

# Sol-Gel Synthesis of Biocompatible TiO<sub>2</sub> doped ZrO<sub>2</sub> Nanoparticles

\*Noreen Iqbal<sup>1)</sup>, Saira Riaz<sup>2)</sup>, Yan-Jun Guo<sup>3)</sup> and Shahzad Naseem<sup>4)</sup>

<sup>1), 2), 4)</sup> *Centre of Excellence in Solid State Physics, University of Punjab, Lahore, Pakistan*

<sup>3)</sup> *National Center for Nanoscience & Technology, CAS, Beijing, 100190, China*

<sup>4)</sup> [shahzad.cssp@pu.edu.pk](mailto:shahzad.cssp@pu.edu.pk)

## ABSTRACT

Nanocrystalline zirconia has gained much attention in recent years for its technological and biological importance as a ceramic material. Tetragonal t-ZrO<sub>2</sub> with high mechanical strength and fracture toughness is a recommended phase for biological applications. However, t-ZrO<sub>2</sub> is high temperature stable phase and transforms to monoclinic ZrO<sub>2</sub> upon cooling. Another problem with zirconia is its bio-inertness. TiO<sub>2</sub> is bioactive material and its addition in ZrO<sub>2</sub> improves the bioactivity of zirconia. In this research work 5wt% TiO<sub>2</sub> is doped in ZrO<sub>2</sub> sol and effect of different reaction temperatures (50, 100, 150, 200 and 250°C) have been studied. XRD results show the formation of pure t-ZrO<sub>2</sub> at relatively lower reaction temperature of 150°C. Crystallite size of TiO<sub>2</sub> doped zirconia is consistent with literature for occurrence of t-ZrO<sub>2</sub>. SEM image shows formation of dense and monodispersed nano sized particles. FTIR spectra reveal the formation of t-ZrO<sub>2</sub> at relatively low reaction temperatures as observed in XRD data. Formation of dense particles leads to higher value of hardness confirmed by Micro Vickers hardness indenter. Frequency dependence of dielectric constant and dielectric loss are investigated at room temperature. Results show linear dependency of dielectric constant with crystallite size.

## 1. INTRODUCTION

The tetragonal monoclinic phase transition of zirconia can also be stimulated by stresses and volume variations. Un-doped and doped zirconia has long been used to enhance the strength and hardness (Garvie and Hannink 1975, Hirvonen et al. 2006, Duszovda et al. 2008). Tetragonal ZrO<sub>2</sub> has high mechanical strength and fracture toughness, therefore is recommended phase for biological applications (Bashir et al. 2015). In spite of good mechanical properties, some negative cases (Allain et al. 1999) pertained to the in vivo phase stability of zirconia implants, and it has poor bioactivity. In this approach bioinertness in zirconia-based implants is the development of new materials by adding bioactive materials to a zirconia matrix. TiO<sub>2</sub> is bioactive material and addition in ZrO<sub>2</sub> improves the bioactivity of zirconia. The idea behind the creation of this material was to take advantage of the good mechanical properties of ZrO<sub>2</sub> and the bioactivity of TiO<sub>2</sub>. Moreover, these oxides are highly soluble to form a homogenous

material (Marchi et al. 2013). In order to retain the stability grain size plays a crucial role (Mahmood et al. 2013). To achieve fine and well dispersed nanocrystalline reaction temperature during synthesis has prominent effect.

In this research paper we have doped  $\text{TiO}_2$  in zirconia to stabilize tetragonal phase. The effect of dopant concentration and reaction temperature on structural, mechanical and dielectric properties is studied.

## **2. Experimental Details**

### *2.1 Materials*

$\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  (Sigma–Aldrich, 99.99% pure),  $\text{TiCl}_4$  (Merck 99.99% pure) and  $\text{NH}_3$  (Sigma–Aldrich, 99.99% pure) were used as starting materials. Deionized (DI) water was used as solvent.

