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Synthesis of nanocrystalline samarium-doped CeO_2 (SDC) powders as a solid electrolyte by using a simple solvothermal route

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Abstract

Samarium-doped CeO_2 is a leading electrolyte for applications in solid oxide fuel cells (SOFCs), which requires a typical sintering temperature of 1400–1600 °C. In this work, fully dense CeO_2 ceramics doped with 10–20 at.% samarium have been fabricated by a simple polyol process. The XRD and SEM results show that a complete solid solution between CeO_2 and samarium was obtained at the sintering temperature of 1300 °C. And also the densification temperature is significantly lower than those (1400–1600 °C) reported for the SDC powders processed by modified sol–gel process and hydrothermal treatment. The resultant ceramics show the sizes of ultrafine grain are lower than 1 μm.

Keywords: Polyol process; Samarium-doped ceria; Solid oxide fuel cells

1. Introduction

Solid oxide fuel cells (SOFCs) have a great potential to be the cleanest, most efficient, and versatile technology for the chemical to the electrical energy conversion. Commonly, solid electrolyte materials which are used in SOFC are; stabilized zirconia (e.g. yttria stabilized zirconia), doped ceria (e.g. samaria doped or gadolinia doped ceria), stabilized Bi_2O_3 and strontium/magnesium doped lanthanum gallate. A typical SOFC which uses yttria stabilized zirconia (YSZ) as the electrolyte requires high operation temperature. The high operation temperature required for YSZ can cause the technological problems, such as mechanical instability, reduced lifetime and undesirable reactions between the cell components (electrolyte, electrodes and interconnecting materials). Doped ceria (CeO_2) compounds are fluorite type oxides with oxygen vacancies, which show an oxide ionic conductivity higher than yttria stabilized zirconia in oxidizing atmospheres and has a low cost in comparison with lanthanum gallate based on electrolytes. The concentration of oxygen vacancy and concominant oxide ion conductivity, in CeO_2 can be increased by the substitution of a lower valent metal such as Sm. As a consequence of this, a considerable interest has been shown in the application of these materials for "low temperature (500–650 °C)" operation of SOFCs. The high ionic conductivity coupled with the low activation energy for the ionic conduction makes the doped ceria an attractive material for its use at temperatures below 800 °C, which would allow greater flexibility in the design of electrode and inter-connectors [1]. Aliovalent substitution of trivalentions into the lattice of ceria results in the formation of oxygenion vacancies, giving a rise to an increase in the ionic conductivity [2].

In the trivalent rare-earth doped ceria, the highest conductivities are observed for $Ce_{1-x}Sm_xO_{2-x/2}$ and $Ce_{1-x}Gd_xO_{2-x/2}$ [3,4]. For this reason, the researches are focused on the ceria based on electrolytes. To obtain these materials, various techniques have been used such as sol–gel [5], combustion [6], mechanochemical [7], hydrothermal [8], microemulsion [9], glycine-nitrate [10] and homogeneous precipitation [11,12]. The SDC powders prepared by a modified sol–gel process have been sintered to a higher relative density even at relatively low sintering temperature of 1300 °C. In this process the gels are treated with octanol [16]. $Ce_{1-x}Sm_xO_{2-x/2}$ and $Ce_{1-x}Ca_xO_{2-x}$ solid solutions were prepared hydrothermally at 260 °C with NaOH solutions. The small particle size (40–68 nm) of the hydrothermally prepared materials allows sintering of the samples into highly dense ceramic pellets at 1400 °C [17].

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Among the various chemical methods, which have been developed for the preparation of metal particles, the polyol process is a promising method with which mono dispersed metal particles can be prepared [13,14]. In this procedure ''polyol'' stands as a general term for polyalcohols (e.g. ethylene glycol, triethylene glycol, etc.) with high boiling temperature and sufficient ability to solve inorganic salts at elevated temperature to a considerable amount. For the preparation of metallic particles the polyol method was applied because of its mild reducing properties. On the other hand, the polyol acts as solvent with a chelating effect which avoids agglomeration of particles during the preparation [15]. Materials, obtained from this method, show homogenous phase composition, narrow particle distribution and high specific surface area. And also morphology controllable synthesis of nanostructred metal compounds can be achieved by adjusting the reaction parameters. Because of its simplicity and the advantage over the most other methods the polyol method has received a considerable attention to prepare the highly pure mixed oxides. For example, the CeO_2 nanospheres, microrods and spindle-like particles were fabricated by using a one step polyol process in the presence of a protective agent, PVP [18].

