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Nd_2O_3 DOPED YTTRIA STABILIZED ZIRCONIA CERAMICS FABRICATED BY CONVENTIONAL AND MICROWAVE SINTERING METHODS

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Cubic 8 mol. % yttria stabilized zirconia (8YSZ) ceramics doped with 9, 12 and 15 wt. % Nd_2O_3 were sintered in a single mode 2.45 GHz microwave furnace at sintering temperature of 1400 °C for 20 min. and by conventional sintering at 1400 °C for 5 h. The microwave sintered samples attained higher densities than the conventional processed ones. The Nd_2O_3 additions have adverse effects on densification of 8YSZ ceramics. The XRD investigations revealed that, cubic phase of 8YSZ remained stable and substitution of Zr^{4+} ions by larger Nd^{3+} ions causes an increase in the lattice parameters with Nd_2O_3 additions. Vickers hardness of 8YSZ decreased with addition of Nd_2O_3 irrespective of the sintering technique.

INTRODUCTION

8 mol. % yttria stabilized zirconia (8YSZ) is one of the most promising ceramic coating materials, and has been used as thermal barrier coating (TBC) for decades [1-4]. This ceramic material gained importance because of its high hardness, high thermal expansion coefficient and low thermal conductivity [5]. Rare earths (RE) doped yttria-stabilized zirconia (YSZ) composites have attracted wide attention with improved thermomechanical properties. RE doping increases the sinterability and decreases the thermal conductivity and it makes the composite most suitable for TBC applications [6]. The effects of Nd_2O_3 on the structural and mechanical properties of YSZ have been studied by many researchers earlier [7-10]. The addition of Nd_2O_3 to YSZ forms pyrochlore crystal structure of $Nd_2Zr_2O_7$. This compound is also considered as a TBC material due to its low thermal conductivity [11]. According to previous studies [7, 11], the Nd_2O_3 + YSZ system has an excellent combination of fracture toughness and hardness; and it inhibits the monoclinic phase formation. Addition of Nd_2O_3 to YSZ lowers the thermal conductivity of YSZ [12]. Microwave sintering (MW) is an advanced sintering technique, developed to increase the sinterability of ceramics. It provides volumetric heating and therefore causes rapid sintering of materials [13]. Also it is believed that higher densification rates were observed in materials which are processed through microwave sintering [14-15]. Additionally, MW provides uniform heat distribution which further decreases the thermomechanical stresses in the materials, unlike in conventional sintering in which heat transfer occurs from the material surface to the interior and may end up with poor thermomechanical properties [16]. Research on the consolidation of ceramic materials processed through MW has been increasing during recent years; however, most of the previous work contributed to the microwave sintering of zirconia-based ceramics [17-19]. From the best of authors' knowledge, microwave sintering of Nd_2O_3 doped 8YSZ composites has not been reported thus far. In this research, Nd_2O_3 was chosen to fabricate Nd_2O_3 + YSZ composites to obtain an excellent combination of phase stability and mechanical properties. In this study we have developed Nd_2O_3 doped 8YSZ composites through conventional and microwave sintering techniques. The effect of Nd_2O_3 on densification, crystal structure and mechanical properties of cubic YSZ was studied.

EXPERIMENTAL

Materials

Crystalline yttria (8 mol. %)-stabilized cubic zirconia and neodymia (Nd_2O_3) powders are the starting materials, which have been purchased from a commercial source (Sigma Aldrich pvt ltd, India). The initial particle sizes of 8YSZ (< 500 μm) and Nd_2O_3 (< 100 nm) are shown in Figure 1. The 8YSZ powder was mixed with 9, 12 and 15 wt. % of neodymium oxide, and blending of powders carried out by ball milling for about 15 min at 300 rpm to ensure uniform mixing. Tungsten carbide balls (60 mm diameter) were used for ball milling; no contamination was observed after ball milling of the powders.

Sample fabrication

The uniformly mixed powders were pressed into cylindrical shaped green pellets (20 mm diameter with 5 mm thickness) by using a hydraulic press with the pressure of about ~ 3 to 5 tons with holding time of 2 minutes. The compacted samples were sintered at 1400 °C for 20 min in a microwave furnace with a heating rate of 45 °C·min^{-1}, and for comparison another set of samples was sintered at 1400 °C with 5 h holding time in a conventional box furnace with a heating rate of 5° C·min^{-1}. The relative densities of sintered samples were measured by using Archimedes method.

