The 2018 World Congress on
Advances in Civil, Environmental, & Materials Research (ACEM18)
Songdo Convensia, Incheon, Korea, August 27 - 31, 2018

Effect of microwave radiations on phase stability of zirconia nanoparticles

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ABSTRACT

Zirconia (ZrO_2) is a strong, osseoconductive and transparent ceramic thus can be used as biomedical implants. Moreover, its ivory color makes it suitable for teeth coatings. Due to the excellent characteristics of zirconia polycrystalline ceramic materials, such as low thermal conductivity, excellent biocompatibility, high fracture toughness and strength, high crack resistance and low wear rates are widely used for many applications. These characteristics of the final hydrous zirconia sols are dependent on the experimental conditions, including intensity of microwave radiations, concentration of reactants, nature of anions along with stirring and aging time. Aim of this study is to prepare transparent, dense and single-phase stabilized zirconia nanoparticles. In-order to investigate the effect of above mentioned parameters on zirconia phase and toughness, microwave radiation of various intensities (17, 33 and 55% of total power) is used. From XRD data it can be inferred that the amorphous structure with humps at 28.2º is an indication of presence of stabilized t-ZrO_2. Crystallite size decreases with increase in intensity of microwave. These as-synthesized dense nanoparticles result in high value of hardness ~988HV under optimized conditions.

1. INTRODUCTION

Microwave heating is the most popular phenomena for synthesis and processing of ceramics. There is a difference in heat transfer mechanism in conventional heating and in microwave heating. Conventional heating involves transfer of heat to the surface via conduction and radiation resulting in high temperature gradient and stresses in components of ceramics while in case of microwave heating there is uniform distribution of heat due to volumetric effect. Microwave heating reduces thermal stresses and speeds up production rate (Clark et al. 2000; Katz, 1992). EA technology

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UK claims least energy consumption in ceramics industry by using microwave assisted fired klins (Shiming and McColm 1997). They have made use of microwave in combination with gas firing in order to produce tiles, pottery and other ceramics with more efficiency and least power consumption.

Microwaves are the part of electromagnetic spectrum corresponding to 1.0 to 1.1mm wavelength and 0.3 to 300 GHz frequency. Major portion of electromagnetic frequencies is used in communication sector while the only frequency in the range 2.45, 5.85, 21.1 GHz is applicable in industry and for medical applications. Microwave field depends on dielectric properties of ceramics due to interaction and heating of materials.

Zirconia is characterized by high strength; high fracture toughness, low thermal conductivity and high crack resistance which makes it suitable material for restoration and implants (Li et al. 2013). Zirconia occurs in three crystal structures which are thermodynamically stable: monoclinic (<1100 ºC), tetragonal (<2370 ºC) and cubic (>2370ºC) (Mamivand et al. 2013). Among all these phases, tetragonal phase unveils better mechanical properties (harder and tougher) than the monoclinic phase (Andrieux et al. 2012) and thus is a potential candidate for biological application as an implant material (Kohal et al. 2006). Zirconia faces issue of stabilization due to aging or LTD because zirconia is a hydrophobic compound and losses its stability due to transformation from tetragonal to monoclinic phase. To stabilize zirconia many techniques are employed including using of organic additives, pH variation, change in crystallite size, addition of dopants and post annealing techniques.

Bodhak et al. (2011) reported better densification and mechanical propertries of microwave sintering in pure mullite and mullite zirconia composites. Ebadzadeh and Valefi (2008) reported dissociation of zirconia is most favourable in microwave heating then in conventional heating. Noh et al. (2003) reported that fraction of monoclinic phase increased with increasing reaction temperature similarly transformation in 5M NaOH solution is much higher than in 1M NaOH solution.

Properties of prepared zirconia nanoparticles strongly depends on the method followed zirconia have been reported by laser ablation (Tan et al. 2011), hydrothermal (Li et al. 2013) co-precipitation (Tani et al. 1983) RF sputtering (Horikawa et al. 1993) and sol- gel (Porozova et al. 2009). We have followed sol gel method for synthesis of zirconia nanoparticles because of its advantages over the other processes which includes that it is a low temperature processing technique, does not require ultra-high vacuum conditions, we have good control over the morphology of resultant nano particles and we can also control the film thickness.

This present work focuses on the mechanical strength due to phase transition in zirconia nanoparticles using water as a solvent and microwave heating for sintering of nanoparticles. The prepared samples are characterized by using X-Ray Diffractrometer (Bukear D8-Advance diffractrometer), elipsometery, FTIR and micro Vickers micro indenter.

