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Effect of Microwave Energy on Titania Doped YSZ

Sonia Mago[1], Chetan Sharma[1], Payal Sharma[1], Kanchan L. Singh[2,*], Anirudh P. Singh[1]
[1]Department of Physics, I. K. Gujral Punjab Technical University, Jalandhar, Punjab, India
[2]Department of Physics, DAV Institute of Engineering and Technology, Jalandhar, Punjab, India

Abstract

Today, Solid State Oxide Fuel Cells (SOFCs) have become a need of the hour owing to higher efficiency, low emissions and versatile applications. Various materials are being explored to increase its performance and long-term stability, especially at high temperatures. Though YSZ has been the state of art anode material, YZT is emerging as a future material under consideration. Theundoped YSZ and the doped YSZ, i.e. 5 mol% YZT, calcined and uncalcined, are synthesized by conventional as well as microwave processing from the precursors prepared by mixed oxide method and then characterized for a comparative analysis by XRD of sintered samples. In the current work, potentiality of microwave energy has been exploited for the synthesis of YSZ and YZT. Higher phase stabilization is noted for microwave sintered samples.

Keywords: *SOFC, YSZ, YZT, XRD, sintering*

****Author for Correspondence*** E-mail:kanchan_69@rediffmail.com

INTRODUCTION

Fuel cells have emerged as beguiled alternatives to combustion engines as these cells also convert chemical energy into electrical energy like a battery, but with organized and somewhat inefficient combustion step [1]. Solid oxide fuel cells (SOFCs) are seeking attention for their clean and reliable electric power generation capacity. These also allow the use of a variety of fuels ranging from hydrogen to hydrocarbons [2]. Multitude of low cost fabrication processes of electrodes and electrolyte for solid oxide fuel cells are used. SOFC development targets cost reduction with the use of low cost materials and alternative processing techniques in terms of long term durability [3].

Several ceria doped and titania doped materials are attracting the researchers as interesting anode materials for SOFCs. Titania doped YSZ i.e. YZT is a mixed conductor found to possess mixed ionic and electronic conductivities [4].

Pure $ZrO_2$is found to exist in the stable tetragonal form at the higher temperatures while monoclinic phase is expected at lower temperatures. Adding Y^{3+} to tetragonal form of zirconia stabilizes the cubic phase as the oxygen vacancies increase around the host Zr^{4+} [5]. Further, the addition of TiO_2 to YSZ leads to the formation of tetragonal zirconia [6].

In the present investigation, the microwave energy is used for preparing YZT to save energy and time without compromising with quality. Microwave processing is a technique employed to lower the sintering time and temperature, aimed at achieving denser products as compared to the conventional process. Consequently, the micro waved products have finer grain size and smaller intrinsic number density [7–16].Also, then on stoichiometry of titania helps it couple very well with microwaves and enhances the dielectric constant of the material [17].In the current work, undoped YSZ and doped YSZ (5 mol% titania) are prepared and are characterized by XRD to study the crystal structure.

MATERIALS AND METHODS

YZT precursors of two compositions $[(ZrO_2)_{0.92}(Y_2O_3)_{0.08}]_{1-x}(TiO_2)_x$, where x=0.00 and 0.05 are synthesized i.e. 0 mol% YSZ and 5 mol% Titania doped YSZ (YZT). The precursors were prepared by mixed oxide

method taking Y_2O_3(99.99% purity), ZrO_2 (99.5% purity) and TiO_2 (98% purity) powders in the stoichiometric ratio. Postliminary, the powders were ball milled for 6 h using zirconia balls in the acetone medium. 2% PVA binder was eventually added to the precursor powders that were pelletized by a hydraulic press under a pressure of about 310 MPa. The work was carried on with uncalcined and calcined samples (900°C, 6 h). The conventional sintering of calcined and uncalcined pellets, five in number, was performed at 1500°C in an electric furnace of IR radiations for about 10 h. Another set offive green uncalcined pellets was taken in an alumina crucible, covered with 8% PVA solution prepared in water acting like a microwave susceptor and fired at 1400°C for 40 min in the microwave furnace so as to evaluate and compare the results to those of the conventionally processed ones. The microwave furnace used here, was a modified domestic multimode oven (LG MS-285SD 1200 W) of frequency 2.45 GHz and maximum 1.2 kW power output. Hence, four types of samples were ready. Two types of samples were prepared by conventional processing and two types of samples were prepared by microwave processing. The conventionally processed samples of compositions $[(ZrO_2)_{0.92}(Y_2O_3)_{0.08}]_{1.00}(TiO_2)_{0.00}$ and $[(ZrO_2)_{0.92}(Y_2O_3)_{0.08}]_{0.95}(TiO_2)_{0.05}$ are designated as YSZ_CON and 5 YZT_CON and the microwave processed ones are designated as YSZ_MW and 5 YZT_MW.The density of calcined and uncalcined products (conventionally sintered) was compared. All the prepared pellets were characterized by XRD to identify the phases present. The apparatus used in this study was an X-ray diffractometer (PANalytical DY 1769, Netherlands) with the Cu K_α radiation (λ=1.54Å) to examine the phase composition of the ceramic composites. The XRD diffract to graphs were collected at room temperature over a range of $20°<2\theta<80°$. The crystallite sizes (D_{XRD}) were calculated using the Scherer equation:

$$D_{XRD}=0.9\lambda/(2\beta \cos(\theta)),$$

Where, λ is the radiation wavelength, $\theta$is the reflection peak angle, and $2\beta$is the full width of half maximum of peak.