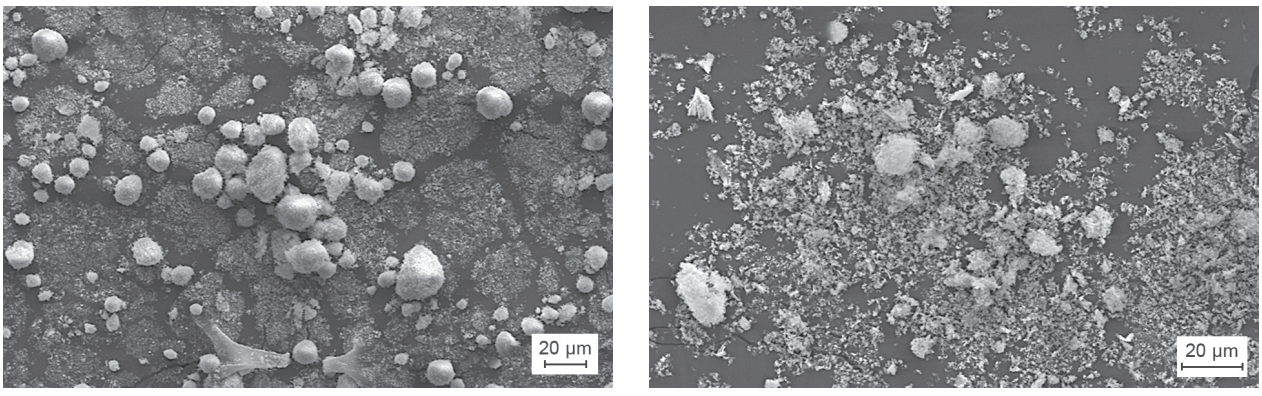
Material characterization and hardness testing

Vickers hardness was measured on a semi-automatic hardness tester by applying a load of 500 gf with dwell time of 10 s. Prior to hardness testing, samples were polished with diamond paste to identify the indentation diagonals clearly. Ten indentations were made randomly across the surfaces of the samples and the average value was taken as the final hardness. The surface morphology of the thermally etched (1200 °C for 1 h) 8YSZ ceramicswere evaluated by using scanning electron microscope (SEM), whereby grain sizes were calculated by using the linear intercept method. In this method grain sizes measured by drawing probe lines on the microstructure, counting the number of intersections with grain boundaries and calculating the mean intercept length from the ratio of length of probe line length to the number of intercepts. The crystal phases of all prepared composites were identified by an X-ray diffractometer with Cu Kα radiation. The XRD pattern was measured for 2 theta ranging from 20° to 90°. The diffraction peaks were indexed by using X'Pert high score software. The lattice parameters of cubic phase were calculated by using interplanar distances and Miller indices of the diffraction peaks.

RESULTS AND DISCUSSION

Densification response

The sintering temperature and soaking time of conventional as well as microwave sintering processes were fixed to compare the relative densities of the as-sintered ceramics. The microwave sintering technique demonstrated that the volumetric heating and uniform heat distribution influence the relative density of the ceramics. Table 1 compares the % theoretical densities of pure 8YSZ and Nd_2O_3 doped 8YSZ ceramics processed through conventional (1400°C for 5 h) and microwave sintering (1400 °C for 20 minutes) techniques. The experimental data (Table 1) revealed that, compared to the pure 8YSZ material, the Nd_2O_3 doped 8YSZ ceramics exhibited poor sinterability. As a result, Nd_2O_3 addition was seen to hinder densification during the processing of 8YSZ ceramics. The decrease of sintered densities with respect to Nd_2O_3 addition might be due to the occurrence of rapid grain growth within the pellets. The microwave-sintered ceramics exhibited higher sintered density values than the corresponding conventional ones. The conventional sintering technique has no electric fields (with 2.45 GHz



a) b)

