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Dielectric Studies on Nano Zirconium Dioxide Synthesized through Co-Precipitation Process

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***Abstract*—**Nano sized zirconium dioxide in monoclinic phase (m-ZrO_2) has been synthesized in pure form through co-precipitation processing at different calcination temperatures and has been characterized by several techniques such as XRD, FT-IR, UV-Vis Spectroscopy and SEM. The dielectric and capacitance values of the pelletized samples have been examined at room temperature as the functions of frequency. The higher dielectric constant value of the sample having larger grain size proves the strong influence of grain size on the dielectric constant.

***Keywords*—**capacitance, dielectric constant, m-ZrO_2, nano zirconia

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I. Introduction

NANO zirconia (ZrO_2) powder has generated a lot of interest in recent years due to its specific optical, thermal, chemical and electrical properties and potential applications including transparent optical devices and electrochemical capacitor electrodes, sensors, synthetic gem stone, fuel cells ,catalysts including photo catalysts and advanced ceramics [1]-[3]. It is a best known industrially important ceramic material of the present generation because of its high refractive index and high oxygen–ion conduction [4]-[7]. These properties have led to the use of ZrO_2 based components in many engineering application such as wire – drawing dies, automobile engine parts and cutting tools. The relatively high coefficient of thermal expansion and low thermal conduction make nano ZrO_2 a suitable material for thermal barrier coating on metal components.The unique high temperature dielectric properties of nano Zirconia (ZrO_2) make it useful in the preparation of a variety of functional ceramic components such as oxygen sensors, piezoelectric, pyroelectric ceramics, ferroelectric ceramics and a variety of transparent toughened structural ceramic products such as ceramic tools, advanced ceramic bearings and engine parts. A great attention is given to the preparation of non-agglomerated, inexpensive nano zirconia with particles homogenous in size and shape. There have been several reports concerning the synthesis of nano size powders described in the literature, such as sol-gel processing, hydrothermal processing, co-precipitation, sonochemical micro emulsion and ion exchange resin manufacture methods [8], [9].

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M.M. Rashad and H.M. Baioumy [9] prepared ZrO_2 nanopowders via three processing routes, namely, conventional precipitation, citrate gel combustion and microemulsion refined precipitation and compared the structural and morphological changes. Gong-Yi Guo, Yu-Li Chen [10] reported a precipitation technique for the preparation of nano crystalline monoclinic zirconia at low temperature. D.G. Lamas *et al.* [11] demonstrated a tetragonal to cubic transition for decreasing crystallite size of nano zirconia prepared through wet chemical route. F. Kazemi *et al.* [12] reported synthesis of tetragonal zirconia nano powder using fructose and sucrose based precursor.

Among the various methods the authors preferred co-precipitation technique as it is an efficient and cost effective method for the mass production compared with the other mentioned techniques. The objective of this research work is to synthesize pure nano crystalline zirconia and also to explore its dielectric properties.

II. Materials and Methods

A. Synthesis

The chemicals zirconium oxychloride octahydrate ($ZrOC_{l2}.8H_2O$) and sodium hydroxide (NaOH) were purchased from Aldrich and were used as purchased for the preparation [9] of nano ZrO_2. Appropriate amount of Zirconium oxychloride octahydrate was dissolved in bi distilled water using hot plate magnetic stirrer. Aqueous solution of 2M NaOH was mixed in the above mentioned precursor solution until the pH value became 8. The precipitate was filtered after 15 minutes and was cleaned with water and acetone many times and then it was dried at 100 °C overnight. The calcination of the ZrO_2 sample thus prepared was done at different temperatures 700°C/hr, 1000°C/hr and 1200°C/hr. The as-prepared sample was coded as Z0 and those calcined at 700°C/hr ,1000°C/hr and 1200°C/hr respectively are coded as Z1, Z2 and Z3.

B. Characterization

The crystalline structure, phase composition and crystallite size of the powder samples were analyzed from XRD patterns obtained using Cu Kα radiation (λ =1.541Å) for 2θ value ranging from 10° to 80° in X-Ray Diffractometer (Model Rigaku Ultima III). General Morphology was examined through Scanning Electron Microscope (JSM 6390).

The Fourier transform Infrared (FTIR) transmission spectra of the powder samples were employed to identify the chemical structure of the samples in a range of 4000 cm^{-1} to 40cm^{-1} using Perkin Elmer Spectrophotometer (Spectrum RX1). The UV-Vis absorption spectra were obtained from UV-vis spectrophotometer (Model: Lambda 35).

