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# Synthesis and dielectric studies on zirconium dioxide nano particles

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**Abstract**
Dielectric properties of nano zirconium di oxide particles were prepared by using modified dip coating method with various temperatures and are reported. The particles are deposited on well cleaned glass substrate. The structural morphology of as prepared samples is analyzed by scanning electron microscope. The size of the nanocrystals and crystalline structure were investigated from XRD equipment. These nano dimension $ZrO_2$ particles are used as a dielectric medium in the fabrication of capacitors. The capacitance and dielectric constant values were studied and calculated using digital LCRZ meter. The transmittance and absorption spectrum of the samples is also examined by UV- Vis spectrograph meter.

**Keywords:** Zirconium dioxide, modified dip coating,nano particles, dielectric materials

## 1. Introduction

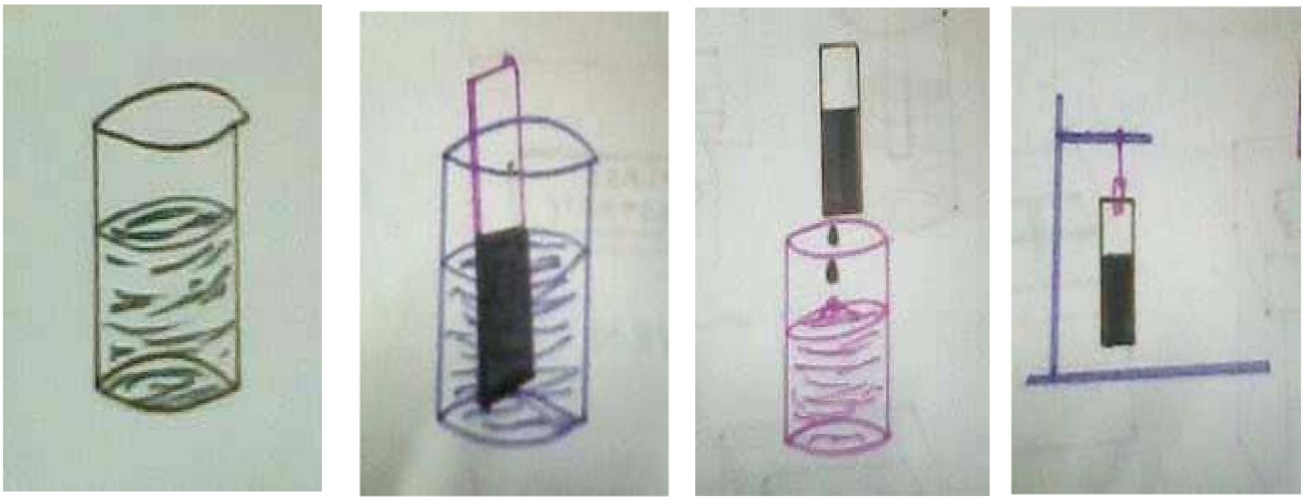
Nano science and nanotechnology is a vigorously developing field in research and technology for past few decades. Nano materials are used in engineering, industrial, electronics and medical field. Zirconia based dielectrics is one of the most promising oxides because of their good thermal stability and large band-offset in direct contact with the silicon substrate , high dielectric constant($\varepsilon_r$) , and wide band gap.It is a wonderful compound which has more potential applications such as sensors, transparent optical devices, artificial gemstones, electrodes [1-3].Nano$ZrO_2$has been studied as storage capacitors in dynamic random access memories [DRAMs], gate oxide in Field Effect Transistor (FET), and so on [4–6]. It is also used as an insulator in transistors in nano-electronic devices [7, 8]. Ultra-thin capacitors are manufactured by UVLSI technique. In the fabrication of capacitors, zirconium dioxide nano particles layer are used as a dielectric medium.

## 2.1 Experiment

### 2.1.1 Sample Preparation Technique

The Zirconium nanomaterials were successfully prepared by simple modified dip coating technique [9]. This setup consists of a magnetic stirrer with hot plate and beaker. Process of dip coating method is shown in fig.1.

Initially 40 ml of distilled water and 1mg of Zirconium were kept in a beaker as shown in fig 1. Then the beaker is placed on the magnetic stirrer. They are stirred for three days with constant rotation and constant temperature. Then the beaker is taken out from the stirrer. Well cleaned glass substrates are noted as A and B and aluminum substrate (1.5cmx1.5cm) is noted as D. The glass substrate A is immersed inside the solution. After 72 hours the substrate is taken out from the solution contained beaker and is desiccated. Further the temperature of the hot plate in magnetic stirrer is increased to 100°C. Then the glass substrate B is placed over the hot plate. The prepared solutions were rolled over the glass plate using glass rod. Due to the high temperature particles were coated on the substrate. Sample D was prepared by drop method with higher thickness for LCR characterization.