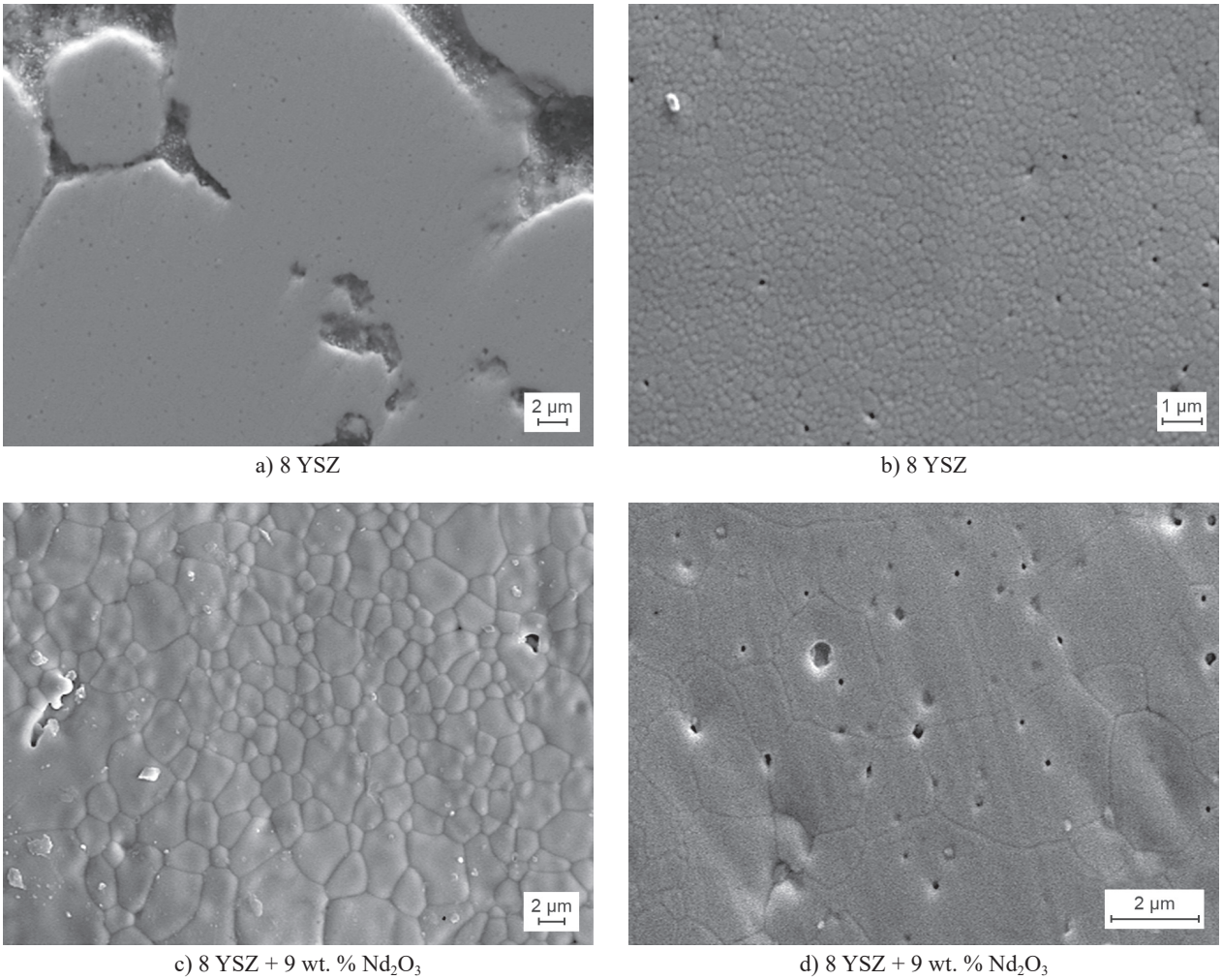
Figure 1. SEM images of as received: a) 8 mol. % YSZ powder, b) Nd_2O_3 powder.

frequency) associated with it, while direct microwave heating has high intensity electric fields. This might be the reason microwave sintered pellets exhibited high sintered densities than the conventional sintered (no electric field) samples. In this work highest relative density of 96.2 % has been obtained for microwave-sintered 8YSZ, which is more than for conventionally sintered 8YSZ with a relative density of 90.5 % after sintering at 1400 °C for 5 h. Previous studies [7, 8, and 20] reported that Nd_2O_3 addition showed adverse effects on the sinterability of YSZ.

Sintered density, lattice parameter and Vickers hardness of 8YSZ with respect to the Nd_2O_3 additions.

