

# Effect of pH on Structural and Dielectric Properties of Zirconia Nanocrystallites

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## ABSTRACT

Application of zirconia ( $ZrO_2$ ) has been quite promising in catalysis and many other areas due to its versatile structural and surface chemical properties as well as good thermal stability. Several procedures have been developed using number of precursors to prepare pure  $ZrO_2$  of desired phase formations with strong acid-base sites and surface areas. Present study describes synthesis of nanocrystalline  $ZrO_2$  using sol-gel method. Effect of acidic and basic nature on  $ZrO_2$  crystallites has been observed by varying the pH of zirconia sol from 1 to 9. Zirconium oxychloride was used as zirconium precursor whereas,  $NH_3$  was used as gelation agent and to vary pH of the  $ZrO_2$  sol. X-ray diffraction results reveal that monoclinic phase becomes less intense with increased tetragonal to monoclinic ratio for basic pH. Hydroxyl ions may have produced increased and/or strong interaction between several species. Such interactions result in volumetric changes along with tetragonal phase rather than monoclinic. Scanning electron microscopy shows decrease in grain size with increased pH. Tetragonal content in zirconia results in increased hardness value confirmed by micro Vickers hardness indenter. Large value of dielectric constant at lower frequency is due to space charge polarization arising at the grain boundary interfaces.

## 1. INTRODUCTION

Zirconia is considered as an attractive material because of its tremendously paramount properties including sufficient chemical stability, mechanical strength and fracture toughness (Grecea et al. 2012). Zirconia is considered as promising candidate in prosthetic and teeth even under harsh conditions. Zirconia based materials show resistance towards deactivation. A major disadvantage in zirconia is occurrence of multi phases that causes cracks and degradation of mechanical strength (Bashir et al. 2015a). Zirconia naturally imperil in the following major phases i.e. cubic, monoclinic and tetragonal. Most stable monoclinic phase of zirconia exists at room temperature. However, with heat treatment up to  $1170^\circ C$ , phase is shifted towards tetragonal that results in large volumetric changes. Moreover, further increase in heat treatment i.e. higher than  $2370^\circ C$ , tetragonal phase is shifted to cubic phase (Bashir et al. 2014).

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Among these phases tetragonal zirconia is considered as most strengthened and dense phase, however, tetragonal zirconia is a metastable phase (Davar et al. 2013).

Researchers have revealed that the structure of chemically synthesized zirconia is affected by the synthesis conditions, e.g. precursor, gelation agent and pH (Stefanic et al. 2000, Denkewicz et al. 1990). The phase transformation mechanisms of tetragonal zirconia to monoclinic in hydrothermal environment are also widely studied. Results can be explained in terms of dissolution/precipitation, structural rearrangement of the tetragonal phase, or simultaneous nucleation of the two phases of  $ZrO_2$ .

Denkewicz et al. (1990) suggested a model for the development of polycrystalline zirconia at different pH synthesized by hydrothermal method. They revealed that at low pH, most expected phase is monoclinic zirconia. While at neutral and less acidic medium re-structuring of amorphous zirconia leads to development of tetragonal zirconia. In basic pH, tetragonal zirconia is formed because of higher energy state of  $Zr(OH)_xO_y$  gel. Formation of monoclinic zirconia results from fast precipitation of the solution as well as from the conversion of t-m $ZrO_2$  under intermediate pH conditions.

Zirconia has high dielectric constant, however, this dielectric constant depends on the phases of zirconia. Among different phases tetragonal zirconia has highest dielectric constant (Zho et al. 2011). Structural properties of zirconia are affected by the variation in crystallite size that leads to phase transition. Variation in pH may cause reduction in crystallite size that results in phase transformation (Garvie 1965).

Variation in pH has great influence on the zirconia phases and its crystalline structure. Recently, with increase in interest for preparation of ultrafine powders researchers are looking for more economical preparation method. Since zirconia has applications in industrial and biomedical fields therefore, preparation method plays an important role. Particularly emphasis has been placed upon sol-gel routes for the synthesis of products with well-defined particle size, morphology, and crystal polymorph. Sol-gel synthesis is a better technique due to its myriad advantages; material's properties can be changed by changing the composition of the precursor, ability to control size and shape of the particles, low processing temperature, excellent control of microstructures, no need of vacuum & fabrication is economically best.

