# Enhancement of Dielectric Properties of Methanol Stabilized Zirconia Nanopowders

Saira Riaz[1)], M Akram Raza[2)], *Shumaila Islam[3)], Yan-Jun Guo[4)]
and Shahzad Naseem[5)]

[1), 2), 5)] *Centre of Excellence in Solid State Physics, University of Punjab, Lahore, Pakistan*
[3)] *Laser Centre, Universiti Tecknology Malaysia, Johor Bahru, Malaysia*
[4)] *National Center for Nanoscience & Technology, CAS, Beijing, 100190, China*
[1)] *saira_cssp@yahoo.com*

## ABSTRACT

Enhancement in dielectric properties and durability of zirconia ceramics can be increased with addition of some additives. In this paper, we report synthesis of stabilized zirconia nanocrystallites by sol-gel method. With the aim to increase durability and hardness of zirconia based ceramics, amount of polymer (methanol) is varied from 1 to 5ml per 100 ml of pre-synthesized zirconia sol. pH of methanol added zirconia sol is fixed at 9 with the addition of ammonia. Ammonia addition causes gelation in zirconia sols. Gels of these sols are dried at room temperature for powder formation. Structural, dielectric and mechanical properties of methanol added zirconia nanoparticles are investigated by x-ray diffractometer (XRD), scanning electron microscopy (SEM) impedance analyzer and hardness vickers indenter, respectively. XRD graphs present mixed zirconia phases (monoclinic and tetragonal) in all samples. However, a decrease in monoclinic content is observed with increase in methanol quantity. Sample with 5 ml content of methanol shows dominant tetragonal zirconia phase with reduced crystallite size ~30nm. SEM images reveal the formation of nanocrystallites like compact structure. At low frequencies a marked increase in dielectric constant from 150 to 400 is most likely related with the onset of dipolar relaxation. Resistance is in the range of $10^6$–$10^7$ correlating to good dielectric constant of 100. Formation of compact microstructure with relatively high density results in higher hardness values.

## 1. INTRODUCTION

Preparation of nanopowders offer an important path to combine different physical and chemical properties of individual components into one system. In particular, unique ability of nanopowders to compensate and reinforce material properties has resulted in extensive research efforts on controlling the design and size of particles (Kim et al. 2009).

Zirconia exists in various crystallographic phases which govern its strength and toughness (Goharshadi et al. 2012). Each crystal structure has precise volume, and decrease in volume with temperature results in transition (Haung et al. 2011, Bloor et al. 1994). At higher temperatures (1100-2300°C) zirconia occurs in cubic structure and at relatively low temperatures (≤1100°C) tetragonal zirconia occurs. At room temperature zirconia occurs in monoclinic phase (Davar et al. 2013). After heating, tetragonal zirconia transforms to monoclinic phase and results in crack propagation. Appearance of cracks leads to tetragonal to monoclinic phase transition (Chevalier and Gremillard 2009). Smaller grain size prevents this crystallographic phase transformation. It can be considered as an increasing contribution of the stress-induced phase transformation. Organic additives have been used to prepare particles with spherical shape. Moreover, use of organic additives resulted in decreased crystallite size from 30 to 10 nm (Heshmatpour and Aghakhanpour 2011). Organic additives act as capping agent and prevent particles from agglomerating. Soft agglomeration or less agglomeration results in small crystallite size, which prevents the transformation of tetragonal to monoclinic zirconia phase (Heshmatpour and Aghakhanpour 2012).

Zirconia has nominal physical properties such as a relatively high dielectric constant (～37 for t-phase). Dielectric properties strongly influenced by zirconia phases. For m-phase dielectric constant is ~20 (Zho et al. 2011). The exclusive high dielectric properties of nano-$ZrO_2$ make this material valuable in the preparation of a variety of functional ceramic components such as oxygen sensors, piezoelectric, pyroelectric ceramics, ferroelectric ceramics. For dielectric study, the dielectric constant is closely pertained to the crystal structures of the material. The connection among the macroscopic characteristics and the microscopic structures is very important for material research. The microscopic study can be investigated through the dielectric properties measurement. Usually layers with high thickness are used as insulator. Higher thickness of oxide layer usually results in decrease in tunneling current. Therefore, for use of new high dielectric constant in ULSI, other factors such as, particle size and capacitance are also considered. Among the high-κ materials, $ZrO_2$ is a promising candidate in multiple gate FinFETS and a lot of research works focus on this material (Nirmal et al. 2010).

