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Synthesis and Characterization of ZrO_2 - ZnO Nanoparticles

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ABSTRACT

Nanosized zirconia powder is prepared by sol-gel method. Zirconia is a material with good electrical, mechanical and biological properties. The improvements in these properties can be achieved by adding some dopants. Here we doped zinc oxide in zirconia sols with different concentrations. Zirconyl chloride was used as precursor of zirconia and NaOH as gelation agent. Zirconia is doped with ZnO, 1% to 5% molar concentrations, in both acidic (pH = 2) and alkaline (pH = 9) medium. X-ray diffraction is employed to check the effect of dopant on structural properties of zirconia while scanning electron microscopy for morphological characteristics of the zirconia nanoparticles. Optical spectra are obtained by using variable angle spectroscopic ellipsometer. XRD patterns demonstrate the formation of tetragonal phase and doping does not affect the crystal structure and lattice parameters of t-zirconia. Crystallite size of the samples increases with the increase in the ZnO content in both acidic and alkaline medium. From the optical spectra up to 90% transmission is observed. It has been observed that zinc oxide doped zirconia has direct band gap. However, ZnO concentration decreases the band gap value as compare to undoped zirconia. Scanning electron microscopy shows that nanoparticles are in the range of 40-50nm. Hence NPs prepared by sol-gel have good optical transmission and direct band gap with stable tetragonal zirconia phase can be employed in opto-electronic devices.

Keywords: Zirconia; ZnO; Nanoparticles; pH

1. Introduction

The materials having nanostructures show very good refractory properties, chemical resistance, mechanical resistance and hardness both at normal and high temperatures (Sanad 2013). The most widely studied type of nanostructures are the nanoparticles (Np's), which are largely used due to their ease and efficiency of production from a variety of materials (Johnston 2010).

Zirconia (ZrO_2) nanoparticles are important material using in the composites and advanced ceramics due to its high strength, high fracture toughness and high hardness. At ambient conditions, pure zirconia exists in three crystal structures, monoclinic,

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tetragonal and cubic (Liu 2013). All these crystal structures are thermodynamically stable at different temperatures ranges. Monoclinic phase (m-phase) is stable at temperature below 1172°C, tetragonal structure (t-phase) stable at temperature range of 1172-2347°C, and cubic structure (c-phase), stable above 2347°C. Different crystal structures and phase transformation has different applications. Cubic phase of zirconia is potentially used for solid oxide fuel cells (SOFCs), oxygen sensors, electrochemical capacitor and electrode sand ferrules because of its ionic, electrical and optical properties. For the reduction reaction tetragonal zirconia is used as a catalyst due to its amphoteric properties (Davar 2013, Li 2013).

Zirconia is good material for the replacement of silica for gate dielectric in microelectronics industry for the CMOS fabrication due to its high dielectric constant, stability with temperature and wide band gap (Balakrishnan 2013). It absorbs photon with two interband transitions: an indirect transition at 5.22 eV followed by a direct transition at 5.87 eV (Heshmatpour 2011). The properties such as high hardness, fracture toughness and high resistance to oxidation make it important mechanical material (Balakrishnan 2013).These mechanical properties of zirconia have been employed for the implantation in biomedical applications. Excellent esthetic properties and limited plaque adhesion make zirconia ceramics an ideal material for implants in the fields of dentistry and orthopedics (Saulacic 2013). Zirconia is a traditional electrolyte of the cell but it requires high temperature to retain oxygen ionic conductivity. On the other hand these high temperatures cause the degradation of cell systems. So in order to get the high performance at intermediate temperatures some dopants are introduced in to the zirconia. In this case metal oxides play an important role to enhance the efficiency of the cell and improve the electronic properties of zirconia (Liu, 2006). ZnO appear to be a sufficient stabilizer. It is chemically stable while its solubility is low (2-3%) in zirconia. However, the presence of ZnO increases conductivity (Marcomini 2012).

