

Magnetic and dielectric properties of Methanol Added Fe₃O₄ –ZrO₂ Nanocomposites

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ABSTRACT

Ceramics such as zirconia find increasing applications in electronic industry and biomedical fields. Fully dense, high-purity zirconia shows good strength, exceptional hardness and wear-resistance. Presently, research has been done to enhance the properties and stability of ZrO₂, specifically the hardness by governing the structure and composition of different additives. For stabilization of zirconia, iron oxide (Fe₃O₄) has already been proven, but it has relatively lower hardness value that can be improved by addition of polymers. In this research work acidic (pH 4) and basic (pH 10) Fe₃O₄ is doped into pre-synthesized ZrO₂ with 2, 4, 6, 8 and 10wt%, whereas methanol was used as additive. Methanol addition leads to relatively higher value of hardness (~1200HV) than previously reported value. XRD confirms the formation of pure tetragonal ZrO₂ with better crystallinity. A sharp decrease in crystallite size has been observed when phase shift takes place at 10wt% of Fe₃O₄. M-H plots show very low value of coercivity and remanence for all dopant content. Dielectric constant is found to increase with Fe₃O₄ content. Dielectric constant of Fe₃O₄ doped zirconia NPs strongly depends on phase and crystallite size.

1. INTRODUCTION

Zirconia was initially referred to as ceramic steel due to its three polymorphous: cubic (c), tetragonal (t) and monoclinic (m). Monoclinic zirconia (m-zirconia) exists at temperatures under 1100°C, tetragonal zirconia (t-zirconia) exists at temperatures between 1100°C–2370°C, and cubic zirconia (c-zirconia) exists at greater than 2370°C and below 2600°C (Bashir et al. 2015a). Among these phases tetragonal zirconia is found to be with higher value of hardness and biocompatibility (Bashir et al. 2014). However, in the biomedical field tetragonal zirconia (t-ZrO₂) application is limited due to hydrothermal degradation (Chevalier and Gremillard 2009, Marro et al. 2009) and it transforms to monoclinic zirconia. But t-ZrO₂ exists at higher temperatures (>800°C). t-ZrO₂ maintenance can be performed at relatively lower temperatures by doping of undersized or oversized atoms (Basahel et al. 2012).

A number of researches have been done to enhance the properties and stability of t-ZrO₂, specifically the hardness by governing the microstructure and composition.

Different dopants have also been used for these purposes. Among several dopants different phases of FeO play critical role because of ferromagnetic and superparamagnetic behavior and its biocompatibility. Ji et al. (1992) studied catalyst properties of Fe/ZrO₂ at different calcination temperatures. They observed small particles below 300°C of Fe³⁺ oxy-hydroxides and Fe³⁺ cations. They revealed that the ions exchanged between hydrated Fe³⁺ oxyhydroxides and surface OH groups of zirconia. Moreover, at 700°C calcination temperature, they observed Fe³⁺ ion exchanged species, crystalline α-Fe₂O₃ and Fe³⁺ oxide clusters.

Chemical deposition technique has been utilized to prepare doped ZrO₂ via controlled hydrolysis of zirconium oxy-chloride precursors in presence of some organic additives. However, direct chemical deposition method based on sol-gel hydrolysis of zirconium oxy-chloride precursors to prepare zirconium oxide often results in the formation of irregular shaped and aggregation of the final particles. Further there is difficulty in controlling the structure of ZrO₂ because of the reason that hydrolysis rates of zirconium oxide precursors are quite fast (Xia and Mokaya 2005). Therefore, it is necessary to control some parameters and additives using feasible method for preparation of controlled zirconia structure with uniform shape, smooth surface and non-agglomerated particles.

