Comparative Study on Conventional Sintering with Microwave Sintering and Vacuum Sintering of Y$_2$O$_3$-Al$_2$O$_3$-ZrO$_2$ Ceramics

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Abstract

The present investigation demonstrated the comparative studies carried out on conventional, microwave and vacuum sintering of alumina added yttria stabilized zirconia (YSZ). The conventional, microwave and vacuum sintered specimens were characterized by density measurement, XRD, SEM with EDX analysis and hardness evaluation. Microwave sintering was proved to be the best efficient sintering technique with respect to energy and time savings. Enhanced densification was observed for the microwave and vacuum sintered specimens at lower temperatures compared to the conventionally sintered ones. Further, it was observed that the particle size had significant influence on the enhancement of densification. The microwave sintered specimen showed the highest hardness compared to conventional and vacuum sintered specimens.

Keywords

1. Introduction

Zirconia (ZrO$_2$) ceramics possess excellent properties such as high fracture toughness, high hardness and wear

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resistance, chemical inertness, low thermal conductivity and ionic conductivity, which allows its use in a range of applications including precision ball valve balls, high-density ball-mill grinding media, rollers and guides for metal tube forming, thread guides, pump seals, oxygen sensors, and solid oxide fuel cell membranes. However, tailored microstructure can be produced through controlled processing of partially stabilized zirconia (PSZ) with alkaline earth or rare earth oxide additions e.g. yttria (Y_2O_3) so that transformation toughening can be achieved by tetragonal ZrO_2 (t-ZrO_2) to monoclinic ZrO_2 (m-ZrO_2) phase transformation [1].

Recently, interest has been growing in the use of microwave energy to sinter ceramic compacts. In conventional thermal processing, energy is transferred to the material through conduction and radiation of heat from the surface. In contrast, microwave energy is delivered directly to the material through molecular interaction with the electromagnetic field. This interaction leads to various beneficial effects, which includes rapid volumetric heating, shorter sintering times, lower sintering temperatures and selective heating. The energy savings are in the range of 25% - 95%. In addition, it is well established that densification of a variety of ceramic materials is enhanced by microwave sintering. Higher densities are being achieved by microwave heating at lower temperatures than that obtained by conventional radiant heating [2]-[7]. Conventional sintering of zirconia at high temperatures above 1600°C results in tetragonal to monoclinic phase transformation on cooling, leading to destruction of the specimen on account of grain enlargement. Sintering at low oxygen partial pressure causes stabilization of high temperature phase of zirconia similar to oxide additives such as Y_2O_3, CaO, MgO, etc. Therefore, stabilization of tetragonal zirconia as well as high densification can be achieved by vacuum sintering method [8] [9].

Few studies were made to investigate the vacuum sintering effect on the phase composition and properties of ceramics compared to the conventionally sintered ones. It was reported that vacuum sintering of plasma-chemical 3 wt.% yttria added zirconia at high temperatures stabilized the tetragonal phase of zirconia in association with obtaining high densification [10] [11]. Sablina *et al*. [12] showed that density increased with increasing temperature and tetragonal to monoclinic phase transformation did not take place on cooling in case of vacuum sintering of ZrO_2-Y_2O_3 and ZrO_2-Y_2O_3-Al_2O_3 based ceramic specimens. Wilson and Kunz [13] evaluated microwave sintering of partially stabilized ZrO_2. They placed ZrO_2 material in SiC susceptors that absorbed microwave energy and transferred heat to the specimen. After initial heating, the ZrO_2 material could then absorb microwave energy and got heated. They showed that cracking of the ZrO_2 material occurred by ultra-rapid heating and observed similar physical properties for conventional and microwave sintered ZrO_2. Janney *et al*. [14] sintered 8 mol% yttria stabilized zirconia (YSZ) using SiC rod as susceptor. Further, Nightingale and Dunne [15] studied the density and grain growth of 3Y-TZP sintered in the conventional and microwave ovens. Sintering of zirconia ceramics using microwaves of various frequencies (2.45 - 60 GHz) has been already studied [5]. Goldstein *et al*. [16] sintered YSZ by microwave directly. They indicated that microwave sintered specimen had a smaller grain size. Upadhyaya *et al*. [17] studied sintering and grain growth of 3Y-TZP and 3Y-TZP with the addition of TiO_2 and MnO_2 in order to improve the microwave coupling at a given temperature. Wang *et al*. [18] used microwave/conventional hybrid heating technique for various ceramics including zirconia. However, grain growth was enhanced during microwave/conventional hybrid heating compared with conventional heating and thereby, suggesting acceleration of the diffusion processes by microwave/conventional hybrid heating. Matsui *et al*. [19] reported that small amount of Al_2O_3 enhanced the densification rate because of the decrease in the activation energy with the change in the diffusion mechanism from grain boundary diffusion (GBD) to volume diffusion (VD).