RESULTS AND DISCUSSION

Different uncalcined pellets of compositions YSZ and 5YZT i.e. 0Ti and 5Ti were sintered conventionally in a muffle furnace at a temperature of 1500°C for 10 h as shown in the Table 1 below:

Table 1: *Density of Calcined/Uncalcined Samples Processed by Conventional as well as Microwave Processing.*

Composition	Density of Calcined Pellets (g/cc)	Density of Uncalcined Pellets (g/cc)
YSZ_CON	2.90	3.92
5 YZT_CON	4.02	4.78
YSZ_MW	3.39	4.12
5 YZT_MW	4.44	5.11

The microwave processed samples were prepared in short period of 40 min of time as compared to 10 h in case of the conventionally prepared samples, thus ensuring energy and time saving. From the observations in Table 1, it was observed that the density of uncalcined products is higher than that of the calcined ones. On sintering for a still greater time, the calcined products stuck to the crucible, so the future work involved only the uncalcined products. Also the density is increasing with higher titania content due to enhanced diffusion. A group of researchers have noted that the grain boundary diffusion leads to densification of the ceramics as a result of sintering [18]. Also, the microwave treatment leads to intensified densification because of better coupling of TiO_2 and Y_2O_3 with microwaves. In fact, in microwave processing, an extra driving force comes to aid in addition to the thermal energy [17].

The sintered products were characterized by X-Ray Diffractometer (XRD) to observe the phase composition. Figures 1 and 2 show the XRD patterns of uncalcined and calcined, conventionally processed samples and microwave processed samples. As indicated by XRD analysis, TiO_2 addition has profoundly influenced the phase composition and distribution, stimulating the formation of mixed phases in binary and ternary ceramic systems [19]. TiO_2 has rutile crystal structure

with tetragonal symmetry and YSZ has fluorite structure with cubic symmetry. The fluorite structure of cubic zirconia is identified by XRD [20]. The cubic phase identified by (111) peak at an angle of 2θ=30.1194° is due to the formation of solid YSZ solution with microwave energy [21]. Apart from the cubic phase, some other phases are also seen. The monoclinic phase is clearly reducing with microwave heating. The results for uncalcined products are better than those for the calcined ones. These results are in agreement that TiO_2 is a microwave susceptor leading to better diffusion and hence greater density.

On observing Figure 2, it is noted that neither anatase nor rutile phase of TiO_2 is present in XRD of any of the conventionally processed 5 YZT and microwave processed 5 YZT. It suggests that titania has been treated completely in the thermochemical process. The XRD peaks at around 2θ=34° were tetragonal, marked as (002) and (200) whereas the middle peak was marked as (200) YSZ/YZT [22]. The Ti^{4+} ion is smaller than the Zr^{4+} ion with the octagonal coordination of oxygen. Titanium ion prefers a coordination of six. Correspondingly, tetragonal zirconia is formed [6, 23, 24]. The pyrochlore and the zirconium titanate phases are not detected by XRD.

Table 2 shows the variation in the crystallite size of conventionally sintered and the microwave sintered products with the addition of titania. The change in the crystallite size is due to the difference in ionic radii of the constituting ions [25].