2. Experimental Details

$ZrOCl_2.8H_2O$ obtained from Sigma–Aldrich and 99.99% pure, was used as a starting material and DI water was used as solvent.

Zirconium oxychloride octahydrate ($ZrOCl_2.8H_2O$) was mixed in deionized water to form 0.1M stock solution. Solution was stirred at 50ºC which results in transparent and shiny sol. In order to check the effect of microwave radiations intensities solution were heated in microwave. Three different intensities were used of power 17, 33, 55 of total power. Subsequently the prepared powders were subjected to different characterizations. Fig.1 shows flow chart for synthesis of zirconia nanoparticles.

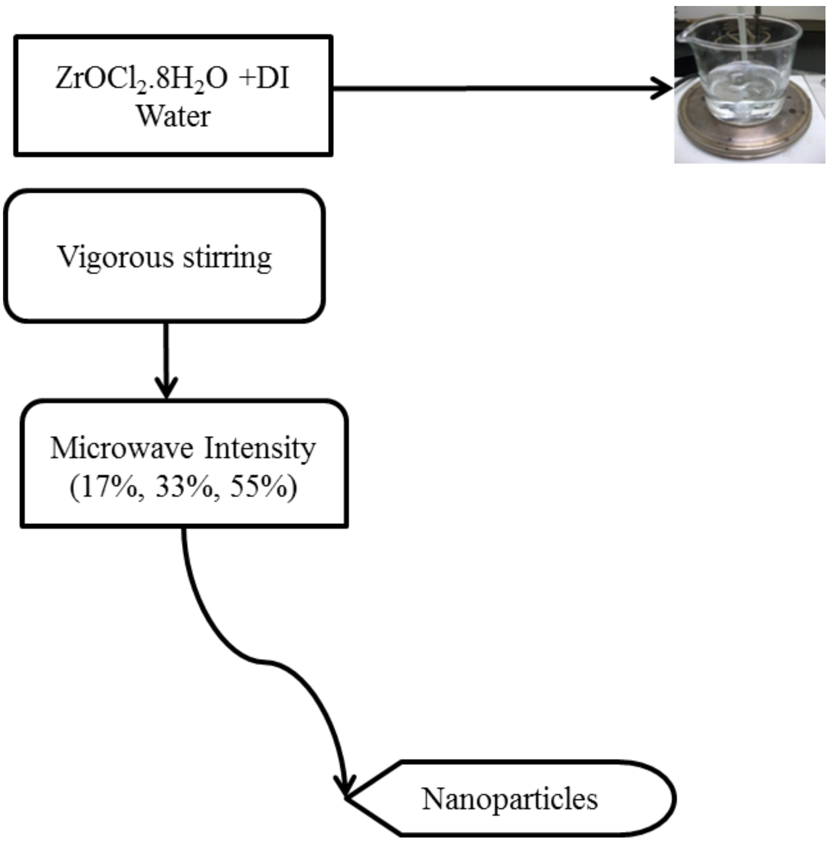

Fig. 1: Schematic representation of zirconia nanoparticles at different microwave intensities

3. Results and Discussion

The main goal of this study is to study effect of microwave power on structural properties of zirconia nanoparticles. XRD analysis is very important parameter for structural analysis of nanoparticles. Fig. 2 shows XRD results of zirconia nanoparticles synthesized with microwave intensities of 17%, 33% and 55%. XRD patterns show amorphous behaviour of synthesized nanoparticles corresponding to all microwave energy ranges and a hump appearing at 28.2º and 41.3º for (111) and (112) plane is a clear indication of formation of stabilized tetragonal zirconia according to JCDP 17-923. It has been observed from data that hump broadening is decreased with increase in microwave intensities indicating reduction in amorphous behavior of zirconia nanoparticles.

This decrease in amorphous behavior is due to generation of stresses induced by rapid microwave heating and has been well explained by Lambert's law providing explanation over exponential decay of energy dissipation. Another cause of decline in amorphous behavior is deletion of hydroxyl ion at higher intensities.

