



Formation and Investigation of Doped Cerium Oxide Thin Films Formed Using E-Beam Deposition Technique

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Abstract. The investigation of new functional materials (ceramics) based on cerium (IV) oxides is a promising field of scientific research. A wide application in the industry received composite materials based on CeO₂–Gd₂O₃ and CeO₂–Sm₂O₃.

Thin ceramic films were formed on the basis of CeO₂ with 10 mol% Gd₂O₃ (GDC10), CeO₂ with 20 mol% Gd₂O₃ (GDC20), CeO₂ with 15 mol% Sm₂O₃ (SDC15), CeO₂ with 20 mol% Sm₂O₃ (SDC20) using e-beam technique in this work. The deposition rate and temperature of the substrate had influence on the formed doped cerium oxide GDC10, GDC20, SDC15, SDC20 thin films structure. Sm and Gd doped cerium oxide thin films were deposited on SiO₂, Alloy 600 (Fe-Ni-Cr), Si (111), Si (100) and Al₂O₃ substrates. Investigations of the formed thin films were carried out using a Scanning electron microscope (SEM), Electron dispersive spectroscopy (EDS), X-ray diffraction (XRD), and Raman spectroscopy. It has been established that the cerium oxide based ceramic retains the crystalline structure, regardless of the concentration of the dopant and used substrate type. The most dominant crystallographic orientation of formed thin films was cubic (111). Raman spectroscopy measurements showed the peak (465 cm⁻¹) of pure ceria corresponding to F_{2g} vibrational mode. First-order peaks, inherent to cerium oxide, were shifted to a region of lower wavenumbers and depend on dopant concentration. The peaks for all formed thin films were similar to each other in form but the position, half width and their intensity varied depending on the dopant concentration. Raman peaks position at 550 cm⁻¹ and 600 cm⁻¹ could be explained as change of oxygen vacancy amount due to the cerium transition between oxidized and reduced forms.

Keywords: Ceramics · Cerium oxide thin films
Doped cerium oxide thin films · Raman spectroscopy

1 Introduction

The creation of new functional materials based on oxides (catalysts, counter electrodes of electrochromic devices, solid oxide fuel cells), including cerium (IV) oxide, is a promising field of scientific research corresponding to priority areas of Lithuania's scientific and technological development "Technologies for the production and processing of functional nanomaterials". The composite materials of cerium oxide doped with gadolinium and samarium are widely used in industry. These materials could have cerium transition between the oxidized and reduced forms [1]. Gd (IV) and Sm (IV) oxides influence this equilibrium, and also increase the thermal stability and transmittance in the visible region of the ceria (IV) oxide spectrum. The known physical and chemical, combined methods for the production of oxide $\text{CeO}_2\text{-CeO}_2\text{-Gd}_2\text{O}_3$ and $\text{CeO}_2\text{-Sm}_2\text{O}_3$ in thin-film states are mainly energy-intensive and require the use of expensive equipment. In our case, we have chosen the method of electron beam evaporation (E-beam deposition). In the method of electron beam evaporation, changes in the deposition rate, pressure and temperature of the substrate affect the properties of oxide films. By changing the application parameters, we could obtain thin films with a homogeneous structure and a homogeneous shape without any defects and cracks [2, 3]. A fuel cell is a device that converts chemical energy into electrical energy. There are different types of fuel cells designed for a specific application, the most important difference between them is the kind of electrolyte they use. This study was carried out using a solid oxide electrolyte, which is a cerium oxide with (Gd_2O_3 and Sm_2O_3) dopant. The properties of a thin film electrolyte in many respects define operational characteristics of the fuel cell. High ionic conductivity, mechanical strength thermal resistance and gas tightness are the main requirements to the electrolyte ensure stable and long-term operation of fuel cells with high electrical performance, preventing the loss of fuel. The purpose of the research is to form a thin film on the basis of cerium oxide (CeO_2) with dopants Sm and Gd using e-beam evaporation technique, to investigate the microstructure and Raman spectra study are the purpose of the research. The early theories, on the basis of which the search for an optimum dopant for CeO_2 was carried out, were generally based on consideration of deformation of a lattice in general and did not take into account local microstructure of a solid electrolyte. With development of new methods of the analysis there was an opportunity to find the additional parameters influencing the properties of solid solution which are not connected with technological features of their production. The method of Raman spectroscopy enabled us to obtain additional information on oxygen vacancies in the investigated solid solutions.