In this study, we report for the first time the preparation of nanocrystalline CeO_2 doped with Sm (0, 10, 15 and 20 mol%) via a simple polyol process without using a protective compound. The dependence of morphology on the nature of metal precursor were also studied. Furthermore, we studied the effect of calcination temperature to find out the evolution of crystal structure. The thermal decomposition behaviors of the products we also examined by thermal gravimetric analysis (Fig. 1).

2. Experimental

2.1. SDC preparation

Cerium(III)acetate hydrate ($(C_2H_3O_2)_3Ce{\cdot}1.5H_2O$, 99.9%, Aldrich), samarium (III) acetate hydrate($(C_2H_3O_2)_3Sm{\cdot}H_2O$, 99.9%, Aldrich), cerium (III) nitrate hexahydrate ($Ce(NO_3){\cdot}6H_2O$, 99%, Aldrich), samarium (III) nitrate hexahydrate ($Sm(NO_3){\cdot}6H_2O$, 99.9%, Aldrich) were used as metal precursors and triethylene glycol, TREG ($C_6H_{14}O_4$, Merck) was used as a solvent and reducing agent. In a typical polyol process; the specified amounts of metal precursors, usually total ion concentration being kept at 0.2 M, were dissolved in 50 ml triethylene glycol. The solution was transferred to a 100 ml three neck spherical glass flask equipped with a refluxing condenser and a thermometer, and placed on a magnetic stirrer. The powders are labeled according to the precursor salt used in the polyol process, SDC1 refers to nitrate anions while SDC2 refers to acetate anions. All the experimental conditions are same for SDC1 and SDC2. First, the metal precursors were dissolved in triethylene glycol at 60–80 °C then the solution was heated to 200 °C and kept for 5 h at this temperature under vigorous stirring. During this time, the color of the liquid turned from white to purple violet then to brown. Then the reaction solution was naturally cooled down to room temperature and the solids separated by the vacuum filtration and washed with deionized water.

2.2. Thermal analysis

The solids were dried at 110 °C for 4 h. The conversion of the so-prepared amorphous precursors into crystalline samarium-doped CeO_2 was achieved by heating the dried solids at a rate between 5 °C min^{-1} to either 300, 500 and 1000 °C, and keeping them at these temperatures for 2 h. The thermal behavior of the SDC1 and SDC2 particles was carried out with SII Exstar 6000 TG/DTA 6300 from 40 to 1000 °C at a heating rate of 10 °C min^{-1} in a flow of air. The results of the differential thermal analysis (DTA) and thermogravimetric analysis (TGA) as a function of temperature were plotted.

2.3. X-ray analysis and crystallite size determination

X-ray diffraction (XRD) technique was used to determine the crystal structure and phase. The precursors were calcined at 100, 300, 500 and 1000 °C for 2 h. The X-ray spectra of samarium-doped ceria particles were obtained over the 2θ range of 20–90° by using Rigaku D/max-2200 ultima X-ray diffractometer with CuKα radiation. From the X-ray diffractograms, phases and the average crystallite sizes, D, of the $Ce_{1-x}Sm_xO_{2-x/2}$ samples were calculated from X-ray line broadening of the reflections of (422) by using the well-known Scherrer equation.

2.4. Density determination

The calcined powders were pressed to disk at 200 MPa with CIP. The compact disk of $Ce_{1-x}Sm_xO_{2-x/2}$ powders were then sintered at 1200, 1300 and 1400 °C for 6 h with a heating rate of 5 °C min^{-1}. The resultant sintered the densities (D_{rs}) of the disks were determined by the Archimedes's method.

$$D_{rs} = \frac{W_{obj}g}{W1 - W2}$$

where W_{obj} is the dry weight, $W1$ is the wet weight (water in body), $W2$ is the body's submerged weight without fine wire and g is the density of the solvent (water at 25 °C 0.997 g cm^{-3}). The value of theoretical density was calculated as 7.16 g cm^{-3}.