In the present investigation, comparative studies have been performed between conventional, microwave and vacuum sintering of alumina added 8 wt.% YSZ ceramics. The objective of this paper is to get full dense YSZ at lower temperature with superior hardness.

2. Experimental

Commercial 8 mol% Y_2O_3-ZrO_2 powder (YSZ, Metallizing Equipment Co. Private Limited, India, particle size 45 ± 10 μm) was mixed with 0.5%, 1%, 1.5% and 2% of alumina (Al_2O_3, Alcoa, USA; 99.99% purity). Alumina was added to enhance the sintering of YSZ. YSZ and Al_2O_3 Powders were milled in a planetary mill to obtain homogenous powder mixture. Powders were then isostatically pressed (EPSI NV, SO, 10,036 Belgium) at 150 MPa to produce disk-shaped green compacts. The green powder compacts were dried at 100°C for 5 h and calcined in an electrical furnace (ELECTROHEAT, Model No.EN170QT, Naskar & Co., Howrah, India) at 1200°C

for 1 h, then cut and finally sintered at 1600°C for various period of time ranging from 2 h to 10 h. Heating and cooling cycle has been shown in **Figure 1**.

Another set of specimens were sintered in a microwave furnace (Enerzi Microwave Systems Pvt. Limited, Bangalore, India) at 1500°C for 20 min. Heating and cooling time was 25°C/min. A multimode microwave furnace with a magnetron having frequency of 2.45 GHz and maximum output power of 3 kW was used for the sintering. SiC powder was used as a susceptor to initiate coupling of microwave with the specimen. The specimens were placed in an alumina disc insulated by microwave transparent casket insulating box. The top cover of the insulating box had a hole of 20 mm diameter to monitor temperature through a non-contact IR pyrometer. Temperature measurement accuracy was ±0.3% of the measured value +1°C with adjustable emissivity (ε: 0.1 - 1.0). Third set of specimens were sintered in a vacuum furnace (Hindhivac Private Limited, Bangalore, India) with a vacuum of 5×10^{-6} mbar at 1500°C for 20 min. Heating and cooling rate was 10°C/min and 7°C/min, respectively. Different temperature programs for conventional, microwave and vacuum sintering were selected to establish the superiority of the microwave and vacuum sintering techniques compared to conventional sintering technique.

The surfaces of sintered specimens were ground using a grinding machine (BAINLINE Belt Linishing machine, Chennai Metco. Limited, Chennai, India) and then polished in a polishing machine (Leco Corporation, USA) with 6 μm, 3 μm and 0.25 μm diamond pastes (Buehler USA). The bulk density of the sintered specimen was measured by Archimedes' principle. Polished specimens were thermally etched at 1300°C for 30 min in an electrical furnace to reveal the microstructure. In order to examine the phase assemblages of the densified bodies X-ray diffraction was performed (PW 1710, Philips Research Laboratory, Eindhoven, Netherlands) with Cu Kα radiation (45 kV, 35 mA). Microstructural observations were performed by scanning electron microscopy (SEM) (Phenom Pro-X, Netherlands) and elemental composition was determined by energy dispersive X-ray (EDX) analysis (Phenom Pro-X, Netherlands). Microhardness was evaluated by a Vickers hardness tester (ESEWAY, 410 series, Bowers group, U.K.) at a load of 100 g with 30 s loading/unloading time. For a particular type of specimen, five specimens were examined. Considerable numbers of data were taken to avoid any error in hardness measurement.