Zirconium oxide (ZrO_2) can be prepared by various techniques such as Sol-gel method, Co-precipitation method and hydrothermal process. The material processing has been improved due to various advantages by using Sol- gel technology. This process covers a verity of materials such as organic, inorganic hybrid and metallic materials (Esposito 2011). Nanostructured coatings developed by the sol gel technique provide enhanced functional or mechanical properties as well as purity, homogeneity and improved microstructure (Costacurta 2011). It does not require vacuum and allow fabricating a large area with low cost and at low processing temperature (Riaz 2013, Saeed 2013).

In this paper, we have synthesized ZnO doped zirconia nanoparticles by sol-gel method with different concentrations of ZnO in acidic and basic medium. Prepared nanoparticles were investigated with different techniques for structural, morphological and mechanical properties.

2. EXPERIMENTAL DETAILS

Zirconyl chloride octahydrate ($ZrOCl_2.8H_2O$) Ethanol, Deionized (DI) water was used as precursors whereas NaOH was used as a gelation agent. All materials were of chemical grade and used without further purification. Zirconyl chloride octahydrate ($ZrOCl_2.8H_2O$) was added in to DI water to form solution of molarity 0.1 M and pH = 2. Solution was stirred and heated at 50°C for 1 hour before and after addition of ethanol. Then ZnO (Saeed 2013) was added drop wise of 1 to 5wt% in to the synthesized sol. All sols were subjected to gel formation by heating at 60°C to form powder of zirconia nanoparticles.

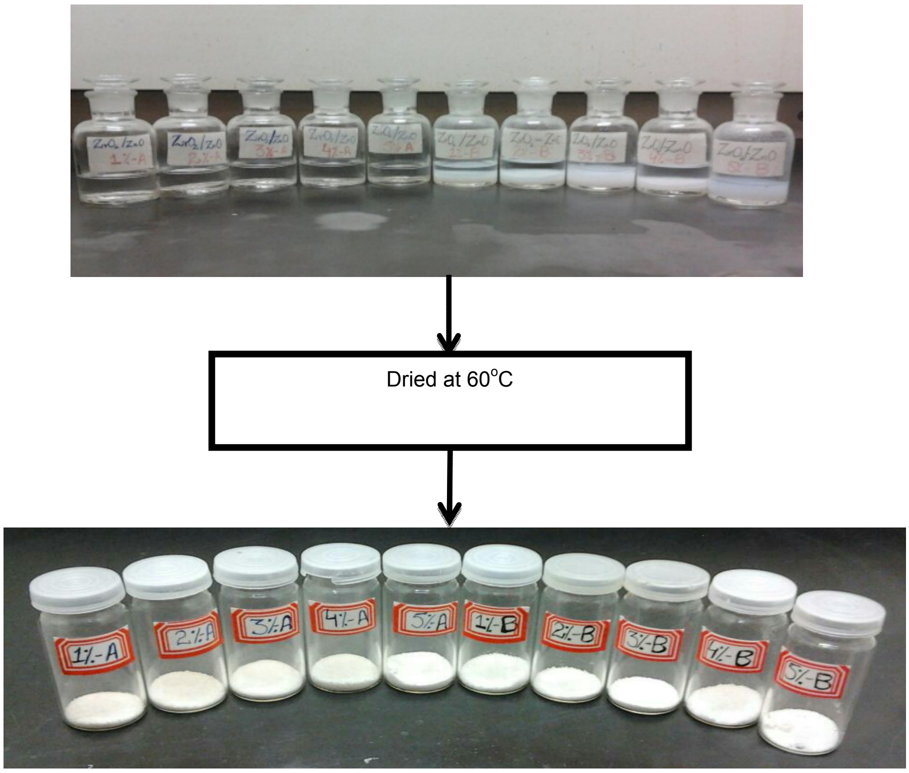

Fig: 1. As-synthesized undoped and ZnO doped ZrO_2 NPs

A wide angle X-ray diffractometer (Bruker D8) was used to study the crystalline structure of the NPs. The Cu K-alpha radiation source was used. K-beta filter was used to eliminate interference peak. For morphological characteristics was studied by Scanning Electron Microscopy (SEM) Model, Hitachi S- 3400N. Optical properties were determined by J.A Woollam M2000 variable angle Spectroscopic Ellipsometer (VASE).