2.5. Scanning electron microscopy (SEM) analysis

The morphology of the sintered samples at 1200, 1300 and 1400 °C was determined by scanning electron microscopy SEM JEOL JSM-6335F. And also the morphology change according to sintering temperature was studied.

2.6. Oxygen conductivity measurements

In order to further investigate the high temperature behavior of this SDC powder, disk-shaped sample of 15 mm diameter and 1 mm thickness was prepared by cold isostatic pressing (CIP) at 95 MPa. Subsequently, the sample was sintered at

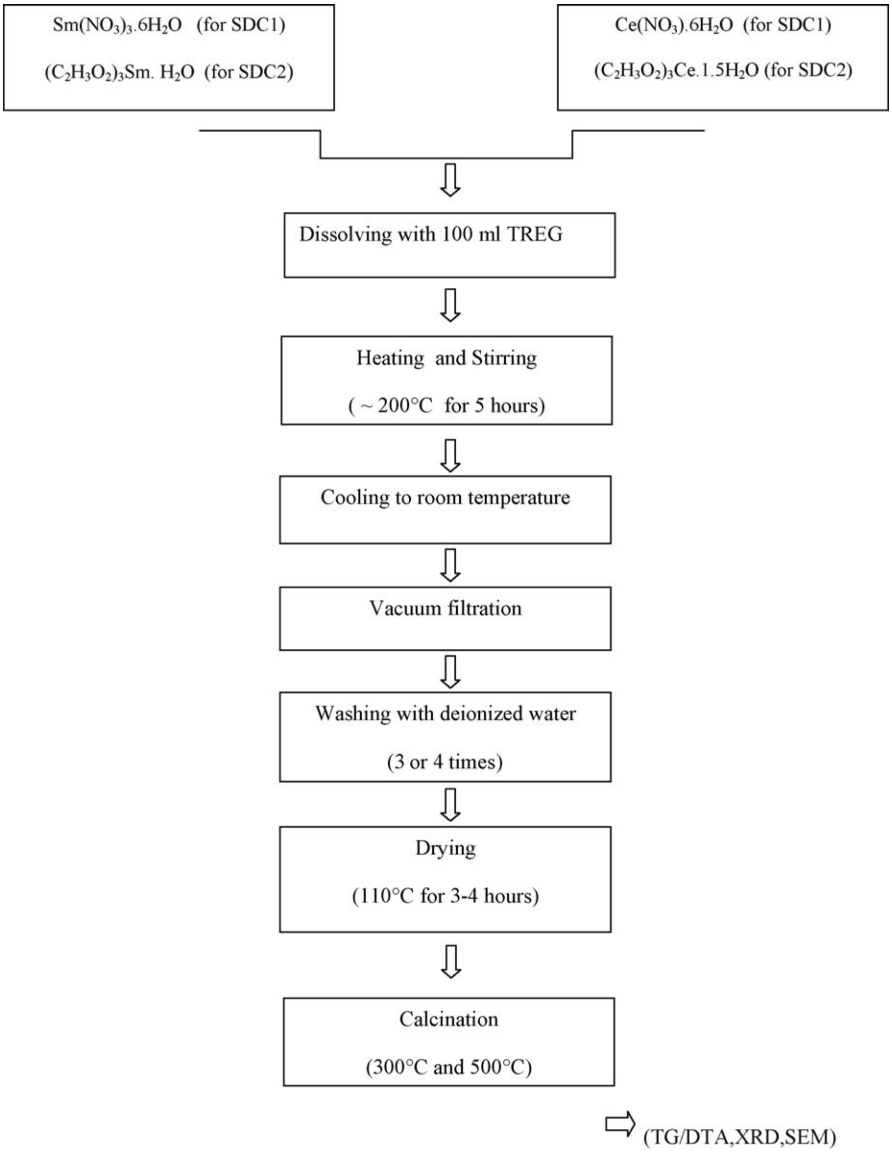

Fig. 1. Flow chart of the polyol process.