This research paper deals with the synthesis of zirconia at room temperature. pH was varied in the of 1 to 9 during synthesis. Variation in structural, mechanical and dielectric properties of zirconia nanocrystallites have been correlated with the variation in pH of zirconia sol.

## **2. Experimental Details**

### *2.1 Materials*

Zirconyl chloride octahydrate ( $ZrOCl_2 \cdot 8H_2O$ , BDH, 99.99% pure), and  $NH_3$  were used as starting materials. Water was deionized (DI) prior to use.

### *2.2 Method*

Zirconyl chloride octahydrate was dissolved in DI water to form 0.1M solution. This stock solution was stirred at room temperature.  $NH_3$  was used to vary pH from 1 to 9 with intervals of 2. Sols were stirred at room temperature for 2 hours for

homogenization. After homogenization, sols were dried at 50°C for powder formation. Reaction mechanism of zirconia powder is shown in Eq. (1). Schematic representation of the route followed is shown in Fig. 1.

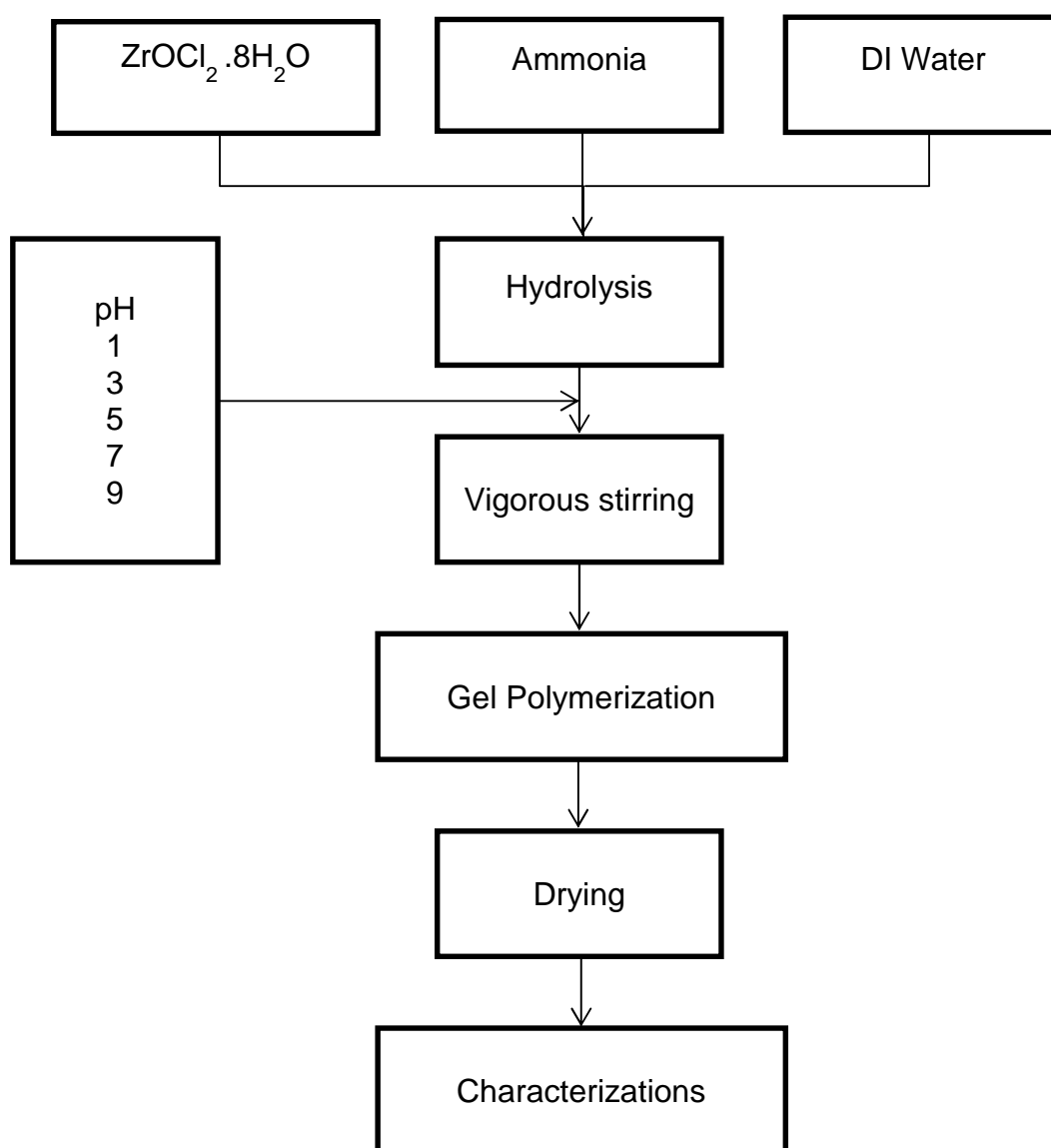
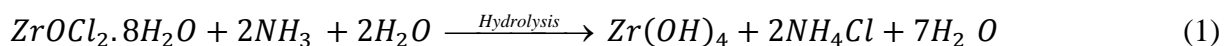