The variation from stoichiometry also influences the electrical behavior of semiconducting oxides such as ZrO₂. Many researchers have reported on stabilization of zirconia but they have compromised with dielectric properties due to presence of oxygen vacancies. Number of oxygen vacancies can be created by the addition of dopants. However, addition of organic additives can introduce some additional mechanisms. Due to addition of organics or polymers, chain network is formed. This chain network hinders the flow of charge, thereby causing high dielectric constant. Moreover, dielectric constant of zirconia is strongly influenced by the crystal structure. Zirconia exhibits high dielectric constant in tetragonal phase (>42), while monoclinic phase has considerably low dielectric constant (~ 20) (Zho et al. 2011).

Very few attempts have been made for preparation of Fe₃O₄ stabilized zirconia. Recently Fe₃O₄ stabilized zirconia was reported by our group (Bashir et al. 2015a) but with relatively low value of hardness. In order to increase its hardness and bio medical era several additives have been incorporated in ZrO₂ (Bashir et al. 2015b). Carbon based compounds have also provide binding sites for Zr⁴⁺ (Philip 2009).

In this research paper, Fe₃O₄ doped zirconia nanocrystallines have been prepared using sol gel method. Organic additive was used to increase the phase stability and dielectric constant of zirconia.

2. Experimental Details

2.1 Materials

Zirconyl chloride octahydrate (ZrOCl₂.8H₂O), FeCl₃.6H₂O, and FeCl₃.4H₂O were used as starting materials. Water was deionized (DI) prior to use and methanol was used as additive.

2.2 Method

ZrOCl₂.8H₂O was dissolved in DI water to make 0.1M solution of pH 1. Stirring was performed at 50°C, which resulted in translucent and glossy sol. Pre-synthesized Fe₃O₄ nanoparticles (NPs) (Riaz et al. 2014) were doped in zirconia sol with 2, 4, 6, 8 and 10wt%. Detailed synthesis of Fe₃O₄ NPs doped zirconia sol has been reported earlier (Bashir et al. 2015a). After that 5ml of methanol was added into each Fe₃O₄ doped zirconia sol that was stirred at room temperature for 5 hours until formation of gel. After that gel of Fe₃O₄ doped zirconia sol was dried at 50°C for formation of powders. These as-synthesized NPs were subjected to different heat treatments without any further treatments.

2.3 Characterization

Structure and phase evaluation of zirconia powders were examined by X-ray diffractometer (XRD) (Bruker D8 advance) by CuK α source ($\lambda=0.1540598$ nm). Shimadzu HMV-2 micro Vickers hardness indenter was used for indentation of the pallets made by hydrolytic pressure of 1 Ton. Dielectric properties of Fe₃O₄ doped zirconia were examined with 6500B Precision Impedance Analyzer. M-H curves were obtained by using Lakeshore 7407 vibrating sample magnetometer.

3. Results and Discussion

XRD patterns of the as-prepared Fe₃O₄ doped ZrO₂ NPs show polycrystalline nature at all concentrations as depicted in Fig. 1. At 2-10wt% concentration of Fe₃O₄, peaks at approximately 21.8°, 31.8°, 39.9° and 46.2° correspond to the (011), (111), (-211) and (20-2) planes of monoclinic zirconia (m-ZrO₂) [JCPDS 81-1314]. However, peaks at 30.6°, 52.6°, 57.9°, 68.8°, 74.4° and 78.3° correspond to the (111), (113), (211), (123), (004) and (330) planes of tetragonal zirconia (t-ZrO₂) [JCPDS 17-923], respectively. Addition of Fe₃O₄ resulted in mixed m-ZrO₂ and t-ZrO₂ phases in as-synthesized NPs. However, as Fe₃O₄ concentration was increased to 8wt%, amorphous zirconia was observed. This is known as non-stable t-phase usually occurring at ~500 °C as reported in the literature (Tyagi et al. 2006). However, it is important to note that non-stable t-phase has been synthesized at room temperature (RT) in this study. Formation of amorphous zirconia is an indication of transformation of monoclinic to tetragonal. At 10wt% of Fe₃O₄ content, intensity of monoclinic peak along with (111) plane decreased and intensity of t(111) increased. This means that Fe₃O₄ stimulates the phase transformation from monoclinic to tetragonal. Reduction in monoclinic content in Fe₃O₄ doped ZrO₂ NPs is due to substitution of Fe ions with Zr ions. When Fe³⁺ / Fe²⁺ ions replace Zr⁴⁺ ions oxygen vacancies are created and distortion in lattice structure is formed. For stabilization of tetragonal zirconia undersized (Fe³⁺, Fe²⁺) or oversized (Y³⁺, Mg²⁺) atoms play an important role. Oxygen vacancies can be created by adding appropriate amounts of dopants. Presence of oxygen vacancies distorted monoclinic structure and formed tetragonal zirconia.

