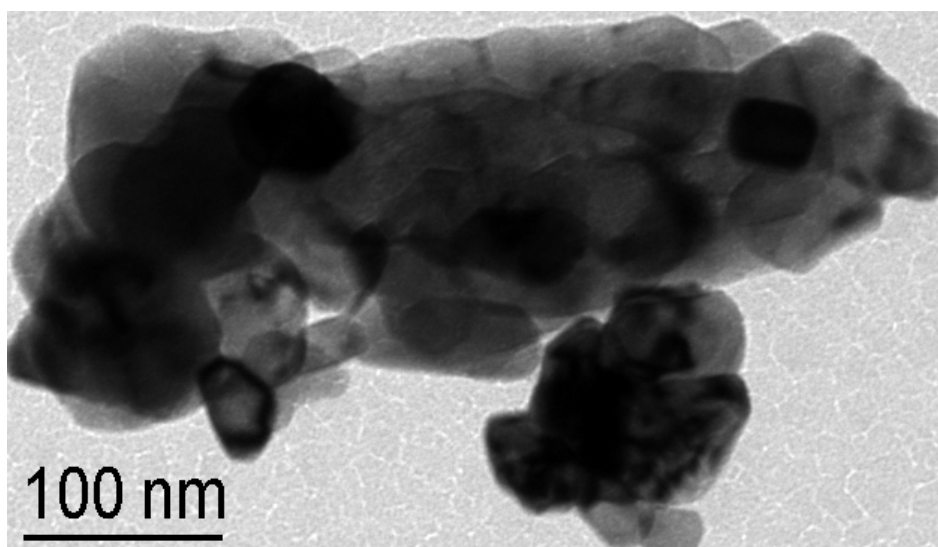


Fig. 3. TEM data for Ln-Co-O system calcined at 1000 °C.

Hence, data obtained revealed formation of nanocomposites composed of two main doped phases with perovskite (dark domains)- and fluorite-like (light domains) structures, their chemical composition and structure parameters being the same after calcination in the range of 900 -1100 °C.

Specific surface area of samples decreases with the calcination temperature from 8-9 m²/g (for annealed at 900⁰ C) up to 2-3 m²/g (for annealed at 1100⁰ C) due to sintering and formation of large nanocomposite particles.

2. The lattice oxygen mobility and reactivity in nanocomposites

For all systems, two main peaks of hydrogen consumption are observed in H₂ TPR curves (Fig. 4), their position and intensities as well as the total hydrogen consumption (Fig. 5) depend on the nature of 3d cation. The temperature of the first peak increases in the order

Co>Mn>Fe, probably being mainly determined by the reactivity, and, hence, bonding strength of the lattice oxygen bound with transition metal cation.

The largest hydrogen consumption was revealed for Ln-Co-O composites (Fig. 5) probably due to an easy reduction of Co^{+3} cations. The increase in calcinations temperature leads to weak variation in the total consumption for Ln-Co-O and Ln-Mn-O composites and to decrease for Ln-Fe-O composite. Nevertheless, the reduction rates at the temperatures of the TPR peaks (peak rates) depend rather strongly on the calcination temperature, especially for Ln-Mn-O system (Fig. 6, 7), decreasing with temperature for the 1st peak and increasing for the 2nd.

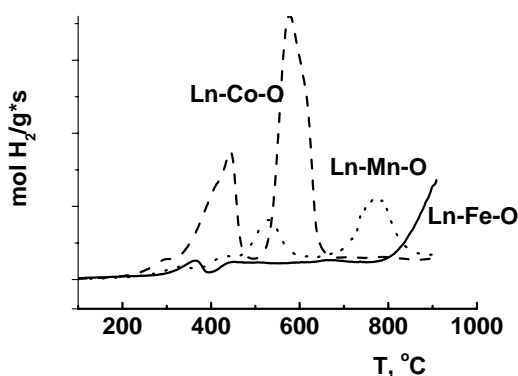


Fig. 4. Typical H_2 TPR curves for Ln-Me-O (Me= Co, Mn, Fe) samples calcined at 1100 °C