Mechanical strength of nanoscale based materials is strongly influenced by the synthesis technique, microstructure of the material, and the effect of interfacial constraint. Nanopowders of methanol added zirconia have been prepared by different techniques such as precipitation and sol gel (Maček et al. 1997) etc. Among all these techniques sol gel synthesis is better technique due to its myriad advantages. It can change the material properties by changing the composition of the precursor. It has ability to control size and shape of the particles, low processing temperature and excellent control of microstructures. In sol gel vacuum is not required so fabrication is economically best (Riaz et al. 2013). Zirconia nanostructures has also been prepared by following several chemical routes. However, phase stability of zirconia at room temperature or at lower temperatures is still a challenging issue.

In the present work, zirconia nanocrystallites have been prepared using sol gel method. Effect of methanol has been studied and correlated with structural and dielectric properties.

## 2. Experimental Details

### *2.1 Materials*

Zirconyl chloride octahydrate ($ZrOCl_2.8H_2O$, BDH, 99.99% pure) was obtained from Sigma Aldrich. Methanol and aqueous Ammonia (32%) were obtained from Merck. 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. Methanol was added as 1 to 5ml per 100ml of zirconia. Ammonia was used to fix the pH at 9. Sols were stirred at room temperature for 4 hours of polymerization. Gels were dried in the temperature range 60-70°C for powder formation.

### *2.3 Characterizations*

Structure evaluation of methanol added zirconia was obtained by X-ray diffractometer (Bruker D8 advance) using Cu kα radiation ($\lambda$=0.1540598 nm). Dielectric properties of zirconia nanocrystallites were studied using 6500B Precision Impedance Analyzer. Mechanical properties were studied by Shimadzu HMV-2 hardness micro Vickers indenter.