3. RESULTS AND DISCUESSION

XRD characterizations have been performed to confirm the phases of the ZrO_2 with the variation of ZnO concentration of acidic and alkaline medium. Crystallization nature of zirconia at pH = 2 and pH = 7 is also discussed. Fig. 2 depicts the XRD patterns of the ZrO_2 - ZnO powders synthesized at different concentrations. The XRD pattern of the zirconia powders (Fig. 2) shows that the powders are mainly composed of ZrO_2

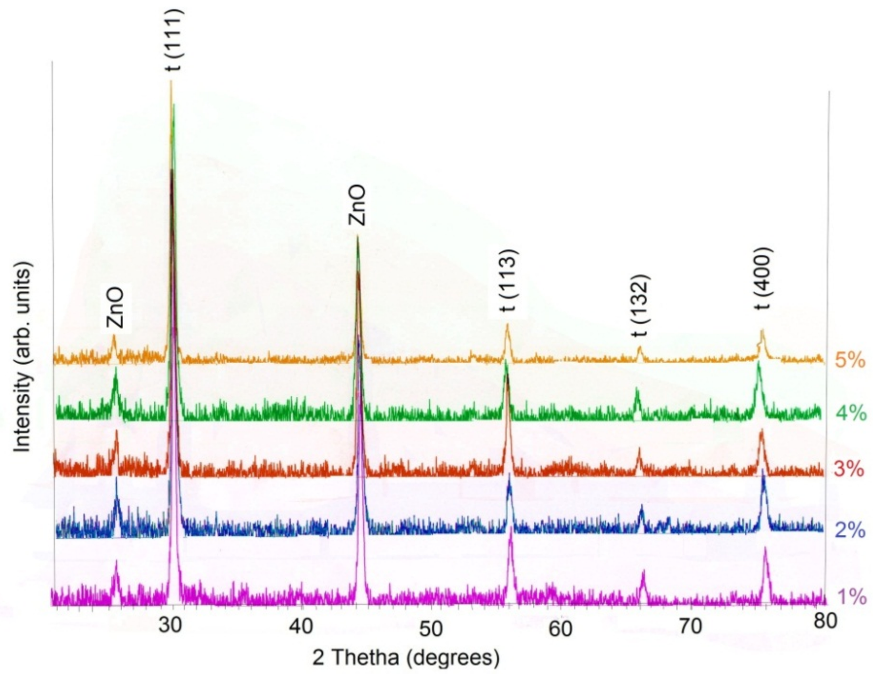

Fig. 2 XRD patterens of ZrO_2-ZnO nanoparticles in acidic medium (pH = 2)

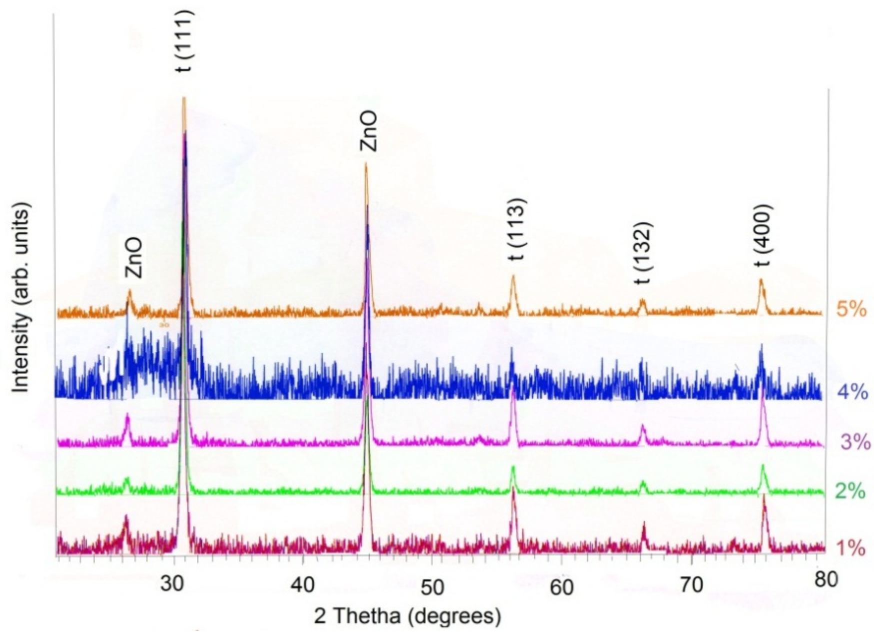

Fig. 3 XRD patterens of ZrO_2-ZnO nanoparticles in basic medium (pH = 9)

