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Short communication

Synthesis of $Ce_{0.75}Zr_{0.25}O_2$ at 100 °C

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Abstract

A simple gel to crystal conversion route has been used for the preparation of $Ce_{0.75}Zr_{0.25}O_2$ phase at 80–100 °C under refluxing conditions. Freshly prepared metal hydroxides gel from cerium and zirconium salt solution is allowed to crystallize under refluxing and stirring conditions for 4–10 h. Formation of nano crystallites of $Ce_{0.75}Zr_{0.25}O_2$ is confirmed by X-ray diffraction (XRD). Transmission electron microscopy (TEM) investigations revealed the average particle size of these powders to be 5 nm.

Keywords: A. Powders: chemical preparation; B. X-ray methods; B. Electron microscopy; D. CeO_2

1. Introduction

The important use of CeO_2 is as an activator in three way catalyst (TWC) for automotive exhaust control [1,2]. CeO_2 based materials also find wide applications in fuel cells and gas sensors [2]. The ability of CeO_2 for activation of water gas shift reaction, thermal stability and its oxygen storage capacity makes it an ideal activator in TWC formulations [3,4]. The key to oxygen storage capacity of CeO_2 based materials is due to its characteristic feature to shift between Ce^{4+} and Ce^{3+} in the stable fluorite structure, which in fact allows release and transport of O^{2-} ions. It has been reported [5] that microstructural stability is improved by doping with suitable cations such as Zr^{4+}, Al^{3+} and Si^{4+}. Compared to CeO_2, $Ce_{1-x}Zr_xO_2$ shows improved ability to store and release oxygen and greater thermal stability. Many wet chemical methods such as co-precipitation, sol–gel, high energy ball milling, micro-emulsion and the hydrothermal method have been employed to synthesize these powders [6–11]. It has also been reported that the catalyst performance depends on phase composition, homogeneity and surface area of the powders [12]. The method of gel to crystalline conversion is reported in the literature for the preparation of multicomponent oxides such as perovskites and spinels [13–15], but this method is not yet reported for the preparation of $Ce_{0.75}Zr_{0.25}O_2$ ceramics. Here we report this simple process of digestion of amorphous hydroxides gel under refluxing conditions at 100 °C for the preparation of nanocrystalline $Ce_{0.75}Zr_{0.25}O_2$.

2. Experimental

All the reagents used in this work are of AR grade. Both ceric nitrate ($Ce(NO_3)_3{\cdot}6H_2O$) and zirconium oxy chloride ($ZrOCl_2{\cdot}8H_2O$) in required quantities were dissolved in distilled water. To this solution ammonium hydroxide is added dropwise to precipitate metal ions as hydroxides. The hydrated hydroxides gel is washed free of anions and transferred to flask fitted with a water condenser. The gel was continuously stirred for 6 h at about 70–100 °C. Then, the crystalline powder formed was filtered and oven dried at 100 °C overnight. Unlike gel, the powders obtained after digestion are crystalline in nature. Various techniques such as XRD (Philips PW 1710 Diffractometer), and BET surface area measurements (Nova 1200 instrument) were employed to characterize these powders. For lattice parameter and interplanar distance (*d*) calculation, the samples were

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scanned in the 2θ range of 10–80° for a period of, 5 s in the step scan mode. Silicon was used as an internal standard. Least squares method was employed to determine the lattice parameters. The TEM picture was recorded with JEOL model 1200 EX instrument at the accelerating voltage of 100 kV. The fine powders were dispersed in amyl acetate on a carbon coated TEM copper grid.