Similarly, commercial nano-sized 8 wt.% Y_2O_3-ZrO_2 powder (YSZ, TOSOH CORPORATION, Japan, particle size 40 ± 20 nm) was conventionally sintered at 1450°C for 2 h in a conventional furnace. Heating rate was 3°C/min and cooling rate was 2°C/min up to 1000°C and 4°C/min up to 600°C. Furnace cooling to room temperature was conducted after 600°C. The sintered nano-YSZ specimen was subsequently characterized in the same manner. Conventional sintering of nano-YSZ specimen was conducted in order to establish the effect of particle size.

3. Results and Discussion

Figure 1 shows that conventional sintering method required ~13 h for the total sintering operation of 0.5 wt.% alumina added YSZ specimen whereas total processing time was ~3 h for the microwave sintered specimen. Total processing time for vacuum sintered similar specimen was ~7 h, which was intermediate among the three processing techniques. **Figure 2(a)** shows the density of YSZ sintered at 1600°C for different period of time with the increase of alumina addition. It was observed that highest density could be achieved by the addition of 0.5 wt.% Al_2O_3 to YSZ. Therefore, 0.5Al_2O_3-YSZ composition was selected as optimum composition for continuing further investigation. **Figure 2(b)** shows the density values for 0.5 wt.% Al_2O_3 added YSZ specimen at 1600°C as a function of soaking time. The 0.5 Al_2O_3-YSZ specimen had 80% density after sintering at 1600°C for 10 h duration whereas 75% density was obtained for the similar specimen sintered at 1600°C for 8 h. The microwave sintered 0.5 Al_2O_3-YSZ specimen at 1500°C for 20 min showed 75% density while it was 70% density in the case of vacuum sintered (1500°C, 20 min) 0.5Al_2O_3-YSZ specimen. It can be said that both microwave and vacuum sintering resulted enhanced densification at lower sintering temperature within shorter processing time leading to energy and time savings. However, highest energy and time savings was observed with the microwave sintering operation. Further, the density of vacuum sintered 0.5 Al_2O_3-YSZ specimen was comparable with that of the microwave sintered 0.5 Al_2O_3-YSZ specimen.

