

# Effect of Stirring Rate on Organic Additives Stabilized Zirconia Nanostructures

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## ABSTRACT

Achievement of stable nanostructures with reproducible properties is a significant direction of energetically developed nanotechnology. Stabilized ZrO<sub>2</sub> nanostructures have found wide applications in biomedical sciences. Problem with zirconia exists in multi-phases occurring simultaneously which degrades its mechanical and microstructural properties (Bashir et al. 2015). In this research work effect of stirring rate on zirconia sol has been examined. 5 ml of methanol is added which helps in reducing grain size of zirconia. Sols are stirred at room temperature for various stirring rates (200 to 600 rpm) during synthesis. Gels of zirconia are dried at 60°C. Phase pure tetragonal ZrO<sub>2</sub> is obtained at stirring frequency of 300 rpm without any further heat treatment as confirmed by XRD data. A sharp decrease in crystallite size has been observed with stirring rate 300 rpm. Dense nanostructures are obtained leading to high value of hardness observed by micro Vickers indenter. A large value of dielectric constant at lower frequency is due to space charge polarization arising at the grain boundary interfaces.

## 1. INTRODUCTION

Achievement of stable nanostructures with reproducible properties is a significant direction of energetically developed nanotechnology (Zaporozhets et al. 2012). These nanostructures have found wide applications in biomedical sciences (Yi et al. 2009), in optoelectronic industry (Wang 2007), catalyst support (Sato et al., 2011) and many more. Zirconia ceramics with different nanostructures have found their applications in dentistry and orthopedics (Hallmann et al., 2012) due to their high value of hardness and anti-corrosion properties (Balakrishnan et al. 2013). The problem with zirconia is its existence in three phases: monoclinic phase, tetragonal phase and cubic phase (Li et al. 2013, Cologna et al. 2011, Zhang et al. 2010). These phases are thermodynamically stable: monoclinic (m) below 1100°C, tetragonal (t) below 2370°C and cubic (c) above 2370°C (Bashir et al. 2014). Tetragonal phase (t-phase) revealed higher hardness than the monoclinic phase (Andrieuxa et al. 2013). Therefore, tetragonal is most important phase for biological application (Kohal et al. 2013). But it transforms to monoclinic zirconia at ambient conditions, so formation of tetragonal zirconia at room temperature is yet a task.

Subsequently, grain size has a strong influence on mechanical properties. Actually grain size is a constraint for the transformation of tetragonal to monoclinic poly-crystals (Li et al. 2012). Organic additive was used to control / alter shape and size of nanoparticles. Decrease in crystallite size from 30 to 10 nm has been reported with the use of organic additives (Heshmatpour et al. 2011).

In the present work, nanofibres of ZrO<sub>2</sub> powders were synthesized by sol- gel method followed by stirring at different frequency ranges. Biocompatible additives, glucose and fructose are used during synthesis.

## **2. Experimental Details**

### *2.1 Materials*

Zirconyl chloride octahydrate (ZrOCl<sub>2</sub>.8H<sub>2</sub>O, BDH, 99.99% pure) was purchased from Sigma Aldrich. Glucose and Fructose were purchased from Merck. Ammonia was purchased from Sigma Aldrich. Deionized (DI) water was used as solvent.

### *2.2 Method*

Zirconyl chloride octahydrate was dissolved in DI water to form 0.1M solution. This stock solution was stirred at room temperature. Ammonia was added drop wise. Then glucose: fructose: water with ratio 1:1:10 were added into the pre-synthesized zirconia. The ratio of glucose, fructose and water was optimized as reported elsewhere (Bashir et al. 2015). Sols were stirred at five different frequencies (200, 300, 400, 500 and 600) which resulted in fluffy sol. These stirred sols were dried in the temperature 60-70°C for powder formation.

Glucose and fructose were used as organic additive with 1:1 ratio, since mostly used organic additive is sucrose and it contains 1, 1 molecule of glucose and fructose. Moreover, 1:1 ratio has already been optimized (Riaz and Naseem 2013). Upon dissolving in water it converts in to mannose which has same configuration as glucose and fructose. Main purpose is the use of glucose and fructose because they are non-toxic, easily available to store at a low temperature, adequately supplied, and water-soluble. These additives have ability to avoid oxidation in acidic pH. The detailed study by using these organic additives has shown that these additives prevents transformation of zirconia from monoclinic to tetragonal by acting as capping agent (Heshmatpour and Aghakhanpour 2011).

