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PREPARATION AND THE ELECTROLYTIC PROPERTIES OF CaO-Sm_2O_3-CeO_2 CERIA SOLID SOLUTIONS

ABSTRACT

Pure CeO_2, samaria doped ceria ($Ce_{1-x}Sm_xO_2$) and co-doped ceria with calcia and samaria $Ce_{1-x}(Ca_{0.5}Sm_{0.5})_xO_2$, wherein x =0.15, 0.20, 0.25, and 0.3 fine powders were prepared by the citrate method. All powders and samples sintered in the CaO-Sm_2O_3-CeO_2 system were found to be ceria-based solid solutions of fluorite type structure. The pellets were sintered at 1500^{o}C for 2h in air. The scanning electron microscopy was used to observe the microstructure of the sintered samples. The electrical conductivity was studied by a.c impedance spectroscopy method in the 200-800^{o}C temperature range. The fracture toughness K_{Ic}, was also determined by Vickers indentation method. It was found that electrical conductivity and fracture toughness in $Ce_{1-x}(Ca_{0.5}Sm_{0.5})_xO_2$ increased with x and reached a maximum for x = 0.2. The co-doped ceria of $Ce_{0.8}(Ca_{0.5}Sm_{0.5})_{0.2}O_2$ seems to be a more suitable solid electrolyte than $Ce_{0.8}Sm_{0.2}O_2$ for application in solid oxide fuel cells and other electrochemical devices operating in 600-800°C temperature range

Key words*: solid oxide fuel cell, solid oxide electrolyte, ceria-based solid solution, electrochemical gas sensors*

INTRODUCTION

For many years, CeO_2-based materials have been mainly used as catalysts and pigments in ceramics or glasses. Today ceria is also applied as an active component in the so-called three-way catalysts (oxidation of CO, oxidation of C_nH_m, reduction of NO_x) for car exhaust [1]. They are also promising materials for gas sensor applications in the automotive industry [2]. Rare earth-doped ceria (RDC) has higher values of ionic conductivity than fully yttria-stabilized zirconia (8YSZ), in the 600-800^{o}C temperature range. Better ionic conductivity can lead to decreased operational temperatures, increases in life-span as well as greater range of choices for constituting material for electrochemical devices such as solid oxide fuel cells and gas sensor [3,4]. The main drawback of these electrolytes is the increased electronic conduction under low oxygen partial pressure, that is accompanied by reduction of $Ce^{4+}$to Ce^{3+} [5]. It has been reported that the reduction of ceria-based materials can be neglected at lower temperature around 600-700^{o}C [6]. However, such low temperature are not suitable for singly doped-ceria operations, as SOFC's electrolyte material has a high resistance. Structural modification of ceria solid solutions is one possible ways to improve their electrical conductivity. Herle, *et all* [7] found that doped ceria with two and more cations showed significantly higher ionic conductivity than the best singly doped ceria. Mori, *et all* reported that due to co-doping small quantities of calcium in the $Ce_{1-x}Sm_xO_2$ solid solutions, the application region (pure oxide ionic conductivity) is shifted by two orders to lower oxygen partial pressure [8]. In spite of such interest in co-doped ceria materials, there has not been much systematic research done on influence of calcia on the structure, microstructure then consequently on electrical and mechanical properties of CeO_2-Sm_2O_3-CaO–based materials.

The aim of this work was to prepare dense samples of ceria-samaria-calcia solid solutions and determine their properties crucial for their application as solid electrolytes in electrochemical devices.

EXPERIMENTAL

The starting materials were $Ce(NO_3)_3{\cdot}6H_2O$ (99.9 % Aldrich), $Sm(NO_3)_3{\cdot}6H_2O$ (99.9 % Aldrich), $Ca(NO_3)_2{\cdot}4H_2O$ (99.9% Aldrich) and citric acid (p.a, POCH Gliwice). The powders were mixed in distilled water in order to prepare pure CeO_2, ceria-samaria solid solutions with formula $Ce_{1-x}Sm_xO_2$, where $0<x<0.30$ or ceria-samaria-calcia solid solutions with formula $Ce_{1-x}(Ca_{0.5}Sm_{0.5})O_2$, wherein $x = 0.15$, 0.2, 0.25, 0.30. The citric acid was added to the solutions. The solutions were evaporated at 70°C to obtain hard gels. The dried gels were calcined at 800°C for 1 h, and then rotary-vibratory milled with zirconia grinding media in dry ethanol. The phase composition of all powders and sintered samples were identified by X-ray diffraction analysis. The specific surface area was measured by one-point BET technique method. Transmission electron microscopy was used to observe the morphology of powders. The ground powders were cold isostically pressed under 250 MPa. Densification behaviour of the powder compacts was monitored in air via dilatometry using a constant heating rate 5°C/min at 25 to 1200°C temperature range. The pellets were sintered at 1500°C for 2 h in air. Scanning electron microscopy was used to observe a microstructure of sintered samples. Apparent density of the sintered bodies was measured by the Archimedes method. The fracture toughness K_{Ic} was determined by Vickers indentation method. Electrical conductivity was studied using a Solatron 1260 Frequency Response Analyser at 200-800°C. To verify the stability of materials prepared under reduction conditions, the CeO_2-based samples were isothermal heated at 800°C for 24 h in (10 % vol H_2-Ar) gas mixture.