Figure 3 represents the XRD patterns of conventional, microwave and vacuum sintered 0.5 Al_2O_3-YSZ specimens. The crystalline phases were identified as tetragonal zirconia (t-ZrO_2), monoclinic zirconia (m-ZrO_2), Y_2O_3 and Al_2O_3 in all the cases. The major crystalline phase was t-ZrO_2 whereas m-ZrO_2, Y_2O_3 and Al_2O_3 were
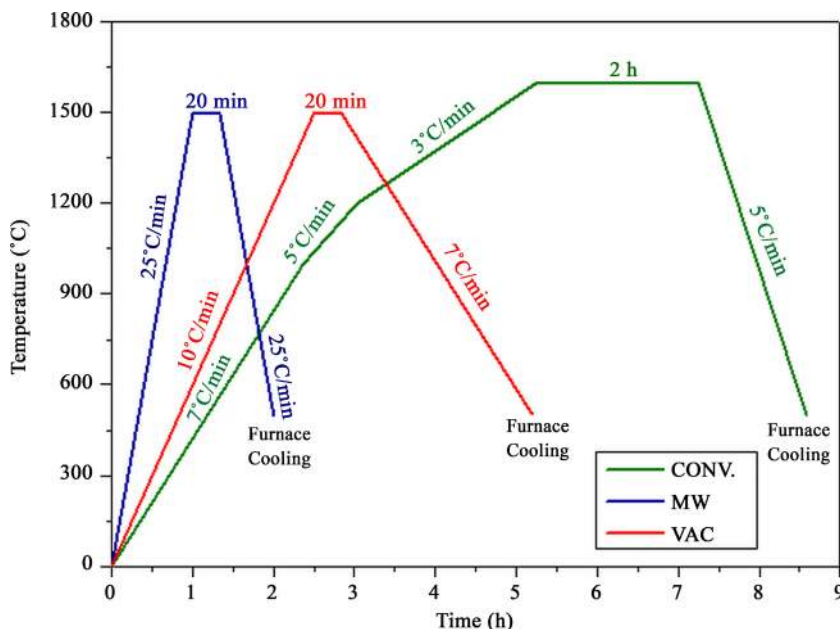
Figure 1. Temperature versus time plots for conventional, microwave and vacuum sintering operations.
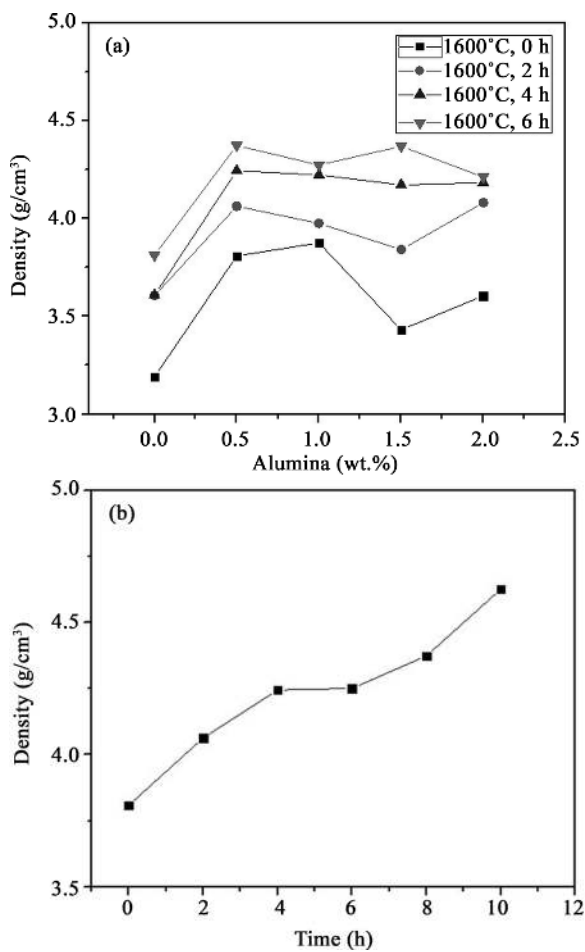

Figure 2. (a) Density of YSZ sintered at 1600°C for different period of time as a function of alumina addition and (b) density versus dwell time plot for YSZ with 0.5 wt. % alumina addition.
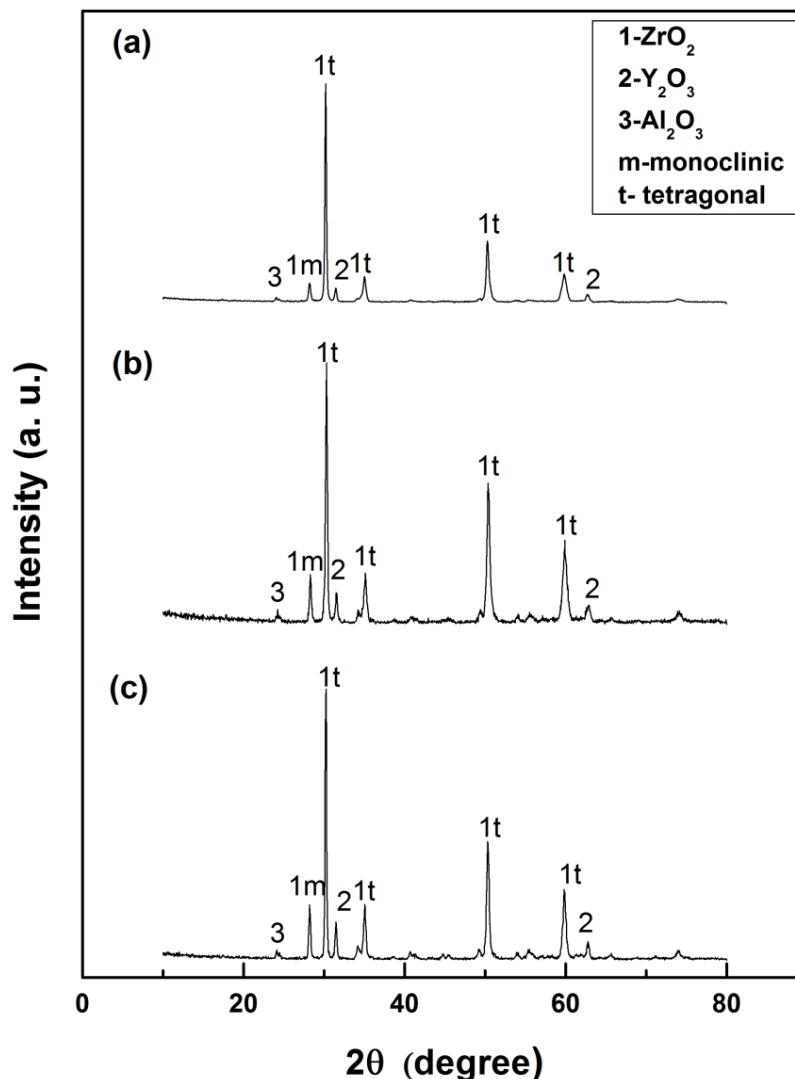
Figure 3. XRD analysis of (a) conventional, (b) microwave and (c) vacuum sintered 0.5Al$_2$O$_3$-YSZ specimens.