(1) (2) (3) (4)

**Fig.1:** Steps for modified dip coating method. (1) Solution (2) immersion (3) ejection (4) drying

### 3.1 Result and Discussion

#### 3.1.1 XRD Analysis

As prepared samples were studied by X-Ray Diffractometer (make:PANalytical) which are shown in figure.2 and figure.3. The d- spacing, particle size and heights of peaks were tabulated as shown in table.1. For sample A, 26 peaks were obtained by changing the angle value from 20° to 80°. A high intense peak is generated at 28.974°. The average interplanar spacing (d) value for sample A is 2.077Å. From the measured FWHM of the diffraction peaks, we computed the particle size using Debye Scherrer equation and are lies between 9.080 nm to 47.183 nm. The average grain size is 26.760 nm. Within the angle 20° to 80°, 12 peaks were generated for sample B. 2.2247Å is the average d – spacing value for sample B. The particle size changes from 7.989 nm to 42.471 nm except one particle of size 112.759 nm and average grain size is 27.028 nm.

**Table 1:** XRD details of Nano $ZrO_2$ (sample A and B)

| S.No | Sample Code | d-spacing [Å] | Rel. Int. [%] | FWHM [°2Th.] | Pos. [°Th.] | Particle Size(D) in nm |
|---|---|---|---|---|---|---|
| 1 | A | 1.348 | 0.740 | 0.979 | 34.863 | 9.080 |
| | | 2.485 | 16.420 | 0.163 | 18.062 | 47.183 |
| 2 | B | 3.625 | 16.010 | 0.937 | 12.281 | 7.989 |
| | | 2.785 | 59.840 | 0.167 | 16.070 | 42.471 |

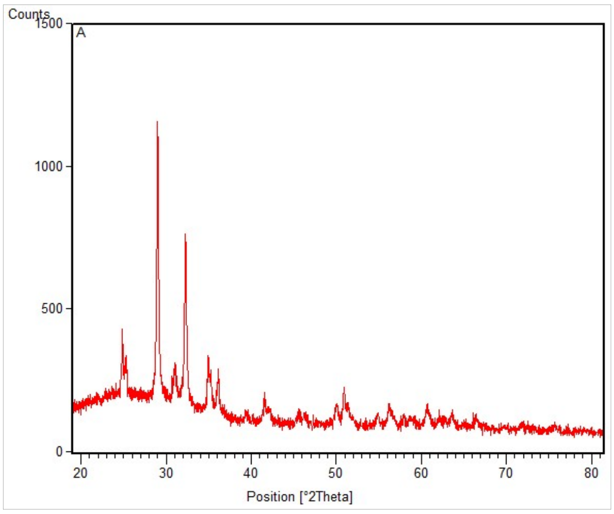



**Fig.2:** XRD pattern of sample A

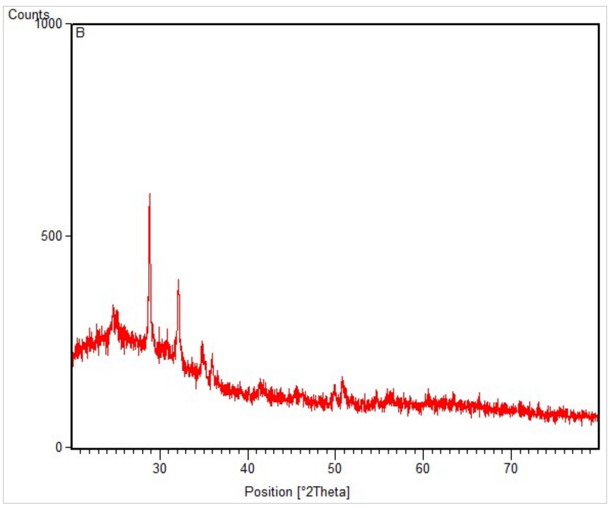



**Fig.3:** XRD pattern of sample B

These results overcome and very close to other results as earlier [10, 11]. Xinyuan Zhao et. al. [12] represented three crystal systems of $ZrO_2$. Axial length (a, b, c) and angle between the three axes (α, β, γ) are given in table