2 Experimental

In the present study Gadolinium and Samarium doped ceria were formed with e-beam physical vapor deposition system "Kurt J. Lesker EB-PVD 75", using 0.2 nm/s ÷ 1.6 nm/s deposition rate and temperatures from 50 °C to 600 °C of SiO_2 , Alloy 600 (Fe-Ni-Cr), Si (111), Si (100) and Al_2O_3 substrates. The $\text{Sm}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$, $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{2-\delta}$ and $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$, $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{1.95}$ powders (Nexceris, LLC, Fuelcellmaterials,

USA) was used as evaporating material. The pellets were placed into crucible and vacuum chamber was depressurised up to $2 \cdot 10^{-9}$ bar. After that, the substrates were treated with Ar⁺ ion plasma (10 min) and preheated up to working temperature. Thickness and deposition rate were controlled with INFICON crystal sensor. Formed thin films ceramic base on Cerium oxides structures and morphology have been studied by X-ray diffraction (XRD) “Bruker D8 Discover” at 2Θ angle in a 20° – 70° range using Cu K α ($\lambda = 0.154059$ nm) radiation, 0.01° step, and Lynx eye PSD detector. EVA Search – Match software and PDF-2 database were used to identify diffraction peaks. The crystallite size was calculated using Scherrer’s equation. Scanning electron microscopy (SEM) “Hitachi S-3400N”, was used to obtain surface topography images and cross-section images Elemental composition was controlled using energy-dispersive X-ray spectroscopy “BrukerXFlash QUAD 5040” (EDS). Raman spectra were recorded at the room temperature, using a Confocal Raman spectrometer Solver Spectrum (NT-MDT). The excitation source was the 532 nm, diameter of laser spot was 2 microns and diffraction grating 1800/500 providing spectral resolution of 1 cm^{-1} . Laser output was 14 mW. Fitting procedure were carried out by the data of Lorentz line shape using a peak fit in the OriginPro software.

3 Results and Discussions

Various concentration of doped gadolinium and samarium were used wishing to determine how concentration of impurities might affect to the microstructure and ionic conductivity of thin films, CeO₂ with 10 mol% Gd₂O₃ (GDC10), CeO₂ with 20 mol% Gd₂O₃ (GDC20), CeO₂ with 15 mol% Sm₂O₃ (SDC15), CeO₂ with 20 mol% Sm₂O₃ (SDC20). XRD measurement of thin films was carried out through the program (DIFFRACTplus EVA) and shown in Fig. 1.

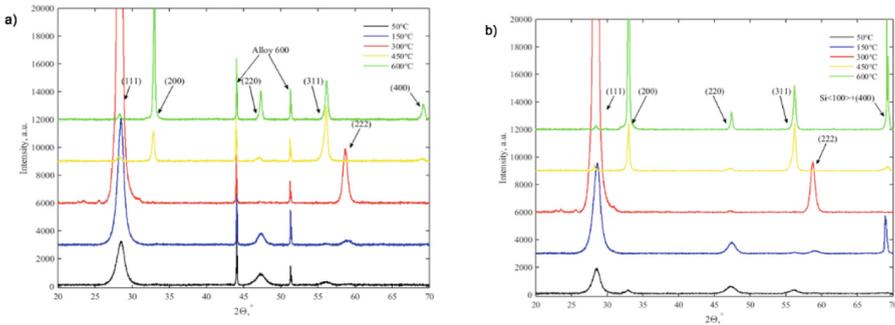


Fig. 1. XRD patterns of SDC20 deposition rate of 1.6 nm/s thin ceramic deposited on a) Alloy 600 and b) Si (100)

The crystallite size was calculated using the program (TOPAS). The results were analyzed by comparison of deposition rate and substrate temperature and detected that,

all thin films (GDC10, GDC20, SDC15, SDC20) based on cerium oxide have a single-phase and fluorite structure with space group Fm3m.