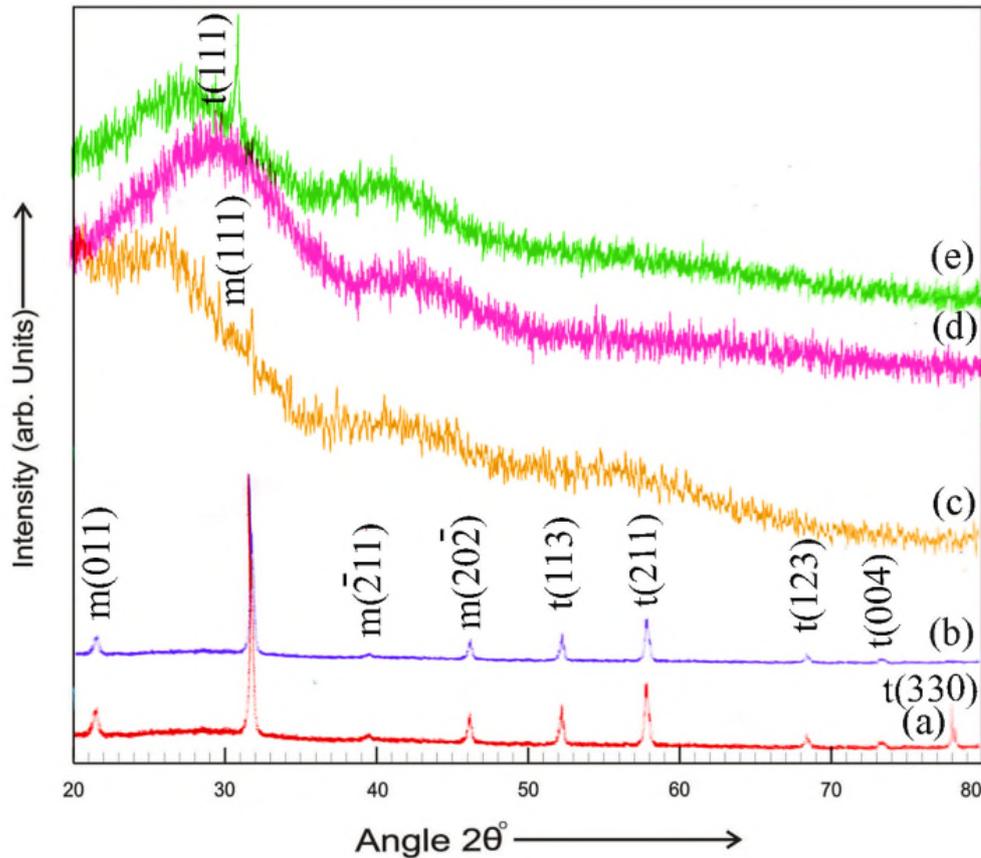


Fig. 1 XRD patterns of methanol added Fe_3O_4 doped zirconia (a) 2, (b) 4, (c) 6, (d) 8 and (e) 10wt%,

Crystallite size of ZrO_2 NPs was estimated using Eq. 1 (Cullity and Stock 2001). Mixed t-phase and m-phase were found at 2wt%-6wt%. Another phase change from mixed to pure t-phase was observed with dopant content 8wt%-10wt%. These phase changes accompanied with decrease in crystallite size. Decrease in crystallite size might have been observed because of re-structuring in materials (Riaz and Naseem 2007). Another cause of decrease in crystallite size is due to substitution of Fe with Zr. The value of ionic radius of Fe^{3+} (0.64 Å) is smaller as compared to ionic radius of Zr^{4+} (0.80 Å). Due to the smaller size of ionic radius, the Zr^{4+} ions can be easily replaced by the Fe^{3+} ions into the ZrO_2 lattice. Dislocation density was calculated using Eq. 2 and plotted in Fig. 3.

