Phase Formation and Electrical Properties of Zinc Titanate Ceramics

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Abstract:
ZnTiO3 was synthesized by employing the solid state reaction between ZnO and TiO2 powders mixed in the 1:1 molar ratio. The dielectric properties such as dielectric constant (εr) and dielectric loss (tan δ) have been studied in the frequency range 200 Hz to 5MHz by varying the temperature from 40°C to 400°C in steps of 10°C. High value of dielectric constant ~ 50 is observed which can be suitable for high charge storage capacitor applications. The optical properties were also studied using FTIR and UV-Visible Spectra. The band gap was calculated from UV-Visible Spectra.

Keywords:
ZnTiO3, Dielectric Constant (εr), Optical Properties, AC-Conductivity

1. Introduction
ZnTiO3 is of a perovskite type oxide structure and has innumerable number of applications because of its diversified electrical, optical and ferroelectric properties. It has many applications such as microwave resonator [1], gas sensor [2] (for ethanol, NO, CO, etc.), microelectronics [3], metal–air barriers [4], and as high performance catalysts [5, 6] for the complete oxidation of hydrocarbons or CO and NO reduction [7] and paint pigment[8]. Commercial electronic systems contain components like capacitors, oscillators and filters. To fabricate these components materials having high dielectric constant, a low dissipation factor, a small temperature coefficient of the resonant frequency (τf) or a small temperature coefficient of the dielectric constant (τε) are required. ZnTiO3 shows interesting dielectric properties that makes it a suitable candidate for high performance components. In this paper, we report the structural, dielectric (dielectric constant and dielectric loss), and electrical properties (ac-conductivity properties) of ZnTiO3.

2. Materials and Methods
Initially, the two precursors, 99.5% pure ZnO and TiO$_2$ (Loba Chemie, India) were mixed in the 1:1 molar ratio. The mixture was grounded for 24 hours and then calcined at 700°C for 12 hours. The powder thus obtained was again grounded for 6 hours. The resulting powder was then pressed into pellets under a pressure of 70 MPa. The pellets were sintered at 800°C for 6 hours. The phase and orientation of bulk ZnTiO$_3$ samples were characterized by X-ray diffractometer (Bruker X-Ray Powder Diffract Meter) using CuKα (λ=1.5407 Å) radiation. The surface morphology was examined by field emission scanning electron microscopy (Hitachi: S-4700), energy dispersive x-ray analyzer (EDAX) (AMETEK system). Absorption spectra had been taken using JASCO UV-Visible spectrophotometer (V-670 PC), FT-IR spectrophotometer (IR affinity-1, Shimadzu). The dielectric measurements at different frequencies were done using HIOKI 3532-50 LCR HiTESTER (Japan). Silver paint was applied on both surfaces of the sample as an ohmic contact. Further, pellet was inserted between the electrodes of the dielectric bridge.

3. Results and Discussion

3.1. Structural Analysis

The diffraction pattern of ZnTiO$_3$ ceramic powder is shown in Fig.1. It can be understood from figure that the observed peaks correspond to rhombohedral perovskite structure. These peaks are in consistent with standard JCPDS file No: 26-1500. These peaks are indexed with miller indices (hkl) and compared with standard JCPDS data as depicted in Fig.1. The maximum intensity of 468 is recorded for (104) plane at a two-theta angle of 32.79°. This peak attributes lattice parameter of a = b ~5.0791 Å and c ~ 13.916 Å [9] for the present material which is almost in close agreement with JCPDS: 26-1500. Furthermore, the average crystallite size (D) is calculated as 47.9 nm using the Scherer formula [10-13].

$$D = \frac{K\lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

Where, k = 0.9, θ is diffraction angle, λ=0.154056 nm and β is full width half maxima.

![Figure 1. XRD of ZnTiO$_3$.](http://www.itspoa.com/journal/am)
Also, the elastic strain (\(\epsilon \sim 0.0015\)) is evaluated from a standard relation mentioned elsewhere [14, 15]. The X-ray density\(d_x\) of \(\sim 5.174\) g/cm\(^3\) is obtained using a formula: \(ZM/Na^3\), where ‘Z’ is the no. of molecules per unit cell \(Z = 1\), ‘M’ is the molecular weight of the composition, ‘N’ is Avogadro’s number \(6.023 \times 10^{23}\) and ‘a’ is the lattice parameter [16]. Further, the bulk density \(d_b\) \(\sim 4.654\) g/cm\(^3\) is evaluated with the help of Archimedes principle [17]. The pore fraction of \(P\) is found to be \(\sim 0.101\) by an equation: \(P \sim 1 - (d_b/d_x)\) [18]. The small value of pore fraction establishes a fact that the present material may be of good dense.

