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Journal of the European Ceramic Society 26 (2006) 397–401

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Nanocrystalline scandia-doped zirconia (ScSZ) powders prepared by a glycine–nitrate solution combustion route

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Abstract

Nanocrystalline scandia doped zirconia (ScSZ) powders were synthesized by a solution combustion route using glycine, zirconyl nitrate and scandia as the starting materials. The properties of the as-synthesized powders are strongly influenced by the molar ratio of glycine-to-nitrate (g/n), where with the g/n ratio increasing from 0.14 to 1.12, the crystallite sizes of the powders decrease from 15.9 to 7.9 nm. 11ScSZ powders of specific surface areas up to 29 m^2/g can be obtained through adjusting the initial g/n to 0.56 or greater. Incorporation of an appropriate amount of PEG dispersant into the starting solution can reduce the tendency of hard agglomeration formation. Investigations showed that powders from start solutions with the PEG incorporation have better sinterability than that of powders without the initial PEG incorporation, e.g., with the incorporation of 1.5 wt.% PEG dispersant in the starting solution, the resultant powders can be sintered to over 96% of theoretical density at 1200 °C, which is nearly 100 °C lower than that of powders without the initial PEG incorporation.

Keywords: Solution combustion; Sintering; Fuel cells

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1. Introduction

Zirconia (ZrO_2)-based ceramics have been widely investigated for applications like solid oxide fuel cells (SOFCs), oxygen sensors, catalysts and as structural materials. Among the ZrO_2-based oxide materials, scandia doped zirconia (ScSZ) possesses the highest oxygen-ion conductivity,[1] and, therefore, is very attractive for intermediate temperature (IT) SOFC applications. A wide variety of methods have been used to synthesize ScSZ powders, such as conventional ceramics method,[2,3] co-precipitation,[4,5] homogeneous precipitation,[6,7] sol–gel method,[8] hydrothermal method,[9] and thermo-decomposition of precursor complexes or gel-combustion process,[10] etc. Solution combustion (SC) synthesis, where a saturated aqueous solution containing certain amounts of salts and organic fuels is combusted to form ceramic powders, is another promising technique for the preparation of complex composition ceramic powders, due to the fact that the process has the advantages of relatively low cost and high composition homogeneity. Although the SC route has been widely applied to synthesize various single, binary and multicomponent oxides,[11–14] to our best knowledge it has not been used to synthesize scandia doped zirconia. In addition, dispersants/surfactants addition in the solution, as commonly employed in normal precipitation synthesis processes, may have strong effects on the properties (particle size, agglomerate status, etc.) of resultant powders, but up to now such effects have not been extensively investigated for the solution combustion process in literature yet.

The aim of the present work is to synthesize homogeneous ScSZ powders via a nitrate–glycine SC route and to explore the potential to optimize properties of ScSZ powders through surfactant incorporation in the start solution.

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doi:10.1016/j.jeurceramsoc.2005.06.007

2. Experimental

2.1. Powder preparation and characterization

Eleven mole percent scandia doped zirconia (11ScSZ) powders were prepared via the SC route. $ZrO(NO_3)_2 \cdot xH_2O$ (analytical reagent grade, Zibo Boshan Yaorong Chem. Plant, China), scandia (Sc_2O_3, 99.99%, Guangdong Huizhou Ruier Chem. Tech. Ltd., China) and glycine (NH_2CH_2COOH, biological reagent grade, Beijing Aoboxing BioTechnologies Co. Ltd., China) were used as the starting materials. Sc_2O_3 was first dissolved in a 65% nitric acid solution to form a $Sc(NO_3)_3$ solution, followed by adding specified amounts of $ZrO(NO_3)_2 \cdot xH_2O$ and glycine into the solution. Various molar ratios of glycine/nitrate (g/n), as listed in Table 1, were studied to investigate the effects of g/n ratios on powder properties. The precursor solution was then heated in a silica basin to 350 °C, where the solution got ignited spontaneously and resulted in porous, foamy and fragile materials. The as-ignited materials were calcined at 700 °C for 2 h in air to remove carbonaceous residues, followed by ball-milling at 600 rpm in ethanol for 24 h and drying at 80 °C for 24 h. To examine the surfactant effects, polyethylene glycol (PEG400:PEG2000 = 1:2 in weight) was added to the starting solution as the dispersant. The concentration of total PEG was chosen as 0.5, 1.5, 3.0, 5.0, 10.0 and 20.0 wt.% of resultant ScSZ powders, respectively.

