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Samarium-Doped Ceria Nanostructured Thin Films Grown on FTO Glass by Electrodepostion

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Electrical, optical or catalytic properties of ceria can be tuned via doping by rare earth elements. The innate properties of ceria-based materials can be further amplified by using nanostructured ceria. In this study, Sm-doped ceria (SDC) coatings were grown on the FTO glass substrate by means of cathodic deposition. Films were obtained from mixed Sm^{3+}/Ce^{3+} aqueous nitrate solutions, applying -0.8V/(SCE) potential for 1 h. Selected conditions gave rise to adherent, homogeneous and well-covering nanostructured SDC thin films. EDX analysis showed that 0.8 and 1.5 mol% Sm^{3+} led to 3.4 and 6.3 at.% Sm in the SDC films. XRD and Raman analysis confirmed the formation of cubic fluorite-type CeO_2. However, Sm-doping decreased the crystallite size of nanostructured ceria. The effect of annealing on SDC film was also studied. An improvement in crystallite quality was found with increasing temperature. Optical absorption properties were studied and the band gap value (E_g) of 3.07 eV was determined for pure ceria. Sm-doped ceria exhibited a red shifting. The E_g values were 2.97 and 2.81 eV, in due order.

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1.Introduction

Ceria and ceria-based materials have been attracting academic and technological attention owing to a wide range of their applications in heterogeneous catalysis, oxygen gas sensors, solid electrolyte fuel cells, and especially, three way catalysts for automobile exhaust systems [1–5]. High performance of ceria is largely based on the ease of reducing Ce^{4+} to Ce^{3+}, high oxygen storage capacity, and high oxygen ion conductivity. Ceria also displays optical properties, which are of great interest for its application. Having band gap energy of ca. 3eV, it exhibits a unique absorbing ability in the ultraviolet range and is used as a blocking material in the UV-shielding [6, 7]. Physical and chemical properties of ceria can be tuned by doping. Great attention has been focused on the doping of ceria by rare earth elements, found to bring an improvement in its electrical, optical, magnetic or catalytic properties [8–10]. In addition, during the past decades, it has been demonstrated that the intrinsic properties of these materials can be further amplified by their nanostructures of specially designed morphologies, in particular a (1D) [11,12]. Naturally, there is an ongoing interest in production of ceria-based low dimensional nanostructures as well, because of their great potentialities as catalysts, sensors, or building blocks in novel devices [13–15]. However, building a pathway to combine both of these advantages, morphology and dopant effect, represents nowadays a research challenge.

Chemical methods are recognized as a promising route to the fabrication of a variety of ceria nanostructures, although often requiring long or harsh experimental conditions [16–19]. Our group has demonstrated recently that a rod-like nanostructured-ceria film can be grown on FTO glass substrate by electrochemical deposition process (ECD) [20]. ECD is a cost-effective technique suitable for producing high-quality ceria thin films. It provides an easy way to monitor process parameters and tailor coating characteristics. The method is based on the reduction of oxygen precursor to form hydroxide ions in the vicinity of the working electrode. In the case of ceria synthesis, the OH^- ions react with the Ce^{3+} cations present in the electrolytic solution, forming, via either $Ce(OH)_2^{2+}$ dehydration or $Ce(OH)_3$ oxidation, a thin oxide layer on the surface of the working electrode [21, 22]. Cathodic method is also applicable to other metal cations taking part in the precipitation at high pH, such as Sm^{3+}. Many teams detailed the ECD of ceria, but only a few studies deal with SDC and Sm films [23–26].

The current study, as an extension of our previous work [20], reports on the possibility of doping nanostructured ceria by Sm^{3+}, in view of enhancing its UV-

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