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

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

Where, θ represents the diffraction angle, λ is the wavelength (1.5406Å), B is Full Width at Half Maximum and δ stands for dislocation density.

Structural changes may also be caused due to localized heating in the material, which may have resulted due to carbonated atoms present in the samples (comes from methanol in this case). Shrinkage in volume results in transformation of t-m zirconia phase. Shrinkage in unit cell volume was also caused by the substitution of undersized atoms with Zr as discussed earlier. Fig. 4 shows relatively less unit cell volume in case of 8 and 10wt%, since tetragonal phase contains relatively smaller unit cell volume [JCPDS card 17-923] as compared to monoclinic phase [JCPDS card 13-307]. Higher density specifies the dense system which has been correlated to the hardness results presented in the latter section. Higher x-ray density is calculated in zirconia powders with 8 and 10wt% of Fe_3O_4 content for pure tetragonal phase [Fig. 5].

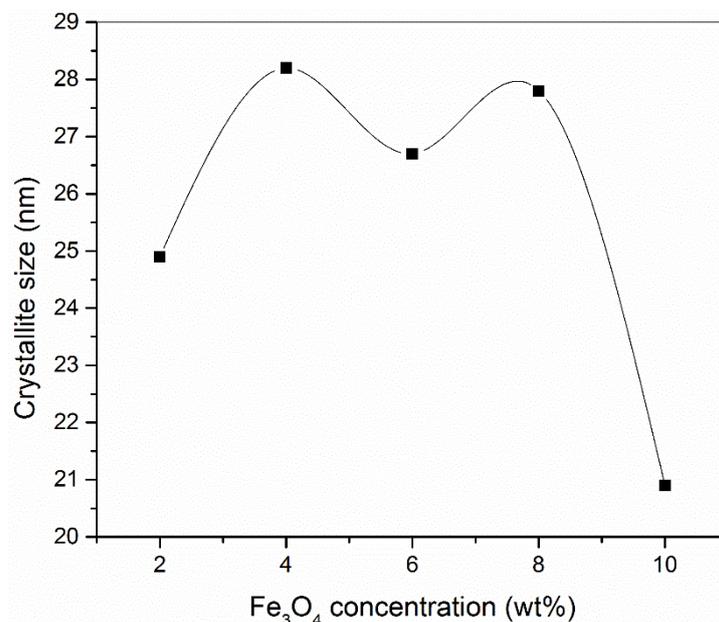


Fig. 2 Crystallite size of ZrO_2 NPs at various Fe_3O_4 content

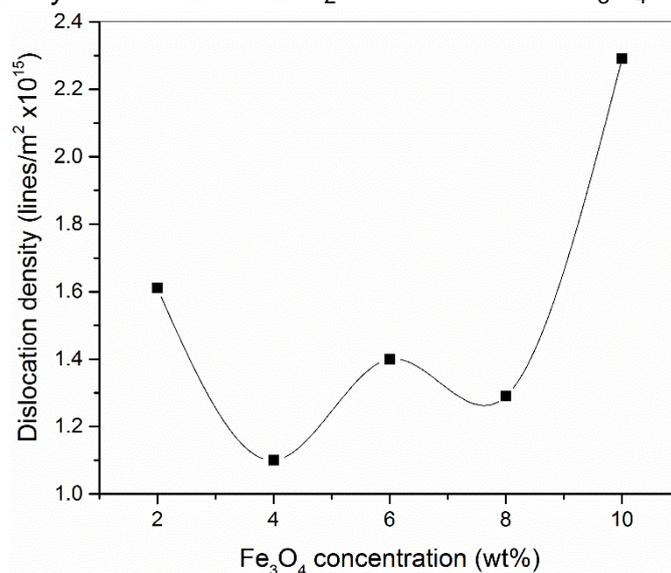