tetragonal phase. Peaks at angles 30.3°, 57.2°, 66.5° and 76.5° which are assigned to (111), (113), (132) and (400) planes respectively are the metastable tetragonal zirconia. They were identified according to JCPDS files no. 17-923. Peaks correspond to angles 45.5° and 28.5° are the indication of the dopants atoms. As from the patterns it can be inferred that ZnO doping up to 5% does not change the crystal structure of the zirconia in both acidic and alkaline medium as Fig. 2 and Fig. 3. ZnO dissolution up to 5% does not significantly change the lattice parameters as the ionic radii of Zr^{+4} (0.84 Å) and Zn^{+2} (0.74 Å) are very close to one another.

The average crystallite size in this research work can be calculated from the XRD line broadening using the Scherrer's formula as fin Eq. (1) (Patterson 1939)

$$C = \frac{0.9\lambda}{\beta \mathrm{Cos}\theta} \tag{1}$$

Where *C* is the crystallite size, *λ* is the wavelength of the Cu K*α* radiation (*k* = 1.5406 Å), *β* is the full width at half maximum (FWHM, in radians) of crystal plane (111) for t-ZrO_2 and *θ* is diffraction angle. The calculated crystallite size of the tetragonal phase of the samples at different concentrations of zinc oxide in both mediums is summarized in Table 1. The Crystallite size of ZnO doped zirconia increased with concentration of zinc oxide for both acidic and alkaline samples. These results show that the tetragonal phase is stabilized below 50 nm. Our results are also in good agreement with Garvie, who reported the formation of metastable tetragonal phase to the critical crystallite size effect (Wang 2013).

Figs. 4(a-b) shows SEM images of undoped and doped zirconia nanoparticles. It can be seen through these images that a decrease in size of nanoparticles to ~ 45-50 nm was observed after doping. However, the shape was observed to be spherical in both of the cases.

Table 1 Variation in Crystallite size with ZnO content

	ZnO Concentration	Crystallite size (nm)		ZnO Concentration	Crystallite size (nm)
Acidic (pH = 2)	1%	28.5	Basic (pH = 9)	1%	21.4
	2%	34.27		2%	42.85
	3%	42.85		3%	28.56
	4%	45.09		4%	34.27
	5%	47.61		5%	35.70