**Table.2** Crystal parameters of Nano $ZrO_2$ (sample A and B)

| Sample Code | Axial lengths [Å] | | | Angles[°] | | | Volume[$Å^3$] |
|---|---|---|---|---|---|---|---|
| | a | b | c | α | β | γ | |
| **A** | 5.28 | 9.04 | 7.29 | 78.6 | 90.5 | 134.04 | 241.7 |
| **B** | 3.34 | 3.86 | 8.52 | 99.09 | 58.27 | 104.97 | 90.65 |

### 3.1.2 Film Thickness

Thickness of the samples was directly measured by Surface Profilometer (SJ Mitutoyo 301) in Bishop Heber College, Trichy. The layer thickness of the Nano sample is 68.5 nm, 99 nm and 3.398μm for sample A, B and D respectively.



### 3.1.3 UV –Vis Spectrograph Analysis

This analysis was carried out using UV-Vis spectrometer (Perkin Elmer, Lambada 35 model). Figure.4 & 5 depicts wavelengths along x axis versus absorptions along y axis for sample A and B respectively. The optical absorption spectrums of samples were obtained within the wavelength range of 300 nm –1100 nm. Since the absorption spectra figures, high peaks noted for sample A and B at 365.53 nm and 346.97 nm wavelength of light radiation respectively.The band gap energy of nano $ZrO_2$ were calculated and presented in table.3 by using the formula [13],

$$E_g = \frac{hC}{\lambda} eV \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \textbf{(1)}$$

These values proved the wide band gap of dielectric materials i.e. more than 3 eV and also has good result compared than previous results which is near to $E_g$ of semiconductor ($E_g$<3eV)[10,14, 15].