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The dielectric characterization was made by LCR meter (model HIOKI 3532-50). For examining the dielectric properties, the ZrO_2 powder sample compressed into pellets of 10 mm diameter, 1 mm thickness by using aqueous PVA solution as a binding agent and also by applying 200 kg/cm^2 pressure for one minute. The pellets were sintered at 500°C for two hours and then silver coating was given on both sides of the pellets in order to provide a firm electrical ohmic contact.

III. Results and Discussion

XRD patterns of the as-prepared (Z0) and calcined samples of nano zirconia (Z1, Z2 & Z3) are shown in Fig.1 It is clear that the as-prepared sample (Z0) exists in amorphous state whereas the calcined samples exist in crystalline state which is evident from the respective presence and absence of distinct diffraction peaks. The intensity of the peaks become more pronounced as a function of temperature, which depicts the increase in the degree of crystallinity with heat treatment. From the diffraction patterns it is found that all the calcined samples exhibit monoclinic crystal symmetry and the peaks are indexed using JCPDS card 37-1484. The lattice parameters of the samples are estimated and presented in Table I. The perusal of them indicates the growth of monoclinic crysallites.

TABLE I
CRYSTAL PROPERTIES

Sample code	a Å	b Å	c Å	a/b:1:c/b	β
Z1	89.9	90.3	87.7	0.99:1:0.97	99°
Z2	90.5	89.6	88.1	1.01:1:0.98	99°
Z3	90.9	88.7	89.6	1.02:1:1.01	99°

There is a weak peak corresponding to tetragonal phase indicating the trace of tetragonal phase t-ZrO2 existing in the sample. The disappearance of those peaks in Z3 confirms the transformation into pure monoclinic phase m-ZrO2 at elevated temperatures.

The average grain size of the crystalline samples Z1, Z2, and Z3 are estimated using Debye Scherrer equation [13, 14] and are 25 nm, 42 nm and 46 nm respectively. It can be observed that the crystallite size increases as the function of annealing temperature which can be ascribed to the increase in the critical size of grain increases with the temperature [15].

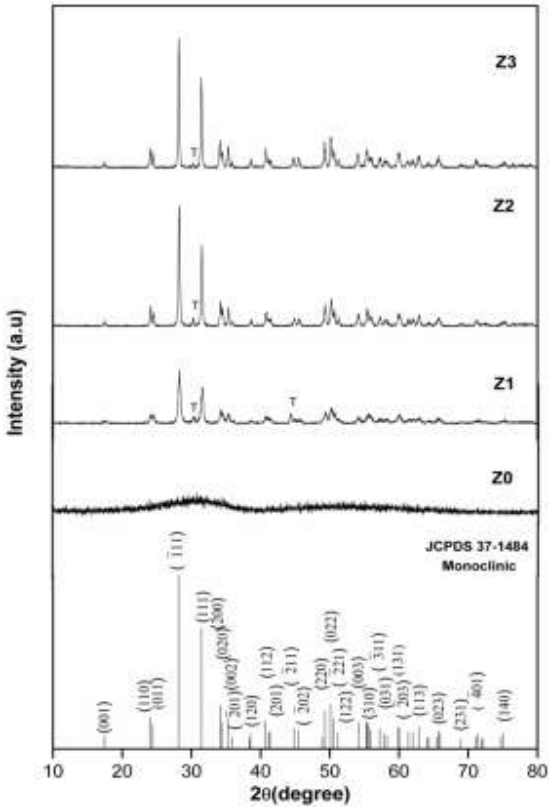


Fig. 1 XRD patterns of nano zirconia samples

The FTIR spectrum obtained for the as prepared and heat treated samples are shown in Fig.2. The as-prepared sample (Z0) has a broad absorption band at 690 cm^{-1} that can be attributed to Zr - O stretches. The IR spectra of crystalline zirconia samples (Z1, Z2 and Z3) show the various stretching frequencies around 508 cm^{-1}, 520 cm^{-1}, 580 cm^{-1}, 740 cm^{-1} as reported earlier [16] and [17].