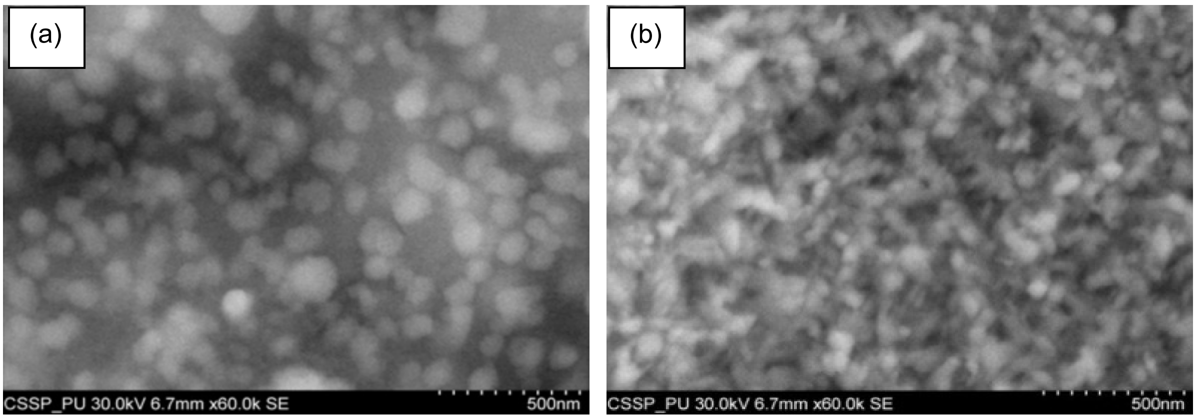

Fig. 4 SEM images of (a) undoped and (b) ZnO doped ZrO_2 nanoparticles

Zirconia is known as most important metal oxide in opto-electronics devices due to its large band gap, high refractive index and low dispersion. For optical studies films surface roughness and transparency are very vital parameters. However, spectroscopic ellipsometery is influential instrument for the analysis of optical properties (Yusoh 2012). The measurements were conducted in the range of 0.68-6.2 eV at 60° incident angle. Figs. 5(a-b) show the optical transmittance of doped zirconia 1%, 2%, 3%, 4% and 5% for pH = 2 and 9. The optical transmittance in the visible region for 3% doped zirconia in acidic medium is greater than 80%. Low value of transmission is due to light scattering caused by poly crystallinity. A slight increase in transmission reveals that zinc oxide doping can increase the transmission of the zirconia as ZnO itself is a good

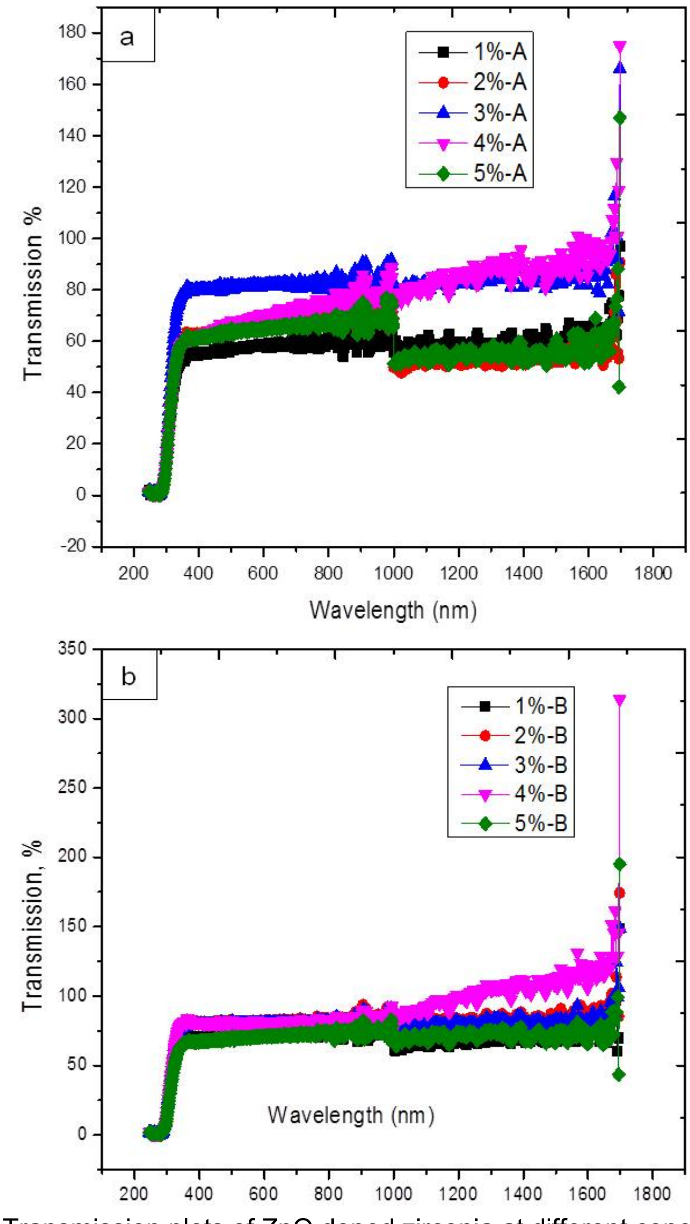

Fig. 5 Transmission plots of ZnO doped zirconia at different concentrations:
(a) Acidic (pH = 2) and (b) Basic (ph = 9)

optical material with direct band gap. Hence doping of suitable metal oxide can enhance the optical properties. Maximum optical transmission up to 90% is observed in basic medium. The transmission plots are in good agreement with Balakrishnan work (Balakrishnan 2013).