3. Results and discussion

Samples before refluxing at 100 °C are X-ray amorphous and no distinct peaks are observed. Fig. 1 shows the XRD for CeO_2 and $Ce_{0.75}Zr_{0.25}O_2$ samples after refluxing at 100 °C. The observed *d*-lines match the reported values for CeO_2 phase. The calculated lattice parameters for CeO_2 and $Ce_{0.75}Zr_{0.25}O_2$ are $a = 5.421$ and 5.385 Å, respectively. This agrees with the decrease in ionic radius when Ce^{4+} (1.11 Å) is replaced by Zr^{4+} (0.98 Å). It is to be noted that the molarity of the solution should be >0.15 M to obtain crystallization in this process. Otherwise it requires long times to form a crystalline product at 100 °C. Fig. 2 shows the slow scan of the (1 1 1) and (2 0 0) XRD peaks which was used for lattice parameter calculations. The shift in the lattice parameters with zirconium substitution in ceria is more discernible in this case as compared to Fig. 1.

The surface area of the $Ce_{0.75}Zr_{0.25}O_2$ powders was found to be 80 m^2/g. The particles are found to be agglomerated and with an average size of 5 nm (Fig. 3) by TEM studies. Crystallite size measurements were also carried out using the Scherrer equation, $D = k\lambda/\beta \cos\theta$ where D is the crystallite size, k is a constant (=0.9 assuming that the particles are spherical), λ is the wavelength of the X-ray radiation, β is the line width (obtained after correction for the instrumental broadening) and θ is the angle of diffraction. The average particle size obtained for $Ce_{0.75}Zr_{0.25}O_2$ from XRD data is 10 nm. These powders, when prepared by the glycine nitrate process [9] have particle size around 35 nm with surface area 40 m^2/g. Microwave-hydrothermal method [8] yielded agglomerated particles of 7 nm in size. The digestion method is thus, superior to above methods as shown by present results. To examine, whether a mesoporous structure is formed by this process low angle X-ray diffraction studies were carried out. Fig. 4 shows the low angle XRD pattern recorded for $Ce_{0.75}Zr_{0.25}O_2$ powders, which indicates the formation of a mesoporous structure (d = 22.7 Å). The mesoporous structure of these powders collapses on heating at 500 °C for 4 h [12].

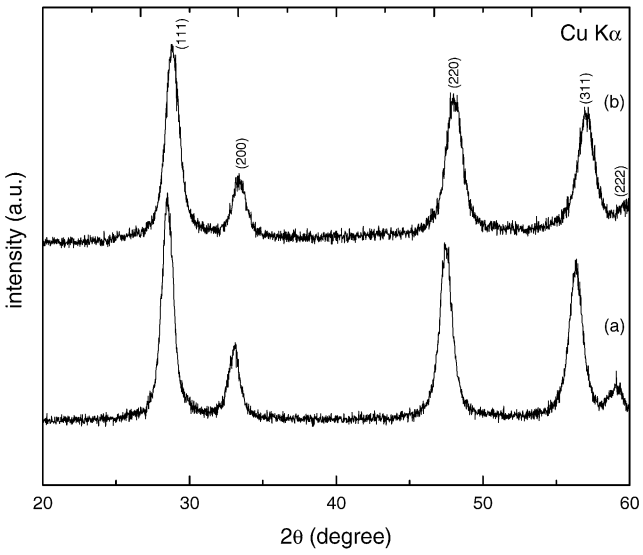

Fig. 1. XRD of (a) CeO_2 and (b) $Ce_{0.75}Zr_{0.25}O_2$ powders.

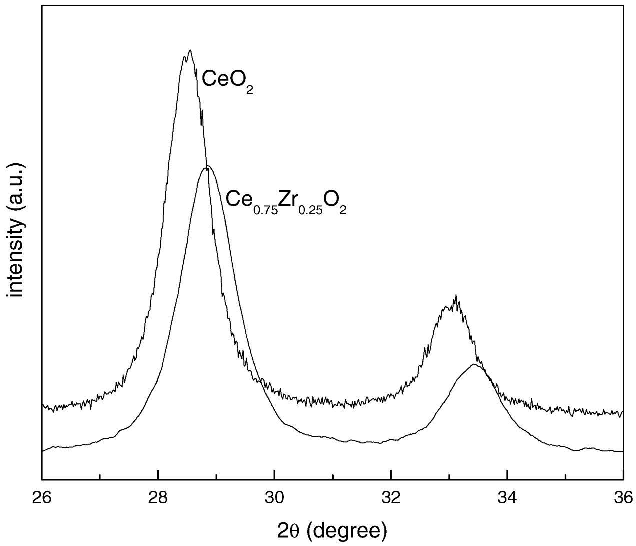

Fig. 2. Slow scan of (1 1 1) and (2 0 0) XRD peaks of (a) CeO_2 and (b) $Ce_{0.75}Zr_{0.25}O_2$.