1400 °C for 6 h. The measurements of the oxygen conductivity were made by AC Impedance analyzer (Solartron 1260 FRA and 1296 interface) at 200 °C.

3. Results and discussion

3.1. Thermal analysis

To further evaluate the composition of the precursor particles and to elucidate their transformation to crystalline $Ce_{1-x}Sm_xO_{2-x/2}$, extensive TGA analyses were carried out. Graphs in Fig. 2 summarize the results of the study for 20% samarium-doped solids which are prepared with $(C_2H_3O_2)_3Ce\cdot 1.5H_2O$ and $C_2H_3O_2)_3Sm\cdot H_2O$ precursors. The TG curve in Fig. 2 shows a minor weight-loss of 3% between 50 and 197 °C which is related to the loss of adsorbed water and acetate. The drastic weight loss of 12% at 200 °C is due to the combustion of organic residues. A slight weight loss is observed between 226 and 351 °C, and could

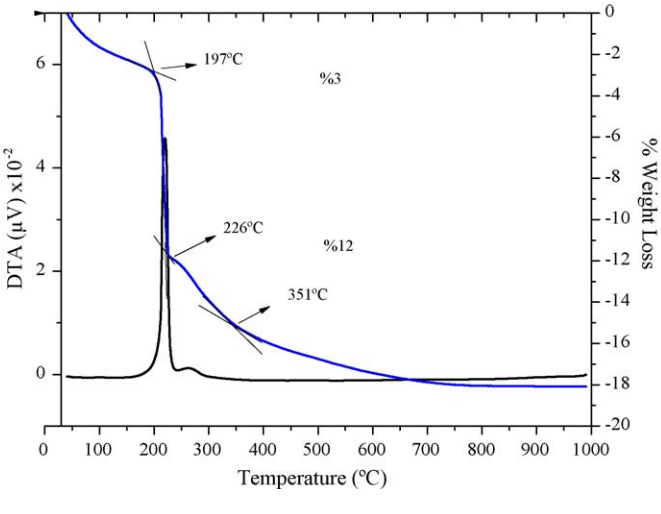

Fig. 2. TG–DTA curves of thermal decomposition of nanocrystalline SDC powder precursors at a heating rate of 5 °C min^{-1} in static air.

Table 1
Some physical properties of the SDC powders calcined at different temperature for 2 h.

Amount of Sm doping (mol%)	Crystallite size (nm)			Lattice constants (nm)	S_{BET} (nm)		
	300 °C	500 °C	1000 °C	1000 °C	300 °C	500 °C	1000 °C
20SDC1	10	11	37	0.5432	113	54	11
15SDC1	11	12	42	0.5431			
10SDC1	9	11	37	0.5428			
20SDC2	11	13	31	0.5440	150	118	11
15SDC2	9	9	36	0.5434			
10SDC2	10	10	42	0.5432			

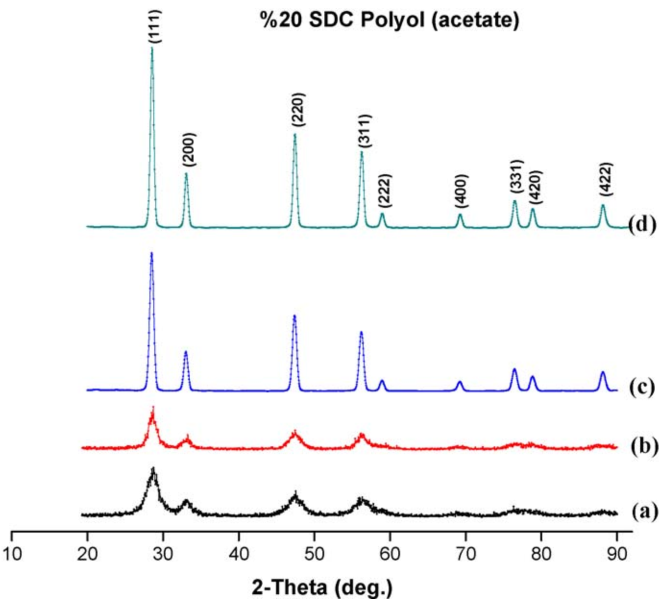

Fig. 3. XRD patterns of nanocrystalline 20% Sm doped SDC(acetate) powders calcined in air for 2 h at (a) 300, (b) 500, (c) 700, and (d) 1000 °C.