The band gaps are calculated from the optical spectra of the samples, from which the direct band gap is calculated by extrapolating the linear portion of the intercept on the energy (X-axis) axis (Fig. 6). A single band gap is noticed for all the samples

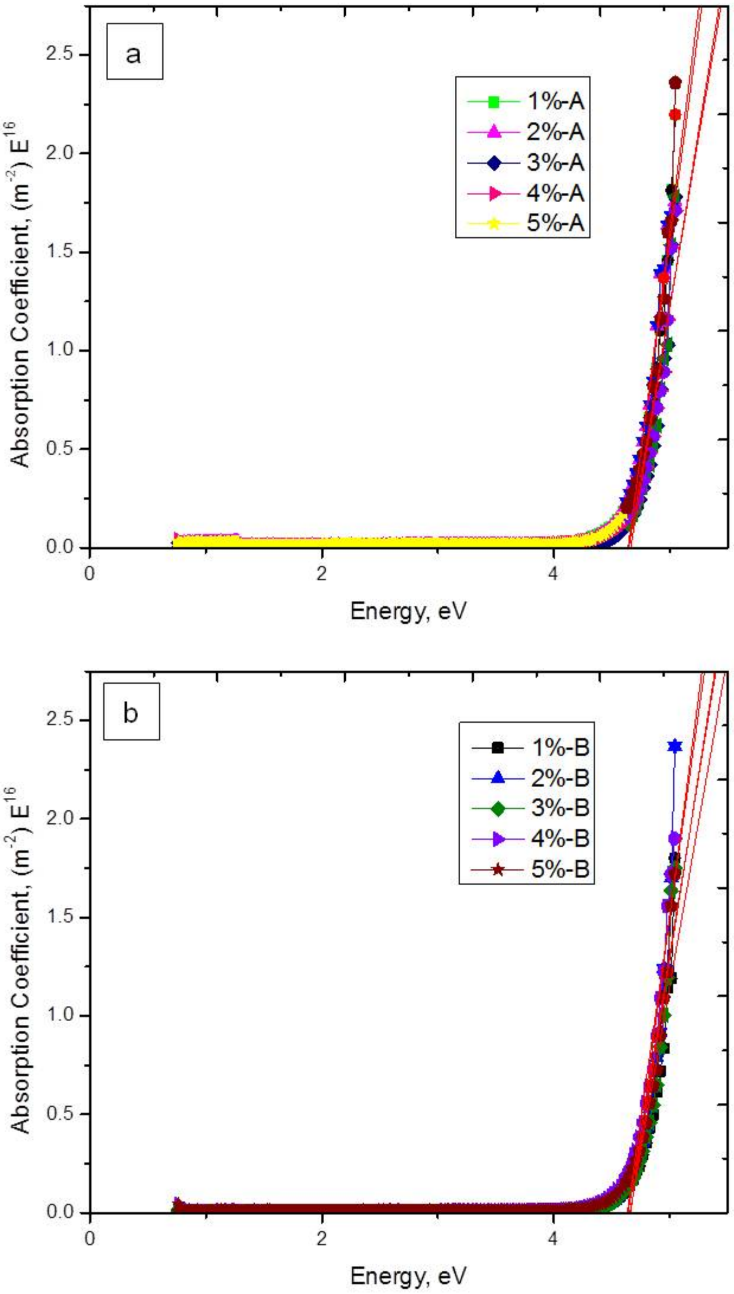

Fig. 6 Band gap of ZnO doped zirconia in (a) acidic (pH = 2); and (b) basic medium (pH = 9)