### *2.3 Characterizations*

Structure of zirconia powders were obtained by X-ray diffractometer (Bruker D8 advance) using Cu K $\alpha$  source ( $\lambda=0.1540598$  nm). Dielectric properties of zirconia nanostructures were examined with 6500 precision Impedance Analyzer. Mechanical properties were studied by Shimadzu HMV-2 micro Vickers hardness indenter. For indentation powders were made in the form of pallets by using hydrolytic pressure of 1 Ton.

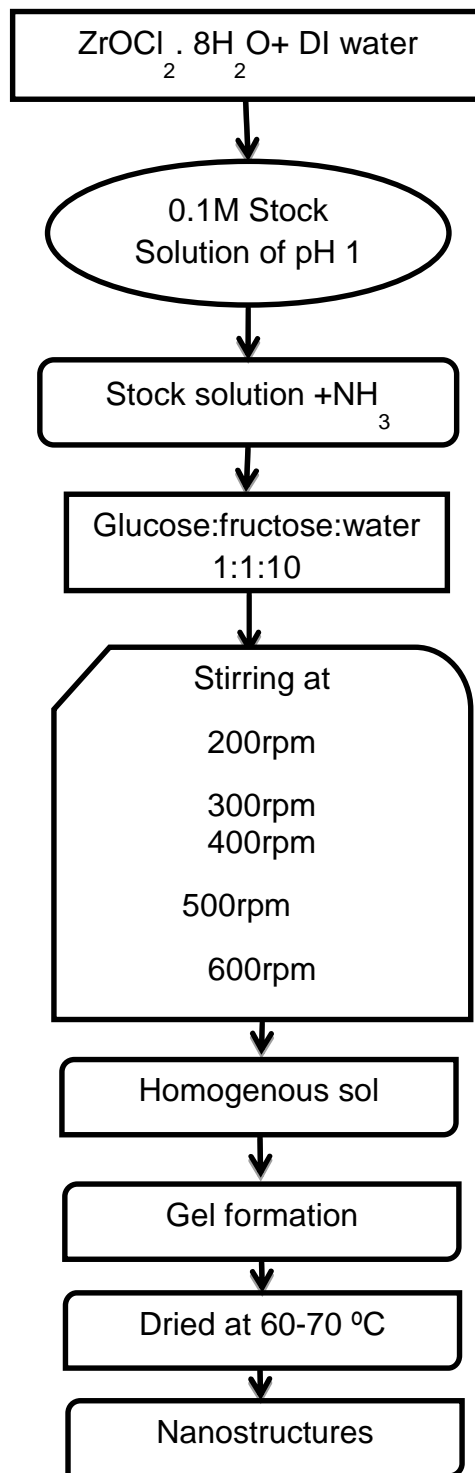


Fig. 1 Schematic approach for synthesis of zirconia nanostructures at various stirring rates

### 3. Results and Discussion

Fig. 2 represents the XRD graphs of  $ZrO_2$  at various stirring rates. XRD graphs of as-synthesized zirconia nanostructures show amorphous behavior for sample stirred at 200rpm [Fig. 2], however, presence of hump at  $\sim 30^\circ$  is a clue for formation of tetragonal  $ZrO_2$  (Catauro et al. 2014). Tyagi et al. (2006) described that transition of amorphous  $Zr(OH)_4$  gel to tetragonal zirconia exists at  $\sim 400^\circ C$ . However, it is important to note that tetragonal zirconia has been obtained at room temperature in organic added zirconia nanostructures. Amorphous zirconia might have observed due to many reasons such that 1) during room temperature synthesis  $Zr(OH)_4$  is formed and it has been considered as a short range structure of isomorphous to tetragonal zirconia. In short range isomorphous tetragonal atoms are arranged to emerge crystallization into tetragonal zirconia. 2) In XRD pattern, a sharp peak is formed due to the periodic arrangement of atoms. But in case of amorphous phase, X-rays scattered in many directions results in large hump distributed over large range of  $2\theta$ . Formation of hump around  $30^\circ$  is due to scattering of X-rays along corresponding planes with many other directions. Actually, XRD patterns consist of sum of all fundamental phases of material. Presence of amorphous behavior is compatible with naturally existing hydroxyapatite layer (Marchi et al. 2013). For sample stirred at 300rpm, pure tetragonal zirconia along with intense peak of tetragonal structure has been found. Shifting in  $2\theta$  values was found due to sufficient