Fig. 3 Dislocation density of ZrO₂ NPs at various Fe₃O₄ content

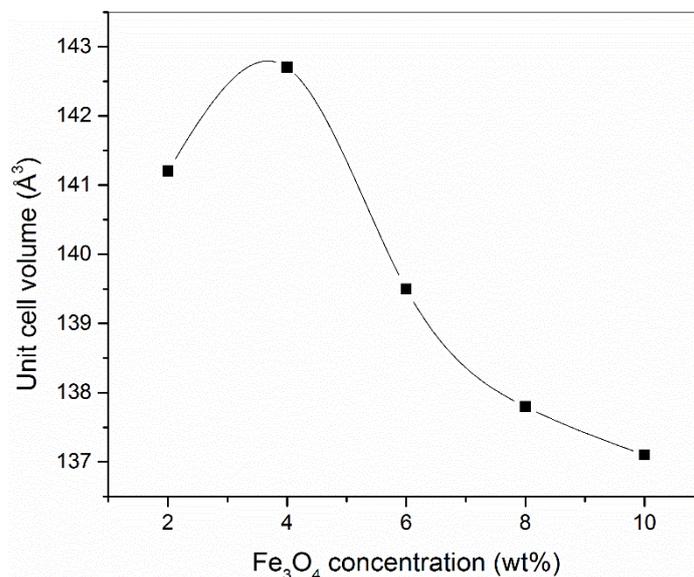


Fig. 4 Unit cell volume of ZrO₂ NPs at various Fe₃O₄ content

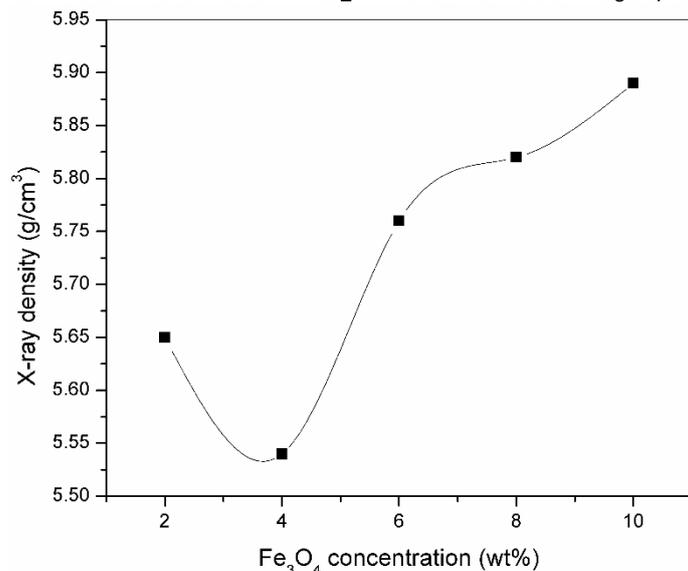


Fig. 5 X-ray density of ZrO₂ NPs at various Fe₃O₄ content

M-H curves of Fe₃O₄ doped zirconia are shown in Fig. 6. Ferromagnetic behaviour with contribution of paramagnetic (coming from zirconia) was observed in Fe₃O₄ doped ZrO₂. Magnetic material doped zirconia can exhibit ferromagnetism caused by RKKY interactions. Such interactions occur between conductive electrons of ZrO₂ and spin polarized electrons of Fe³⁺ ions in case of Fe₃O₄ doped ZrO₂. The magnetism due to this interaction causes spin polarization of conductive electrons of ZrO₂ host lattice. After exchange interaction with local spin polarized electrons of Fe²⁺ and Fe³⁺ ions, these local spin polarized electrons exhibit same spin direction as

conductive electrons after long range exchange interaction (Bashir et al. 2014). These interactions are caused by host electrons and dopant spin polarized electrons (Bashir et al. 2014). Moreover, because of such exchange interactions zirconia exhibits ferromagnetic behaviour. Graphs for saturation magnetization and coercivity are plotted in Fig. 7.