3.2. SEM Analysis

The Scanning Electron Microscope (SEM) provides the surface morphology of powder specimen. It is seen from Fig.2 that all the grains are of almost spherical in shape. The average grain size \(G_a\) is found to be \(714\) nm using linear intercept method [19].

\[
G_a = 1.5L/MN
\]  
(2)

Where \(L\) is the test line length, \(N\) is the number of intersecting grains and \(M\) is the magnification.

![Figure 2. SEM image of ZnTiO\(_3\) ceramic.](image_url)

3.3. FTIR Analysis

Fourier Transform Infrared Spectroscopy (FTIR) spectrum is generally used for the determination of metal oxide bonds of ceramics [20]. The FTIR spectrum of barium titanate ceramics sintered at \(800^\circ\)C is recorded in the range of 400-4000 cm\(^{-1}\) as shown in Fig.3 and showed metal oxide absorption bands at 489.9 cm\(^{-1}\) and 504.6 cm\(^{-1}\) corresponding to Zn-O and Ti-O, respectively [21, 22].
3.4. UV-Visible Spectrum

The diffuse reflectance spectrum (DRS) is recorded in the range of 200-1600 nm as depicted in Fig.4 for finding optical band gap energy of powder samples. Kubelka-Munk function of reflectance F(r) is used to determine band gap [23-25].

\[ F(r) = \frac{(1-r)^2}{2r} \]  

(3)

The maximum absorption wavelength is recorded to be 295 nm.

\[ (\alpha h\nu)^n = m (h\nu - E_g) \]  

(4)
Where, $m$ = Energy- independent constant that depends on transition probability, $E_g$ = optical band gap energy, $n$= the kind of transition i.e. $n = 2$ for direct transition, $2/3$ for direct forbidden transition, $1/2$ for indirect transition, $1/3$ for indirect forbidden transition and $h\nu$ = photon energy [29]. In this study direct and indirect transitions are considered. $E_{op}$ value is evaluated from the linear portion that is extrapolated towards X-axis for $(\alpha h\nu)^2$ versus photon energy $h\nu$(eV) plot as $\alpha$ tends to zero (Fig.5). The optical band gap energies for direct and indirect transitions are calculated as 3.03eV and 2.83eV, respectively.

![Figure 5. The ‘hv’ versus ‘(ahv)^n’ plot of ZnTiO\textsubscript{3} ceramic.](image)

### 3.5. Dielectric Properties

The variation of dielectric constant ($\varepsilon'$) and loss ($\varepsilon''$) of ZnTiO\textsubscript{3} is shown in Fig.6&7, respectively, as a function of both frequency (200 Hz-5 MHz) and temperature (313-673K). It can be seen from the figures, that the dielectric constant and loss is found to increase slowly with the increase of temperature up to 600 K and above 600K a sharp increasing trend in both the cases is observed. The constant variation of dielectric constant and loss was mainly attributed to the weak response of the charge carriers for the provided input temperature. For further increase of temperature the charge carriers will get activated and therefore they will be moved to the excited level which in turn leads to the enhancement of electrical properties. The sharp increase can be attributed to the interfacial or space-charge polarization effect [30, 31]. In addition, $\varepsilon'$ and $\varepsilon''$ were found to decrease with increase of frequency. This happens due to ineffective space-charges at the grain boundary interface. At room temperature, for f~ 5 MHz the present specimen showed dielectric constant of ~50. In general, the polarization due to grain boundaries are more active at the lower frequencies, and as the frequency increase the polarization due to grains will be more. Up to 100 Hz frequency, the space-charge or Maxwell-Wagner interfacial polarization becomes predominant and for further increase of frequency, the effectiveness of space-chargers will be diminished. Thus, the dielectric constant as well as loss will be decreased. The transition temperature is noticed at ~663 K at which the structural transformation usually occurs. Normally, at the transition temperature all the charge carriers will be accumulated at the grain boundary interface and therefore the resistivity of the grain
boundary decreases. Hence, the breakage of grain boundary takes place which can again responsible for the peak value of dielectric constant or loss. At this juncture the entropy may be in general found to be very high. After transition temperature, the charge carriers will gradually come to the normal position. That is, the relaxation of charges may take place. In addition, the dielectric constant and loss plots (temperature dependent plots) reveal the distortion behavior at few temperatures. This can be attributed the presence of defect centers, strain variation, grain size variation etc. In other words, the imperfections will work as scattering centers to the charge carriers and hence the huge value of dielectric constant or loss may be obtained. The loss was also showing the similar trend as that of permittivity in all respects. This kind of high \( \varepsilon' \) and high \( \varepsilon'' \) values noticed at room temperature are most suitable for filter, charge stored capacitors and absorber applications [32].