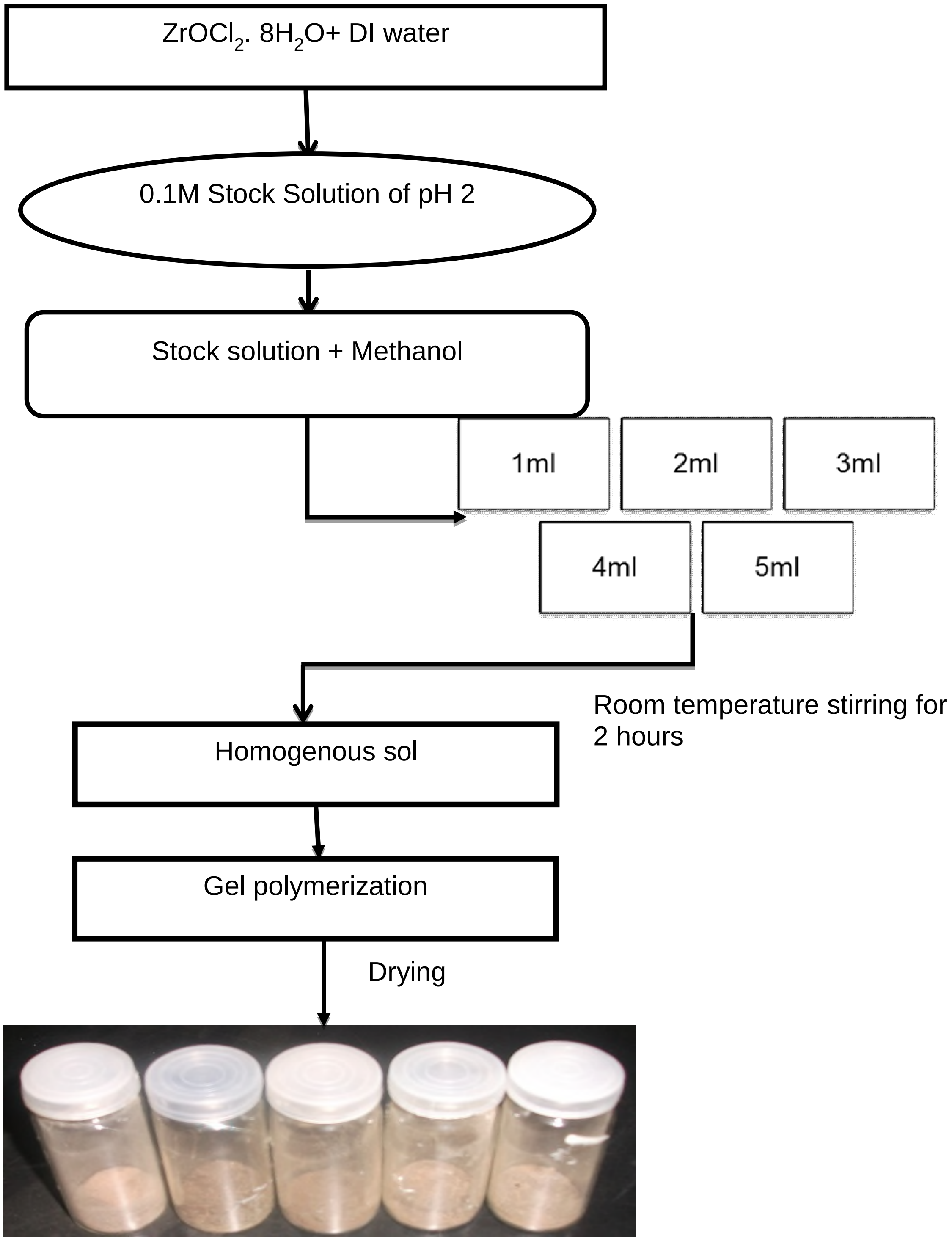

Fig. 1: Schematic approach for synthesis of zirconia nanocrystallites at various content of methanol

## 3. Results and Discussion

These synthesized zirconia powders were checked for their crystal structure at different content of methanol as shown in Fig. 2. XRD patterns of methanol added zirconia powders are a mixture of monoclinic and tetragonal at low content of methanol as illustrated in Fig. 2(a-d). Peaks appearing at approximately 28. 2°, 31.6° and 45.5° $2\theta$ values correspond to the (11-1), (111), and (20-2) planes of monoclinic zirconia (m-$ZrO_2$) [JCPDS card no. 13-307], respectively. However, peaks at 30.2°, 55.5° 66.2° and 76.4° correspond to (111), (113) (123) and (300) planes of tetragonal zirconia (t-$ZrO_2$) [JCPDS card no. 17-923]. As methanol content was increased up to 5ml phase pure tetragonal zirconia was observed. An increase in methanol content to a certain limit suppresses the monoclinic content by coating the particles. Formation of tetragonal zirconia at room temperature is due to diminution of particle size. With increasing amount of methanol, the distance between the crystallized primary particles becomes larger, making it possible to prevent agglomeration.