X-ray diffraction patterns of SDC20 thin films have characteristic peaks, corresponding to crystallographic orientations (111), (200), (220), (311), (222), and (400). For the formed thin films, preferential orientations are (111) and (222). However, investigated ceramic thin films do not retain the same structure and orientation, since the deposition parameters were different, they change into (200) or (311) (Figs. 1, 2), i.e., it was observed that the change appear at high substrate temperatures (450 °C and 600 °C) and at high deposition rates (1.2 nm/s and 1.6 nm/s). Analysis of thin films of identical components at different deposition parameters might give different structure and orientation.

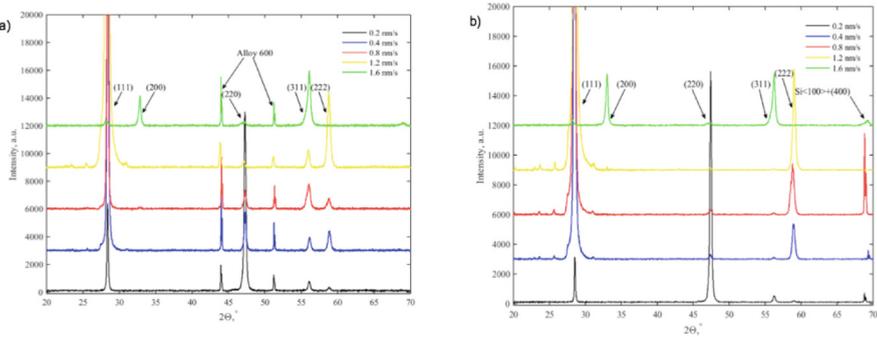


Fig. 2. XRD patterns of SDC20 deposition rate of 0.2 nm–1.6 nm thin ceramic deposited on (a) Alloy 600 and (b) Si (100), substrates temperature $T_{\text{sub}} = 450$ °C

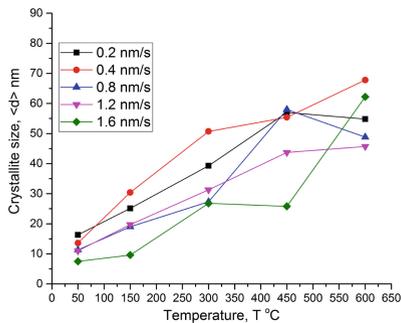


Fig. 3. Temperature dependence of crystallite size at different deposition rate by 0.2 nm/s ÷ 1.6 nm/s thin ceramics deposited on Alloy 600

SDC20 dominant crystallographic orientation (222) the intensity of the peak increases and in some cases, are disappear. This orientation may be associated with deposition energy of the particles, which can migrate into larger clusters changing the

dominant peak intensity. In the analysis of XRD, the more intense peaks of a narrow line width shown in Figs. 2 and 3 may indicate an increase in the grain and crystallite size with an admixture of Sm^{3+} .

The calculation of the crystallite size, were prove the statement that by increasing the substrate temperature the crystallite size increases (6.2 nm \div 80.1 nm) (Fig. 3). The deposition rate also, have influence on crystallite size. The crystallite size shows almost the same value with increasing the deposition rate if temperature of the substrates, are under 300 °C and crystallite size decreases with increasing deposition rate if substrates temperatures are 450 °C and 600 °C.