present as minor phases. Therefore, transformation toughening can be obtained for the sintered specimen as a consequence of t-ZrO$_2$ to m-ZrO$_2$ phase transformation. **Figure 4** shows the microstructures of conventional, microwave and vacuum sintered 0.5 Al$_2$O$_3$-YSZ specimens.

Conventionally sintered specimen demonstrated highest grain growth having grain size of 2.5 ± 0.25 μm (**Figure 4(a)**, **Figure 4(b)**). The microwave sintered specimen had finest grain size of 0.8 ± 0.1 μm (**Figure 4(c)**, **Figure 4(d)**). Whereas the vacuum sintered specimen showed a grain size of 1.2 ± 0.2 μm (**Figure 4(e)**, **Figure 4(f)**). In addition, significant difference in the morphologies of the conventional, microwave and vacuum sintered specimens was observed. The microwave sintered specimen displayed uniform grain size. In contrast, the conventional and vacuum sintered specimens showed non-uniformity in the grain size.

Present study showed that 100% dense YSZ specimen was achieved by 2 h soaking at 1450°C in the conventional route through particle size tuning of the starting powder from micron-size to nanometer-size range. **Figure 5(a)** shows the typical XRD analysis of nano-YSZ specimen conventionally sintered at 1450°C for 2 h, which was identical to those obtained for conventional, microwave and vacuum sintered micron-sized 0.5 Al$_2$O$_3$-YSZ specimens. The total processing time was analogous to that maintained for conventional sintering of micron-sized 0.5 Al$_2$O$_3$-YSZ specimen. The SEM image and corresponding EDX analysis have been shown in **Figure 5(b)**. The SEM microstructure showed that the grain morphology of nano-YSZ specimen was spherical. The EDX pattern confirmed the presence of Zr and O elements only.