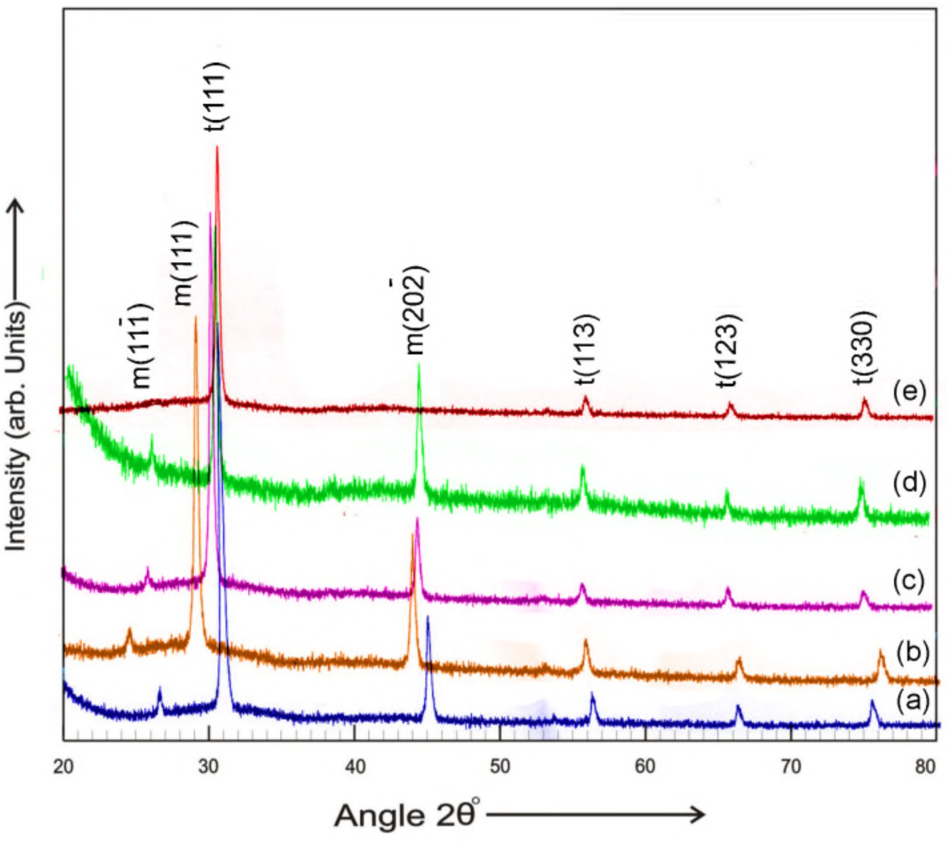

Fig. 2 XRD patterns at methanol content (a) 1ml, (b) 2ml, (c) 3ml, (d) 4ml and (e) 5ml

Crystallite size was estimated using Eq. 1 (Cullity 1956). Crystallite size of $ZrO_2$ powders synthesized by varying the methanol content is shown in Fig. 3. A sharp decrease in crystallite size has been observed in sample with methanol content 5ml due to phase transition (Riaz and Naseem 2007). Increase in amount of methanol favored decrease in crystallite size by increasing the distance between cations. Relative dislocation density was calculated using Eq. 2 for methanol added zirconia powders as shown in Fig. 3. The presence of low dislocation density is essential for implant applications.

$$D = 0.9\lambda / B Cos\,\theta \qquad (1)$$

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

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.

Unit cell volume calculations [Fig. 4] reveal decreasing behavior with increased methanol content. These variations are consistent with phase transition in the material. It has already been discussed in XRD results that higher tetragonal content has been observed at methanol content of 5ml. Therefore, unit cell volume of such sample sharply decreased as compared to other samples. Since monoclinic phase has slightly larger unit cell volume than tetragonal. Decrease in volume leads to increase in density especially for sample synthesized at methanol content 5ml [Fig. 4] with phase purity. For biological applications relatively higher densities are required because denser the material, more compact the powder and higher hardness of samples can be achieved.

