Doping of Sm into CeO_2 nanotubes up to 50%

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Abstract

Introduction: Ceria and Materials based on ceria (CeO_{2-x}) have attracted much attention due to many applications in different fields such as fuel cells, catalysis, etc.. Doping of some elements for example Sm**,** into ceria has improved some properties of this compound such as electrical conductivity, catalytic behavior, etc..

Aim: Syntheses and characterization of Sm doped CeO_2 nanotubes at room temperature

Materials and Methods: Crystalline phases were determined by X-ray diffraction (XRD) and morphology of the prepared samples was studied by SEM and TEM. Elemental analysis of the prepared samples was carried out using ICP method.

Results: The XRD patterns of the Sm doped CeO_2 nanotubes were compared with that of CeO_2 (JCPDS, 43-1002). Comparison of these patterns indicated that all samples had cubic flurorite structure. Sm-doped CeO_2 patterns showed that Sm could be doped into CeO_2 up to 50%. The EDAX and ICP analysis of the samples indicated that Sm was doped into the CeO_2. The SEM and TEM images of the synthesized samples confirmed formation of Sm doped ceria nanotubes. The calculation of unit cell parameter (a) indicated that by doping of Sm into CeO_2, "a" increased. This increase could be due to Sm ionic radii (r_{Sm}^{III}= 0.96Å), which is more than that of Ce (r_{Ce}^{IV}= 0.87 Å).

Conclusion: The XRD patterns of Sm-doped CeO_2 showed that Sm could be doped into CeO_2 up to 50% (This doping level is obtained in this work for the first time). By doping Sm into CeO_2, lattice parameter of the unit cell of the samples ("a") increased.

Keywords: Inorganic nanotubes, Gas-liquid co-precipitation, Ceria, Sm-doped ceria

Introduction

Recently, the applications of nanometric size ceria and doped ceria materials improved some properties such as electrical conductivity, catalytic behavior, etc.[1] Thus, these materials have received enormous attention because of their applications in various fields. Cerium oxide has a fluorite structure stable up to its melting point, a large diffusion coefficient and good corrosion-resistance when compared with other pure oxides having oxygen ion conductivity. Among doped ceria materials, the Sm_2O_3/CeO_2 system (SDC) shows the highest electrical conductivity, since Sm-

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doping induces the least distortion of the parent lattice. Also used as an oxygen buffer in the automotive three-way catalysts (TWCs), as a promoter for gas phase oxidation/ reduction reactions.[2-5]

Recently, various methods have been developed to synthesize CeO_2 and doped nanomaterials with various shapes, including: co-precipitation, sol-gel process, hydrothermal synthesis, sono-chemical, hydrothermal treatment, gas–liquid co-precipitation, etc. [6-15]. In this work, Sm doped CeO_2 compounds were synthesized and characterized by conventional methods.

Experimental

Cerium nitrate, $Ce(NO_3)_3.6H_2O$ (98.5% Merck), samarium oxide (Sm_2O_3) (99% Fluka), and NH_4OH (25% Merck) were used as the starting materials. Samarium nitrate solution was prepared by dissolving samarium oxide in minimum amount of dilute nitric acid, and appropriate amount of cerium nitrate and samarium nitrate were mixed to give $Ce_{1-x}Sm_xO_{2-\delta}$ (x=0.2,0.3 and 0.5) compounds. For example, according to the stoichiometric ratio of $Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC), cerium nitrate and samarium nitrate solution were mixed in a beaker. This beaker and another beaker containing ammonia solution (25%) were put into a sealed vessel. This sealed vessel was maintained at ambient temperature about 2 days. Finally, the precipitate was centrifuged, washed with de-ionized water and absolute ethanol alternatively for three times, and dried in vacuum at room temperature. The phase and purity of the products were examined by X-ray diffraction (XRD) using an X-ray diffractometer with CuKα radiation λ=1.5405Å (on Rigaku, D / Max 2500 V/PC). The morphology of the products were observed using a scanning electron microscope (SEM Philips XL 30) and a transmission electron microscope (TEM) (Philips EM 208) and elemental analysis of the sample was carried out by using inductively coupled plasma (ICP) technique.

