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Synthesis of nanocrystalline 8 mol% yttria stabilized zirconia by the oleate complex route

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Abstract

Nanocrystalline 8 mol% yttria stabilized zirconia (YSZ) powder has been synthesized by the oleate complex route. Oleate complexes of zirconium and yttrium were formed in the hexane rich layer by the reaction of sodium oleate with zirconyl chloride and yttrium chloride at the interface of the two ternary solutions in water–ethanol–hexane system. The zirconyl oletae and yttrium oleate complexes on heating decomposed to oxide through the formation of carbonate intermediates. The powder obtained by calcination at 600 °C for 2 h was cubic YSZ with surface area of 42 m^2/g. The YSZ powder contained primary particles of ~300 nm size and the primary particles were aggregate of crystallites of 5–10 nm. The compacts prepared from the YSZ powder were sintered to ~99% TD (theoretical density) at 1400 °C. The sintered YSZ had a low average grain size of 0.73 μm.

Keywords: Solid oxide fuel cell; Yttria stabilized zirconia; Organic precursor synthesis

1. Introduction

Eight-mole percent yttria stabilized zirconia (8YSZ) is a proven electrolyte material for Solid Oxide Fuel Cells (SOFC) [1–5]. The SOFC requires highly dense 8YSZ in the form of thin film (5–20 μm) on anode substrate or in the form of a thin sheet (100–200 μm) for its anode supported and electrolyte-supported designs, respectively [1–9]. The 8YSZ used in anode supported design need to be sintered to full density at temperature as low as possible since the co-sintering of anode support and YSZ layer at high temperature results in warpage. It is well known that nanocrystalline ceramic powders are highly reactive and may be sintered to their near theoretical density (TD) at relatively low temperatures. Wet-chemical methods have been used for the synthesis of these nanocrystalline ceramic powders. A number of wet-chemical methods such as sol–gel, co-precipitation, hydrothermal, spray drying, spray pyrolysis, freeze drying, combustion synthesis, auto ignition process, polymer precursor synthesis and oxalate precipitation have been reported for the preparation of yttria doped zirconia powders [10–24].

Recently, a versatile method for the synthesis of nanocrystals of metals and metal oxides from complexes of corresponding metals with the long chain fatty acids such as oleic acid and linoleic acid has been reported [25–26]. The method offers synthesis of nanocrystals of a number of materials in a range of crystallite size. The present work reports synthesis of nanocrystalline 8 mol% yttria stabilized zirconia by the oleate complex route.

2. Experimental procedure

Zirconium oxychloride ($ZrOCl_2{\cdot}8H_2O$, 99.99%) and yttrium oxide (Y_2O_3, 99.99%) were procured from Indian Rare Earth Ltd., India. The sodium hydroxide (CDH, India), hydrochloric acid (Merck, India), oleic acid (CDH, India), ethanol (Merck, India) and hexane (Merck, India) used were of analytical reagent grade. Double distilled water was used for preparation of solutions.

Yttrium chloride solution was prepared by dissolving the yttrium oxide powder in hydrochloric acid solution at 60 °C. Sodium oleate was prepared by mechanically stirring a mixture of oleic acid, sodium hydroxide and ethanol in the mole ratio

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1:1:5 in a reaction kettle at room temperature until it forms a homogeneous solution. Sodium oleate was precipitated from the solution by adding excess ethanol. The precipitate was filtered and dried at room temperature.

The zirconyl oleate and yttrium oleate complex was prepared using the procedure reported by Park et al. [25]. Six liters of a solvent mixture containing water, ethanol and hexane in the ratio 1:1.33:2.33 by volume was contained in a 10 l three-necked round bottom (RB) flask fitted with a water condenser and mechanical stirrer. 2.32 moles of the sodium oleate was added to the solvent mixture and stirred for 1 h at 60 °C. One liter of aqueous solution containing 0.92 moles of $ZrOCl_2$ and 0.16 moles of YCl_3 were added to the RB flask under continuous stirring. Stirring was continued for 24 h while maintaining the temperature at 60 °C. The upper layer (hexane rich layer) from the reaction mixture was separated using a separating funnel and washed 4–5 times with deionized water to ensure the removal of chloride ions. Nearly 15 l of water was used for one washing. Further, the washed mixture was heated in a vacuum oven at 50 °C to evaporate off the hexane leaving a waxy solid of zirconyl oleate and yttrium oleate.