Composition	Sintering method	Relative density (in % of theoretical density)	Lattice parameter (Å) (Cubic YSZ Phase)	Grain size (μm)	Vickers hardness (Hv)
8 mol. % YSZ	CS	90.5 ± 1	5.13	10.24 ± 0.24	1268 ± 74
	MW	96.2 ± 0.4	5.09	0.278 ± 0.01	1332 ± 175
8 mol. % YSZ +	CS	86.4 ± 2.2	5.1	2.19 ± 0.1	1261 ± 85
+ 9 wt. % Nd_2O_3	MW	91 ± 2.3	5.09	1.61 ± 0.02	1263 ± 127
8 mol. % YSZ +	CS	86 ± 1	5.14	5 ± 0.3	1224 ± 107
+ 9 wt. % Nd_2O_3	MW	88 ± 1	5.12	2.21 ± 0.5	1236 ± 118
8 mol. % YSZ +	CS	77.4 ± 2	5.14	3.1 ± 0.2	1194 ± 132
+ 9 wt. % Nd_2O_3	MW	82.6 ± 2	5.13	2.4 ± 0.4	1159 ± 82

CS – Conventional Sintering; MW – Microwave Sintering



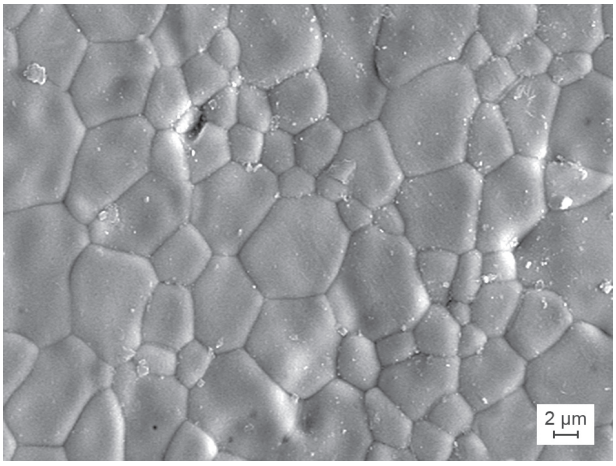
a) 8 YSZ

b) 8 YSZ

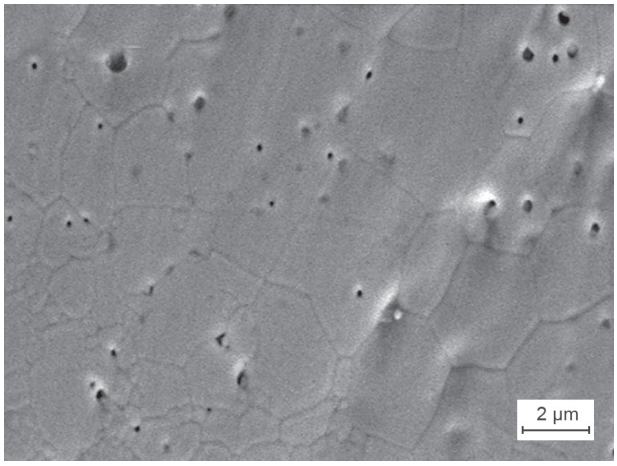
c) 8 YSZ + 9 wt. % Nd_2O_3

d) 8 YSZ + 9 wt. % Nd_2O_3

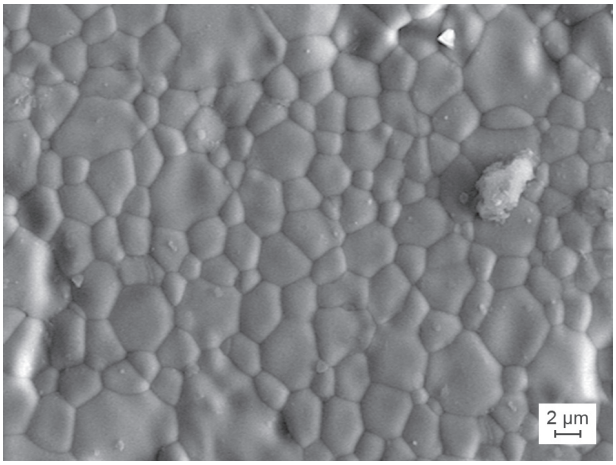
Figure 2. SEM micrographs of sintered: a) 8 mol. % YSZ and b) 9 wt. %, c) 12 wt. %, d) 15 wt. % Nd_2O_3 doped 8YSZ compacts; left hand side conventional and right hand side microwave sintered samples. *(Continue on next page)*