The phase structure of the as-synthesized powders was analyzed by an X-ray diffractometer (X'Pert MPD Pro, PANalytical, The Netherlands). The line broadening method was used to determine the grain size of the powders, according to the Scherrer equation as[15]:

$$d_{\mathrm{XRD}} = \frac{0.9\lambda}{(\beta \cos\theta)} \tag{1}$$

where λ is the wavelength of Cu Kα radiation, β is the calibrated full width at half maximum (FWHW) of the (1 1 1) peak (in radian) and θ is the Bragg angle. Microstructures of various powders were observed by field-emission scanning electron microscopy (FESEM, JSM-6700F, JEOL, Japan). Specific surface areas of powders were characterized by the BET method (Autosorb-1, QUANTACHROM, USA).

Table 1
Effect of g/n molar ratios on the properties of 11ScSZ powders

$\text{Nitrate}_{\text{initial}}$ (mmol)	$\text{Glycine}_{\text{initial}}$ (mmol)	g/n[a]	Color of the as-ignited product	d_{XRD} (nm)
80.2	11.2	0.14	White	15.9
80.2	22.4	0.28	Offwhite	11.0
80.2	44.9	0.56	Brown	8.2
80.2	67.4	0.84	Black	8.2
80.2	89.8	1.12	Black	7.9

[a] Initial molar ratio of glycine/nitrate.

2.2. Powder sintering and microstructure observation

The as-synthesized 11ScSZ powders were uniaxially pressed into cylindrical specimens of ϕ 6.5 × 5 mm^3 at 500 MPa. The green densities were determined by the dimensions and weights of compacts. Sintering behaviors of the cylindrical specimens were measured on a dilatometer (L75/1550, LINSEIS, Germany), from room temperature to 1500 °C at a heating rate of 10 °C/min and a cooling rate of 30 °C/min. The relative density of the powder compact, ρ_{r}, can be determined from the green density, ρ_0, and the measured linear shrinkage, $\Delta L/L_0$, using the following equation:

$$\rho_{\mathrm{r}} = \frac{\rho_0/\rho_{\mathrm{th}}}{(1-\Delta L/L_0)^3} \times 100 \tag{2}$$

where L_0 is the initial sample length and $\Delta L = L_0 - L$, where L is the instantaneous sample length. Herein the theoretical density ρ_{th} is 5.69 g/cm^3 for 11ScSZ.[16]

Isothermal sintering was performed on green compacts pressed at 500 MPa using a heating rate of 5 °C/min and a dwell time of 4 h at 1200 and 1300 °C. Microstructures of the sintered materials were observed via FESEM.

3. Results and discussion

During the solution combustion process, glycine acts as the complexing agent to ensure compositional homogeneity of metal ions[14] and the fuel for combustion as well, and nitrate ions normally act as oxidizers for the combustion. According to the propellant chemistry,[17] the g/n molar ratio for stoichiometric combustion of the 11ScSZ precursor solution is 0.56, as expressed by Eqs. (3) and (4).

$$\begin{aligned} &ZrO(NO_3)_2 + \tfrac{10}{9}NH_2CH_2COOH_{(aq)} \\ &\quad \rightarrow ZrO_{2(s)} + \tfrac{20}{9}CO_{2(g)} + \tfrac{14}{9}N_{2(g)} + \tfrac{25}{9}H_2O_{(g)} \end{aligned} \tag{3}$$

$$\begin{aligned} &Sc(NO_3)_{3(aq)} + \tfrac{5}{3}NH_2CH_2COOH_{(aq)} \\ &\quad \rightarrow \tfrac{1}{2}Sc_2O_{3(s)} + \tfrac{10}{3}CO_{2(g)} + \tfrac{7}{3}N_{2(g)} + \tfrac{25}{6}H_2O_{(g)}. \end{aligned} \tag{4}$$

As the fuel-to-oxidizer ratio was reported to strongly affect powder properties in the synthesis of other powders,[12,13] systematical variation of the g/n ratio, from 0.14 (fuel lean) to 1.12 (fuel rich), was employed to study the g/n effects in the present investigations. Experiments revealed that with the g/n ratio of 0.14 the combustion process was difficult to proceed due to the lack of sufficient fuel. The combustion behavior is similar to that of nitrate solution without glycine, where only the decomposition of nitrates was observed. The resultant powder from the g/n ratio of 0.14 is amorphous, which is also quite similar to that of decomposition products of the nitrate solution without glycine, as demonstrated in Fig. 1. When the g/n ratio is 0.28 or greater, the solution can be easily ignited after being heating to 350 °C and the combustion