Thermo gravimetric analysis (TGA) and differential scanning calorimetric analysis (DSC) (Set-Sys 16, France) of the zirconyl oleate and yttrium oleate was carried out in air atmosphere at a heating rate of 10 °C/min. The zirconyl oleate and yttrium oleate mixture was heated in a muffle furnace at 600 °C for 2 h to burnout the organics resulting in the formation of the crystalline phase.

X-ray diffraction (Philips–XRD PW 2770/00, Holland) analysis of the calcined powder was carried out to confirm the cubic phase formation. The mole percentage of zirconia and yttria in the YSZ powder was measured by X-ray fluorescence spectroscopy (Oxford MDX 1000, UK). The calcined powder was deagglomerated using planetary ball milling in ethanol medium using zirconia grinding media of 10 mm diameter. The charge to ball ratio of 1:3 was used for deagglomeration. The surface area of the YSZ powder was measured by BET method (Sorptomatic 1990, Thermo Finnigan, Italy). Crystallite size in the powder particles was measured using a Transmission Electron Microscope (Philips USA).

Pellets were prepared by pressing the powder at 50 MPa pressure in a hardened steel die. The pellets were sintered at temperatures in the range of 1300–1500 °C for 4 h. Heating rate used was 5 °C/min up to the sintering temperature. Density of the sintered pellets was measured using Archimedes principle. Microstructure of the YSZ powder and polished and thermally etched surfaces of the sintered ceramics were observed using a scanning electron microscope (LEO 1455, UK).

3. Results and discussion

The solvent mixture containing water, ethanol and hexane formed two solutions, which are immiscible and therefore separated in to two layers. One layer is a hexane rich and the other layer is water rich. The sodium oleate dissolved in the hexane rich layer when stirred with the solvent mixture in the RB flask at 60 °C. When the solution containing $ZrOCl_2$ and YCl_3 was added to the RB flask, the reaction of sodium oleate and the metal chlorides took place at the interface of water rich layer and hexane rich layer to form zirconyl oleate, yttrium oleate and sodium chloride. This reaction at the interface resulted in the transfer of zirconium and yttrium ions from the water rich layer to the hexane rich layer and the sodium ions from the hexane rich layer to the water rich layer. The exchange reactions occurring at the interface are schematically represented in Fig. 1.

The waxy solid obtained by evaporation of the solvent from the hexane layer showed a peak at 1710 cm^{-1} in the IR spectrum. This confirms the formation of zirconyl oleate and yttrium oleate complexes [25]. Fig. 2 shows TGA–DSC plot of the oleate complexes. The oleate complexes showed weight loss mainly in two stages. In the first stage, nearly 62% of the weight loss is observed in the temperature range of 150–460 °C and in the second stage nearly 18% weight loss observed up to 560 °C. An exothermic peak corresponding to the first weight loss and an endothermic peak corresponding to the second weight loss are observed in the DSC plot. It is well known that metal carboxylates on heating produce ketones and metal carbonates [27]. In the present case, it appears that, thermal decomposition of the zirconyl oleate and yttrium oleate complexes resulted in the formation of long chain ketones