Fig. 1 Schematic approach for synthesis of zirconia nanocrystallites at various pH

### 2.3 Characterizations

Structural analysis of zirconia was obtained by X-ray diffractometer (Bruker D8 advance) using Cu  $\text{k}\alpha$  radiation ( $\lambda=0.1540598$  nm). Mechanical properties were studied

by Shimadzu HMV-2 micro Vickers Hardness Indenter. Dielectric properties were studied by 6500B Precision Impedance analyzer using parallel plate configuration.

### 3. Results and Discussion

Fig. 2 depicts XRD patterns of  $ZrO_2$  powders at different pH. It can be seen that for pH 1 to 7 powders, under as-synthesized condition, are mixtures of monoclinic and tetragonal zirconia. For pH 1, 3, 5, and 7 a  $Zr^{4+}$  solution is formed and large concentration of  $Zr^{4+}$  leads to higher  $Zr(OH)_xO_y$  solubility. Higher  $Zr(OH)_xO_y$  solubility favors the formation of monoclinic  $ZrO_2$  instead of tetragonal  $ZrO_2$  by a dissolution / precipitation mechanism. The formation of monoclinic  $ZrO_2$  at low pH using zirconyl salts have earlier been reported by many researchers (Mahmood et al. 2013, Kurapova and Konako 2014). At pH 9,  $Zr(OH)_xO_y$  solubility is minimum which causes formation of tetragonal  $ZrO_2$ . Therefore, appearance of tetragonal  $ZrO_2$  results from hydrolysis and condensation of  $Zr(OH)_xO_y$  due to high electronegativity (Wang et al., 2007).

Furthermore, under basic conditions, the crystal surfaces can adsorb the  $OH^-$  ions from the solution and produce hydrated amorphous zirconia along with tetragonal as shown in Fig. 2(e). Formation of hydrated amorphous zirconia acts as barrier for transformation of tetragonal to monoclinic zirconia. Apart from  $OH^-$ ,  $NH_4^+$  ions might have been incorporated into the vacant sites on the crystal surface and thus stabilize tetragonal zirconia.