Table 1 shows the density and hardness values for conventional, microwave and vacuum sintered 0.5 Al_2O_3-YSZ specimens (micron-sized) and conventionally sintered nano-sized YSZ specimen. Conventionally sintered nano-sized YSZ specimen exhibited 100% density at lowest temperature with highest hardness *i.e.* 1345 ± 25 VHN (13.19 ± 0.25 GPa). The hardness of conventionally sintered 0.5 Al_2O_3-YSZ specimen for 10 h duration was 660 ± 20 VHN (6.47 ± 0.20 GPa) while it was 433 ± 15 VHN (4.25 ± 0.15 GPa) in case of similar specimen conventionally sintered for 8 h. The hardness of microwave sintered (1500°C, 20 min) 0.5 Al_2O_3-YSZ specimen was 440 ± 17 VHN (4.32 ± 0.17 GPa) whereas it was 417 ± 18 VHN (4.09 ± 0.18 GPa) in case of vacuum sintered (1500°C, 20 min) specimen.
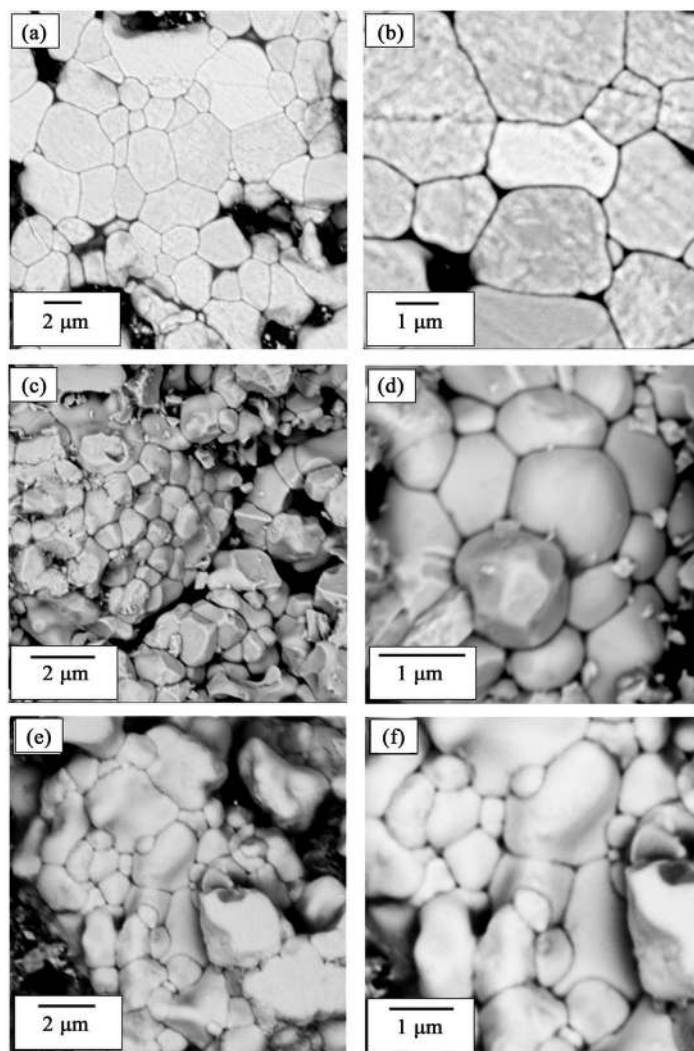

Figure 4. SEM images of (a)-(b) conventional, (c)-(d) microwave and (e)-(f) vacuum sintered 0.5 Al_2O_3-YSZ specimens.

Table 1. Properties of conventional, microwave and vacuum sintered zirconia.