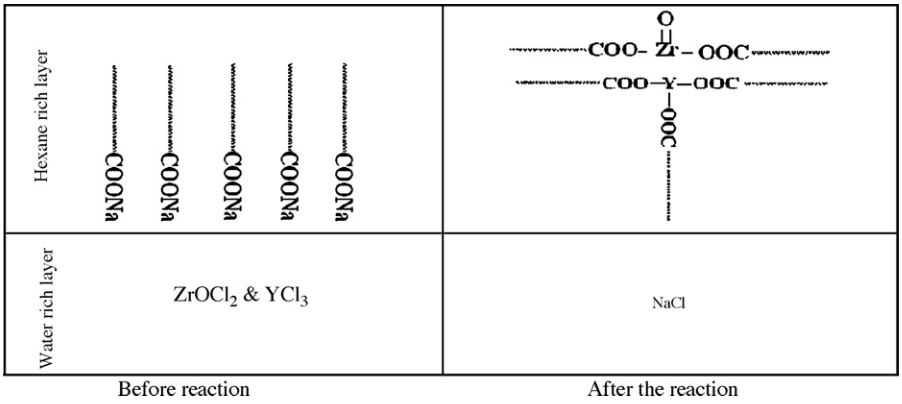

Fig. 1. Schematic representation showing the reaction of sodium oleate with zirconium oxychloride and yttrium chloride at the immiscible aqueous–organic interface.

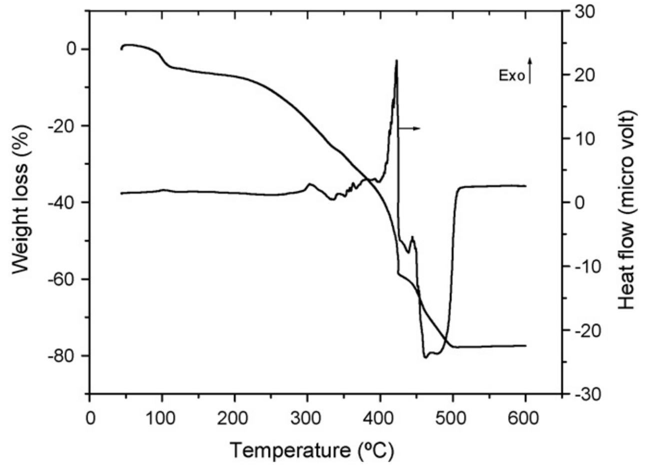

Fig. 2. TGA–DSC plot of the zirconyl oleate and yttrium oleate complexes.

and the metal carbonates. The strong exothermic peak observed in the DSC is due to the combustion of the long chain ketones. The carbonates thus generated undergo thermal decomposition at temperature in the range of 460–560 °C to form the oxide. The endothermic peak observed in the DSC is corresponding to the decomposition of the carbonates. The formation of carbonate intermediate is confirmed by the fact that the residue obtained by heating the zirconyl oleate and yttrium oleate complexes at 350 °C for 30 min in a muffle furnace produced brisk effervescence when treated with dilute HCl due to the formation of carbon dioxide gas. Further, the residue showed a peak at 1424 cm^{-1} in the IR spectrum corresponding to the ionic carbonate.

The oleate complex when heated at 600 °C in a muffle furnace burnt with a strong sooty flame. The product calcined at 600 °C for 2 h showed well defined peaks of cubic YSZ phase in the XRD spectrum. The yttria content in the YSZ is confirmed as 7.98 mol% by X-ray fluorescence spectroscopy. Fig. 3 shows XRD spectrum of the 8YSZ prepared by the oleate complex route. The broad peaks in the XRD spectrum indicate nanocrystalline nature of the product. The crystallite size calculated from XRD data by Scherer equation is 6.5 nm [28].

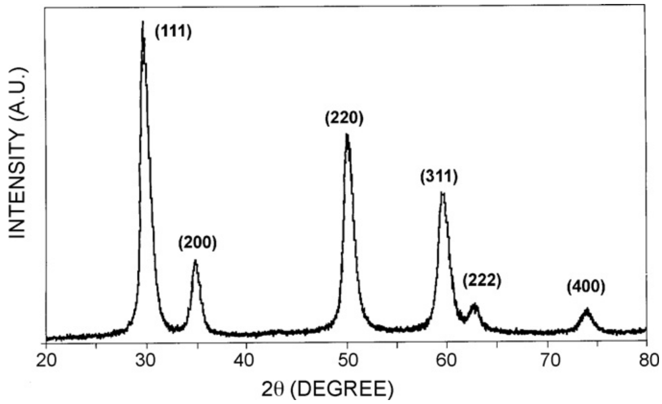

Fig. 3. XRD spectrum of the 8YSZ powder prepared from the zirconyl oleate and yttrium oleate complex.