### *2.2 Method*

$\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  was dissolved into DI water to form stock solution of molarity 0.1M and pH 1. Solution was stirred at constant stirring at room temperature to form a transparent and shiny solution. Then pre synthesized 5wt%  $\text{TiO}_2$  (Riaz and Naseem 2015) was added drop wise into the prepared  $\text{ZrO}_2$  solution. Subsequently  $\text{NH}_3$  was added drop wise which leads to sol formation. The effect of reaction temperature on  $\text{TiO}_2$  doped zirconia five different reaction temperatures were used i.e. 50°C, 100°C, 150°C, 200°C and 250°C. These as-synthesized powders were subjected to different characterizations without any further treatments.

### *2.3 Characterizations*

Structure analysis was obtained by X-ray diffractometer (Bruker D8 advance) using  $\text{Cu } \alpha$  ( $\lambda=0.1540598$  nm). Dielectric properties of zirconia powders were studied with 6500 Precision Impedance Analyzer. Mechanical properties were studied by Shimadzu HMV-2 micro vickers hardness indenter.

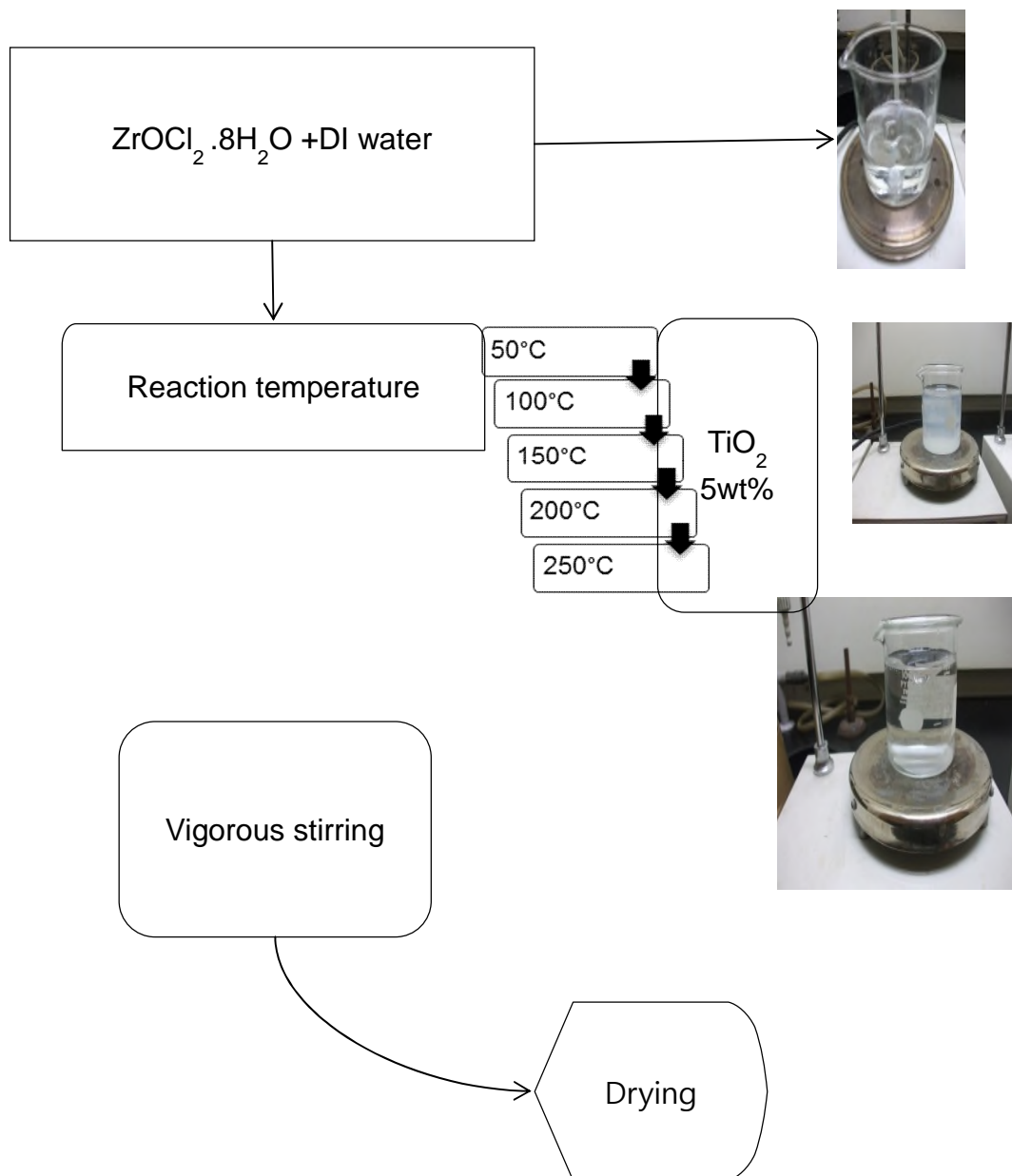


Fig. 1 Schematic approach for synthesis of TiO<sub>2</sub> doped zirconia nanoparticles at various reaction temperatures

### 3. Results and Discussion

The synthesized zirconia powders were checked for their crystal structure at different reaction temperatures as shown in Fig. 2. XRD patterns of  $\text{TiO}_2$  doped zirconia powders are a mixture of monoclinic and tetragonal phases at low reaction temperature as illustrated in Figs 2 (a and