be attributed to the removal of residual TREG (the remaining polyol molecules in the precursor) in the simple whose boiling point is around 280 °C. Almost no weight loss is observed at above 700 °C, suggesting the formation of crystalline $Ce_{1-x}Sm_xO_{2-x/2}$ as a decomposed product. The XRD results also verify this finding.

3.2. X-ray analysis and crystallite size results

The phase evolution of the precursors upon calcination was studied using the most heavily doped sample (20% Sm SDC2 acetate) as an example (Fig. 3). In accordance with the results of DTA/TG, crystallization of the powder occurred by calcination at 700 °C, and almost all the characteristic diffraction peaks corresponding to the fluorite structure of CeO_2 (JCPDS Card No. 34-394). It is clearly seen that the reflection peaks become sharper and narrower with increasing calcination temperature, indicating that the crystal sizes increases and the crystallinity of the powders become better-defined during the calcination process. Heating the powders to 500 °C has a little effect on peak width and intensity, indicating a little change in crystallite size as shown in Table 1. However,

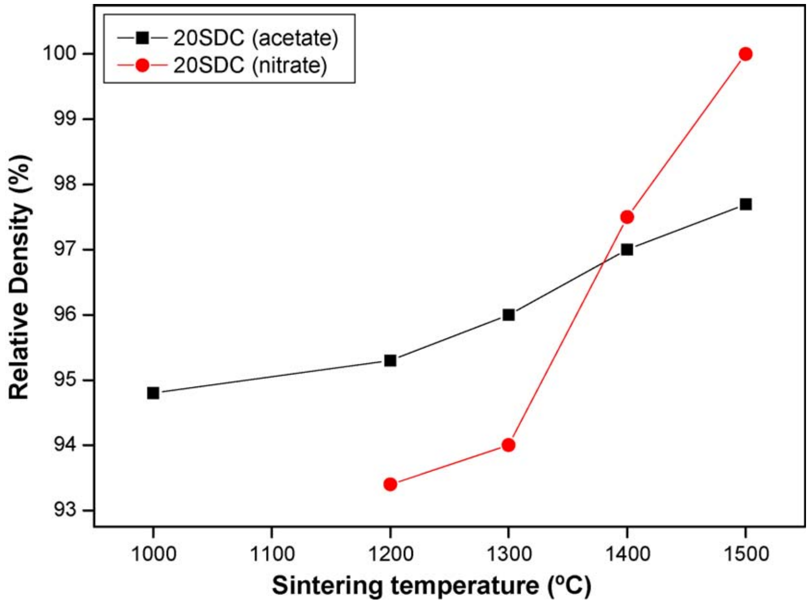

Fig. 4. Relative density as a function of sintering temperature.