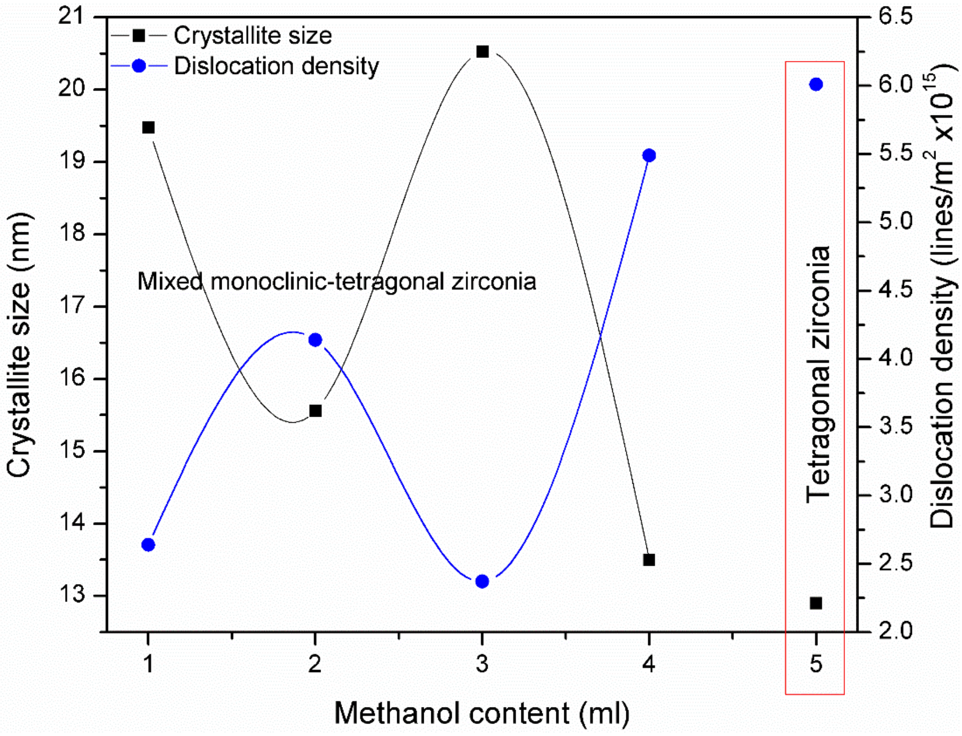

Fig. 3 Crystallite size and dislocation density of zirconia nanocrystallites at various methanol contents

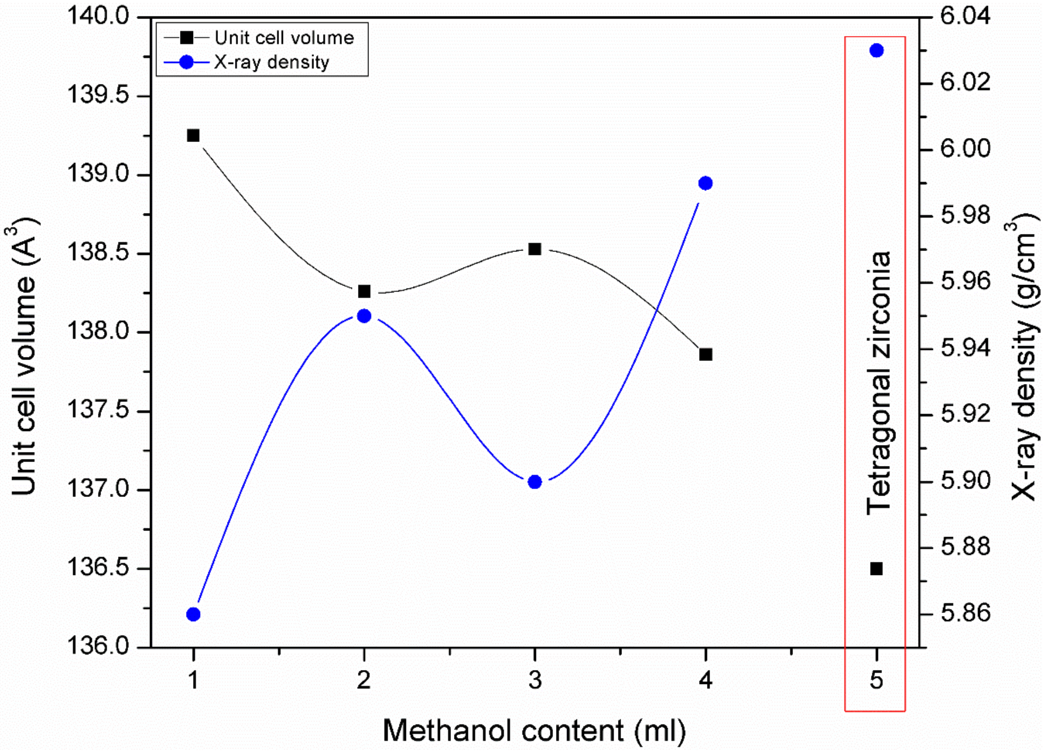

Fig. 4 Unit cell volume and x-ray density of zirconia nanocrystallites at various methanol contents