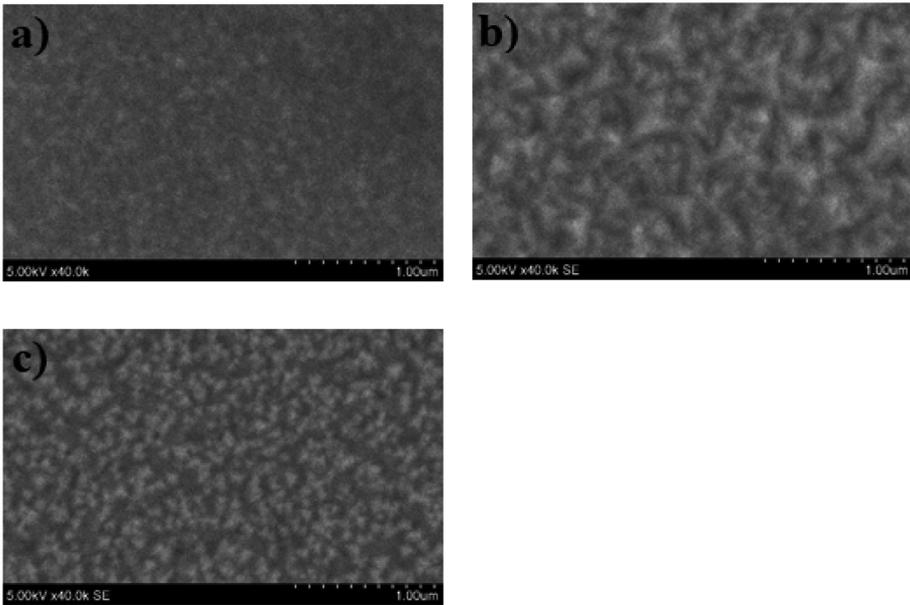


Fig. 4. SEM picture of SDC20 thin ceramic films deposited on optical quartz substrates (SiO_2) using (a) 0.2 nm/s, 50 °C (b) 0.8 nm/s, 300 °C (c) 0.8 nm/s, 600 °C

Depending on the temperature of the substrate, the grain size of the thin film changes as shown in Fig. 4. When the temperature of the substrates increases, the grain sizes increase, but this process occurs up to a certain temperature, in our case to 450 °C, and after that at a temperature of 600 °C, were notice a decrease in the grain size. This is due to the increased influence of the growth rate at high temperatures. As shown in Fig. 4, all the thin films are uniform and do not have any defect or cracks. The obtained results are in good agreement with other authors results [5, 6].

Main peak of pure ceria presents on 465 cm^{-1} on F_{2g} vibrational mode. In this mode can be move only oxygen atoms around the cerium ions Ce^{4+} [7]. As were know in the fluorite lattice only oxygen atoms can be mobile, and the frequency of this mode should not depend on the mass of the cation. It is for this reason that the characteristics

of the peaks are very sensitive to disorder induced in the oxygen ion sublattice of the oxide, in particular, the peak position and the width of the peaks [8]. Doping the crystal lattice of cerium with rare-earth Gd and Sm elements, were got a defect in the crystal lattice that affected the environment of oxygen around the metal ions. As a result, were received changes in the position of peaks and width of peaks in the Raman spectra. Considering thin films of cerium oxide doped with Sm and Gd, it is seen that the F_{2g} modes, in particular, first-order peaks inherent to cerium oxide, shifted to the region of lower wavenumbers (Fig. 5).