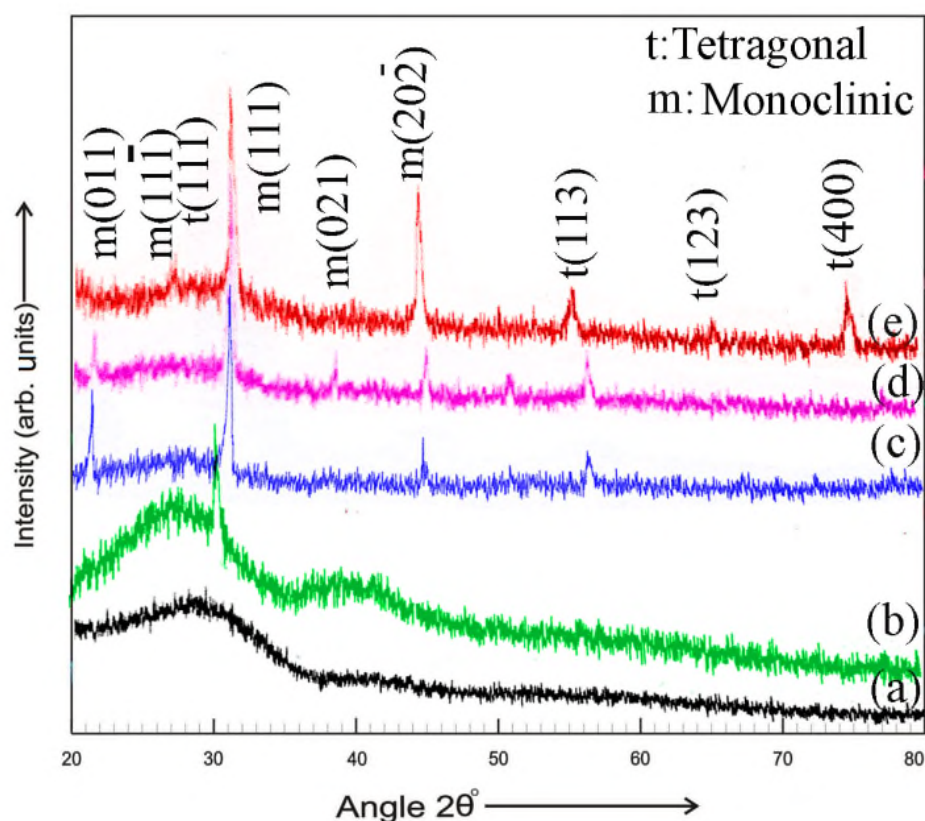


Fig. 2 XRD patterns at stirring rate (a) 200rpm, (b) 300rpm, (c) 400rpm, (d) 500rpm and (e) 600rpm

amount energy with the increase in stirring rate. Such shift towards higher angles causes phase transition from tetragonal to monoclinic. In fact, at higher stirring rate sufficient high mechanical energy is an important source of temperature. At higher stirring rate temperature increases and creates chemical driving force. This chemical driving force is sufficient to produce the strain energy associated with transformation.

Crystallite size of the zirconia nanostructures was estimated using Eq. 1 (Cullity 1956) and is plotted in Fig. 3. Crystallite size of phase pure tetragonal zirconia at 300rpm [Fig. 3] is 31.26nm. Crystallite size is in agreement with literature according to which tetragonal zirconia occurs below 30 nm (Garvie 1965). An increase in stirring rate in organic additives zirconia causes phase shift from phase pure tetragonal zirconia to mixed (monoclinic-tetragonal) phase. An increase in crystallite size has observed with increase in stirring rate. As discussed earlier, higher stirring rates provide higher mechanical energy / strength. With the increase in temperature chemical driving force leads to lowest surface energy due to diffusion of two different nuclei and migration of grain boundaries. This lowest surface energy and coalescence of nuclei leads to stable polycrystalline state of a material (Raiz and Naseem 2007). Relatively lower dislocation lines/m<sup>2</sup> (dislocation density) were calculated, using Eq. 2, for organic additives zirconia powders as shown in Fig. 3.

$$D = 0.9\lambda / B \cos \theta \quad (1)$$

$$\delta = 1/D^2 \quad (2)$$

Where D is crystallite size,  $\lambda$  is wavelength of X-rays used (1.5406Å), B is full width at half maximum,  $\theta$  is diffraction angle and  $\delta$  is dislocation lines/m<sup>2</sup>.