b). Peaks at approximately  $28.2^\circ$ ,  $31.6^\circ$  and  $45.5^\circ$  correspond to the (11-1), (111), and (20-2) planes of monoclinic zirconia ( $\text{m-ZrO}_2$ ) [JCPDS card no. 13-307] respectively. However, peaks at  $30.6^\circ$ ,  $56.5^\circ$ ,  $66.6^\circ$  and  $75.2^\circ$  correspond to the (111), (221), (231) and (004) planes of tetragonal zirconia ( $\text{t-ZrO}_2$ ) [JCPDS card no. 17-923]. As the reaction temperature proceeds, chemical shift occurs. Peak at  $31.6^\circ$  shifts to lower angle of  $30.6^\circ$ , which causes phase transformation from monoclinic to tetragonal at  $150^\circ\text{C}$  of reaction temperature and retains this phase up to  $250^\circ\text{C}$ . Phase shift occurs due to removal of OH ions. In  $\text{TiO}_2$  doped  $\text{ZrO}_2$ ,  $\text{Ti}^{4+}$  ion occupying a zirconium site ( $\text{Zr}^{4+}$ ) introduces oxygen vacancy in a different way than others e. g.  $\text{Y}^{3+}$  and  $\text{Ca}^{2+}$  etc. where oxygen vacancies are created due to difference in valences of host and dopants. But zirconium ion and titanium ion are isovalent, having same valences. The ionic radius size of  $\text{Ti}^{4+}$  ( $0.68 \text{ \AA}$ ) is lesser than  $\text{Zr}^{4+}$  ( $0.79 \text{ \AA}$ ) and consequently this size difference could encourage the creation of oxygen vacancies. This phenomenon is often called as "size effect". It is normally recognized that the size difference between dopant and host ions causes the distortion of lattice structure and in crystal structure by creating oxygen vacancies.