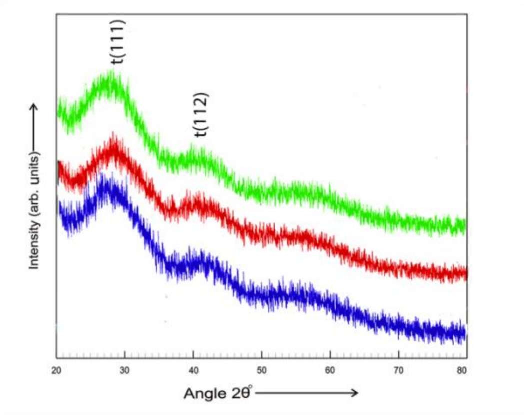

Fig. 2: XRD pattern of zirconia nanoparticles synthesized at microwave intensities of 17%, 33% and 55%.

The crystalline size (D) of nanoparticles is calculated by using Scherer equation (Cullity and Stock 1956);

$D=k\lambda/BCos\theta$ (1)

Where k=0.9, a correction factor, B =full width half maximum of most intense diffraction peaks, λ is the wavelength of x-ray and θ the Bragg angle.
Dislocation densities are measured by using equation;

Dislocation density $=1/D^2$ (2)

Fig. 3 shows variations in crystalline size with respect to different microwave intensities of 17%, 33% and 55%. At 17% of total power of microwave crystalline size of 14.4nm has been found. Tyagi et al. 2006 and Gravie 1965 reported that crystalline size for zirconia below 30nm is stable tetragonal phase and is well suited for biomedical applications (Tyagi et al. 2006 and Gravie 1965). Decrease in crystallite size with increased microwave power leads to increase in dislocation density which is due to decrease in XRD humps with increase in intensity of microwave power as also clear from XRD data [Fig. 2]. Dislocation lines/m^2 is calculated by using equation 2 and shown in Fig. 4. Dislocation lines are measure of number of dislocations in a unit volume. Behavior observed for dislocation lines/m^2 is opposite to that of crystallite size. Relative increase in dislocation lines/m^2 is observed with increase in microwave intensity. Corresponding to 17%, 4.6 x10^{15}/m^2 has been observed. Relative increase in dislocation density results in increase in strength due to generation of high shear stress and consequently results in decrease in hardness of material (Jiang et al. 2010).

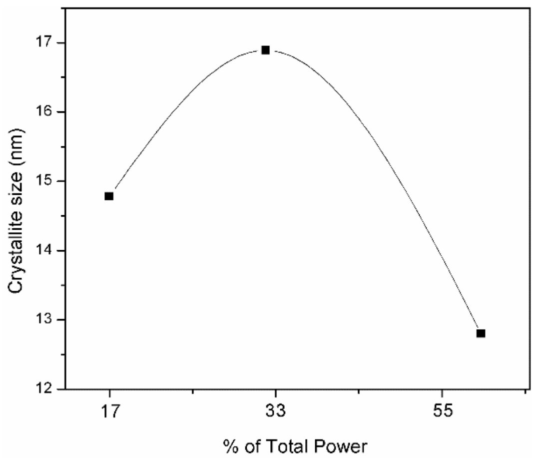

Fig. 3: Crystallite size of ZrO_2 as a function of different microwave intensities

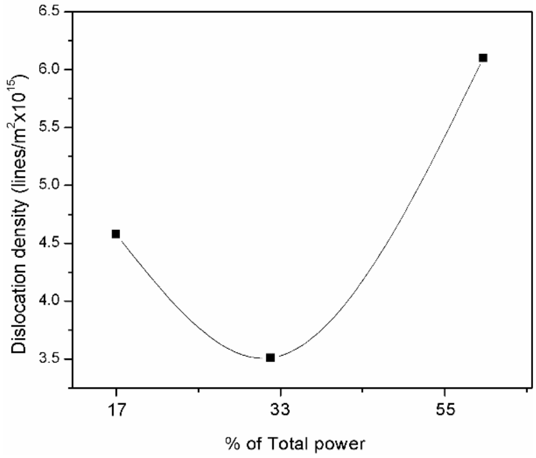

Fig. 4: Dislocation density of ZrO_2 as a function of different microwave intensities