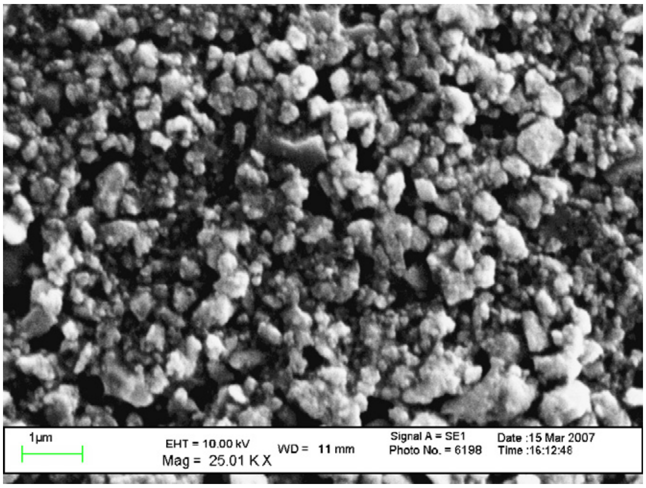

Fig. 4. SEM photograph of the 8YSZ powder prepared by the oleate complex route showing particulate clusters of ∼300 nm.

Fig. 4 shows SEM photograph of the YSZ powder prepared by the oleate route. Fine particle clusters of size nearly 300 nm are clearly seen in the SEM photograph. TEM analysis shows these clusters are aggregates of nanocrystallites in the size range of 5–10 nm. The crystallite particles size observed in TEM is in agreement with that calculated from XRD data using Scherer formula. Fig. 5 shows the TEM photograph of the YSZ powder. Surface area of the YSZ powder measured by BET method is 42.3 m^2/g.

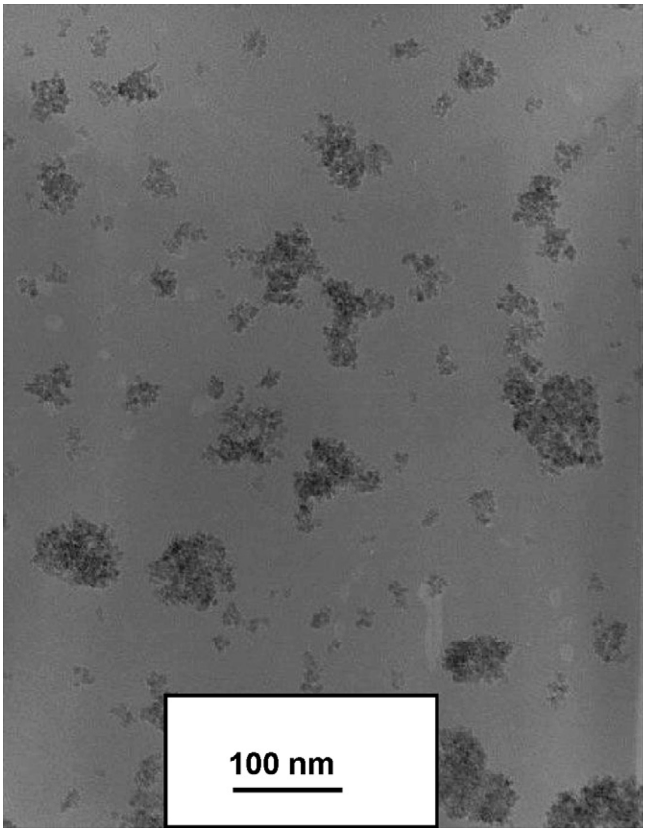

Fig. 5. TEM photograph of the 8YSZ powder prepared by the oleate complex route.