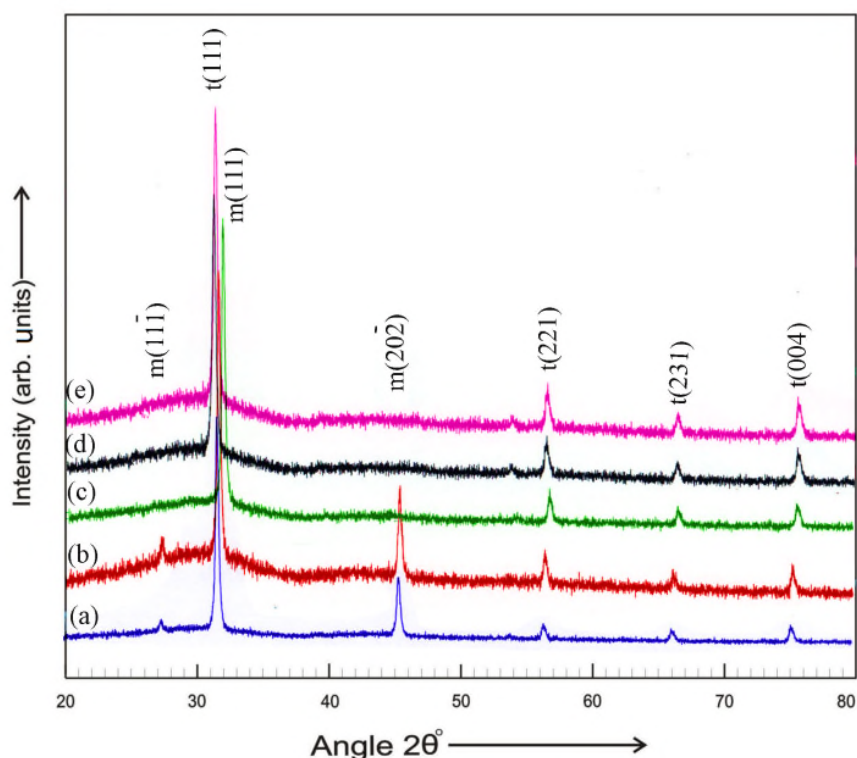


Fig. 2 XRD patterns of  $\text{TiO}_2$  doped zirconia at reaction temperatures (a)  $50^\circ\text{C}$ , (b)  $100^\circ\text{C}$ , (c)  $150^\circ\text{C}$ , (d)  $200^\circ\text{C}$  and (e)  $250^\circ\text{C}$

The crystallite size of zirconia powder was estimated using Eq. 1 (Cullity 1956). Crystallite size of TiO<sub>2</sub> doped ZrO<sub>2</sub> powders synthesized by varying the reaction temperature is shown in Fig. 3. As reaction temperature increases, crystallite size shows a sharp decrease at 150°C due to phase transition (Riaz and Naseem 2007). After the phase stabilization crystallite size begins to increase due to coalescence of nuclei. Researchers (Wang et al. 2013, Chrask et al. 2000, Chen and Chiao 1983) had observed that crystallite sizes below 10 –15 nm tended to be tetragonal at room temperature. Calculated crystallite size (~ 13nm) at 150°C of reaction temperature is in good agreement with literature. Relatively lower dislocation density was calculated using Eq. 2 for TiO<sub>2</sub> doped zirconia powders as shown in Fig. 3

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

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

Unit cell volume calculations [Fig. 4] revealed decreasing behavior after treatment at reaction temperature 150°C. These variations are consistent with the appearance of different zirconia. It has already been discussed in XRD results that higher tetragonal content has been observed at 150°C. Therefore, unit cell volume of such sample sharply decreases as compared to other samples. Removal of OH<sup>-</sup> ions causes shrinkage in unit cell volume at relatively high reaction temperatures. Decrease in volume leads to increase in density especially for sample synthesized at reaction temperatures 150, 200 and 250°C [Fig. 4] with phase purity. For biological applications relatively higher densities are required because dense the material, more compact the powder and higher hardness of samples.