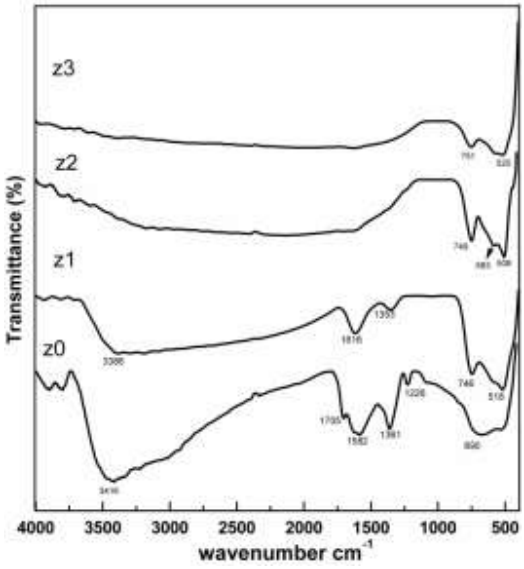


Fig. 2 FTIR spectra of nano zirconia samples

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The features particularly at 740 cm^{-1} and 500 cm^{-1}, due to Zr–O_2–Zr asymmetric and Zr–O stretching modes respectively, confirm the formation of ZrO_2 phases [16]. The extended spectrum in the 1000–4000 cm^{-1} region signified the mesostructure with an amorphous surface of the sample with chemisorbed H_2O molecules [9] and it is found that the traces of water disappeared for samples treated at elevated temperature.

In general, all ZrO_2 polymorphs are very similar in vibrational structure. A minor variation in their band frequencies or intensities infers small differences in the Zr^{4+} distribution ZrO sites and the oxygen vacancies and other structural defects [9], [18]. In the present work, the difference of the spectral appearance can be attributed to the transformation of the crystal lattice to a pure monoclinic phase from the mixed state.

The UV-visible absorption spectrum of Z1, Z2, and Z3 are shown in Fig.3. Pronounced absorption peaks are obtained at 212, 201, 217 and 236 cm^{-1} for the monoclinic phase.

The band gap is determined from the equation [19]

$$\alpha(h\upsilon) = A\,(h\upsilon - E_g)^{m/2} \quad (1)$$

where $\alpha(h\upsilon)$ is the absorption coefficient at the $h\upsilon$ energy photon, Eg the band gap, m a coefficient which is 1 for a direct transition and 4 for an indirect transition. From the spectra a straight line is extrapolated to zero absorbance where Eg = $h\upsilon$ and the band gap value is found to be 5.7 eV for the samples which is in good agreement with the value reported earlier [16].

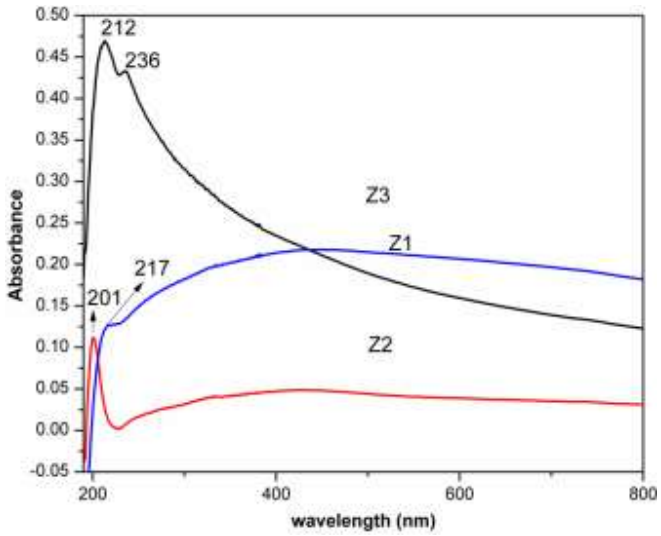


Fig. 3 UV-vis absorption spectra of nano zirconia samples

The micrographs obtained for the samples Z1 and Z3 are shown in the Fig.4. Both of them show a slightly different morphology. The former has formed primary agglomerates of average size 48 nm and secondary agglomerates of larger size. The later exhibiting monoclinic structure has formed primary agglomerates of average size 156 nm and of shape varying from spherical to elongated, angular to sub rounded [9]. In general, in pure monoclinic phase the grains are larger in size when compared to the mixed phase.