RESULTS AND DISCUSSION

Only cubic CeO_2 phase was identified by the XRD analysis in all the powders and samples sintered. No other phase than cubic CeO_2 was found in X-ray diffraction patterns of the samples exposed in a (H_2-Ar) gas mixture. Basis characteristics of the starting powders are shown in Table 1.

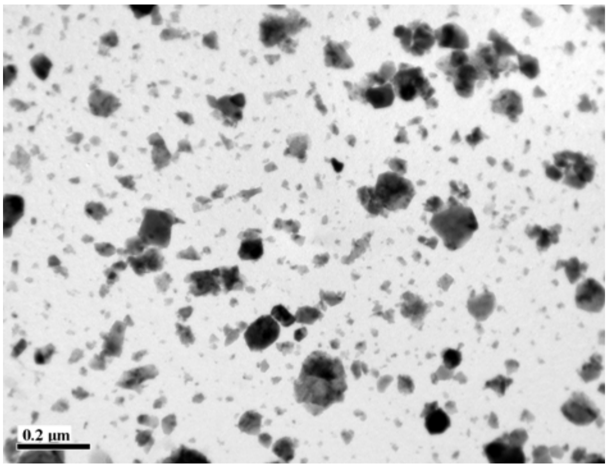

Fig. 1. The TEM morphology of $Ce_{0.8}(Ca_{0.5}Sm_{0.5})_{0.2}O_2$ powder

Table 1. *Average crystallite sizes of powders determined by XRD and BET specific surface measurements*

Composition	$d_{(hkl)}$, nm	$d_{(BET)}$, nm
CeO_2	17.1	18.4
$Ce_{0.85}Sm_{0.15}O_2$	18.4	20.8
$Ce_{0.8}Sm_{0.2}O_2$	20.1	22.6
$Ce_{0.75}Sm_{0.25}O_2$	24.3	26.3
$Ce_{0.7}Sm_{0.3}O_2$	19.4	22.5
$Ce_{0.85}(Ca_{0.5}Sm_{0.5})_{0.15}O_2$	24.4	29.6
$Ce_{0.8}(Ca_{0.5}Sm_{0.5})_{0.2}O_2$	26.1	27.5
$Ce_{0.75}(Ca_{0.5}Sm_{0.5})_{0.25}O_2$	29.2	32.4
$Ce_{0.7}(Ca_{0.5}Sm_{0.5})_{0.3}O_2$	24.5	26.3

The data in table 1 shown that, the particle sizes ranged from ~ 17 to about 32 nm. The consistency of particle sizes determined by X-ray analysis and BET specific surface measurements suggest that the powders were composed of isometric and rather weakly agglomerated crystallites. The typical morphology of $Ce_{0.8}(Ca_{0.5}Sm_{0.5})_{0.2}O_2$ powder is presented in Fig 1. The distribution of isometric particles (20 to 40 nm in size) and some forms of agglomerates was observed. Further observations of the all powders allowed us to state that no distinct differences in morphology are present. Fig 2. shows the densification behaviour of compacts heated at constant rate 5^o/min at 25 to 1200^{o}C temperature range. The results indicated that for all samples investigated, pellet shrinkage began at 200^{o}C and during further heating intensive densification of CeO_2-based materials started from about 800-850ºC. The comparison of all dilatometric curves showed that the introduction of CaO into $Ce_{1-x}Sm_xO_2$ solid solution form did not cause a considerable change in behavior of sintering pellets. Only for sample $Ce_{0.7}(Sm_{0.5}Ca_{0.5})_{0.3}O_2$ a deterioration of sinterability was observed.