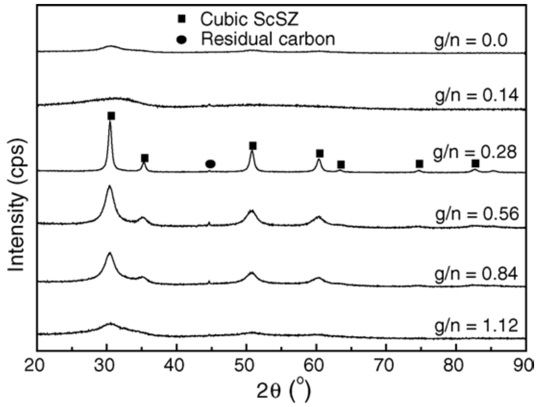

Fig. 1. XRD patterns of the as-ignited samples prepared at various initial *g*/*n* molar ratios.

lasts only a few seconds, after which porous, foamy products could be obtained. However, careful investigations showed that combustion intensity decreased with increasing the *g*/*n* ratio, as evidenced by: (1) the XRD intensity of the as-ignited powders decreased with increasing the *g*/*n* ratio (Fig. 1), inferring the decreases of flame temperatures with increasing the *g*/*n* ratio; (2) the amount of residual carbon in the as-ignited products, as could be identified from the color of the products, increases with increasing the *g*/*n* ratio (Table 1). For the stoichiometric *g*/*n* ratio of 0.56, the presence of residual carbon in the resultant products indicates that the combustion does not exactly follow the theoretical equations of (3) and (4). Partial decomposition of nitrates during the combustion process may be one of the causes of the departure from the theoretical equations. The existence of residual carbon also demonstrated that oxygen in air was not significantly taken part in the combustion process and the fuel was mainly oxidized by the nitrates. So, the decrease of flame temperature could be mainly attributed to the decrease of nitrates concentration with increasing fuel/oxidant ratios.

The as-ignited powders were then calcined at 700 °C in air for 2 h to remove the residual carbon. Typical morphologies of the as-calcined 11ScSZ products are shown in Fig. 2, where for the *g*/*n* ratio of 0.14, the as-formed agglomerates are relatively dense as illustrated in Fig. 2(a). For the products from the *g*/*n* ratio of 0.28, the aggregates are partially dense and contain porous foam-like islands as shown in Fig. 2(b). When the *g*/*n* ratio is greater than 0.28, the as-formed aggregates are loose with bubble-like microstructures as demonstrated in Fig. 2(c) and (d). High magnification image in the inset of Fig. 2(c) revealed that the diameters of the bubbles are of ∼1 μm with the wall thickness of several nanometers, indicating that the walls are consisted of nanometer grains. These porous aggregates can be easily crashed into powders through ball milling to achieve specific surface areas greater than 20 m^2/g. The as-calcined products were milled into powders through ball milling and were subjected to XRD characterization. As shown by the XRD patterns in Fig. 3, these powders are all in the cubic structure. Crystallite size calculated according to the Scherrer equation showed that small crystallite sizes of ∼8 nm can be obtained when the initial *g*/*n* ratio is greater than 0.28, as listed in Table 1. These investigations showed that 11ScSZ powders