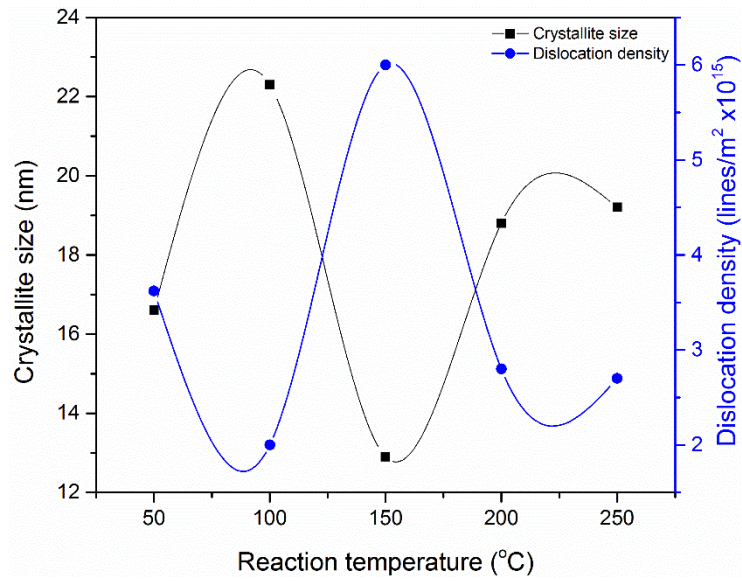


Fig. 3 Crystallite size and dislocation density of TiO<sub>2</sub> doped zirconia at various reaction temperatures

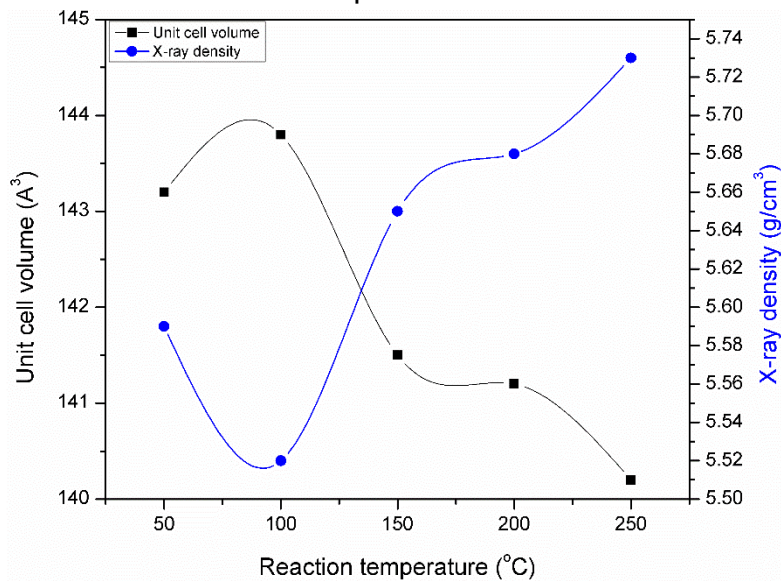


Fig. 4 Unit cell volume and x-ray density of TiO<sub>2</sub> doped zirconia at various reaction temperatures

Hardness of the samples was observed to be in the range of 400HV to 965HV. Maximum hardness was observed for the sample with reaction temperature at 250°C. A small variation in hardness was observed with the increase in reaction temperature. These results are in close agreement with the XRD data presented in Fig 2. It has already been shown in the XRD results that suppression of the monoclinic phase started at reaction temperature 150°C and strengthens after that temperature. Relation between phase transformation and hardness can be explained by chevalier's model (Chevalier 2006) which says that transformation begins in individual particles on the

surface through a mechanism of stress corrosion. The initial transformation of specific particles can be related to a state of imbalance: greater particle size, specific guidance from the surface, the presence of residual stress, or even the presence of a cubic phase. Table 1 summarizes the hardness values.

**Table 1** Hardness of TiO<sub>2</sub> doped zirconia powders at various reaction temperatures

Reaction temperature (°C)	Hardness (HV) at constant load and time ASTM C-1327-99
50	590
100	400
150	710
200	849
250	965

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

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

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

Dielectric constant and tangent loss decreases as frequency of applied field increases and becomes constant at high frequencies thus exhibiting normal dispersion behavior. The dielectric constant at low frequency for prepared samples is relatively high. From this result we infer that the dielectric constant of TiO<sub>2</sub> doped zirconia strongly depends on phase and crystallite size (Sujit et al. 2010). Like dielectric constant, tangent loss also decreases with frequency for synthesized samples. Observed high tangent loss in the low frequency region may be due to a high defect charge density existing in material (Pazhani et al. 2011). At low frequencies a marked increase in dielectric constant is most likely related with the onset of dipolar

relaxation. Different studies have shown that oxygen vacancies are more likely to sit nearest neighbor to Zr.