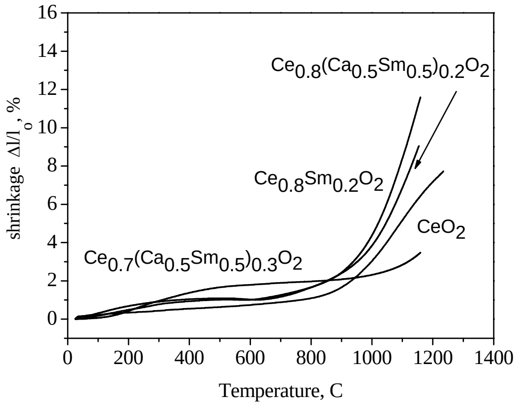

Fig. 2. Dilatometric curves recorded for selected CeO_2-based pellets

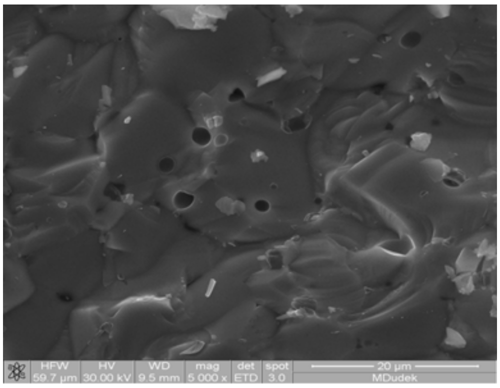

Fig. 3. Microstructure of $Ce_{0.8}(Ca_{0.5}Sm_{0.5})O_2$ ceramic sintered at 1500^{o}C for 2h in air.

Generally, all of the samples sintered at 1500°C for 2 h achieved more than 97 % of theoretical density. In sample $Ce_{0.7}(Ca_{0.5}Sm_{0.5})_{0.3}O_2$ the decrease of relative density to 93 % was observed. The microstructure of $Ce_{0.8}(Sm_{0.5}Ca_{0.5})_{0.2}O_2$ sample sintered with isometric grains about 12 -18 μm and small close porosity is presented in Fig. 3. The SEM observations of the sample heated in hydrogen containing atmosphere were also carried out. Contrary to pure CeO_2 and $Ce_{1-x}Sm_xO_2$, no cracks and additional pores were no detected by SEM microphotogaphs recorded for co-doped ceria with calcia and samaria. These results indicated that addition calcium in $Ce_{1-x}Sm_xO_2$ solid solutions could improve their stability under reduction conditions. Only gas-tight ceramic elements (without open porosity and cracks) should be applied as solid electrolytes in electrochemical devices.

The lattice parameter of $Ce_{1-x}Sm_xO_2$ or $Ce_{1-x}(Sm_{0.5}Ca_{0.5})_xO_2$ (Fig.4) linearity increased with x, but the slope is lower for the doubly doped ceria with Ca^{2+} and Sm^{3+} than only Sm^{3+} singly doped ceria. The additional heat-treatment in (H_2-Ar) gas mixtures caused decrease cell parameters for all CeO_2-based samples investigated. It was found that a relatively smallest change of cell constant values was observed in the $Ce_{0.8}(Ca_{0.5}Sm_{0.5})_{0.2}O_2$ sample.

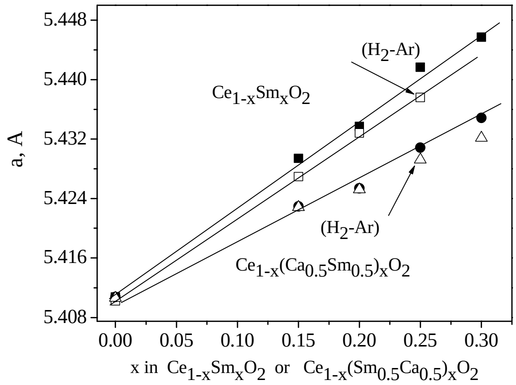

Fig. 4. Dependence of lattice constant on the composition x of $Ce_{1-x}Sm_xO_2$ or $Ce_{1-x}(Sm_{0.5}Ca_{0.5})O_2$ based samples