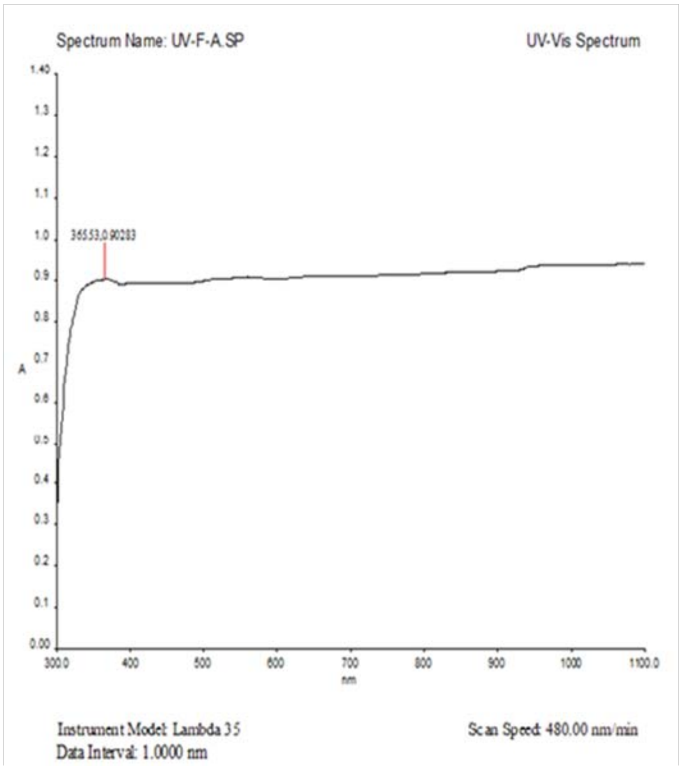



**Fig.4** Absorption Spectrum of sample A

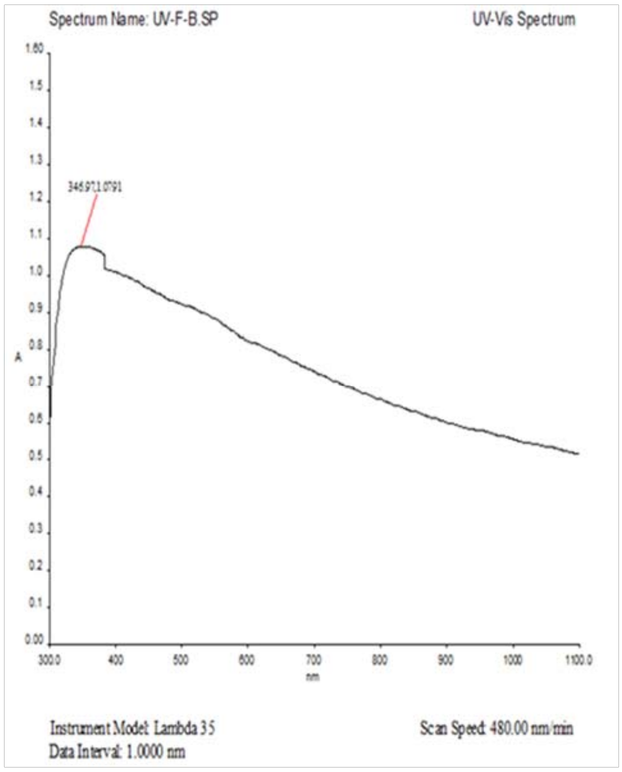



**Fig.5** Absorption Spectrum of sample B

**Table.3** Calculation of Energy band gap of $ZrO_2$ film

| Sample Code | Wavelength(λ) obtained from absorption spectrum in nm | Band gap energy $E_g$= hc/λ in x$10^{-19}$ J | Band gap energy $E_g$= hc/λ in eV |
|---|---|---|---|
| A | 365.53 | 5.437 | 3.337 |
| B | 346.97 | 5.728 | 3.575 |
| h = Plank's constant = 6.626 x $10^{-34}$ Joules sec | | C = Speed of light = 3.0 x $10^{8}$ meter/sec | |

### 3.1.4 SEM Analysis

Further, the structural morphology of samples were analyzed and reported by scanning electron microscope. The different magnification of SEM photographic results are reported in the series of zirconia structures is represented in figure.6 and figure.7 for sample A and B respectively.