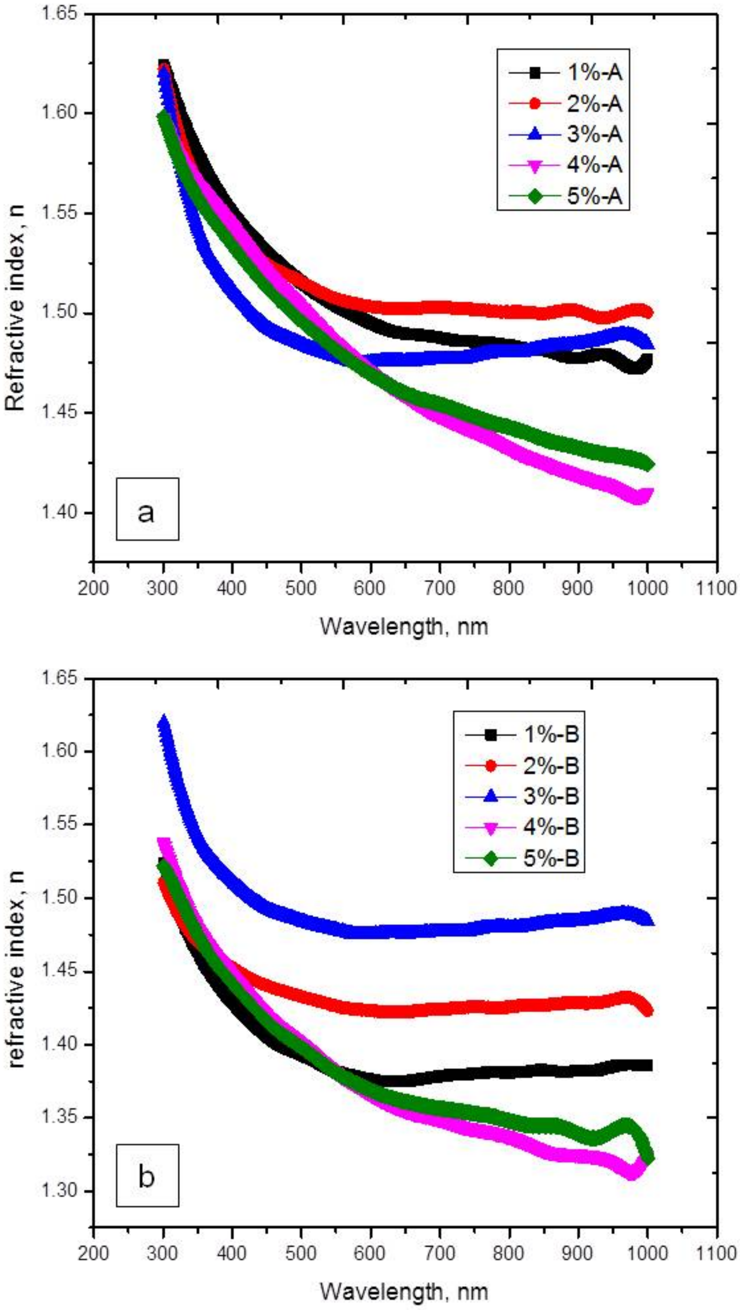

Fig. 7 Refractive index (a) acidic (pH = 2) and (b) basic medium (pH = 9) as a function of wavelength

prepared at different doping conditions, since these samples contain only tetragonal hase, which is also inferred from the XRD data. Figures illustrate the direct band gap at 4.6 eV since with doping zirconia band gap has reduced. Practically, the exitonic transitions emitted by the relative recombination of e-h pairs in a particular system and their emission characteristics strongly depend upon the particle size.

Calculation of the optical constants, e.g., refractive index, thickness and extinction coefficient is a topic of major and technological importance in optical study. Usually optical constants can be calculated from physical and optical model by comparing with experimental data. For the refractive index calculations Cauchy dispersion relation is used. This optical model is generally suitable to describe optical constants in visible and infrared regions. From the Fig. 7 it is depicted the decrease in refractive index particularly in the basic medium. The reason behind is low packing density and weak bonding between atoms.