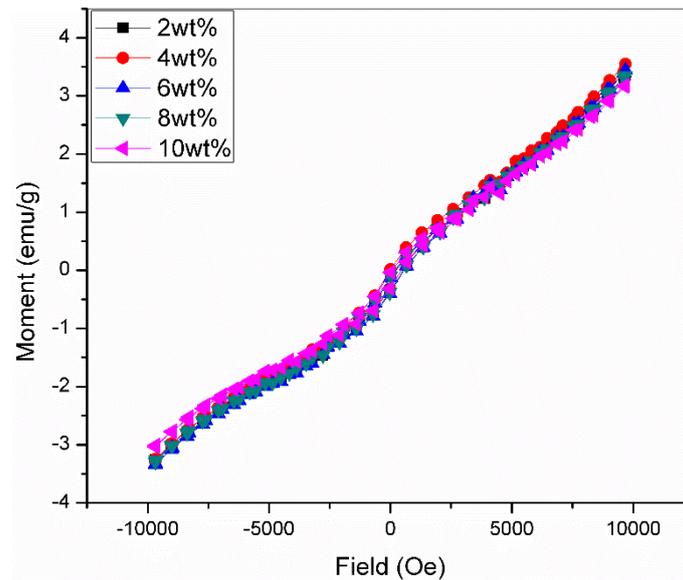


Fig. 6 VSM graphs of zirconia NPs at various Fe_3O_4 content

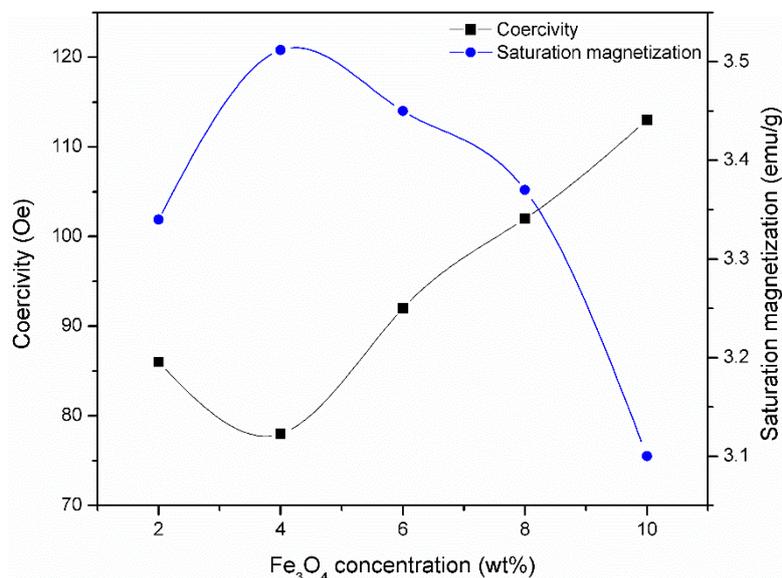


Fig. 7 Coercivity and saturation magnetization of zirconia NPs at various Fe_3O_4 content

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). From Fig. 5 dense structure was observed at 8 and

10wt%. Methanol addition leads to relatively higher value of hardness than reported earlier (Bashir et al. 2015a) as revealed by Micro Vickers [Table 1].

Table 1 Hardness of the samples in comparison of earlier report of Fe₃O₄ stabilized zirconia without methanol addition

Fe₃O₄ Content (wt%)	Hardness (HV) With methanol	Hardness Without methanol
2	789	310
4	677	450
6	854	680
8	950	945
10	1279	962

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 dielectric properties the dielectric constant and dielectric 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 is the capacitance, d is width of disk, ε_0 is the permittivity of free space, A is the area, f is the frequency and ρ is the resistivity.