Figure 6. The variation of dielectric constant (\( \varepsilon' \)) with temperature.

Figure 7. The variation of dielectric loss (\( \varepsilon'' \)) with temperature.
Figure 8 shows the variation of ac conductivity as a function of reciprocal of temperature at different frequencies (400 Hz-3 MHz). As the temperature increases, the ac conductivity increases owing to the hopping of charge carriers and hence this can be governed by the Arrhenius equation [33]:

\[ \sigma_{ac} = \sigma_0 \exp \left( \frac{-E_a}{kT} \right) \]  

(5)

where, \( K = 8.6 \times 10^{-5} \text{eV} \), \( \sigma_0 \) = pre exponential factor, and \( T \) = absolute temperature.

In general, \( \sigma_{ac} \) can be calculated using the equation [34]:

\[ \sigma_{ac} = \varepsilon_0 \varepsilon_r \tan \delta, \]

where \( \varepsilon_r = 8.9 \times 10^{12} \text{F/m} \), \( \omega = 2\pi f \) and \( \tan \delta = \text{loss tangent} \). The \( \ln \sigma_{ac} \) and 1000/T plots almost show a curve shape. The intersecting point of these two curves in general termed as the transition point [35]. Two slopes were taken on either side of curves as shown in plots. Normally, above the transition temperature, a definite change of conductivity is observed. These two slopes provide two activation energies i.e. 0.125 and 0.418 eV. The smaller activation energy was noticed in the high temperature region (>384 K) while higher activation energy is observed in the low temperature region (<384 K). This kind of variation of activation energy was mainly due to the conductivity behavior at lower and higher temperatures. Similar kinds of observations were made by Naidu et al. [35].

![Figure 8. The ln(\(\sigma_{ac}\)) and 1000/T plots of ZnTiO\textsubscript{3} ceramic.](image)

The frequency dependence of ac conductivity was depicted in Fig.9. It is noticed that the conductivity was increasing with frequency. This variation can be governed by the power law relation [35-37]:

\[ \sigma_{ac}(\omega, T) = \sigma_0(T) + A\omega^n, \]

where \( A \) = constants and \( n \) is exponent (varying between 0 -1). The term \( \sigma_0(T) \) indicates the dc conductivity which is independent of frequency. The power law fit revealed the dc conductivity of 2.20x10\(^8\) S/cm at room temperature (313 K). The \( \sigma_0 \) is varying between 2.20x10\(^8\) - 1.18x10\(^{10}\) S/cm. The exponent values were increasing with temperature from 0.24-0.67. This confirmed that the ‘n’ value was greater than zero and less than one. Within the frequency independent region or DC-conductivity region ‘n’ becomes zero, whereas the same showed greater than one, when the correlated barrier hopping (CBH) conduction mechanism took place in the sample as a function of frequency due to translation motion of charges. Hence, it was confirmed...
that the electrical hopping type of conduction mechanism was accomplished in the present materials [36, 37].

![Figure 9. The logσ versus frequency plots of ZnTiO3 ceramic.](image)

4. Conclusions

The zinc titanate (ZT) ceramic material is synthesized via conventional solid state reaction method. The rhombohedral structure is confirmed form diffraction study. A high optical band gap of 3.03eV is attributed to ZT when a direct transition is considered. However, these kinds of materials comprising wide optical band gaps can provide applications in optoelectronic devices, photo catalytic and sensor devices. The SEM micrographs confirmed the formation of almost spherical shape grains. In addition, the average grain size was noted to be approximately 720 nm. The obtained high permittivity and loss values provide dielectric absorber and charge stored capacitor applications. The two kinds of activation energies on either side of Arrhenius plots were seen which may be attributed to the change of slope and gradient line before and after transition temperature. The power law fit revealed the dc-conductivity of 2.20x10⁻⁸ S/cm at room temperature (313 K). Further, the exponent values were increasing with temperature from 0.24-0.67. The exponent value achieved less than unity indicated the existence of hopping conduction mechanism among the charge carriers.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

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