Extinction coefficient of doped zirconia obtained from data has been shown in Fig. 8. The value of extinction coefficient is in the range of 0.00 to 0.06 for acidic and 0.0075 to 0.035 for alkaline samples observed at wavelengths 300nm to 1000nm. Extinction coefficient depends upon the absorption.

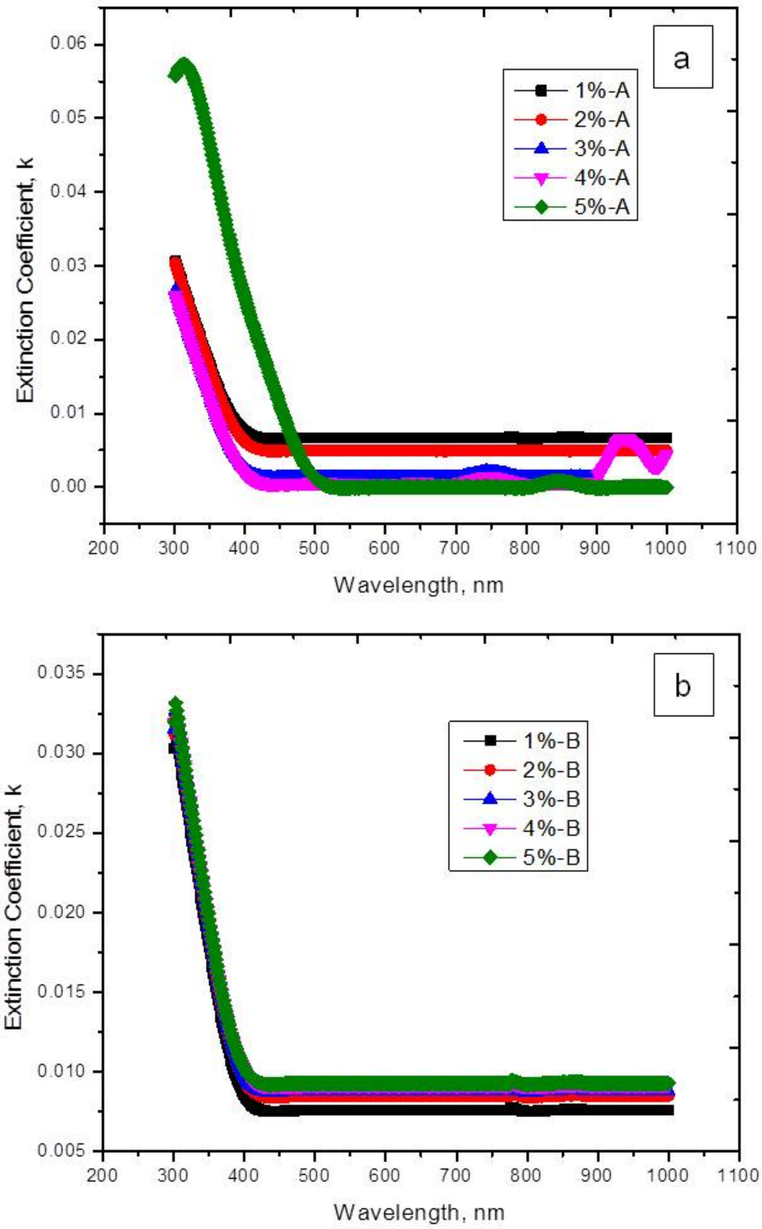

Fig. 8 Extinction coefficient of basic (pH = 9) ZnO-Zirconia as a function of wavelength

4. CONCLUSIONS

In this research work we have synthesized nanoparticles of ZnO doped zirconia by sol- gel method. We also checked the effect of pH on the size and phase of the zirconia. From the XRD patterns it can be inferred that stabilized t-ZrO_2 was obtained. ZnO doping concentration had not significant effect on crystal structure and lattice parameters of zirconia. Optical spectra demonstrated the high value of transmission up to 90% in basic medium. ZnO doping reduced the band gap of the zirconia as compare to undoped however, direct band gap was observed in all the samples. SEM micrographs revealed the nanoparticle size in the range of 40-50 nm.

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