For Fe₃O₄ doped zirconia, dielectric constant shows a similar effect for all samples. At low frequencies, the value of dielectric constant is maximum but with increase in frequency, its value decreases and than at high frequencies remains almost constant. This effect might have been observed because of the reason that space charge carriers need time to align in the direction of field. Since at low frequencies these space charge carriers have sufficient time for alignment. But at high frequencies space charge carriers have not sufficient time.

For 8wt%, at low frequencies relatively high dielectric constant was observed. This increase in dielectric constant is mainly due to some reasons i.e. 1) The presence of organic (methanol) chain polymer network causes hinerance that results in high dielectric constant. 2) Fe has covalent bonding with Zr having low coordination. The covalent bonding means that the main defects are dangling bonds, and the low coordination allows the ZrO₂ network to relax to remove any dangling bonds by

rebonding the network (Robertson 2004). Tangent loss in the presence of dopant showed a decrease with increase in frequency [Fig. 9].

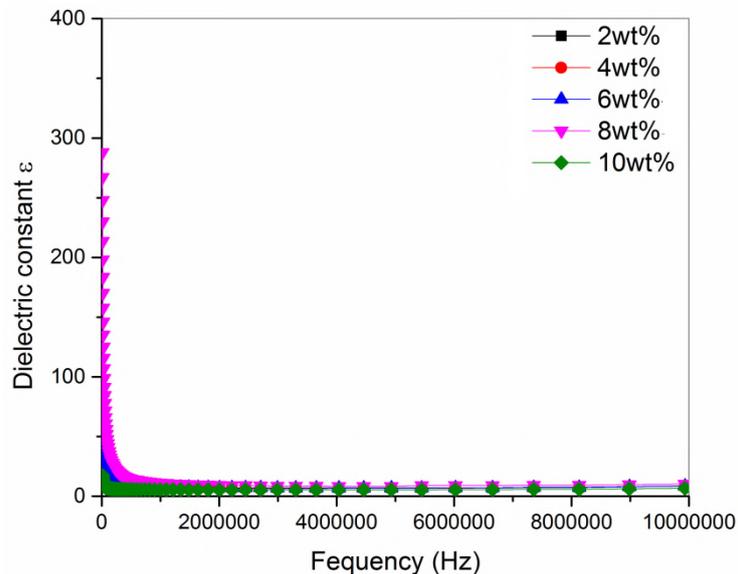


Fig. 8 Dielectric constant of ZrO_2 NPs at various Fe_3O_4 content

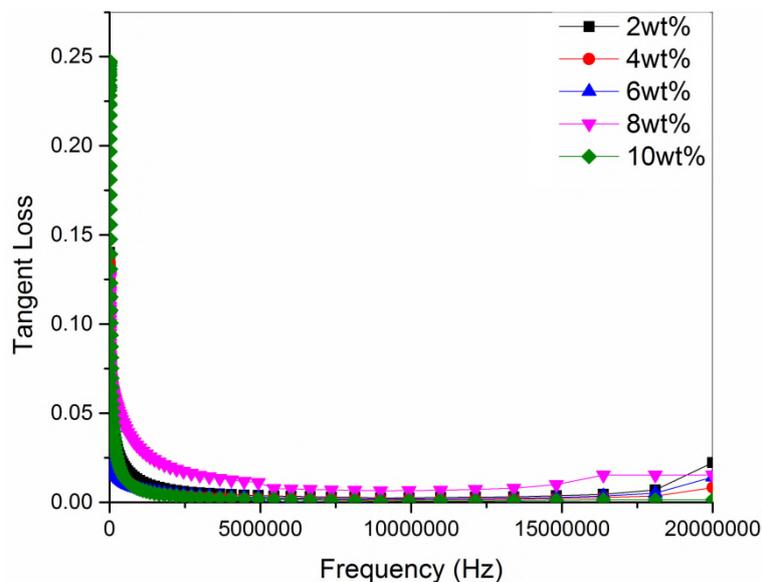


Fig. 9 Tangent loss of ZrO_2 NPs at various Fe_3O_4 content

3. CONCLUSIONS

Fe_3O_4 doped zirconia NPs were prepared by sol-gel method. (1) Five different sols at different concentrations of Fe_3O_4 (2, 4, 6, 8 and 10wt%) were prepared. (2) XRD results showed that zirconia powders were a mixture of m- ZrO_2 and t- ZrO_2 at low content of Fe_3O_4 whereas, phase pure tetragonal zirconia was obtained at 8 and 10wt%. (3) Crystallite size showed sharp decrease with phase transition due to restructuring. (4) Hardness of Fe_3O_4 doped ZrO_2 was observed to be in the range of

789HV-1279HV. (4) Doped zirconia NPs showed high dielectric constant at lower frequency and an increasing behavior was observed with increase in dopant concentration. (5) Magnetic properties revealed ferromagnetic behavior.

REFERENCES