Metal hydroxide gels are in general polymeric chains forming an entangled network in which solvent is entrapped. It is the osmotic pressure, which is the sum of rubber elasticity, polymer–polymer affinity and hydrogen ion pres-

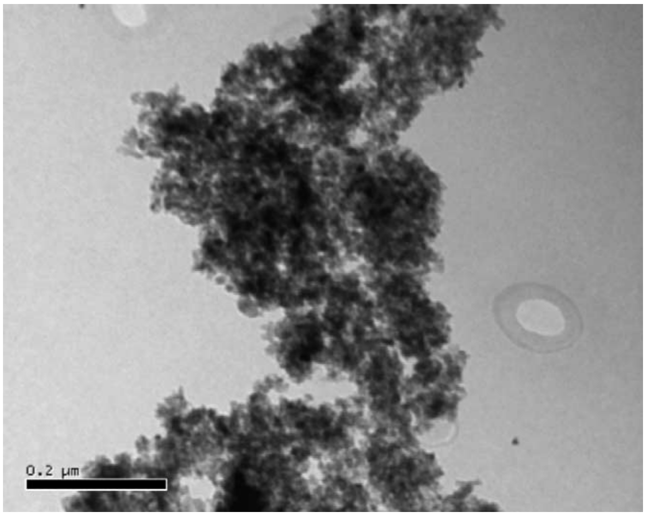

Fig. 3. TEM micrograph $Ce_{0.75}Zr_{0.25}O_2$ powders.

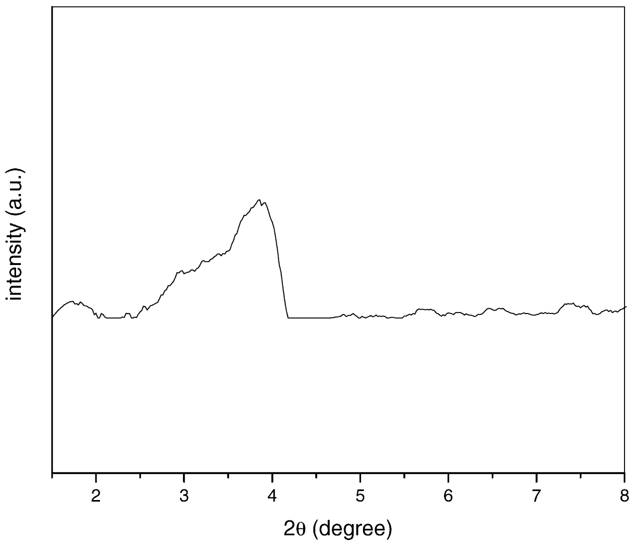

Fig. 4. Low angle XRD for $Ce_{0.75}Zr_{0.25}O_2$ powders.

sure that contributes to stability of the gel. If any one of the factors is altered, the gel collapses irreversibly. The continuous influx of solvent breaks the gel network and small crystalline regions are created. This crystallization is favoured because of reduction in the free energy. Thus, crystalline $Ce_{0.75}Zr_{0.25}O_2$ phase is formed at 100 °C.

4. Conclusion

Nanocrystalline $Ce_{0.75}Zr_{0.25}O_2$ was obtained from their amorphous hydroxide precipitates by simple digestion at 100 °C. The average particle size obtained by TEM is 5 nm. Low angle XRD studies show the formation of mesoporous structure ($d = 22.7$ Å) which collapses on heating at 500 °C for few hours.

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