Table 3. *The fracture toughness K_{Ic} determined for CeO_2-based samples*

Composition	K_{Ic}, MPa·m$^{0.5}$	
	starting	(H_2-Ar) test
CeO_2	1.3 ± 0.2	0.7 ± 0.1
$Ce_{0.85}Sm_{0.15}O_2$	1.9 ± 0.3	1.5 ± 0.2
$Ce_{0.8}Sm_{0.2}O_2$	2.3± 0.1	1.6± 0.2
$Ce_{0.75}Sm_{0.25}O_2$	2.0± 0.3	1.3± 0.4
$Ce_{0.85}(Ca_{0.5}Sm_{0.5})_{0.15}O_2$	2.2± 0.2	1.9 ± 0.1
$Ce_{0.8}(Ca_{0.5}Sm_{0.5})_{0.2}O_2$	2.6 ± 0.2	2.2± 0.1
$Ce_{0.75}(Ca_{0.5}Sm_{0.5})_{0.2}O_2$	1.9± 0.3	1.8± 0.1
8YSZ	3.1± 0.3	2.8± 0.2

The good mechanical properties of CeO_2-based ceramics are also necessary for application as solid electrolytes in electrochemical devices. The fracture toughness K_{Ic} measurements (Tab.3) revealed a small increase in fracture toughness with increasing samaria or (calcia and samaria) in $Ce_{1-x}Sm_xO_2$ or $Ce_{1-x}(Sm_{0.5}Ca_{0.5})_xO_2$ solid solutions for x = 0.20. However, they have slightly worse mechanical properties than 8YSZ electrolyte, which is commonly used as a component in electrochemical devices (solid oxide fuel cells, gas sensors).

The impedance spectroscopy enabled to determine of the bulk (σ_b) and grain boundary ionic (σ_{gb})conductivities of CeO_2-based samples. Respective values of the conductivities at temperature 600°C are given in Table 4. The values of the activation energy (Ea), calculated for 200-800°C temperature range and data for zirconia stabilized with 8 % mol yttria (8YSZ) are also given.

It can be seen from Table 4, that the bulk and grain boundary conductivity of $Ce_{1-x}Sm_xO_2$ and $Ce_{1-x}(Sm_{0.5}Ca_{0.5})_xO_{0.2}$ increased up to x = 0.20 a then fell towards smaller values. Contrary changes of activation energy was noticed. The total electrical conductivity (calculated as sum grain boundary and bulk conductivity) reached a maximum ($8.0 \cdot 10^{-3}$ S/cm at 600°C) for $Ce_{0.8}(Sm_{0.5}Ca_{0.5})_{0.2}O_2$. This values are over 50 % higher than total conductivity of 8YSZ at 600°C ($1.46 \cdot 10^{-3}$ S/cm)

Table 4. *Electrical conductivity at 600°C of the CeO_2-based solid solutions*

Composition	σ(S/cm), 600°C		Ea, eV	
	bulk	brain boundary	bulk	grain bounadry
CeO_2	$6.16 \cdot 10^{-5}$	$1.21 \cdot 10^{-6}$	1.51	1.81
$Ce_{0.85}Sm_{0.15}O_2$	$1.72 \cdot 10^{-3}$	$1.13 \cdot 10^{-3}$	0.85	0.94
$Ce_{0.8}Sm_{0.2}O_2$	$3.21 \cdot 10^{-3}$	$2.11 \cdot 10^{-3}$	0.78	0.90
$Ce_{0.75}Sm_{0.25} O_2$	$2.18 \cdot 10^{-3}$	$9.85 \cdot 10^{-4}$	0.85	0.95
$Ce_{0.7}Sm_{0.3}O_2$	$4.41 \cdot 10^{-4}$	$2.67 \cdot 10^{-4}$	0.98	1.12
$Ce_{0.85}(Ca_{0.5}Sm0_{.5})_{0.15}O_2$	$3.11 \cdot 10^{-3}$	$1.86 \cdot 10^{-3}$	1.11	1.16
$Ce_{0.8}(Ca_{0.5}Sm0_{.5})_{0.2}O_2$	$5.31 \cdot 10^{-3}$	$2.68 \cdot 10^{-3}$	0. 75	0.86
$Ce_{0.75}(Ca_{0.5}Sm_{0.5})_{0.25}O_2$	$1.81 \cdot 10^{-3}$	$1.08 \cdot 10^{-3}$	0.84	0.98
$Ce_{0.7}(Ca_{0.5}Sm_{0.5})_{0.3}O_2$	$5.21 \cdot 10^{-4}$	$4.53 \cdot 10^{-4}$	0.95	1.02
8YSZ	$8.11 \cdot 10^{-4}$	$6.52 \cdot 10^{-4}$	0.90	1.01

CONCLUSION

The results presented in this paper indicated that co–doped ceria with calcia and samaria leads to small improvements their electrolytic properties compared to only samaria-doped ceria. This material seems to be a promising solid electrolyte for electrochemical devices operating in intermediate temperature range (600- 800°C).

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