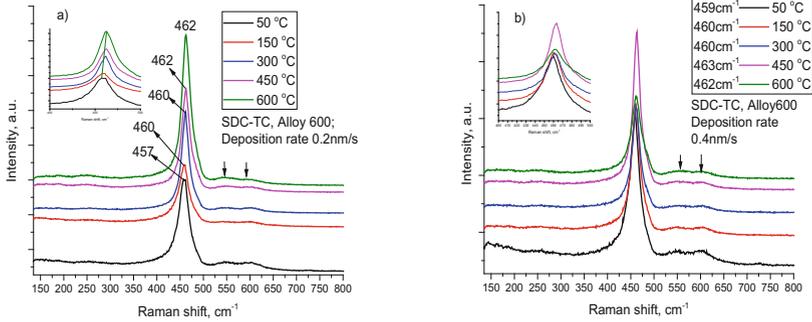
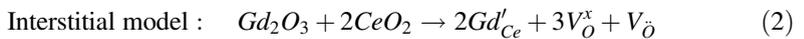
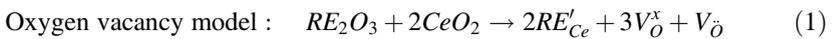
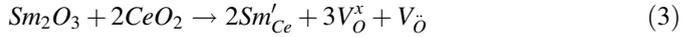


Fig. 5. Raman spectra of Sm doped ceria (SDC20) on Alloy600 substrate at different temperatures by 50 °C to 600 °C and deposition rate: (a) 0.2 nm/s, (b) 0.4 nm/s

The Raman peak position shift consists from 2 cm^{-1} to 9 cm^{-1} of a low-frequency wave (Fig. 5). The peaks for all the samples were similar to each other in form but the wave numbers and their intensity varied depending on the studied sample. The observed intense bands for doped cerium oxides are due to the Raman regime F_{2g} of fluorite dioxide belonging to the space group $Fm\bar{3}m$. The shift of peak position to the region of lower wavenumbers shows that the F_{2g} mode corresponds to the symmetric vibrations of oxygen ions around Ce^{4+} ions in octahedral CeO_8 [8]. The peaks for all the samples were similar to each other in a form. Peak position due to the F_{2g} symmetry and shift in the F_{2g} mode is explained by the change in M-O vibration frequency after the doping with Gd and Sm rare-earth elements [9]. Some additional broad peaks expressed in all samples at 530–550 and around 600 cm^{-1} might be explained by presence of oxygen vacancies [9] are created as charge compensation defects induced by the introducing of other metal cations into the crystal lattice of cerium. Peaks at around 600 cm^{-1} could be explained by non-stoichiometry oxygen vacancy in cerium oxide. The appearance of oxygen vacancy in Gd and Sm doped ceria, could be explained by reaction:





In the Raman study, peak positions are determined by fitting the data to the Lorentz line shape using a peak fit.

4 Conclusions

SDC20 thin films have a single-phase and fluorite structure with space group Fm3m peaks corresponding to crystallographic orientations (111), (200), (220), (311), (222), and (400). The crystallite size of formed SDC20 thin films increases with increasing temperature of the (Alloy 600 and SiO₂) substrates, the smallest crystallite size is $d = 6.2$ nm when the temperature of substrate is $T_{\text{sub}} = 50$ °C and biggest crystallite size $d = 80.1$ nm when $T_{\text{sub}} = 450$ °C). SEM analysis of SDC20 thin films shows that the substrate temperature has the influence on grain size of the formed thin films, the grain size increases till 450 °C substrate temperature and starts to decrease with further increase of the substrate temperature till 600 °C. The main Raman peak of pure ceria is presents at 465 cm^{-1} and corresponds to the F_{2g} vibrational mode. The peaks for all the samples were similar to each other in form, but the wave numbers and their intensity varied depending on the investigated sample. The Raman peak (465 cm^{-1} corresponding to pure ceria) shifts to the lower side from 1 cm^{-1} to 9 cm^{-1} for the formed (GDC10, GDC20, SDC15, SDC20) thin films. That could be influenced by an increase of oxygen vacancies. The most significant shift, 456 cm^{-1} is registered for Sm doped ceria (SDC 15) thin films deposited on SiO₂ and Alloy 600. Raman peaks position at $530\text{--}550 \text{ cm}^{-1}$ and around 600 cm^{-1} might be explained as change of oxygen vacancy amount due to the cerium transition between oxidized and reduced forms of $\text{Ce}^{3+} \rightleftharpoons \text{Ce}^{4+}$.

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