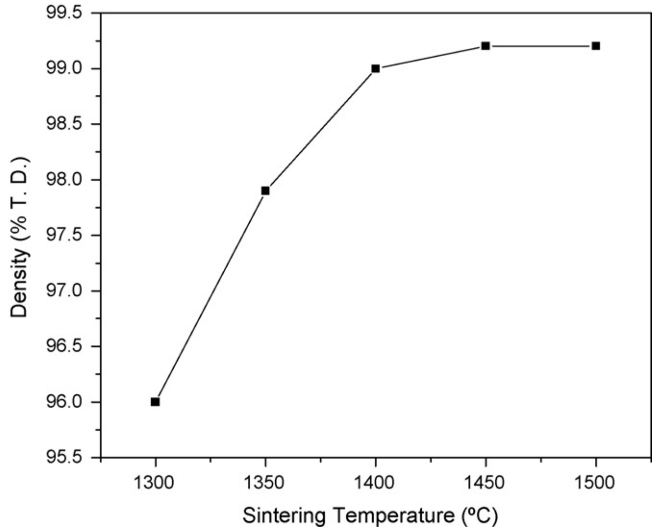

Fig. 6. Density versus sintering temperatures of 8YSZ powder compacts (holding time, 4 h).

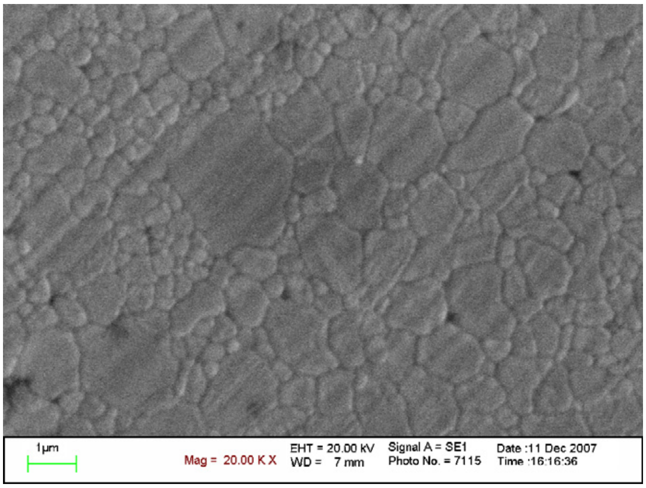

Fig. 7. SEM photograph of polished and thermally etched surface of the 8YSZ ceramic sintered for 4 h at 1400 °C.

Fig. 6 shows density versus sintering temperatures of the compacts obtained by uni-axial pressing of the 8YSZ powder prepared by the oleate route. The powder compacts showed a green density of 54% of the theoretical density and attained a density of 96% TD during sintering at 1300 °C for 4 h. The density of the compacts further increased with sintering temperature and reached a value of 99% TD at 1400 °C. Further increase in sintering temperature did not produce considerable increase in density. Fig. 7 shows SEM photograph of the polished and thermally etched surface of the 8YSZ sample sintered for 4 h at 1400 °C. The sintered YSZ ceramic has a fine-grained microstructure. Grain size observed in SEM is in the range of 0.3–2.3 μm. The average grain size calculated from the SEM by linear intercept method is 0.73 μm.

4. Summary and conclusions

Reaction of zirconyl chloride and yttrium chloride with sodium oleate at the interface of water rich layer and hexane rich layer in water–ethanol–hexane solvent mixture system resulted in the formation of zirconyl oleate and yttrium oleate complexes. Thermal decomposition of the zirconyl oleate and yttrium oleate complexes to the oxide takes place through the formation of a carbonate intermediate. The cubic YSZ obtained after heating at 600 °C contained particles of ~300 nm size and the particles are aggregates of nanocrystallites of 5–10 nm. Compacts prepared by pressing the 8YSZ powder sintered to 99% of the theoretical density at 1400 °C. The average grain size calculated from the microstructure of polished and thermally etched surface of the 8YSZ sample sintered for 4 h at 1400 °C is 0.73 μm.

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