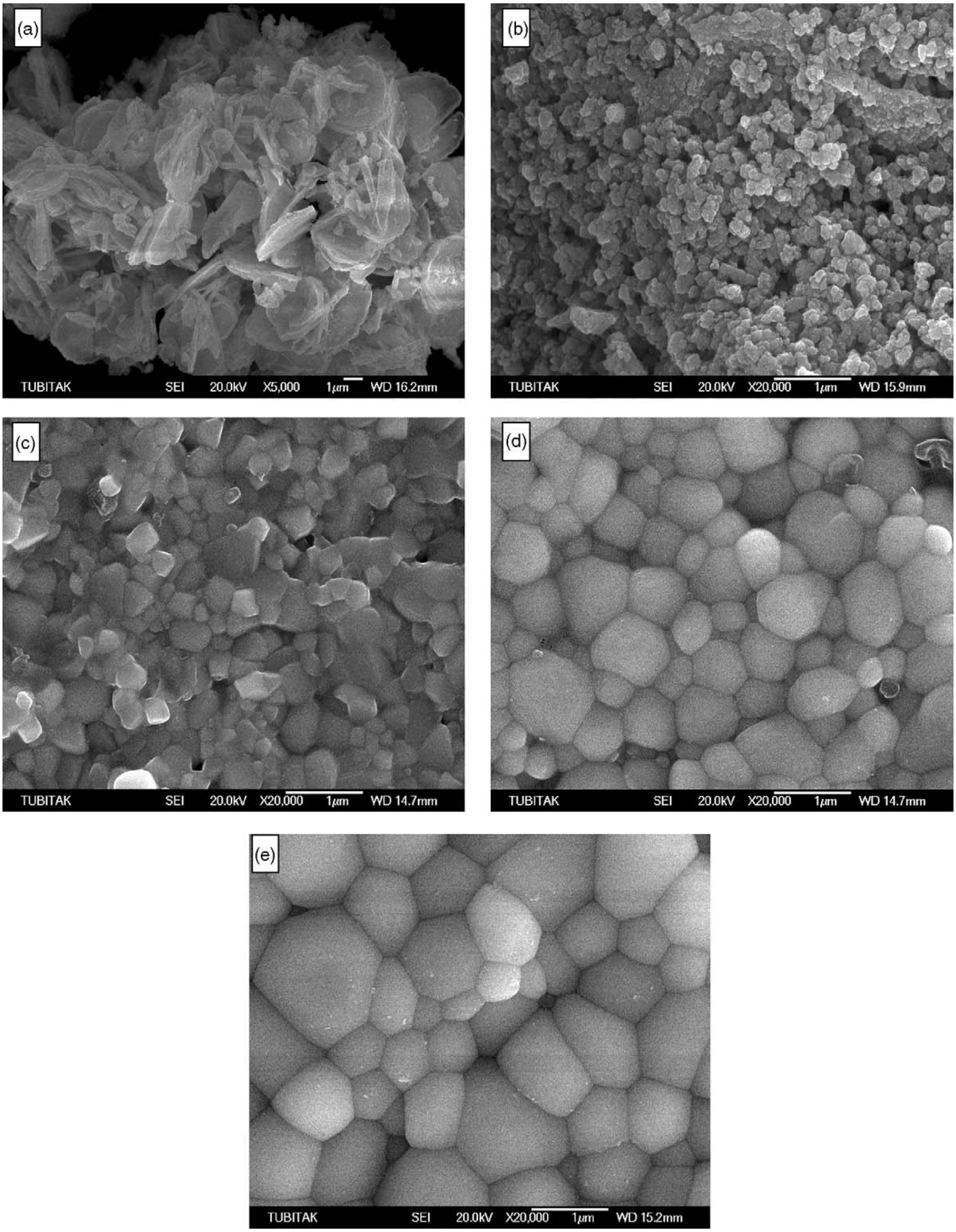

Fig. 5. SEM micrographs of 20% SDC2(Ac) showing morphology change of the nanoparticles annealed at (a) 300, (b) 500, (c) 1200, (d) 1300, and (e) 1400 °C.

after heating 1000 °C, the peaks' widths become very narrow and intense, indicating a rapid increase in the growth of the crystallite size. The powders have the average crystallite sizes of around 11 nm at 500 °C, though the one with lower samarium concentration shows a slightly finer crystallite size. The crystallite sizes as calculated by Debye-Scheerrer equation were found to be 36.74 nm for SDC1(nitrate) powder, compared to 30.54 nm for SDC2(acetate) powder. Results show that the nanocrystalline powders were produced by the polyol process. However, the powders prepared by using acetate precursors composed of crystallite size that is 17% smaller than that prepared by using nitrate precursors. Table 1 gives the unit cell values of the solid solution oxides calcined at 1000 °C. Clearly Sm doping induces a gradual expansion in the unit cell. It is noteworthy that the maximum unit cell is obtained as 5.440 nm for 20 SDC(2).