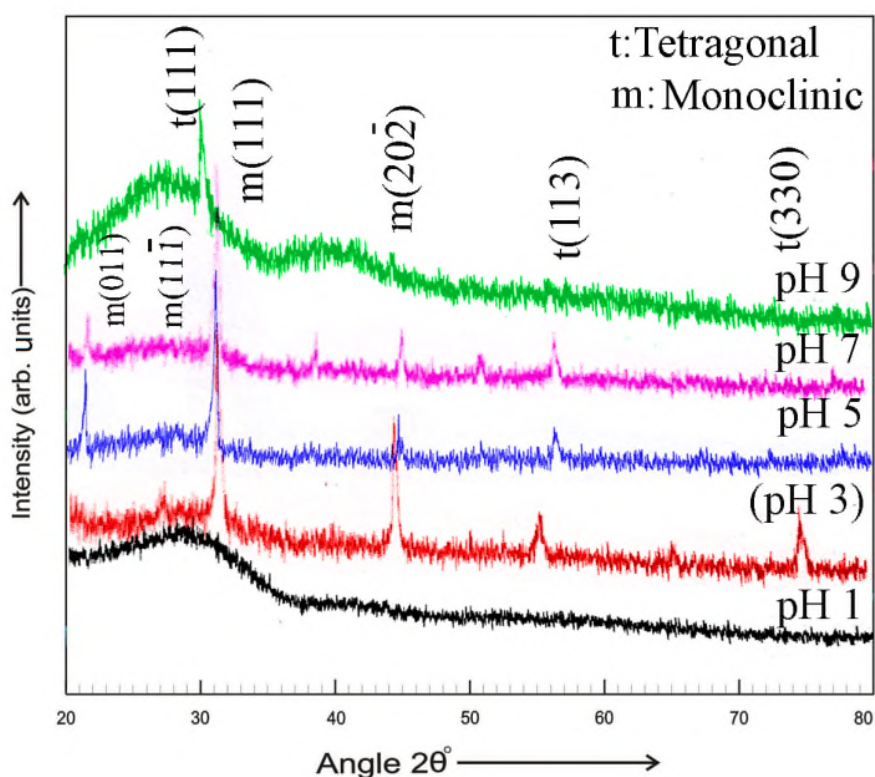


Fig. 2 XRD patterns at various pH (a) 1, (b) 3, (c) 5, (d) 7 and (e) 9

Crystallite size of zirconia was calculated using Scherer's formula given in Eq. 2 (Cullity 1956). Crystallite size of  $ZrO_2$  powders synthesized by varying the pH from 1 to 9 and using  $NH_3$  as gelation agent is shown in Fig. 3. With the increase in pH, crystallite size of the samples increases initially. In the sol-gel process crystallite size is strongly influenced by rate of hydrolysis. A sharp decrease in crystallite size has been observed in sample with pH 9 due to phase transition. Samples prepared using  $NH_3$  exhibit better crystallinity and phase purity under as-synthesized conditions as compared to the ones prepared without  $NH_3$  (Maheswari et al. 2013). Structural rearrangement is affected by the presence of  $NH_4^+$  in terms of steric hindrance. The rate of rearrangement increases with an increasing concentration of MOH mineralizer, which results in decrease of the size of crystals. Therefore, pure tetragonal zirconia can be produced via in-situ structural rearrangement of  $Zr(OH)_xO_y$ .

$$D = 0.9\lambda / B \cos \theta \quad (2)$$

Where  $D$  is crystallite size,  $\lambda$  is wavelength of X-rays used ( $1.5406\text{\AA}$ ),  $B$  is full width at half maximum and  $\theta$  is diffraction angle.

Unit cell volume calculations [Fig. 4] revealed average increasing behavior with pH. These variations are consistent with phase occurrence. It has already been discussed in XRD results that higher tetragonal content has been observed at pH 9. Therefore, unit cell volume of such sample sharply decreases as compared to other samples since monoclinic has slightly larger unit cell volume than tetragonal. Decrease in volume leads to increase in density especially for sample synthesized at pH 9 [Fig. 5] with phase purity. For biological applications relatively higher densities are required because dense the material, more compact the powder and higher hardness of samples.

