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Structural and cathodoluminiscent properties of $Zr_{0.95}Ce_{0.05}O_2$ nanopowders prepared by sol–gel and template methods

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ABSTRACT

Nanopowders of $Zr_{0.95}Ce_{0.05}O_2$ composition have been prepared by a standard Pechini-type sol–gel process and by means of a colloidal crystal template approach. In the latter method, inverse opal $Zr_{0.95}Ce_{0.05}O_2$ powders were fabricated employing poly(methyl methacrylate) (PMMA) colloidal crystals as a template. The effects of the two different synthesis routes on the structure and microstructural characteristics of the prepared nanopowders were evaluated by X-ray diffraction and scanning electron microscopy. For both preparation routes, the X-ray diffraction analysis has shown that a tetragonal fluorite structure is formed with a crystallite size of ~35–40 nm. The scanning electron microscopy measurements indicate that the powder obtained by the sol–gel Pechini-type process is comprised of nanoparticles that are arranged in agglomerates with shape and size relatively uniform whereas the inverse opal $Zr_{0.95}Ce_{0.05}O_2$ nanopowders exhibit the formation of macropores with a mean size of ~100 nm. The cathodoluminescence spectra of the prepared $Zr_{0.95}Ce_{0.05}O_2$ nanomaterials have been measured in the 300–800 nm wavelength range. The powder prepared by sol–gel method yields a broad emission band centered at 482 nm whereas the emission from the inverse opal preparation is considerably less intense.

1. Introduction

Zirconium oxide is a widely studied material with many actual and potential technological applications because of its specific properties such as superior hardness, good chemical and photochemical stability, high resistance to corrosion, low thermal conductivity, high thermal expansion coefficient, high thermomechanical resistance, a large dielectric constant, a high refractive index and a high optical transparency in the 0.3–8.0 μm range with two direct band-to band transitions at 5.2 and 5.8 eV ([1,2] and references therein). At ambient pressure ZrO_2 exists in three polymorphs. Monoclinic zirconia (m-ZrO_2) shows a transition to a tetragonal phase (t-ZrO2) at 1150 °C. Above 2300 °C a cubic fluorite-type structure (c-ZrO_2) is observed. Many studies on the stabilization of high temperature zirconia phases have been carried out employing ceria (CeO_2) as a dopant [2–8] because it improves its mechanical and electrical properties such as toughness, strength, thermal-shock resistance, ionic conductivity and catalytic performance. The amount of dopant content and the synthesis route may determine whether the tetragonal, the monoclinic or the cubic phases are stabilized. It is broadly accepted that the stabilization process of the tetragonal phase in the ceria–zirconia system occurs because oversized tetravalent Ce^{4+} ions (the effective ionic radius is 0.97 Å for eightfold coordination) replace the smaller hosts Zr^{4+} (0.84 Å) and causes to expand the cation network, leading to a decrease in strain energy, which favors tetragonal symmetry.

Nowadays, nanocrystalline particles have attracted broad attention from researchers in various areas both for their fundamental size dependent properties and for many important technological applications. These nanocrystalline materials exhibit size dependent characteristics, and often novel electronic, magnetic, optical, chemical and mechanical properties that cannot be achieved using their bulk counterparts. In this context, the sol–gel method has been successfully used to prepare nano-sized and homogenous zirconia materials [9–14]. This is a straightforward preparation method and has the advantage that the constituent materials can be easily and homogenously mixed at the atomic level by properly controlling the hydrolysis and condensation processes.

Furthermore, as it is known, the fabrication of nanostructured materials using colloidal crystals as templates is a relatively new and promising technique in materials science area. Inverse opals

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can be obtained by infiltrating the solution of precursors inside the opal voids followed by the removal of the organic matter. The resulting material consists of a network that is formed by nanometer-sized pores yielding large surface areas and with a crystalline inorganic phase as pore wall. The obtained meso- and macroporous architectures can be useful in applications where large surface areas are to be preserved during high temperature operations as, for instance, in heterogeneous catalysis. Several experimental studies have been reported on the successful formation of the macroporous photonic crystals of zirconia, ceria–zirconia and rare-earth doped zirconia and the modification of spontaneous emission of the embedded luminescent species in the photonic crystals [13–16].

The optical gap of ZrO_2 is commonly affected by the incorporation of rare-earth ions that generally induce new optical properties in the host material. Moreover, ZrO_2 has very low dominant phonon energy of about 470 cm^{-1}, which decreases the probability of non-radiative multi-phonon relaxation of excited rare-earth dopant ions throughout the vibrational bands of the host lattice. This mechanism is considered one of the most competitive non-radiative relaxation processes for optical activator ions in a luminescent material. Therefore, luminescence studies can provide important information about intrinsic and impurity defects in pure and doped ZrO_2 [17–18]. The techniques employed to study the optical properties of lanthanide ion-doped ZrO_2 materials include cathodoluminescence [12,18–20], photoluminescence [13–16,21–27] and thermoluminescence [12,28–32] spectroscopies. Light emission from rare-earth ions is mainly due to electric and magnetic dipole optical transitions within the 4f manifolds or involving configurations such as $4f^{n-1}$ and 5d [17]. The outer 5s and 5p subshells shield the 4f electrons from the influence of external fields and, as a result, the emission spectra consist of relatively sharp lines. Although the f–f transitions of lanthanide ions are, in principle, forbidden, the crystal field surrounding the rare-earth ions relaxes the selection rules so that luminescence emission can be observed even at room temperature.