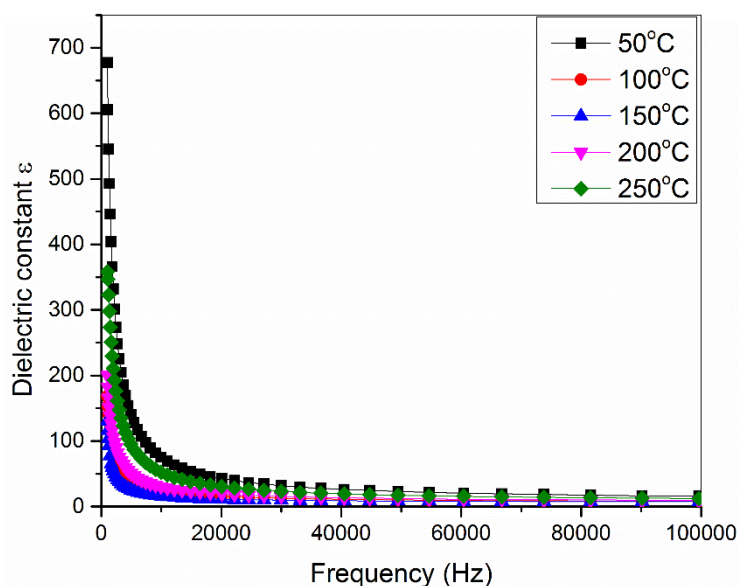


Fig. 5 Dielectric constant of  $\text{TiO}_2$  doped zirconia at various reaction temperatures

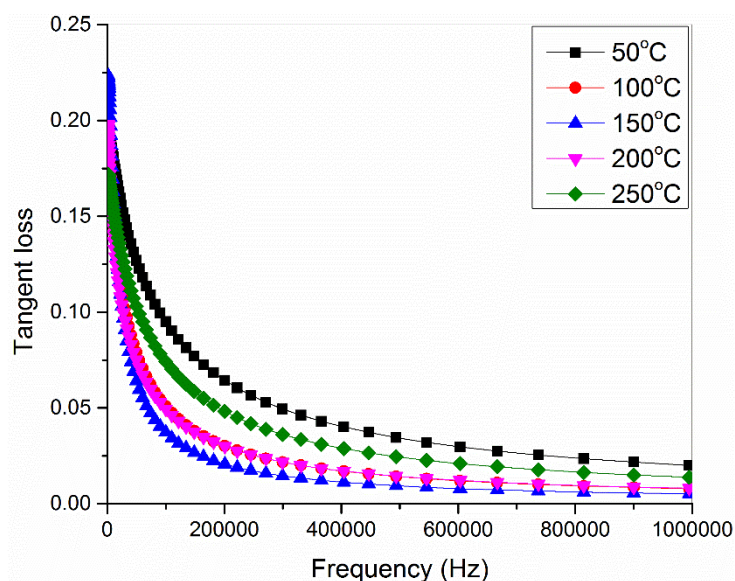


Fig. 6 Tangent loss of  $\text{TiO}_2$  doped zirconia at various reaction temperatures

### 3. CONCLUSIONS

(1) Zirconyl chloride octahydrate was used as precursor of zirconia, whereas pre-synthesized  $\text{TiO}_2$  was added 5wt%. Five different sols by varying the reaction temperature from 50 to 250°C were prepared. (2) XRD results showed that doped zirconia powders are a mixture of monoclinic and tetragonal  $\text{ZrO}_2$  at low reaction



temperatures (50 and 100°C) whereas, phase pure tetragonal zirconia has been obtained as temperature reached to 150°C and remained stable up to 250°C. (3) Crystallite size showed sharp decrease with phase transition due to restructuring and after stabilization of phase it started to increase. (4) Maximum hardness of the zirconia was 965HV. Samples with phase pure tetragonal zirconia exhibited high value of hardness. (5) Zirconia nanocrystallites prepared using sol gel method showed higher dielectric constant value at lower frequency.