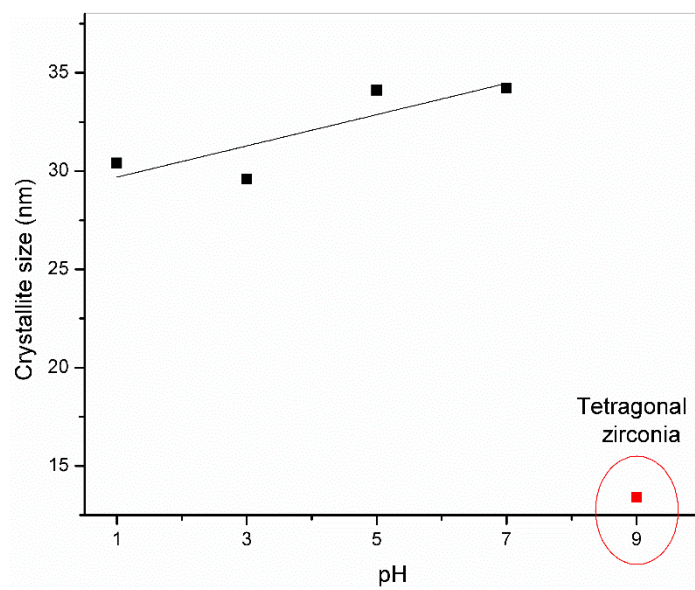


Fig. 3 Crystallite size of zirconia nanocrystallites as a function of pH

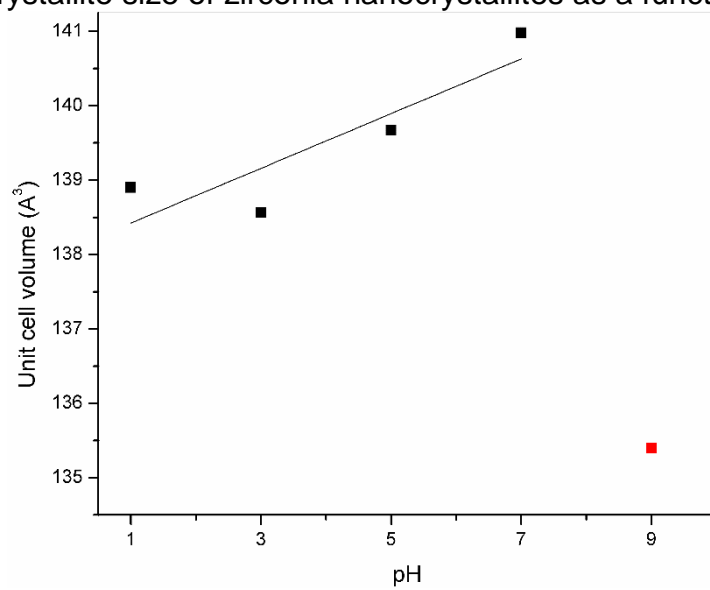


Fig. 4 Unit cell volume of zirconia nanocrystallites as a function of pH

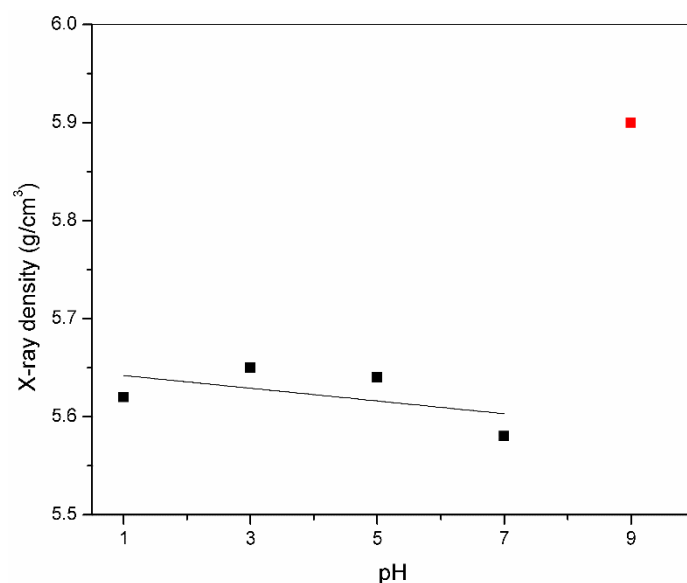


Fig. 5 X-ray density of zirconia nanocrystallites as a function of pH

For hardness measurements Vickers indentation under 4.9N load for 15 seconds dwell time was performed according to American Society for Testing and Materials (ASTM C-1327-99). The hardness of zirconia samples is strongly related to phase formation. The close packing of atoms due to reduction in volume also results in higher value of hardness. Maximum hardness obtained at pH 9 is 1290HV [Table 1].

**Table 1** Hardness of zirconia NPs as a pH

<b>pH</b>	<b>Hardness (HV) at constant load and time ASTM C-1327-99</b>
1	866
3	726
5	666
7	846
9	1290

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 constant and tangent loss Eqs.3 and 4 were used.

$$\varepsilon = Cd / \varepsilon_0 A \tag{3}$$

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

To carry out dielectric measurements, the powder samples were prepared in the form of circular disk shaped pellets. 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 specimen as is observed in our case in Fig. 6. Further, the space charge carriers require some time to get aligned in the direction of externally applied electric field. At high frequencies, space charge carriers do not follow the alteration of externally applied field thus results in low polarization and as a result dielectric constant and tangent loss become constant at high frequencies (Majid et al. 2015, Shah et al. 2014, Riaz et al. 2015). Observed high tangent loss in the low frequency region is because of high defect charge density existing in the material. Variation in tangent loss with the change in frequency is shown in Fig. 7.