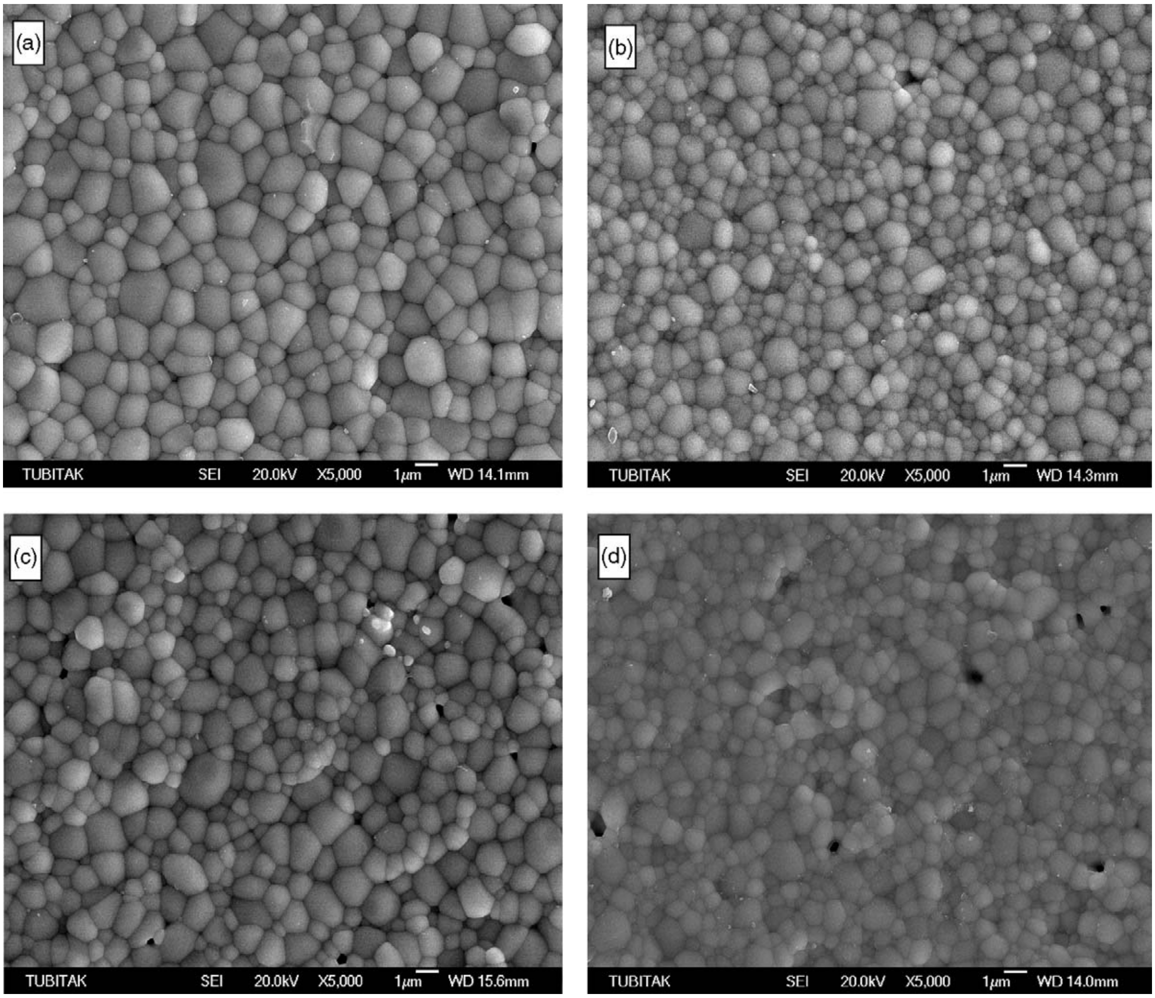

Fig. 6. SEM micrographs of SDC2(Ac) annealed at 1400 °C (a) 10% Sm, (b) 15% Sm, (c) 20% Sm doped, and (d) 20% Sm SDC1(nitrate).