The present work reports on the influence of the synthesis route on the crystalline structure and cathodoluminescent properties of ceria (CeO_2) doped zirconia powders obtained by the Pechini-type sol–gel method and by inverse opal preparation using 3D arrays of PMMA particles as template. The synthesized samples were characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM). Additionally, the cathodoluminescence (CL) response of the synthesized $Zr_{0.95}Ce_{0.05}O_2$ nanomaterials has been analyzed and discussed.

2. Experimental

Nanopowders of $Zr_{0.95}Ce_{0.05}O_2$ composition were prepared by the Pechini method [33] using $ZrOCl_2 \cdot 8H_2O$ (Aldrich, Purity 99.99%) and $Ce(CH_3COO)_3$ (Aldrich, Purity 99.99%) as starting materials with citric acid and ethylene glycol as polymer agents. 5 g of citric acid was dissolved into 40 ml of water followed by the addition of stoichiometric quantities of $ZrOCl_2 \cdot 8H_2O$ and $Ce(CH_3COO)_3$. After 1 h of stirring, 4.5 ml of ethylene glycol was added. The solution obtained was heated at 80 °C for 30 min and then the temperature was slowly increased up to 140 °C to promote polyesterification and to remove water excess. After 1 h, a white aerogel was obtained that was aged during 4 days. The pyrolysis and subsequent calcination in air at 750–850 °C yielded a yellow crystalline powder.

For the inverse opal preparation, the sol–gel precursor solution containing Ce–Zr–CA complex, prepared as in the Pechini-type synthesis, was infiltrated within a poly(methyl methacrylate) (PMMA) colloidal crystal template prepared as described in Ref. [34]. The $Zr_{0.95}Ce_{0.05}O_2$ inverse opal was isolated after removal of the organic template by calcination between 750 and 850 °C for 3 h.

Powder X-ray diffraction (XRD) patterns of the prepared materials were collected on a Philips X'Pert MPD diffractometer, Ni filtered Cu K_α radiation, with a PW 3050/00 goniometer. A step scan of 0.04° (2θ) in the range 10–120° and a counting time of 15 s for each step were employed. The goniometer was connected to a PC controlled by the commercial program PC-APD (Analytical Powder Diffraction Software 4.0).

Scanning electron microscopy (SEM) was used to characterize the powders using a JEOL-6400 electron microscope operating at 20 kV. The sample was dusted on an adhesive conductive carbon disk attached to a mount and was coated with a gold film prior to examination.

Cathodoluminescence (CL) investigations were performed in a Hitachi S-2500 SEM. Measurements were carried out at an accelerating voltage of 20 kV and temperatures between 85 and 295 K. CL spectra in the visible range of wavelengths were recorded using a charge coupled device camera with a built-in spectrograph (Hamamatsu PMA-111) and corrected for the system response. The spectral resolution of the system used is 0.4 nm.

3. Results and discussion

3.1. XRD and SEM structural characterization

Fig. 1 displays the XRD patterns of the cerium-doped zirconia nanopowders of $Zr_{0.95}Ce_{0.05}O_2$ composition synthesized by both the sol–gel Pechini-type process and the PMMA colloidal crystal template method. In the case of powders obtained by sol–gel Pechini-type method, the X-Ray diffraction patterns show reflections that can be indexed to a tetragonal symmetry. By contrast, the powders synthesized via PMMA inverse opal present reflections that can be indexed to a mixture of tetragonal and monoclinic symmetries without any indication of impurities. Evidence of the tetragonal symmetry might be obtained in the high-angle region of the XRD pattern, i.e., a non-symmetric line-shape at around $2\theta=35°$, which is originated from the splitting between [0 0 2] and [1 1 0] peaks.

The X-ray diffraction data of nanopowders obtained by the two preparation routes were analyzed by means of the Rietveld refinement method and using the FULLPROF program [35]. The XRD data of nanopowders obtained by the sol–gel process were indexed and

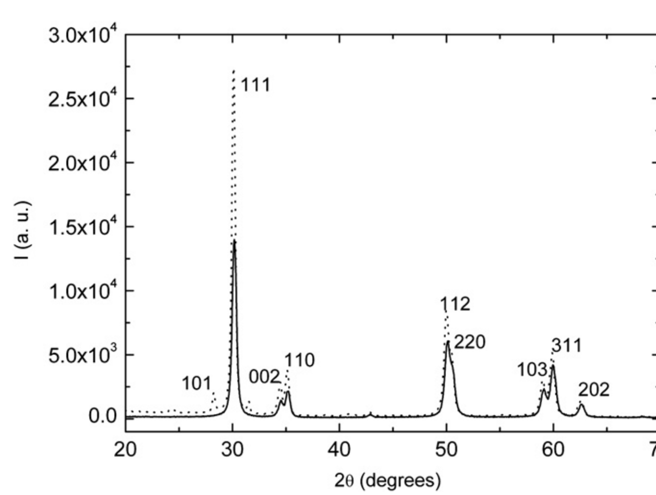

Fig. 1. XRD patterns of synthesized $Zr_{0.95}Ce_{0.05}O_2$ oxides. Solid: Pechini-type sol–gel method; dashed: inverse opal powder.