Unit cell volume calculations [Fig. 4] revealed periodic behavior with stirring rate. These variations are consistent with phase occurrence. It has already been discussed in XRD results that phase pure tetragonal zirconia was observed at stirring rate 300rpm. Therefore, unit cell volume of such sample sharply decreased as compared to other samples. Samples stirred at other rpm showed slightly larger unit cell volume with the fact that monoclinic has slightly larger unit cell volume than tetragonal. Decrease in volume leads to increase in density especially for sample synthesized at stirring rate 300rpm [Fig. 5] with phase purity. A small increase in unit cell volume was observed with the further increase in stirring rate. This might have occurred because of the chemical transformation in the samples that resulted in relatively increased monoclinic to tetragonal ratio. At relatively higher temperatures oxygen vacancies present in tetragonal zirconia are filled, thus resulting in lattice distortion leading to phase transformation from tetragonal to monoclinic. For biological applications relatively higher densities are required because more dense the material, more compact the powder and higher hardness of samples.

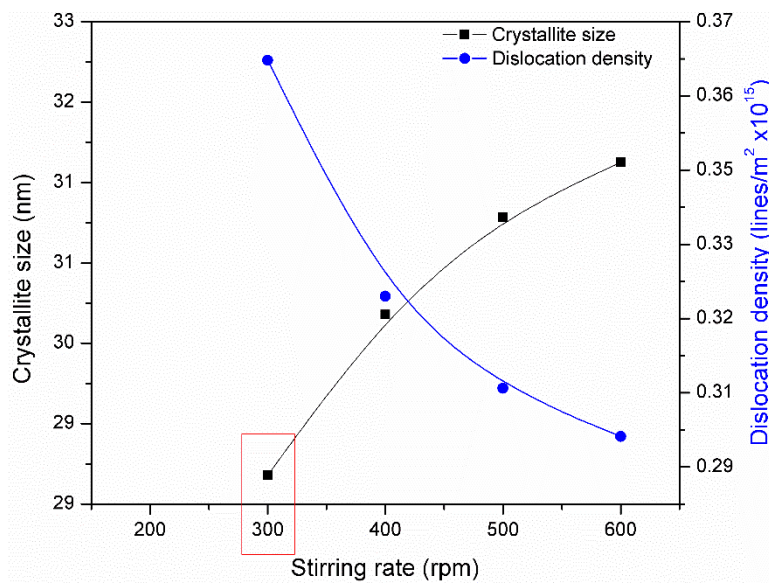


Fig. 3 Crystallite size and dislocation density of zirconia nanostructures as a function of stirring rate: Rectangle shows the phase pure tetragonal zirconia