Lattice parameter (a) was calculated by the following formula:

$$d^2 = a^2/ (l^2+k^2+h^2)^2$$

Where, a refers to the CeO_2 (FCC) lattice parameter, h, k, l are Miller indices and d is crystalline face space.

Results and discussion

In Fig. 1, the XRD patterns of the Sm doped CeO_2 nanotubes dried at room temperature (298 K) are compared with that of CeO_2 (JCPDS 43-1002). Comparison of these patterns indicates that all samples have single phase of cubic flurorite structure and no additional peaks observed

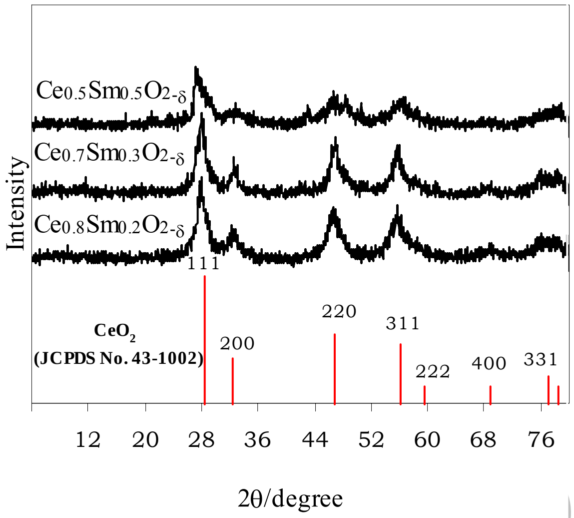

Fig. 1- XRD patterns of the Sm-doped ceria dried at room temperature.

In order to confirm the phase purity of the obtained product, the synthesized $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ sample were calcined at 973 K. Fig. 2 shows the XRD patterns of this sample dried at room temperature (298K) and 333K, and calcined at 973K. It is observed that the XRD pattern reflections of the Sm-doped ceria sample before calcination are very broad, which is due to very fine crystalline size, but after calcinations, sharp peaks are appeared. The XRD patterns of CeO_2 and the other Sm-doped CeO_2 samples calcined at 773K are indicated in Fig. 3. Sm-doped CeO_2 patterns (Fig. 1 and 2) show that Sm could be doped into CeO_2 up to 50%.

EDAX analysis of the $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ is shown in Fig. 4. This figure indicates that the Sm is doped into the CeO_2. The exist of ZnK peaks is due to impurity of $Ce(NO_3)_3.6H_2O$ compound used for synthesis of the sample.

From ICP analysis of $Ce_{0.5}Sm_{0.5}O_{2-\delta}$, it was found that the Ce:Sm ratio in the final calcined product was around 45/50. This result indicates that there is only a slight difference in the Ce/Sm ratio, that can be due to presence of Zn in the $Ce(NO_3)_3.6H_2O$ compound as impurity.

Fig. 5 shows the SEM image of the $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ calcined at 973K. This figure indicates the Sm doped ceria nanotubes. However, there are also some nanoparticles in this image. Fig. 6 (a-e) shows TEM images of CeO_2 and 20% and 50% Sm-doped ceria at room temperutre and calcined at 773K.

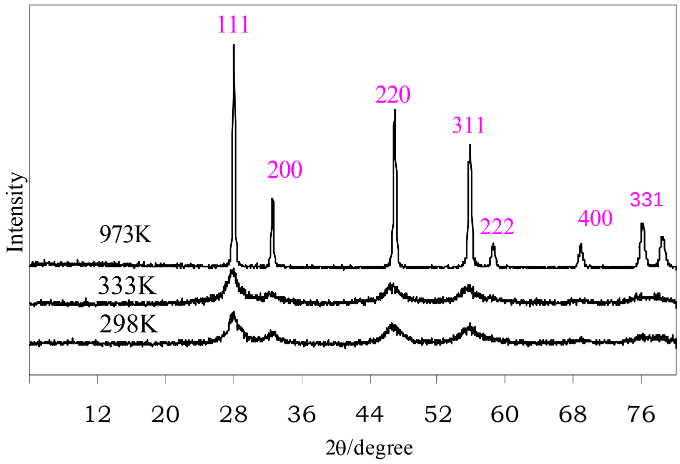

Fig 2- XRD patterns of the $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ sample.