## REFERENCES

- Allain, J., Le-Mouel, S., Goutallier, D. and Voisin, M.C. (1999), "Poor eight-year survival of cemented zirconia-polyethylene total hip replacements," *J. Bone Joint. Surg.* **81**, 835–842.
- 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.
- 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.
- Catledge, S.A., Cook, M., Vohra, Y., Santos, E.M., McClenny, M.D. and Moore, K.D. (2003), "Surface crystalline phases and nanoindentation hardness of explanted zirconia femoral heads," *J. Mater. Sci. Mater. Med.*, **14**, 863–867.
- Chen, I.W. Chiao, Y.H. (1983), "Martensitic nucleation in ZrO<sub>2</sub>," *Acta Metall.* **31**, 1627-1638.
- Chrask, T., King, A.H. and Berndt, C.C. (2000), "On the size-dependent phase transformation in nanoparticulate zirconia," *Mater. Sci. Eng. A*, **286**, 169-178.
- Chevalier, J. (2006), "What future for zirconia as a biomaterial," *Biomaterials*, **27**, 535-543.
- Cullity, B. D. and Stock, S.R. (2001). *Elements of X-Ray Diffraction*, Prentice Hall, USA
- Duszovda, A.; Dusza, J.; Tomasek, K.; Blugan, G.; Kuebler, J. Microstructure and properties of carbon nanotube/zirconia composite. *J. Eur. Ceram. Soc.*, **28**, 1023-1027.
- Garvie, R. C.; Hannink, R. H.; Pascoe, R.T. (1975), "Ceramic steel," *Nature*, **258**, 703-704.
- Haraguchi, K., Sugano, N., Nishii, T., Miki, H., Oka. K. and Yoshikawa, H. (2001), "Phase transformation of a zirconia ceramic head after total hip arthroplasty," *J. Bone Joint. Surg.* **83**, 996–1000.
- Hirvonen, A., Nowak, R., Yamamoto, Y., Sekino, T. Niihara, K. (2006), Fabrication, structure, mechanical and thermal properties of zirconia-based ceramic nanocomposites. *J. Eur. Ceram. Soc.*, **26**, 1497-1505.
- Mahmood, Q., Afzal, A., Siddiqi, H. M. and Habib, A. (2013), "Sol-gel synthesis of tetragonal ZrO<sub>2</sub> nanoparticles stabilized by crystallite size and oxygen vacancies," *J. Sol-gel Sci. Technol.*, **67**, 670-674.
- Marchi, J., Amorima, E.M., Lazar, D. R. R., Ussui, V., Bressiani, A. H. A. and Cesarc, P.F. (2013), "Physico-chemical characterization of zirconia-titania composites coated with an appetite layer for dental implants," *Dent. Mater.*, **29**, 954-962.
- Pazhani, R., Padma Kumar, H., Varghese, A., Moses Ezhilraj, A. and Solomon, S., Thomas, J. K. (2011), *J. Alloy. Compd.* **509**, 6819–6823.
- Riaz, S. and Naseem, S. (2007), "Effect of reaction temperature and time on the structural properties of Cu(In,Ga)Se<sub>2</sub> thin films deposited by sequential elemental layer technique," *J. Mat. Sci. Technol.*, **23**, 499-503.
- Riaz, S. and Naseem, S. (2015), "Controlled nanostructuring of TiO<sub>2</sub> nanoparticles: a sol-gel approach," *J. Sol-Gel Sci. Technol.*, **74**, 299-309.
- Sujit, M., Ghosal, T. and Del, S.K. (2010), "Room temperature stabilized cubic zirconia nanocrystals: Gaint dielectric material," *J. Phys. D: Appl. Phys.*, **43**, 1–6.

Wang, X., Wu, G., Zhou, B. and Shen, J. (2013), "Effect of crystal structure on optical properties of sol-gel derived zirconia thin films," *J. Alloy Compd.*, **556**, 182-187.