For hardness measurement Vickers indentation under 4.9N load for 15 seconds dwell time was performed according to American Society for Testing of Materials standard (ASTM C-1327-99). Hardness of methanol stabilized zirconia was found to be in the range of 1063HV to 1425HV. Maximum hardness was observed for the sample with methanol content of 5ml. A small variation in hardness was observed with increase in methanol content. These results are in close agreement with XRD data presented in Fig. 2. It has already been shown in the XRD results that suppression of the monoclinic phase started at methanol content 4ml, whereas, phase pure tetragonal was observed at 5ml of methanol content. Table 1 summarizes the hardness values.

**Table 1** Hardness of zirconia powders as a function of methanol content

| **Methanol content (ml)** | **Hardness (HV) at constant load and time ASTM C-1327-99** |
|---|---|
| 1 | 1065 |
| 2 | 1249 |
| 3 | 1224 |
| 4 | 1063 |
| 5 | 1425 |

Dielectric properties are 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.

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

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

Dielectric constant and tangent loss decreases as frequency of applied field increases and becomes constant at high frequencies thus exhibiting normal dispersion behavior. This dispersion can be explained on the basis of Maxwell Wagner two layered model. According to this model, a polycrystalline specimen contains two layers: 1) Grains and 2) Grains boundaries (Majid et al. 2015, Shah et al. 2014, Riaz et al. 2015). Role of grains dominate at high frequencies while grain boundaries contribute more at low frequencies. In addition grains exhibit high conductivity as compared to grain boundaries because of which, normal dispersion arises in polycrystalline specimens as observed in our case in Fig. 5. Further, the space charge carriers require some time to get aligned in the direction of externally applied electric field. At high frequencies, space charge carries do not follow the alteration of externally applied field thus resulting in low polarization and as a result dielectric constant and tangent loss becomes constant at high frequencies (Majid et al. 2015, Shah et al. 2014, Riaz et al. 2015).

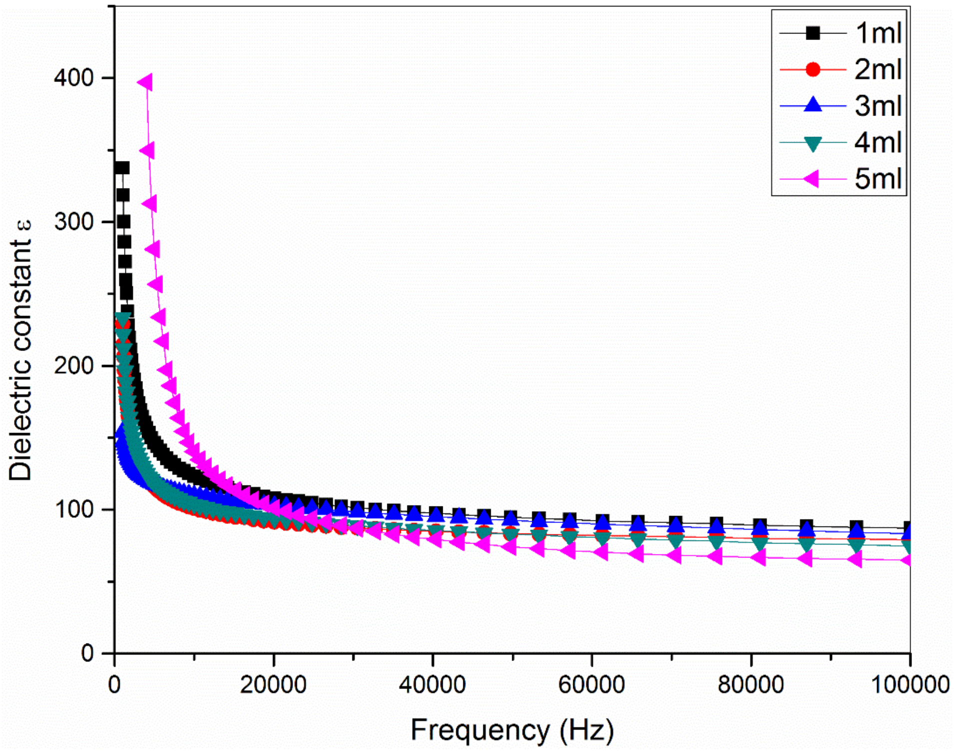

Fig. 5 Dielectric constant of zirconia nanocrystallites at various methanol contents