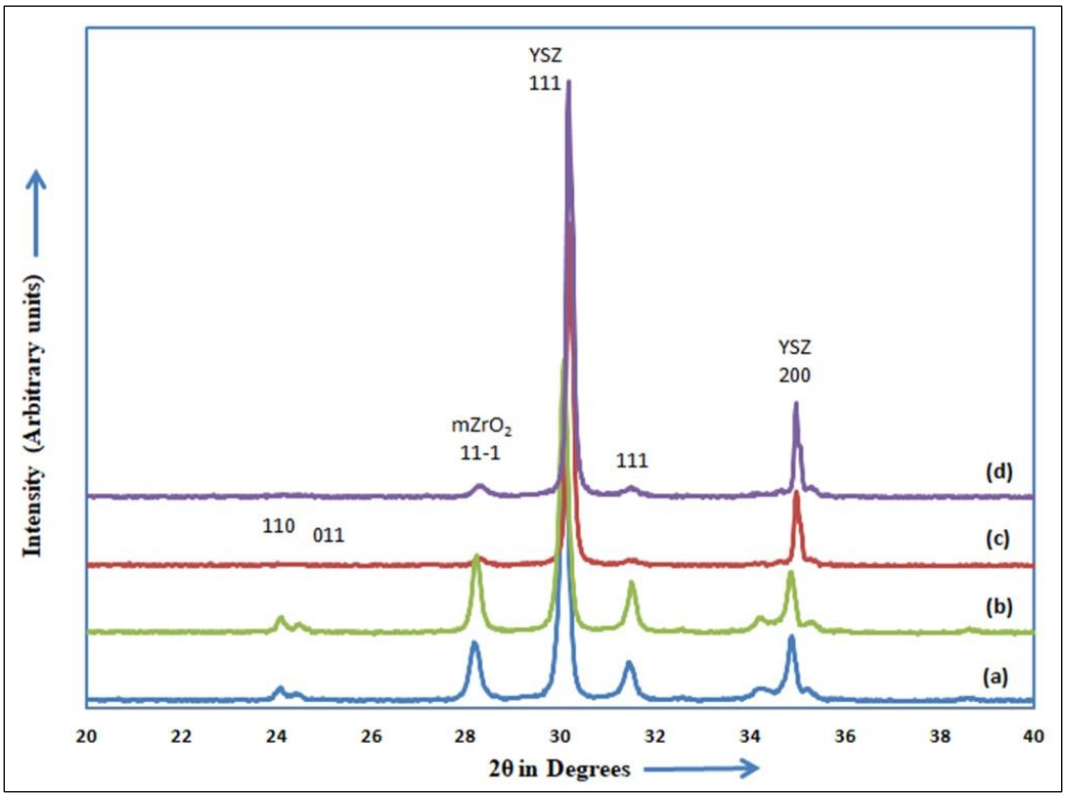

Fig. 1: *XRD of YSZ (0 Ti)* ***(a)*** *Uncalcined Conventionally Sintered;* ***(b)*** *Calcined Conventionally Sintered;* ***(c)*** *Uncalcined Microwave Sintered;* ***(d)*** *Calcined Microwave Sintered.*

Table 2: *Variation of Crystallite Size with the Composition.*

Composition	Conventional Sintering Crystallite Size (nm)	Microwave Sintering Crystallite Size (nm)
YSZ	74.65	41.25
5 YZT	107.9	50

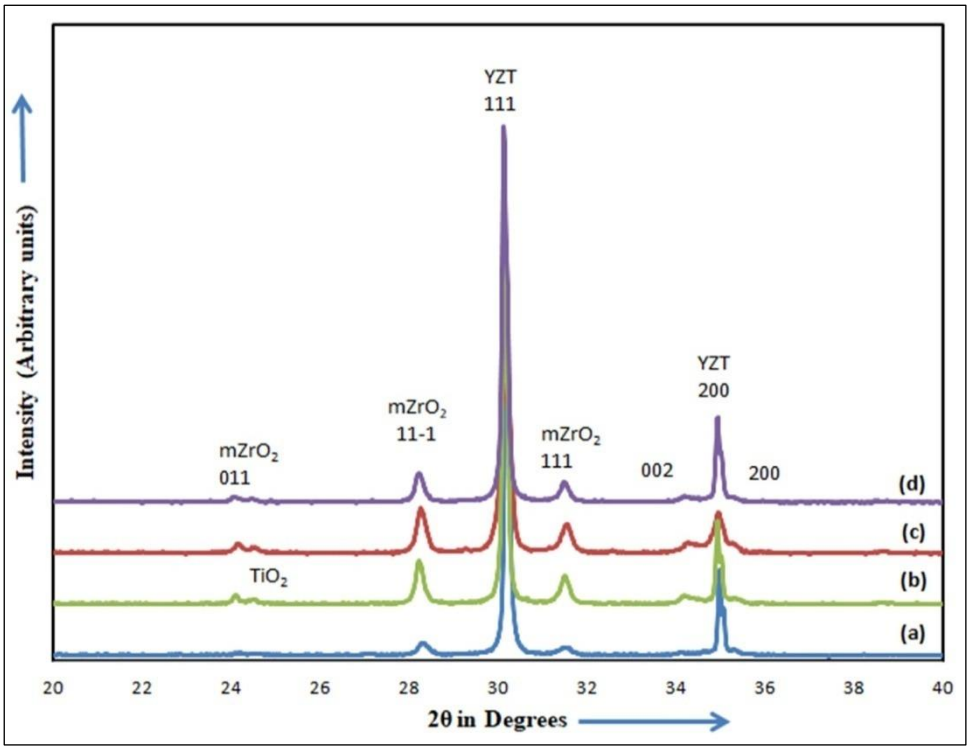

Fig. 2: *XRD of 5 YZT**(a)** Uncalcined Conventionally Sintered;**(b)** Calcined Conventionally Sintered;**(c)**Uncalcined Microwave Sintered;**(d)** Calcined Microwave Sintered.*

CONCLUSION

We have successfully synthesized Ti-doped YSZ samples using the mixed oxide method and studied the density and phase in comparison to that of YSZ samples in comparison to that of YSZ samples after the conventional as well as the microwave sintering. Microwave energy not only enhances the sintering kinetics but also involves molecular interaction with electromagnetic field. This treatment results in effective densification and better phase stability of microwave processed products compared to that of the conventionally sintered products.

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