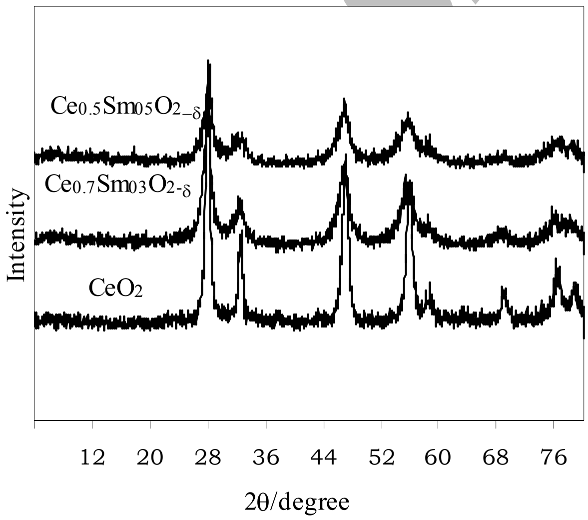

Fig. 3- XRD patterns of the Sm-doped ceria at 773K.

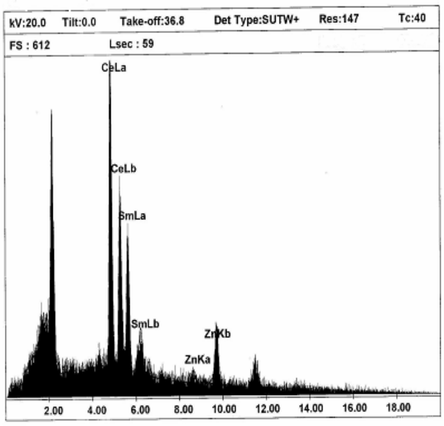

Fig. 4- EDAX analysis of $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ at 973K.

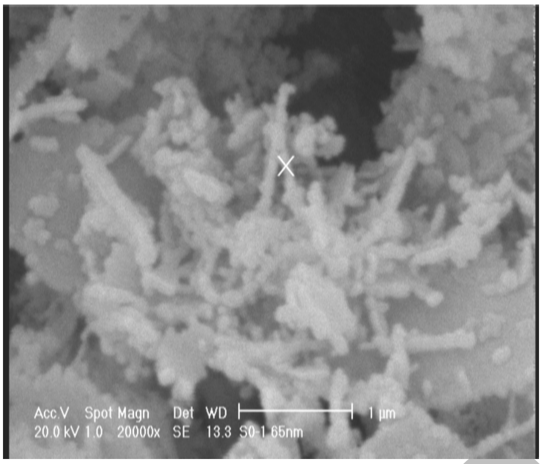

Fig. 5- SEM image of the $Ce_{0.8}\ S_{0.2}O_{2-\delta}$ at the 973K.

Lattice parameter of the samples calculated using XRD data. Table1 shows "*a*" values of the unit cell of the prepared samples. This table indicates that by doping Sm into CeO_2, "*a*" increased. This increase could be due to Sm ionic radii (r_{Sm}^{III}= 0.96Å), which is more than that of Ce (r_{Ce}^{IV}= 0.87 Å).