Dielectric properties plays critical role for use in bio-medical applications. Dielectric properties were measured by using impedance analyzer in parallel plate configuration. Data has been collected in frequency ranging from 200000-1000000Hz. Parallel capacitance with resistance were measured which helped in measurement of dielectric constant 'Ɛ' and dielectric loss 'tanδ' were calculated using following equations

$$\mathcal{E} = \frac{C*d}{\varepsilon_0 * A} \tag{3}$$

$$\tan\delta = \frac{1}{2\pi\varepsilon\varepsilon_0\rho} \tag{4}$$

Here C donates capacitance, d is for thickness of sample; A is for area, $\mathcal{E}_o$ donates the permittivity of free space and ρ is for resistivity in above equations. Dependence of dielectric constant verses frequency at different microwave power is shown in Fig. 5. Noteworthy observation collected from data is the high dielectric constant is observed for high frequency while microwave power is constantly increasing in the range from 17- 55% and it becomes almost constant at mid and rapidly increase at high frequency. Dielectric constant shows an increasing behavior with intensities of microwave. This variation observed in dielectric constant is in consistent with Debye model. If applied frequency is less than 1/τ of Debye relaxation time then charge carriers are fully involved in mechanism of polarization. However, if value of applied frequency is larger than 1/ τ then charge carriers are not involved in mechanism of polarization and cause dielectric constant to decrease with increase in frequency. Grain size is responsible for difference in dielectric constant due to increase in microwave power which has caused easier domain wall motion (Goharshadi and Hadadian 2012). Tangent loss with respect to different applied frequencies for different microwave powers has been plotted in Fig. 5 and is calculated by using equation 4 corresponding to low frequency high values of tangent loss have been observed and for 55% of microwave power 0.20 of tangent loss is reported in this research [Fig. 6].

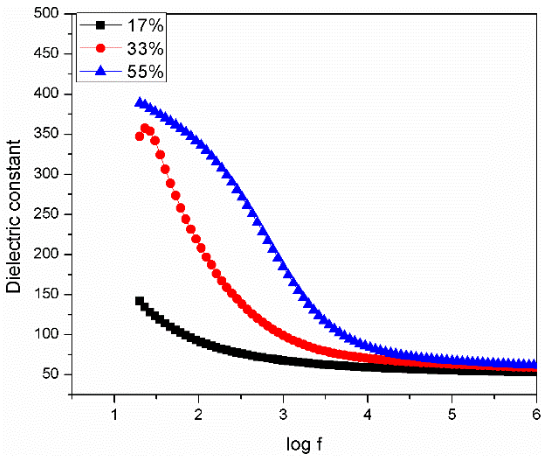

Fig. 5: Dielectric constant of ZrO_2 as a function of different microwave intensities

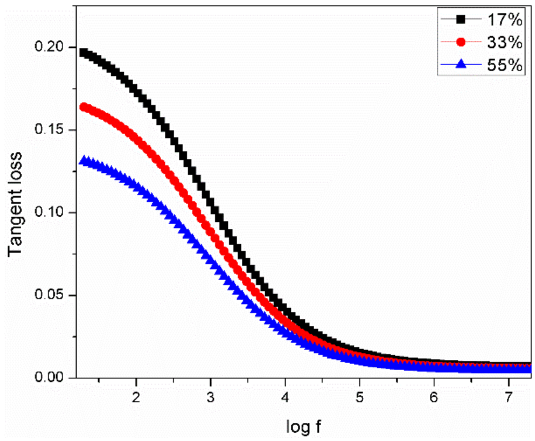

Fig. 6: Tangent Loss of ZrO_2 as a function of different microwave intensities

For measurement of mechanical properties of microwave assisted zirconia nanostructures micro indention method is used under 4.9N load for 15 seconds dwell time was performed according to American Society for testing of materials standard. Hardness is observed in the range from 988 HV to 782 HV. Maximum hardness has been observed for 17% which are in consistent with XRD data which shows that corresponding to 17% maximum of t-phase of zirconia is found which consequently leads to high value of hardness and maximum density. Decrease in hardness is observed with increased microwave power which is inconsistent with XRD data and crystallite size verses dislocation density.

Table 1. Relation between Hardness and microwave power of zirconia nanoparticles at different microwave powers

Microwave Power (%)	Hardness (HV)
17%	988
33%	845
55%	782

3. Conclusions

Zirconia nanoparticles have been prepared using sol gel method accompanied with microwave heating of various intensities (17, 33 and 55% of total power). From XRD data it can be inferred that the amorphous structure with humps at 28.2º is an indication of presence of stabilized t-ZrO_2. Crystallite size decreases with increase in intensity of microwave. Dielectric analysis showed normal behaviour of prepared samples with highest dielectric constant and lowest tangent loss for 55% microwave power intensity. These as-synthesized dense nanoparticles result in high value of hardness ~988HV under optimized conditions.