3.3. Density result

Fig. 4 presents the relative densities of the compact disks from SDC(1) and SDC(2) powders. At the calcination temperature of 1200 °C, the relative density of SDC(2) powders becomes higher than that of SDC(1) powder (95.3% of the theoretical value). And also the densification temperature is significantly lower than those (1400–1600 °C) reported for the SDC powders processed by modified sol–gel process and hydrothermal treatment [16,17]. The two kinds of compact disks seem to have the same relative density (∼97–97.5%) at the calcination temperature of 1400 °C. And above 1400 °C, the density of the compact disk of SDC(1) powder becomes fairly close to the full relative density.

3.4. SEM results

Typical particle morphology of the SDC(2) samples calcined and sintered at different temperature for 6 h are shown in Fig. 5a–e. The sample calcined at 300 °C shows hardly agglomerated flake-like structure. The particle size determined by Debye-Scherrer equation is 10.45 nm. The micrographs of the samples calcined at 500 °C showed loosely agglomerated highly spherical structure. The specimen sintered at 1200 °C resulted in grain growth, these are grown from 36.74 nm to approximately 200 nm, but no sharp grain boundary is observed. Sintering at 1300 °C resulted in more grain growth and more densification (over 96% of the theoretical value). At 1400 °C final grain growth and densification were observed. The average particle size was calculated as 970 nm from the SEM micrograph. The microstructures of the SDC ceramics sintered at 1400 °C for 6 h with different samarium doping are compared in Fig. 6. All the materials are nearly fully dense with very few residual pores. The well-developed straight grain boundaries, and the very low porosity are typical micro-structural features of a ceramic in the final stage of sintering. There is no exaggerated grain growth and the average particle size observed from micrographs is approximately 1 μm. The calculated relative density for all samples is more than 97% of the theoretical value. As all of the samples had already densified at sintering condition, so effects of Samaria content on densification was not clear [19].

3.5. Conductivity results

The complex impedance plot of SDC(2) for 200 °C is seen in Fig. 7. It was observed that grain boundary resistivity is lower

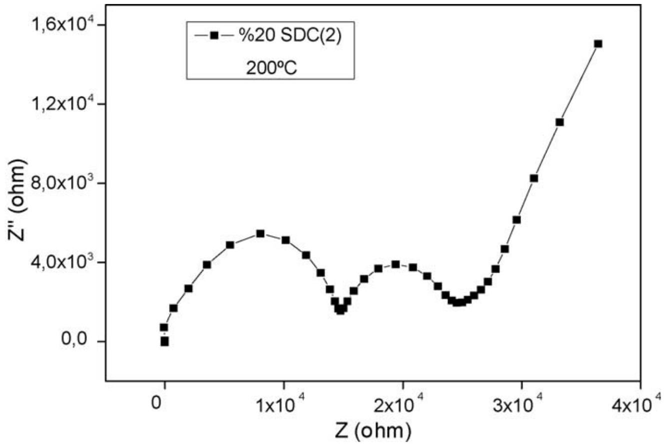

Fig. 7. Impedance spectra obtained at 200 °C for SDC(2).

than grain interior resistivity. The value ratio of resistivity is 1.58. The size of the small grain, e.g. 1 μm of SDC ceramics prepared by the polyol process may cause smaller grain interior thickness. Because the decrease of intergranular thickness with decreasing grain size. Therefore it provides the higher grain boundary conductivity.

4. Conclusion

CeO_2 powders doped with 10–20 at.% of samarium have been synthesized via simple polyol process in which a relatively low calcination temperature was needed, compared with conventional sol–gel process and hydrothermal treatment, to form the single-phase fluorite structure. Only triethylene glycol is used and no further reducing agent or a protecting agent is used which made this process easy to scale-up for mass production. The study of experimental conditions revealed that the crystallite sizes and the sintering behavior of the SDC powders are not directly affected by metal precursor anion being used as the opposite finding mentioned for Cu/ZnO nanopowders in literature [20].

Acknowledgments

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