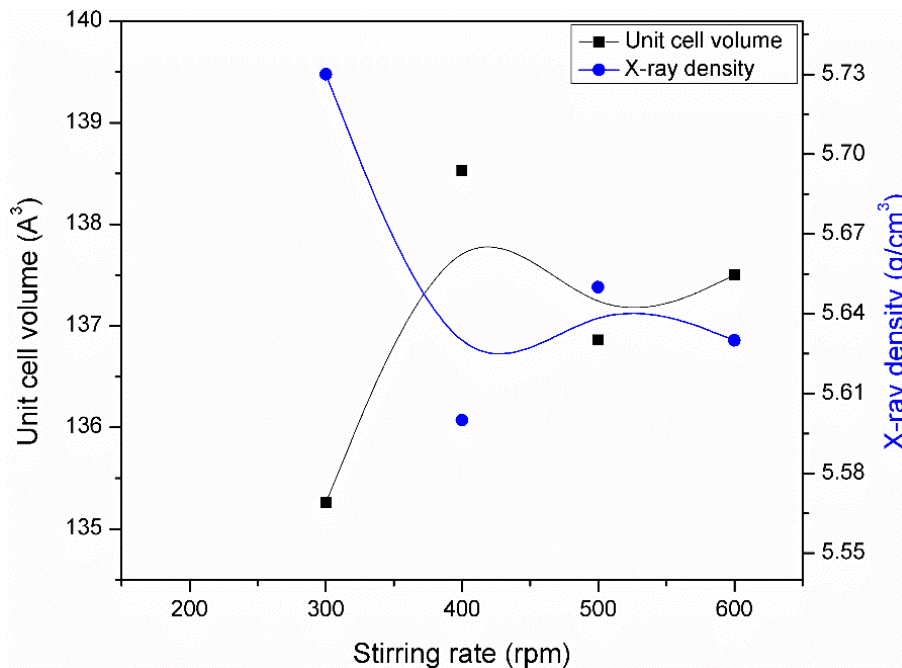


Fig. 4 Unit cell volume and x-ray density of zirconia nanostructures as a function of stirring rate

The method of choice and a starting point for measuring the mechanical properties of organic additives zirconia by many biomedical researchers is the micro indentation

method. Over many years, there have been a number of breakthroughs in the instrumentation, methodology and micro indentation. This technique is now considered to be an effective and simple means of determining the hardness of the samples. From Fig. 4 higher x-ray density was calculated for sample stirred at 300rpm. This higher x-ray density causes higher hardness as shown in Table 1. Samples prepared by using organic additives show relatively very high value of hardness ~1543HV. Hardness of the samples is in the range of 1181HV to 1543HV [Table 1]. However, maximum hardness values were observed in sample stirred at 300rpm. Decrease in value of hardness is observed with increase in stirring rate due to presence of mixed tetragonal – monoclinic phases as shown in XRD graphs [Fig. 2].

**Table 1** Hardness of zirconia nanostructures as a function of stirring rate

<b>Stirring rate (rpm)</b>	<b>Hardness (HV) at constant load and time ASTM C- 1327-99</b>
200	1275
300	1543
400	1219
500	1289
600	1181

Dielectric properties are very crucial for any oxide material to be used in bio-medical applications. The environment such material may create in body and their stability plays a critical role. For studying the dielectric properties the dielectric constant and tangent loss were calculated using Eqs. 3 and 4;

$$\varepsilon = Cd / \varepsilon_0 A \quad (3)$$

$$\tan \delta = 1 / 2\pi f \varepsilon \varepsilon_0 \rho \quad (4)$$

Where,  
C = capacitance,  
d =thickness,

A= area,  
 $\epsilon_0$ = permittivity of free space  
 $\rho$  =resistivity

From Figs. 5 and 6 a decrease in dielectric constant and tangent loss with increasing frequency has been observed. Under the application of external field, dispersion occurs in space-charge carriers. These space charge carriers are required some time to get aligned in the applied field. Since at low frequencies these space charge carriers have sufficient time for alignment. But at high frequencies space charge carriers do not get sufficient time to follow field thus results in low dielectric constant. For sample prepared at 300rpm, relatively high dielectric constant was observed at low frequencies. This massive increase / difference in dielectric constant with organic additives can be endorsed to increase in grain size (Nair et al. 2003). The increase in grain size with increase in stirring rate assists easier domain wall motion (Riaz et al. 2015) leading to an increase in dielectric constant.

In fact, dielectric properties of organic additives is governed by charge distribution and change in temperature gradient. Basically, polarization phenomenon is combination of ionic, electric and dipole polarization. As from XRD data, amorphous and crystalline structure has observed. In case of crystalline, binding chains of molecules (due to presence of organic additives) move with greater hindrance due to presence of different hindral structural units (Yadav et al. 2010). Therefore, samples with amorphous nature has less dielectric constant as compare to crystalline.