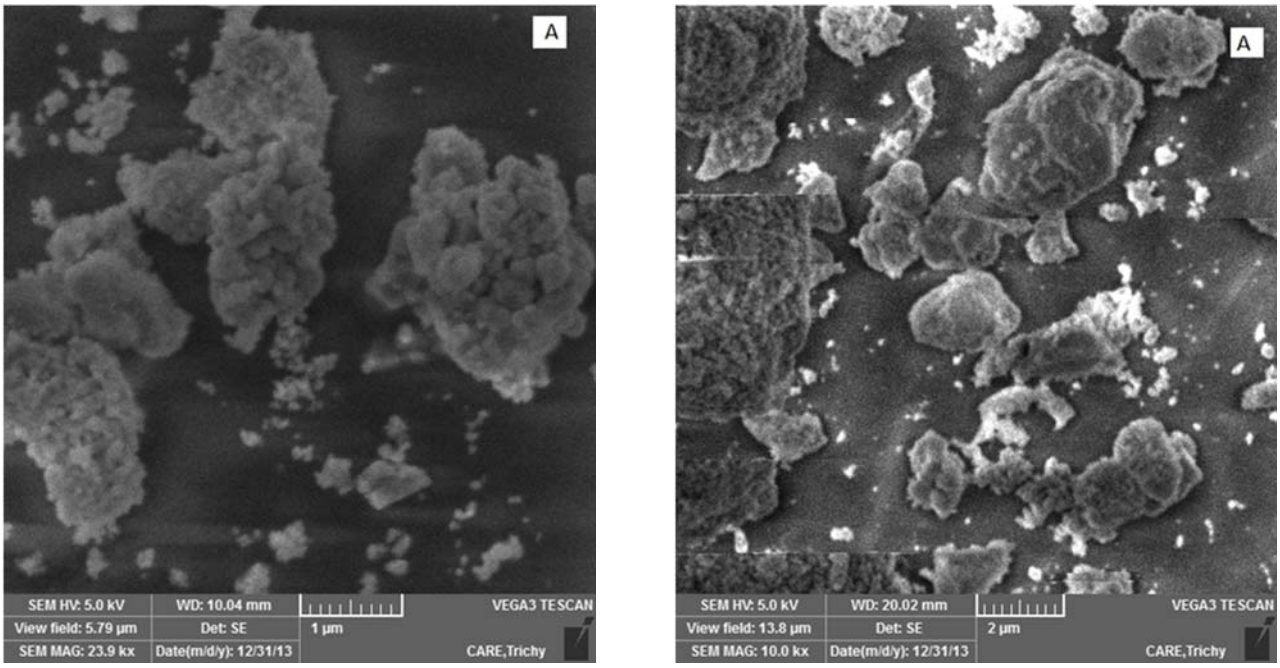



**Fig.6** Series of SEM Images of $ZrO_2$ films (sample A) with various magnifications

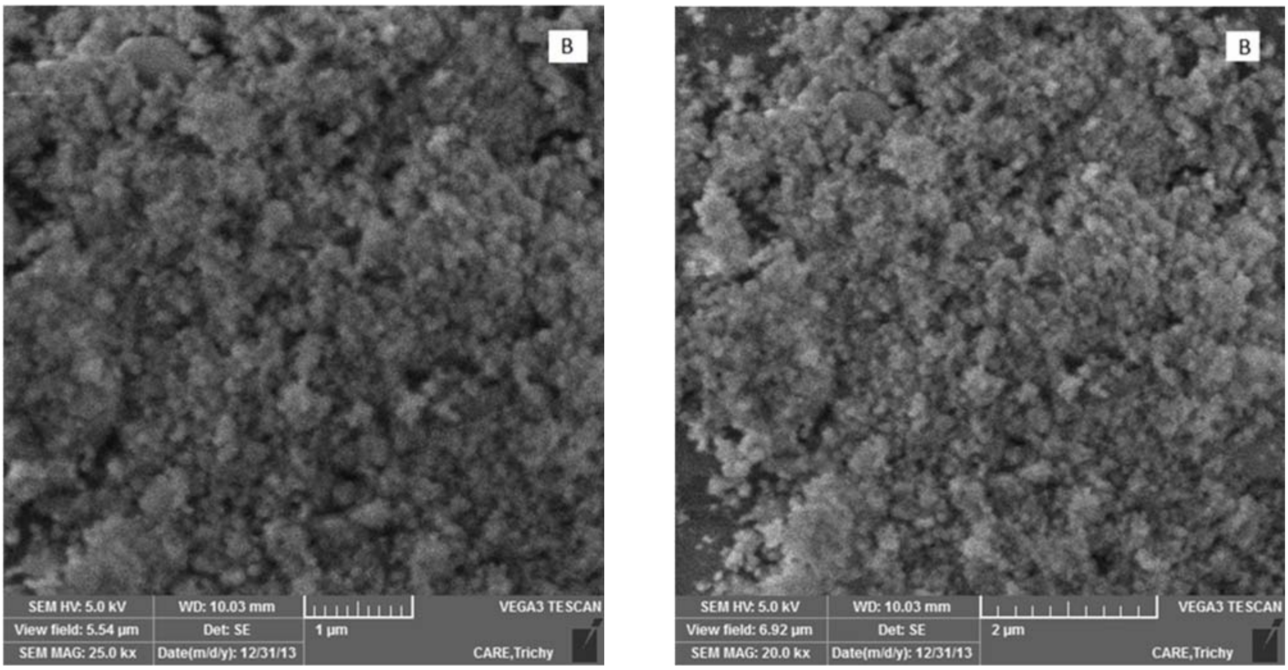



**Fig.7** Series of SEM Images of $ZrO_2$ films (sample B) with various magnifications

### 3.1.5 Digital LCRZ Characterization

The capacitance characterization is studied by digital LCRZ Bridge. Al substrate coated with $ZrO_2$ particle is employed in between the sample holder of LCRZ meter. By varying the frequency range from 50 Hz to 200 kHz capacitance were noted. From the LCR observation the dielectric constant ($\varepsilon_r$) can be computed by the relation,

$$\varepsilon_r = \frac{Cd}{\varepsilon_o A} \qquad (2)$$

Let C, d, A and $\varepsilon_o$ be the capacitance, film thickness of the film, area of the sample and permittivity of free space respectively.

Figure.8 & 9 reported the dependence of capacitance and dielectric constant of the material with frequency. From the plot, if the frequency increases, both capacitance and dielectric constant values decreases gradually i.e. capacitance value varies from 896pF to 25pF and dielectric constant value changes from 193 to 5.