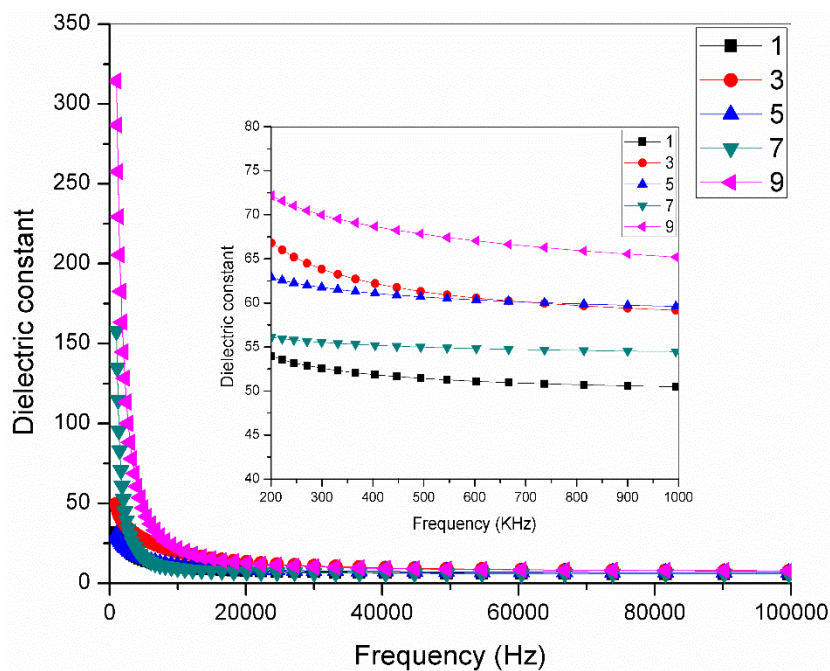




Fig. 6 Dielectric constant of zirconia nanocrystallites as a function of pH: Inset shows the variation in dielectric constant high frequencies

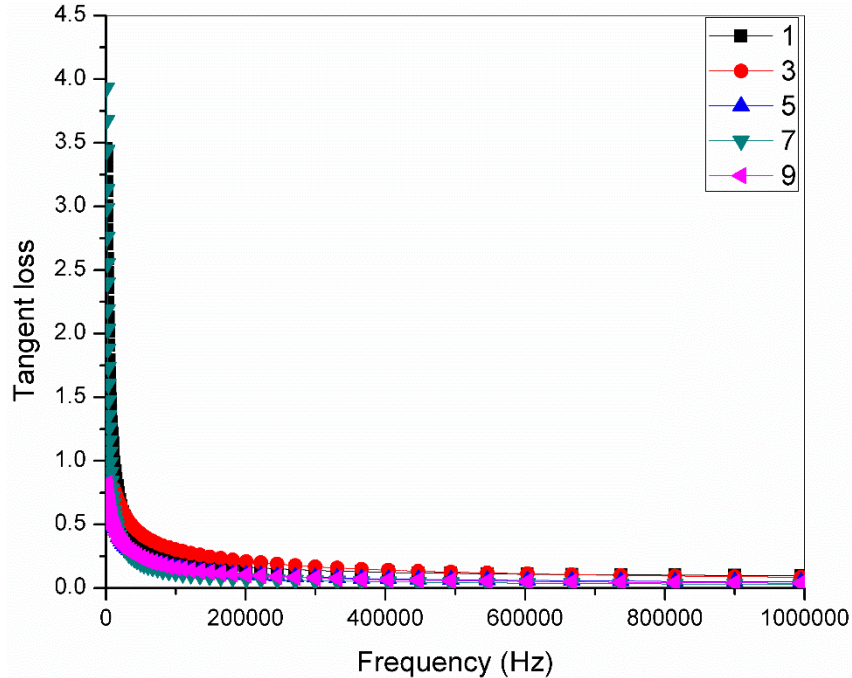


Fig. 7 Tangent loss of zirconia nanocrystallites as a function of pH

### 3. CONCLUSIONS

(1) Five different sols of pH 1, 3, 5, 7 and 9 were prepared. (2) XRD results showed that zirconia nanocrystallites were a mixture of monoclinic and tetragonal  $ZrO_2$  whereas, phase pure tetragonal zirconia was obtained at pH 9 (3) Crystallite size showed sharp decrease with phase transition due to restructuring. (4) Hardness of the samples was in the range of 650HV to 1290HV. 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 225 at lower frequency. Whereas, dielectric constant of  $\sim 60$  was observed at 20kHz.

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