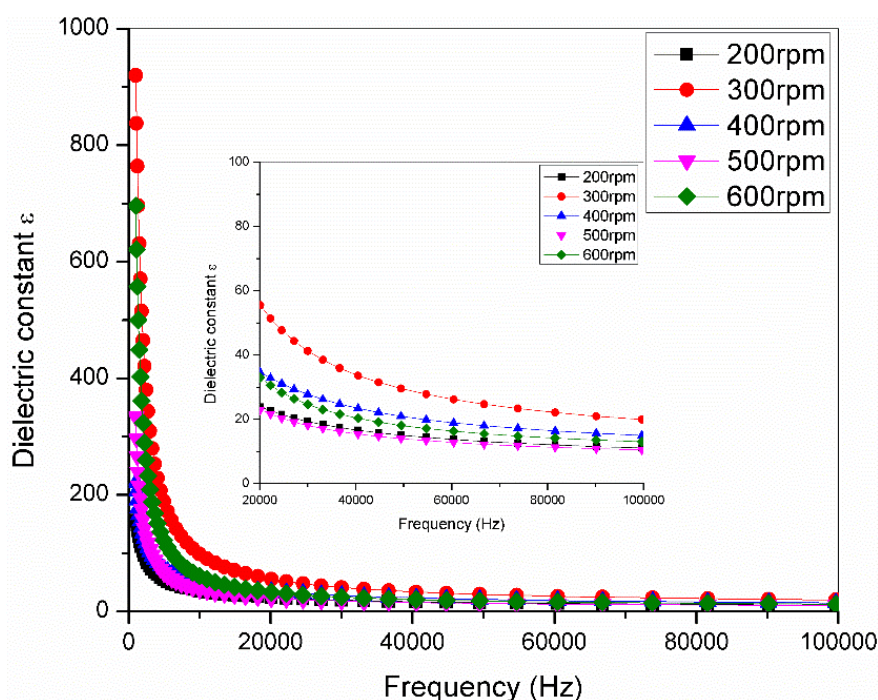


Fig. 6 Dielectric constant of zirconia nanostructures as a function of stirring rate: Inset shows the variation in dielectric constant high frequencies



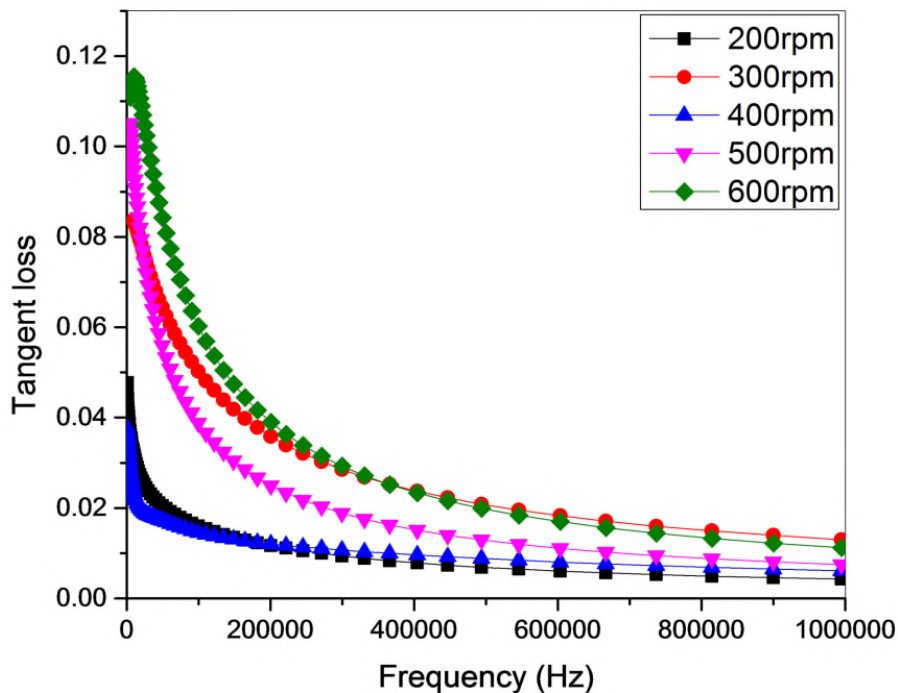


Fig. 7 Tangent loss of zirconia nanostructures as a function of stirring rate

### 3. CONCLUSIONS

(1) Zirconyl chloride octahydrate was used as a starting material. Five different sols at different stirring rates 200, 300, 400, 500 and 600rpm were prepared. (2) XRD results showed that zirconia powder was a mixture of monoclinic-tetragonal  $ZrO_2$  phase at high stirring rates. Whereas, phase pure tetragonal zirconia was obtained at stirring rate 300rpm (3) Crystallite size showed sharp decrease with phase transition due to restructuring. (4) Hardness of the samples was in the range of 1181HV to 1543HV. Sample with phase pure tetragonal zirconia exhibited high value of hardness. (5) Zirconia nanocrystallites prepared using sol gel method showed higher dielectric constant value of 900 at lower frequency. Whereas, dielectric constant of  $\sim 58$  was observed at 20kHz.

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