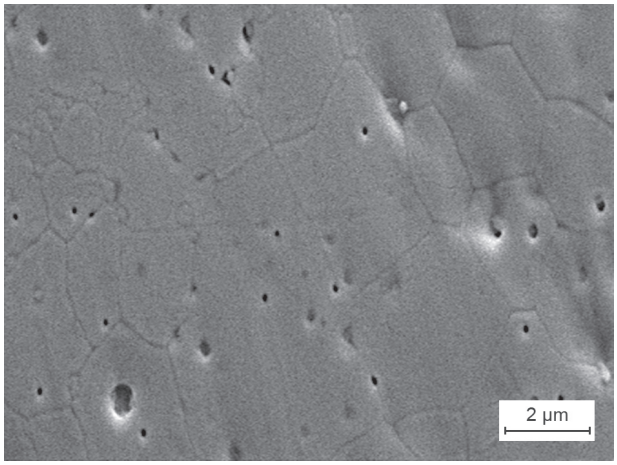
e) 8 YSZ + 12 wt. % Nd_2O_3



f) 8 YSZ + 12 wt. % Nd_2O_3



g) 8 YSZ + 15 wt. % Nd_2O_3



h) 8 YSZ + 15 wt. % Nd_2O_3

Figure 2. SEM micrographs of sintered: a) 8 mol. % YSZ and b) 9 wt. %, c) 12 wt. %, d) 15 wt. % Nd_2O_3 doped 8YSZ compacts; left hand side conventional and right hand side microwave sintered samples.

SEM Analysis

The SEM micrographs of microwave and conventional sintered specimens of 8 mol. % YSZ and its doped ceramics with 9, 12 and 15 wt. % of Nd_2O_3 are shown in Figure 2. The microstructure of the pure 8YSZ and the Nd-doped ceramic samples exhibited a homogenous matrix with clearly visible grain boundaries. The sizes of matrix grains are coarser in CS than MW sintering due to the longer holding times. Most of the samples exhibited dense morphology, since very little porosity was observed. Similar grain morphologies were observed in the previous work [7, 8, 21]. Larger grains comprising most area percent of the microstructure are embedded in a fine grained matrix. Grains sizes of the pellets were less affected by the neodymia content. The surface of all conventionally sintered samples appeared to have a denser morphology than that of the microwave-sintered samples; from this it may be concluded that the differences in densities of differently sintered pellets are not caused by porosity. The matrix grains of conventionally sintered samples exhibited bubble type, whereas flat microstructures were observed for the microwave-sintered ceramics.

XRD Analysis

Figure 3 presents the XRD analysis results of the microwave-sintered and conventionally sintered 8YSZ and the Nd_2O_3 doped 8YSZ ceramics. From the evaluated peaks, it is observed that 9, 12 and 15 wt. % of Nd_2O_3 is enough to stabilize the cubic phase of 8YSZ after sintering carried out at 1400/20 min (MW) and 1400/5 h (CS). All peaks (111), (200), (220), (311), (222), (400), (331) and (420) corresponded to cubic crystal structure, suggesting that these ceramics are single-phase materials, similar to the results found by other authors in a previous study [9]. There are no secondary phases found in the Nd_2O_3 doped ceramic materials, suggesting that the Nd-containing ceramics is a single-phase material. The combination of Nd_2O_3 and yttria

dopants resulted in fully cubic phase ceramics, which is known as Nd-Y stabilized cubic zirconia polycrystals. However, compared to neodymia-free 8YSZ ceramics, Nd_2O_3 doped ceramics exhibit distinct lattice shift towards lower diffraction angles. This peak shift can be observed in Figure 4. The peak shift towards lower angle 2θ demonstrates unit cell expansion caused by Nd_2O_3 doping, since the large Nd^{3+} ion replaces the much smaller Zr^{4+} ions. The ionic radii for Zr^{4+}, Y^{3+} and Nd^{3+} ions are 0.84, 1.019, and 1.109 Å, respectively. This phase shift has been further confirmed by lattice parameter measurement, where Nd_2O_3 doped YSZ ceramic samples have been shown to exhibit a larger lattice parameters than neodymia-free 8YSZ [8].