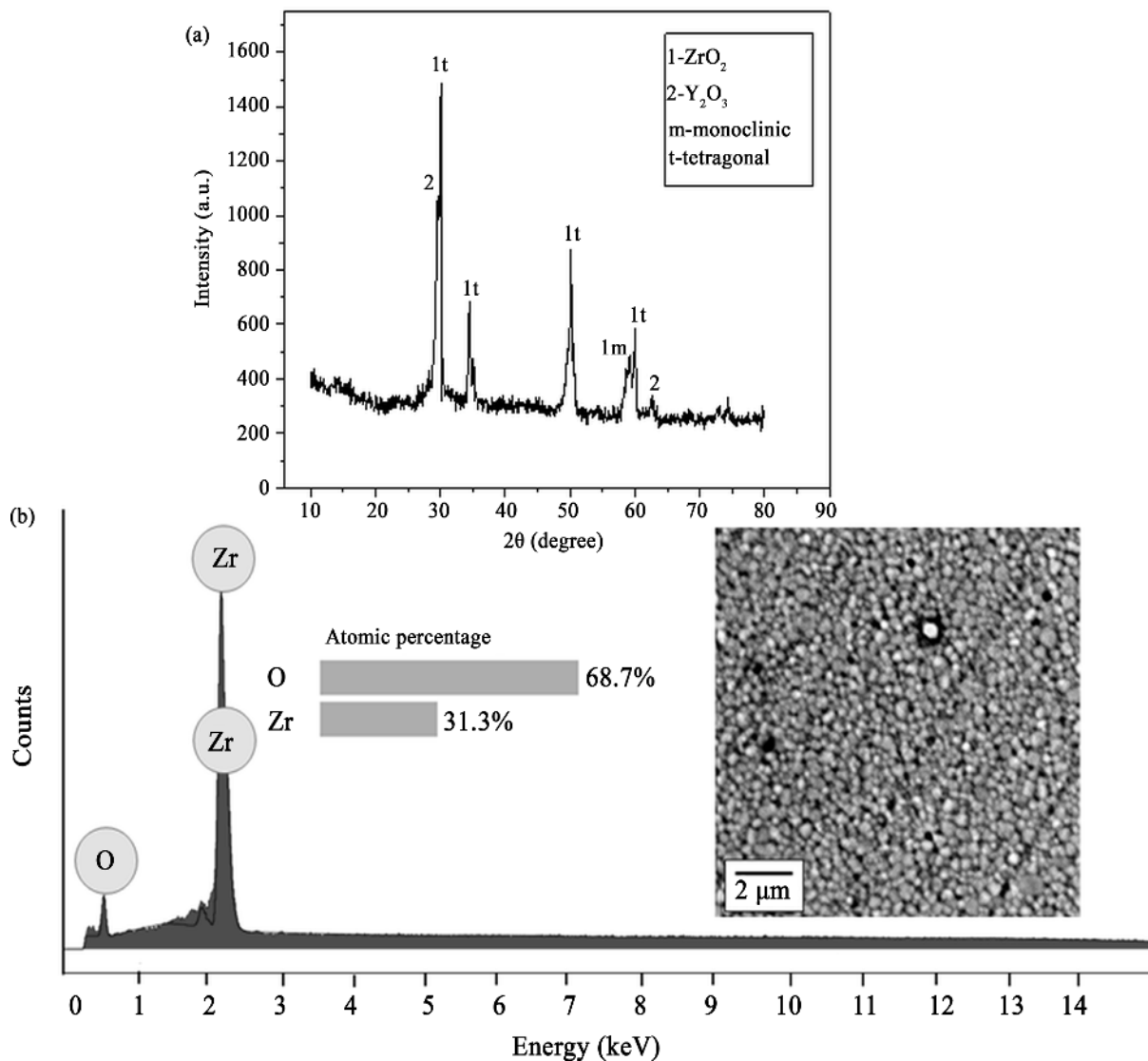| Processing Method	Properties			
	Particle Size	Density (g/cm^3)	Hardness (VHN)	Hardness (GPa)
Conventional (1600°C, 10 h)	45 ± 10 μm	4.8 (80%)	660 ± 20	6.47 ± 0.20
Conventional (1600°C, 8 h)	45 ± 10 μm	4.5 (75%)	433 ± 15	4.25 ± 0.15
Microwave (1500°C, 20 min)	45 ± 10 μm	4.5 (75%)	440 ± 17	4.32 ± 0.17
Vacuum (1500°C, 20 min)	45 ± 10 μm	4.2 (70%)	417 ± 18	4.09 ± 0.18
Conventional (1450°C, 2 h)	40 ± 20 nm	6.0 (100%)	1345 ± 25	13.19 ± 0.25

Figure 5. Typical (a) XRD plot and (b) EDX pattern in association with SEM image (shown in inset) of sintered nano-YSZ specimen.

4. Conclusion

The present investigation showed that microwave and vacuum sintering techniques offered enhanced sintering at lower temperatures compared to conventional sintering technique in case of the micron-sized 0.5 Al₂O₃-YSZ specimen. However, microwave sintering technique appeared as the best sintering technique in comparison to the conventional and vacuum sintering techniques. Further, conventional sintering of nano-YSZ specimen imparted 100% density at 1450°C for 2 h soaking. In contrast, conventionally sintered micron-sized 0.5 Al₂O₃-YSZ specimen revealed 80% density after 10 h soaking at 1600°C. The current study also established the particle size effect on densification of the conventionally sintered YSZ specimen. Thus, the present study showed some possible means through which hard zirconia based ceramics can be manufactured for suitable applications in dentistry.

Acknowledgements

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