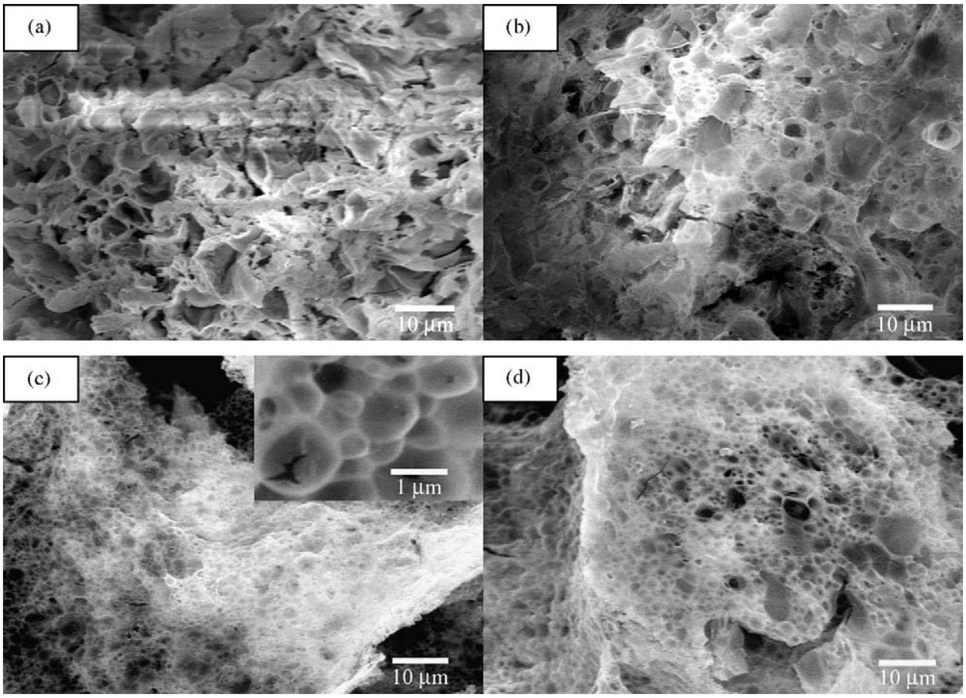

Fig. 2. SEM micrographs of the as-calcined 11ScSZ powders after calcining at 700 °C for 2 h, with the initial *g*/*n* ratios of (a) 0.14, (b) 0.28, (c) 0.56 and (d) 0.84.

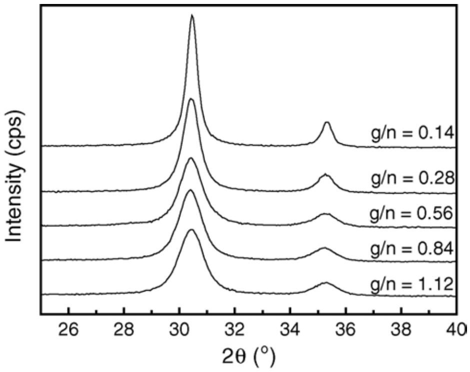

Fig. 3. Low angle region of XRD patterns of the as-calcined samples prepared at various initial *g*/*n* ratios.

with small nanocrystallites and weak agglomerates could be obtained through adjusting the initial *g*/*n* ratios to 0.56 or greater.

Dispersants are commonly employed in the synthesis of nano powders from solutions to reduce the tendency of hard agglomeration formation, but they are seldom incorporated in combustion synthesis routes. In the present investigation, PEG was employed up to 20 wt.% (percentage of PEG to the resultant 11ScSZ) to study the influence of the PEG concentration on the properties of synthesized powders at a constant *g*/*n* molar ratio of 0.56. Investigations showed that the PEG incorporation in the start solution can significantly reduce the tendency of hard agglomeration formation for resultant powders, as confirmed by BET measurements. Fig. 4 shows the influence of the PEG concentration on the specific surface areas of the 11ScSZ powders after ball milling at 600 rpm in ethanol for 24 h, where the specific surface areas increase quickly from ∼29 to ∼34 m^2/g with only 1.5 wt.% PEG addition. Further increasing the PEG concentration in the start solution showed little effects on the specific surface areas. It should be pointed out that the PEG incorporation has little effect on the crystallite sizes of the resultant powders, since the crystallite size is mainly determined by the flame temperature during combustion, while the small addition of PEG does not significantly affect the *g*/*n* ratio that determines the flame temperature. The underlying mechanism for the specific surface area improvement has not yet been totally understood. It might be related to the dispersing effects that keep sol particles separated from each other due to steric hindrance of PEG molecules adsorbed on the sol particles.

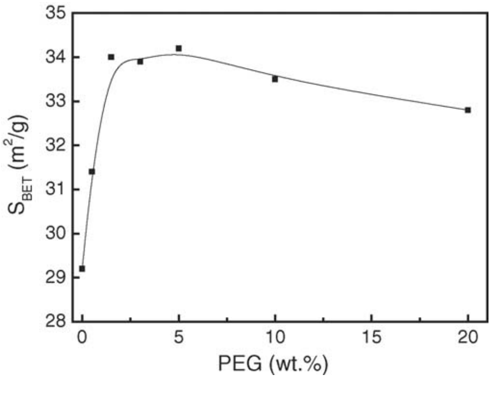

Fig. 4. The influence of PEG dispersant on the specific surface area of the as-synthesized 11ScSZ powders at the initial *g*/*n* ratio of 0.56.

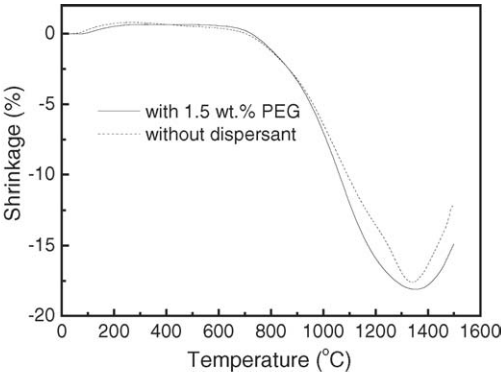

Fig. 5. Densification behaviors of 11ScSZ powders prepared at the *g*/*n* molar ratio of 0.56 without and with 1.5 wt.% PEG incorporation.