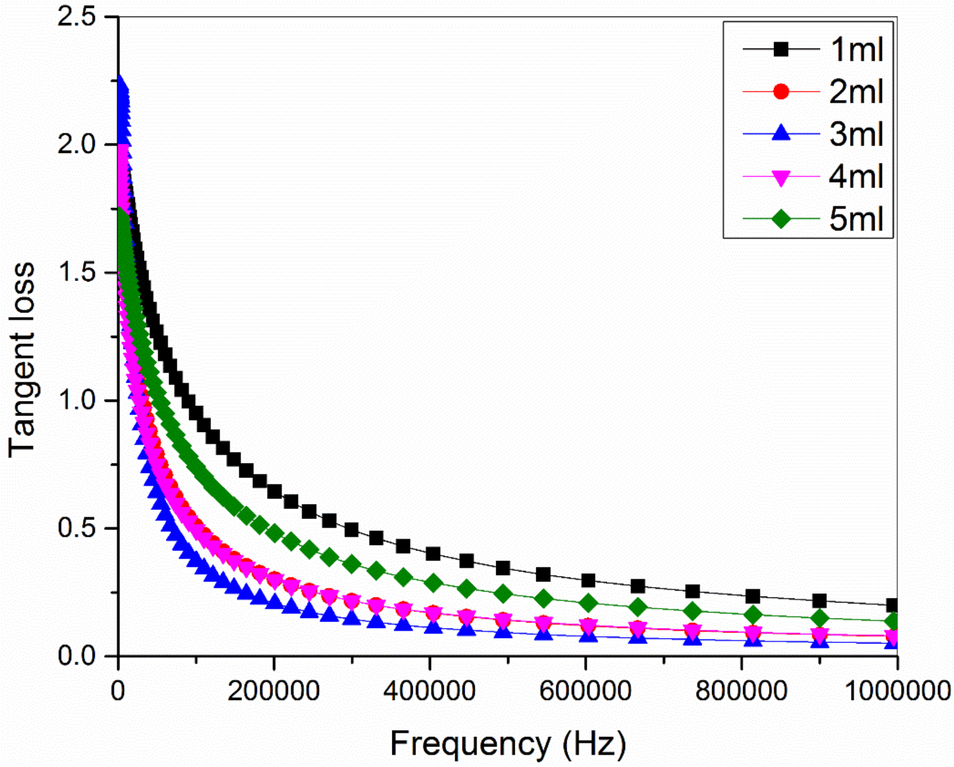

Fig. 6 Tangent loss of zirconia nanocrystallites at various methanol contents

## 3. CONCLUSIONS

Five different sols were prepared by varying the methanol content 1 to 5ml. (2) XRD results showed that zirconia nanocrystallites were a mixture of monoclinic and tetragonal $ZrO_2$ at low content of methanol, whereas phase pure tetragonal zirconia was obtained at 5ml of methanol content. (3) Crystallite size showed sharp decrease with phase transition due to restructuring. (4) Hardness of the samples was in the range of 1063HV to 1425HV. 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 400 at lower frequency.

## REFERENCES

Bashir, M., Riaz, S., Kayani, Z. N. and Naseem, S. (2015), “Effects of the organic additives on dental zirconia ceramics - Structural and mechanical properties,” J. Sol-Gel Sci. Technol., 74, 289-298.

Bloor, D., Brook, R. J., Flemings, M. C. and Mahajan, S. (1994). Encyclopedia of Advanced Materials. Pergamon Press. Oxford.

Chevalier, J. and Gremillard, L. (2009), “Ceramics for medical applications: A picture for the next 20 years,” *J. Eur. Ceram. Soc.,* **29**, 1245-1255.