- Basahel, S.N. Ali, T.T. Narasimharao, K. Bagabas, A.A. and Mokhtar, M. (2012), "Effect of iron oxide loading on the phase transformation and physicochemical properties of nanosized mesoporous ZrO₂", *Mater. Res. Bull.*, **47**, 3463–3472.
- Bashir, M. Riaz, S. and Naseem, S. (2014), "Structural and magnetic properties of Fe₃O₄ stabilized zirconia", *IEEE Trans. Magn.*, **50**, 2201104, 1-4.
- Bashir, M. Riaz, S. and Naseem, S. (2015a), "Fe₃O₄ stabilized zirconia: Structural and optical properties" *J. Sol-Gel Sci. Technol.*, **74**, 281-289.
- Bashir, M. Riaz, S. Kayani, Z.N. and Naseem, S. (2015b), "Effects of the organic additives on dental zirconia ceramics - Structural and mechanical properties", *J. Sol-Gel Sci. Technol.*, **74**, 289-298.
- 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.
- Ji, W. Kuo, Y. Shen, S. Li, S. and Wan, H. (1992), "Proc. 10th International Congress on Catalysis", Budapest, 2059.
- Marro, F.G. Chintapalli, R. Hvizdos, P. Soldera, F. Mücklich, F. and Anglada, M. (2009), "Study of near surface changes in yttria-doped tetragonal zirconia after low temperature degradation", *Int. J. Mater. Res.*, **100**, 92–96.
- Philip, D. (2009), "Honey mediated green synthesis of gold nanoparticles" *Spectrochim. Acta Mol. Biomol. Spect.*, **73**, 650-653.
- Riaz, S. and Naseem, S. (2007), "Effect of reaction temperature and time on the structural properties of Cu(In,Ga)Se₂ thin films deposited by sequential elemental layer technique", *J. Mat. Sci. Technol.*, **23**, 499-503.
- Riaz, S. Bashir, M. and Naseem, S. (2014), "Iron oxide nanoparticles prepared by modified co-precipitation method", *IEEE Trans. Magn.*, **50**, 4003304, 1- 4.
- Robertson, J. (2004), "High dielectric constant oxides", *Eur. Phys. J. Appl. Phys.*, **28**, 265–291.
- Tyagi, B. Sidhpuria, B. Shaik, B. and Jasra, R.V. (2006), "Synthesis of nanocrystalline zirconia using sol-gel and precipitation techniques", *Ind. Eng. Chem. Res.*, **45**, 8643–8650.
- Xia, Y. and Mokaya, R. (2005), "Hollow spheres of crystalline porous metal oxides: A generalized synthesis route via nanocasting with mesoporous carbon hollow shells", *J. Mater. Chem.*, **15**, 3126-3131.
- 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.