Sintering behaviors of the 11ScSZ powders from various conditions were investigated using non-isothermal sintering techniques. It generally showed that powders from start solutions with the PEG incorporation have better sinterability, as demonstrated by Fig. 5. This fact was also confirmed by isothermal sintering experiments. Fig. 6 shows the typical microstructures of compacts sintered at 1200 °C for 4 h. For powders without the initial PEG incorporation, pores were frequently observed and evenly distributed in the microstructure after sintering at 1200 °C (Fig. 6(a)). The relative density reached only 92% of theoretical value after sintering at 1200 °C for 4 h. While for the compacts from powders with the initial 1.5 wt.% PEG incorporation, the sintered body is nearly fully dense after being sintered at 1200 °C for 4 h, as shown in Fig. 6(b), e.g., the relative density reached over 96% of theoretical value, demonstrating much better sintering activity for powders with initial PEG incorporation. Investigations showed that for the powders without the initial PEG incorporation, a sintering temperature of 1300 °C is necessary for the densification of the green compacts. It is well known that the densification behavior of a powder compact is mainly influenced by the particle size/crystallite size and the extent of agglomeration of the starting powders.[18] The higher sinterability of the powders with initial PEG incorporation can be mainly attributed to the high surface area and weaker agglomerations. Improving the sinterability of synthesized powders through adding dispersant in the starting solution for the solution combustion synthesis is beneficial to practical applications as it allows the fabrication of dense ScSZ or other ZrO_2-based materials with lower temperatures and reduced production cost. Furthermore, unfavorable interface reactions with other components can be avoided through the sintering temperature reduction.

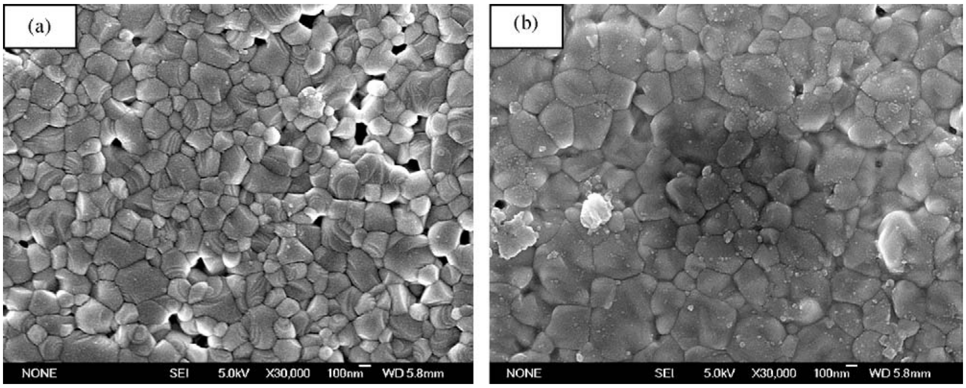

Fig. 6. FESEM microstructures of 11ScSZ ceramics sintered 1200 °C for 4 h in air, where the figure shows sintering behaviors of (a) powders synthesized without the initial PEG incorporation and (b) powders synthesized with 1.5 wt.% PEG incorporation.

4. Conclusions

Nanocrystalline scandia doped zirconia powders with a nominal composition of $(ZrO_2)_{0.89}(Sc_2O_3)_{0.11}$ were prepared with starting materials of $ZrO(NO_3)_2{\cdot}xH_2O$, Sc_2O_3 and glycine by a solution combustion route. The properties of the as-synthesized powders are influenced strongly by the g/n molar ratio, where with the g/n ratio increased from 0.14 to 1.12, the crystallite sizes of the powders decrease from 15.9 to 7.9 nm. When g/n is greater than 0.28, foamy products with loose and bubble-like microstructures can be obtained. The as-formed products can be easily crashed into powders with specific surface areas greater than 20 m^2/g. An appropriate amount of PEG incorporation can reduce the agglomeration of the as-synthesized powders, and thus improve sintering activity of the powder, e.g., with the incorporation of 1.5 wt.% PEG dispersant in the starting solution the resultant powders can be sintered to over 96% of theoretical density at 1200 °C, which is nearly 100 °C lower than that of powders without the initial PEG incorporation.

Acknowledgements

This work was supported in part by Ministry of Science and Technology of China (Grant No. 2003AA323010), and by National Natural Science Foundation of China (Grant No. 20221603).

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