Cullity, B. D. and Stock, S.R. (2001). Elements of X-Ray Diffraction, Prentice Hall, USA

Davar, F., Hassankhani, A. and Loghman-Estarkic, M.R. (2013), “Controllable synthesis of metastable tetragonal zirconia nanocrystals using citric acid assisted sol–gel method,” *Ceram. Int.,* **39**, 2933–2941.

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

Heshmatpour, F. and Aghakhanpour, R. B. (2011). Synthesis and characterization of nanocrystalline zirconia powder by simple sol–gel method with glucose and fructose as organic additives, *Powder Technol.,* **205**, 193-200.

Heshmatpour, F. and Aghakhanpour, R. B. (2012), “Synthesis and characterization of superfine pure tetragonal nanocrystalline sulfated zirconia powder by a non-alkoxide sol–gel route,” *Adv. Powder Technol.,* **23**, 80–87.

Huang, W.Z., Yang, J.L., Meng, X.S., Cheng, Y.L., Wang, C.J., Zou, B., Khan, Z.H., Wang, Z. and Cao, X. Q. (2011), “Effect of the organic additions on crystal growth behavior of $ZrO_2$ nanocrystals prepared via sol–gel process,” *Chem. Eng. J.,* **168**, 1360–1368.

Kim, J.M., Chang, S.M., Kim, S., Kim, K.S., Kim, J. and Kim, W.S. (2009), “Design of $SiO_2/ZrO_2$ Core-Shell Particles using the Sol-Gel Process,” Ceram. Int., **35**, 1243-1247.

Liu, E., Locke, A.J., Martens, W.N., Frost, R.L. and Yang, X. (2012), “Fabrication of Macro-Mesoporous Zirconia-Alumina Materials with a One-Dimensional Hierarchical Structure”, *Crys. Growth Des.,* **13**,1402-0410.

Maček, J., Marinšek, M. and Novosel, B. (1997), “Study of the drying zirconia gel-precipitates using thermal analysis”, *J. Therm Anal.,* **48**, 675-682.

Majid, F., Riaz, S. and Naseem, S. (2015), “Microwave-assisted sol–gel synthesis of $BiFeO_3$ nanoparticles,” *J. Sol-Gel Sci. Technol.,* **74**, 329-339.

Nirmal, D., Nalini, B. and Vijaya Kumar, P. (2010), “Nanosized high κ dielectric material for FINFET,” *Int. Ferro,* **121**, 31–35.

Riaz, S. and Naseem, S. (2007), “Effect of reaction temperature and time on the structural properties of $Cu(In,Ga)Se_2$ thin films deposited by sequential elemental layer technique,” *J. Mat. Sci. Technol.,* **23**, 499-503.

Riaz, S., Bashir, M., Hussain, S. S. and Naseem, S. (2013), “Effect of Mn doping concentration on the structural & magnetic properties of sol–gel deposited ZnO diluted magnetic semiconductor”, Amsterdam, The Netherlands: Atlantis Press, 518–522.

Riaz, S., Shah, S.M.H., Akbar, A., Atiq, S. and Naseem, S. (2015), “Effect of Mn doping on structural, dielectric and magnetic properties of $BiFeO_3$ thin films.” *J. Sol-Gel Sci. Technol.,* **74**, 310-319.

Shah, S.M.H., Riaz, S., Akbar, A., Atiq, S. and Naseem, S. (2014), “Effect of Solvents on the Ferromagnetic Behavior of Undoped $BiFeO_3$ Prepared by Sol-Gel.” *IEEE Trans. Magn.,* **50,** 2200904.

Zhang, C., Guo, R., Liu, Z., Cai, Z., Guo, W. and Wu, C. (2015), “Calculation and Analysis of the Lattice, Electronic Structures, and Dielectric Functions for Monoclinic $ZrO_2$ under High Pressure,” *Chinese J. Phys.,* **53**, 1208031-11

Zho, C., Zhao, C. Z., Werner, M., Taylor, S. and Chalker, P. R. (2011). “Advanced CMOS Gate Stack: Present Research Progress”, ISRN *Nanotechnol.,* **2012**, 689023, 1-35.