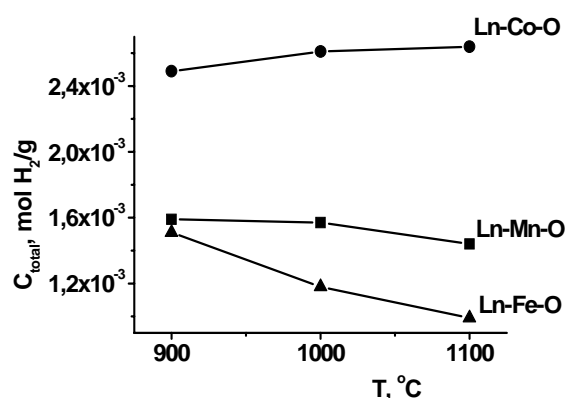


Fig. 5. Total hydrogen consumption (C) for Ln-Me-O (Me=Co, Mn, Fe) samples versus calcinations temperature.

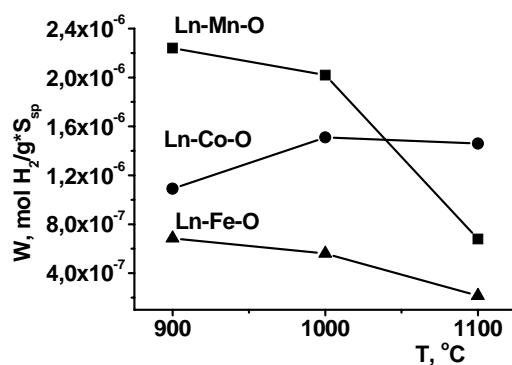


Fig. 6. Reduction rate (W) in the 1st peak for Ln-Me-O (Me=Co, Mn, Fe) samples versus their calcinations temperature

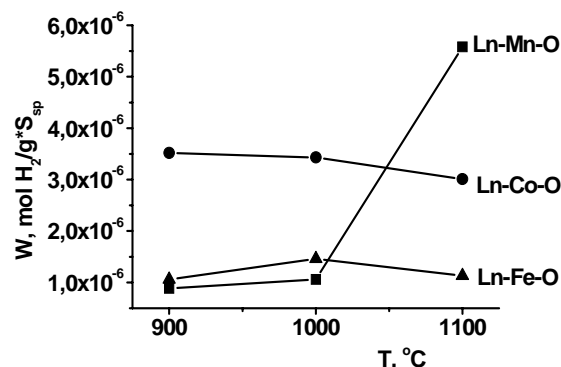


Fig. 7. Reduction rate (W) in the 2nd peak for Ln-Me-O (Me=Co, Mn, Fe) samples versus their calcination temperature

The peak reduction rates for Ln-Mn-O nanocomposites greatly (more than 30 times) exceed those for pure lanthanum manganite [8], while for Ln-Fe-O system this difference is more moderate (ca 3 times). They are also higher than typical values of peak reduction rates determined for pure or doped ceria phases [9]. This increase in the peak reduction rates for Ln-Mn-O and Ln-Fe-O nanocomposites demonstrates the increase of oxygen mobility due to formation of mixed ionic-electronic conducting nanocomposites [1, 10]. For Ln-Co-O nanocomposite, the reduction rate in the 1st peak is lower than that observed for pure LaCoO_3

perovskite [8], probably due to a rather low content of LaCoO_3 in composite ($\sim 30\%$) along with a pronounced effect of LaCoO_3 doping with Nd and Ce cations (Table 2) decreasing the lattice oxygen mobility. However, it remains to be reasonably high. Apparently, a high thermal stability of nanocomposite is important as well.

CONCLUSIONS

Mechanical activation of the mixture of complex inexpensive lanthanide LnO_x oxide with transition metal oxides followed by calcination at a rather moderate (900°C) temperature generates nanocomposites comprised of domains with the fluorite and perovskite structures. Hence, MC activation method allows to easily obtain from the solid raw materials the same phases as wet precipitation or nitrate decomposition routes [11]. Estimation of the oxygen mobility and reactivity by H_2 TPR revealed that for low temperature ($400\text{--}600^\circ\text{C}$) application, Ln-Co-O system could be the most attractive. This system is also characterized with a weak dependence of the lattice oxygen reactivity on the calcination temperatures. For applications at higher temperatures, Ln-Mn-O and Ln-Fe-O systems could be promising as well.

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