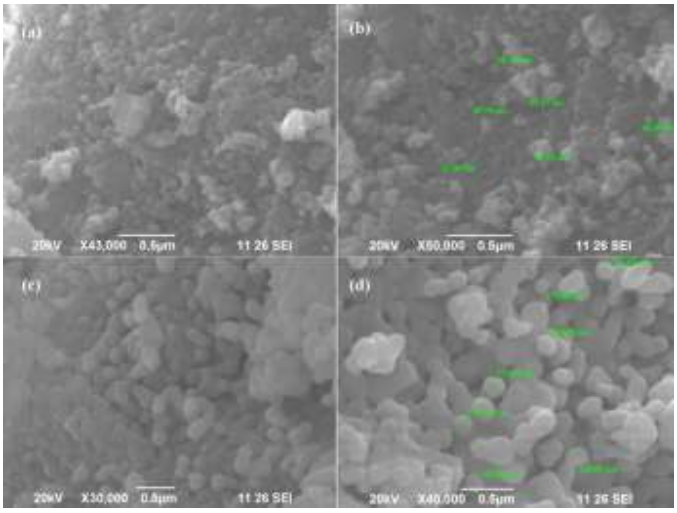


Fig. 4 SEM micrographs (a) & (b) of sample Z1, (c) & (d) of sample Z3 at various magnifications

The pelletized samples of Z1 and Z2 placed between copper electrodes acted like a capacitor. The capacitance and dielectric constant values were calculated using LCR meter in the frequency region from 100 Hz to 100 kHz at room temperature. Fig.5 shows the variation of the capacitance and dielectric constant as functions of frequency. In both the plots the capacitance and dielectric constant decrease with the increase of frequency, which was in agreement with the reported value [20].

It is observed that the dielectric constant changes from 244 to 25 as the frequency changes from 100 Hz to 100kHz. From 100 Hz to 20000 Hz there is a rapid decrease in the dielectric constant value and beyond which it remains almost constant at 25. Sample Z2 exhibits a similar trend but with higher values than those of Z1.The values change from 1000 to 58 for the variation of 100 Hz to 20000 Hz. For higher frequency values it remains constant at 58. The higher value of dielectric constant of Z2 can be attributed to its larger grain size. The dielectric constant strongly depends on the grain size and hence the sample Z2 (of grain size = 42 nm) has higher dielectric constant than sample Z1 (of grain size = 25 nm). The dielectric constant of materials is due to the electronic, ionic, dipolar, and surface charge polarizations, which depend on the frequencies. The large value of dielectric constant at lower frequency may be due to space charge polarization arising at the grain boundary interfaces.

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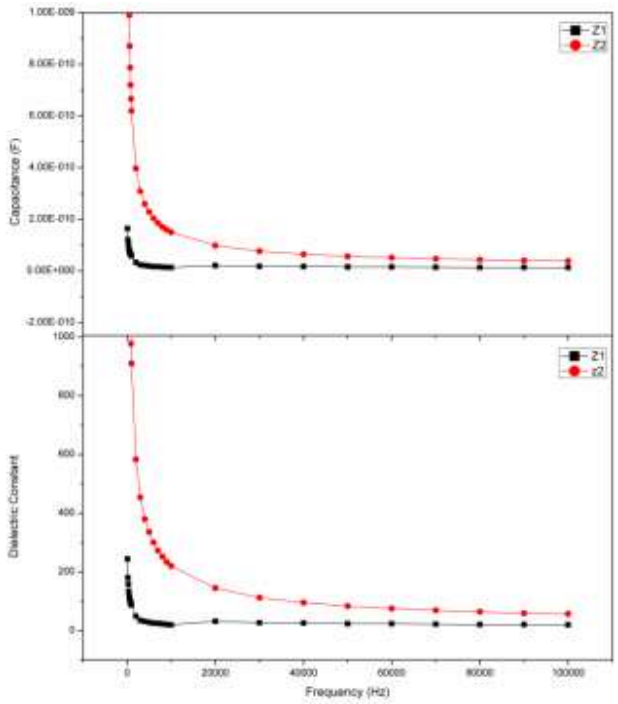


Fig. 5 Variations of Capacitance and Dielectric constant with respect to frequency

IV. CONCLUSION

In the present study, nano zirconium dioxide has been prepared using co-precipitation process. The XRD result confirms the pure monoclinic phase (m-ZrO_2). The phase purity is further ensured by FTIR spectra. The band gap value of the sample is found to be 5.7 eV. The variations of capacitance and dielectric constant with respect to frequency changes have been studied at room temperature. The dielectric constant of materials is due to the electronic, ionic, dipolar, and surface charge polarizations, which depend on the frequencies. The large value of dielectric constant at lower frequency is due to space charge polarization arising at the grain boundary interfaces. Sample with larger grain size has higher dielectric constant value which proves the strong influence of grain size on the dielectric properties.

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