REFERENCES

Andrieux, M., Ribot, P., Gasquères, C., Servet, B. and Garry, G. (2012), “Effect of the oxygen partial pressure on the toughness of tetragonal zirconia thin films for optical applications”, *Appl. Surf. Sci.* **263**, 284-290.

Bodhak, S., Bose, S. and Bandyopadhyay, A. (2011), “Densification Study and Mechanical Properties of Microwave-Sintered Mullite and Mullite–Zirconia Composites”, *J. Am. Ceram. Society,* **94** (1), 32-41.

Clark, D. E., Folz, D. C. and West, J. K. (2000), “Processing materials with microwave energy”, *Mater. Sci. Eng. A,* **287** (2), 153-158.

Cullity, B., and Stock, S. (1956), “The directions of diffracted beams. *Elements of X-ray diffraction”, Addison-Wesley Publishing Co., USA*, 78-103.

Ebadzadeh, T., and Valefi, M. (2008), “Microwave-assisted sintering of zircon”, *J. Alloys Compd,* **448** (1-2), 246-249.

Garvie, R. C. (1965), “The occurrence of metastable tetragonal zirconia as a crystallite size effect”, *J. Phys. Chem,* **69** (4), 1238-1243.

Goharshadi, E. K., and Hadadian, M. (2012). Effect of calcination temperature on structural, vibrational, optical, and rheological properties of zirconia nanoparticles. *Ceramics International, **38*** (3), 1771-1777.

Horikawa, T., Mikami, N., Makita, T., Tanimura, J., Kataoka, M., Sato, K. and Nunoshita, M. (1993), “Dielectric properties of (Ba,Sr)TiO_3 thin films deposited by RF sputtering”, *Jpn. J. App. Phys,* **32** (9), 4126.

Jiang, H., Gomez-Abal, R. I., Rinke, P. and Scheffler, M. (2010), “First-principles modeling of localized d states with the G W@ LDA+ U approach”, *Phys. Rev. B*, **82** (4), 045108.

Katz, J. D. (1992), “Microwave sintering of ceramics”, *Annu. Rev. Mater. Sci,* **22**(1), 153-170.

Kohal, R. J., Klaus, G. and Strub, J. R. (2006), “Zirconia implant supported all ceramic crowns withstand long term load: a pilot investigation”, *Clin. Oral Implants Res,* **17**(5), 565-571.

Li, C., Li, K., Li, H., Zhang, Y., Ouyang, H., Liu, L.and Sun, C. (2013), “Effect of reaction temperature on crystallization of nanocrystalline zirconia synthesized by microwave-hydrothermal process”, *J. Alloys Compd,* **561**, 23-27.

Mamivand, M., Zaeem, M. A., El Kadiri, H. and Chen, L.-Q. (2013), “Phase field modeling of the tetragonal-to-monoclinic phase transformation in zirconia”, *Acta Mater,* **61**(14), 5223-5235.

Noh, H.-J., Seo, D.-S., Kim, H. and Lee, J.-K. (2003), “Synthesis and crystallization of anisotropic shaped ZrO_2 nanocrystalline powders by hydrothermal process” *Mater. Lett,* **57**(16-17), 2425-2431.

Porozova, S., Krasnyi, B., Tarasovskii, V., and Krasnyi, A. (2009), “Preparation of zirconia ceramics from powder synthesized by a sol-gel method”, *Refract. Ind. Ceram,* **50**(6), 438-440.

Shiming, F., and McColm, I. (1997), “Development of a low cost microwave system for rapid sintering of clay based ceramics”, *Br. Ceram. Trans,* **96**(5), 188-194.

Tan, D., Lin, G., Liu, Y., Teng, Y., Zhuang, Y., Zhu, B., Zhao,Q. and Qiu, J. (2011), “Synthesis of nanocrystalline cubic zirconia using femtosecond laser ablation”, *J. Nanoparticle. Res,* **13**(3), 1183-1190.

Tani, E., Yoshimura, M. and Sōmiya, S. (1983), “Formation of ultrafine tetragonal ZrO2 powder under hydrothermal conditions”, *J. Am. Ceram. Society,* **66**(1), 11-14.

Tyagi, B., Sidhpuria, K., Shaik, B. and Jasra, R. V. (2006), “Synthesis of nanocrystalline zirconia using sol− gel and precipitation techniques”, *Ind. Eng. Chem. Res,* **45**(25), 8643-8650.