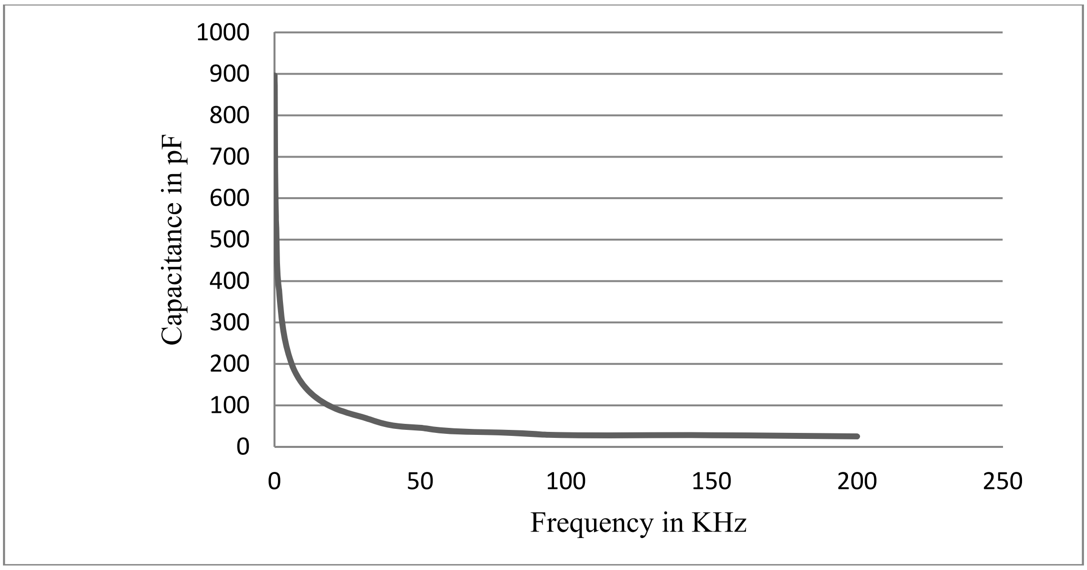



**Fig.8** variation of capacitance with its corresponding frequency

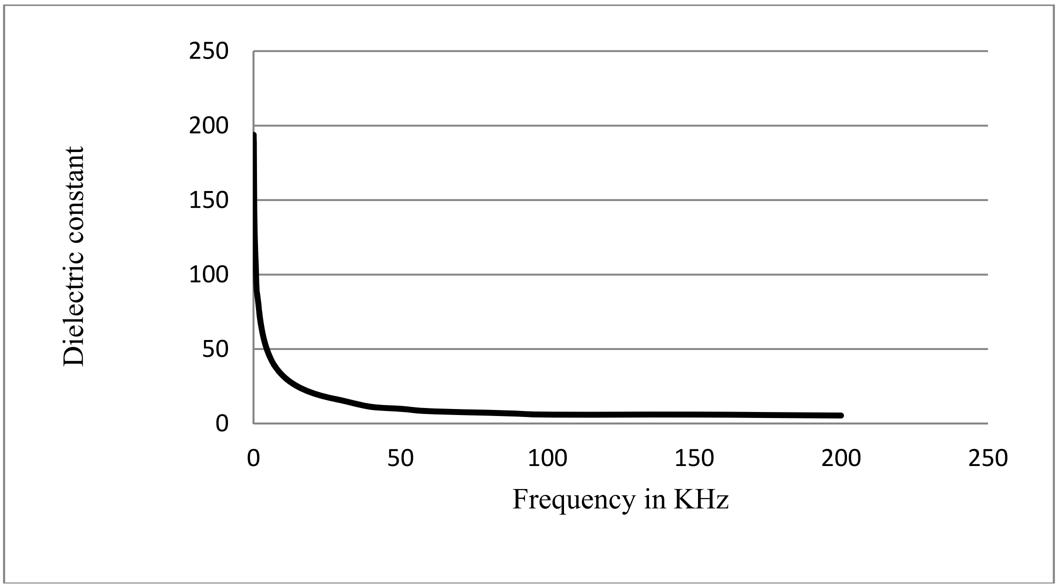



**Fig.9** Variation of dielectric constant with its corresponding frequency

The electronic, ionic, dipolar and space charge polarizations are occurs at lower frequencies. Average dielectric constant value of $ZrO_2$ is 70. The dielectric constant value is purely depends on size of the particle [16]. For very low grain size of $ZrO_2$ we obtained very low dielectric constant about 5. Here the relative permittivity ($\varepsilon_r$) value vigorously varies from 42 to 20 as a function of frequency is shown in fig. 9.

### 4.1 Conclusions

Nano Zirconia ($ZrO_2$) samples were deposited on the silicon substrate by modified dip coating method and are characterized by X-ray Diffraction, Scanning Electron Microscope, UV-Vis Spectrograph and Digital LCRZ meter at room temperature. Furthermore, the improved results are discussed. The band gap energy value of nano zirconia sample is more than 3 eV. At room temperature both capacitance and dielectric constant are changes drastically with frequencies. Mass of the nano particles is very less so that it can easily polarized, when field is applied. The dielectric constant is high at lower frequency due to four types of polarizations and also grain size of the particle. These characterizations proved the nano zirconia will be used as a dielectric media for capacitor.

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