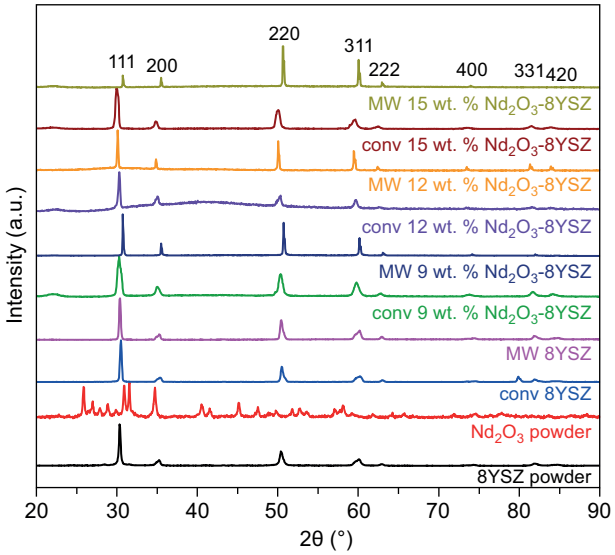


Figure 3. XRD plots for powders and conventionally (conv) and microwave (MW) sintered ceramics.

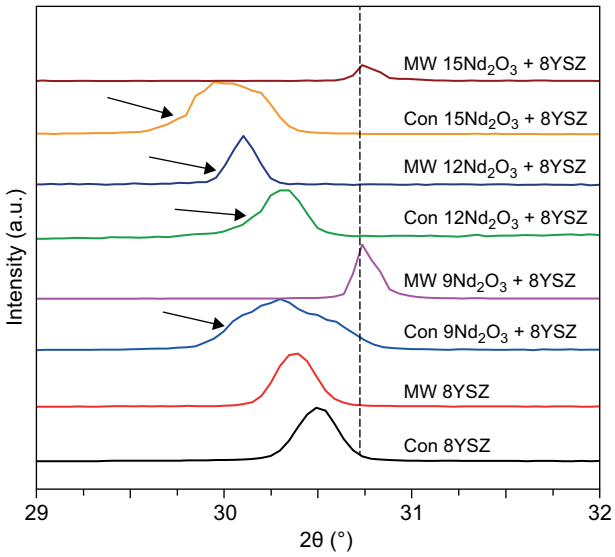


Figure 4. XRD phase shift of Nd_2O_3 doped 8YSZ Composites (Con – conventionally sintered, MW – microwave-sintered).

Vickers hardness

The dependence of Vickers hardness on the Nd_2O_3 content in 8YSZ samples is listed in Table 1. Vickers hardness of 8YSZ ceramics decreased with addition of Nd_2O_3. Most of the microwave sintered samples exhibited higher hardness values than conventionally sintered specimens. In the conventional sintering technique, a temperature difference exist between surface and interior of the pellets, and also the non-uniform heating rate in the samples results in reduced hardness. Microwave-sintered samples may undergo rapid grain growth that could be responsible for the high closed porosity observed. The hardness of the Nd_2O_3-YSZ ceramics decreased with increasing Nd_2O_3 content. This decreasing hardness may be influenced by many factors. Increasing Nd_2O_3 concentration was observed to expand the lattice and to develop microcracks. The combined effect of microcracks and densification behavior results in lower hardness values. The highest hardness value of 1332.6 Hv has been obtained for MW-sintered 8YSZ samples, but hardness decreases to 1263, 1236 and 1159 Hv with the addition of 9, 12 and 15 wt. % Nd_2O_3, respectively. Similarly, in conventionally sintered samples hardness values decrease with the addition of Nd_2O_3 [7, 8].

CONCLUSION

In this paper, 8 mol. % YSZ ceramics with the addition of 9, 12, and 15 wt. % of Nd_2O_3 were prepared via microwave sintering. Densification, microstructure and hardness of the as-sintered specimens were investigated. The findings of this research are the following:

- The addition of Nd_2O_3 to 8YSZ hindered the densification during microwave and conventional processing. Maximum relative density of 96.4 % was obtained for 8YSZ pellets processed by microwave sintering at 1400°C/20 min.
- Nd_2O_3 addition has adverse effects on Vickers hardness of Nd_2O_3-8YSZ ceramics, the maximum hardness 1332.6 Hv being obtained for MW sintered 8YSZ samples.

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