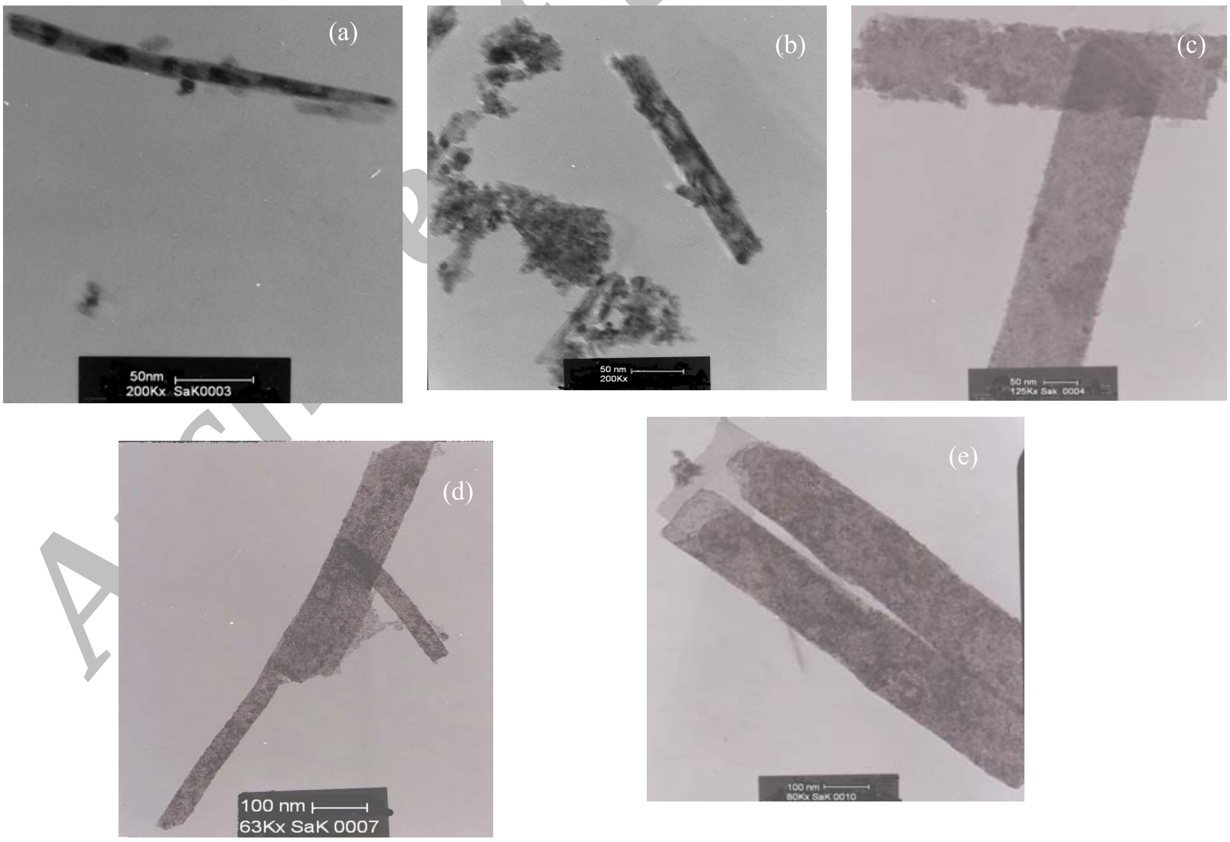

Fig.5- TEM images of CeO_2 (a-b), $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ as-dried at room temperature (c) and calcined at 773K (d), and $Ce_{0.5}Sm_{0.5}O_{2-\delta}$ calcined at 773K (f).

Tabel 1 -Lattice parameter a (Å) of CeO_2 and Sm doped CeO_2 nanotubes.

Sample	a (Å)
CeO_2	5.4122
$Ce_{0.5}Sm_{0.5}O_{2-\delta}$	5.4210

Conclusion

The XRD patterns of Sm-doped CeO_2 showed that Sm could be doped into CeO_2 up to 50% (This doping level is obtained in this work for the first time). By doping Sm into CeO_2, lattice

parameter of the unit cell of the samples ("*a*") increased. The XRD patterns of Sm-doped ceria sample before calcination were very broad, but after calcinations sharp peaks were appeared.

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