Enhancing of Electrical and Dielectric Properties of Barium Zirconate Titanate/Poly (Vinylidene Fluoride) Nano-Composites

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Abstract: The effects of poly (vinylidene fluoride, PVDF) on barium zirconate titanate nanoparticles has been studied. Different concentrations of (BZT-PVDF) nanocomposites using the formula \( [x \text{ (PVDF)/(1 } - x) \text{ BZT}] \) (where \( x = \text{zero, 0.2, 0.4, 0.6, 0.8 and 1} \)) were prepared using the hot pressing method. The BZT nanoparticle was prepared using the tartrate precursor route method. The DC resistivity as a function of reciprocal temperature \((1000/T) \text{ K}^{-1}\) for the composite samples has been studied. The dielectric constant \((\varepsilon)\) increases with the amount of BZT, which can be described as the increase of interfacial space charge polarization between (PVDF-BZT) nano-composites and the increase in the ionic mobility of the polymer. The ferroelectric hysteresis of prepared nano-composites has been investigated. The increase of BZT content raises the slope of the hysteresis loop and hence the dielectric polarization, which may be attributed to the dominance of smaller grain size and tetragonality. The increasing in dielectric properties for the prepared samples is very useful in industrial applications, such as sensors, actuators and transducers.

Keywords: PVDF; BZT; nano-composite; DC resistivity; AC conductivity; tartrate precursor route

1. Introduction

Numerous scientific researchers have been drawn to the study of a novel material with high dielectric permittivity and good mechanical properties for incorporation into electronic devices throughout the past few decades. Ferroelectric ceramics have lower dielectric breakdown strengths and substantially greater dielectric values than polymers, but they also have poor mechanical qualities. Despite having a relatively low dielectric permittivity, polymers are flexible, resistant to high fields, and simple to work with [1–3].

A new generation of polymer/ceramic nano-composite materials has many applications due to their promising properties, which make them suitable for a wide range of applications such as for the production of transducers, sensors, energy storage devices and actuators, etc.; additionally, they are environmentally friendly. Although high dielectric permittivity is obtained by adding BZT nanoparticles with the PVDF polymer, the high content may cause damage to the breakdown strength and cause them to lose their flexibility and uniformity [4–6].

Recently, more and more polymers, such as polyethylene, polystyrene, and poly (vinylidene fluoride, PVDF) have been shown to have wide applications as voltage capacitors due to their high breakdown voltages [7]. PVDF is considered to have a stronger piezoelectric response compared with other polymers due to its chemical stability, resistance to organic solvents, high elastic modulus, high permittivity, dielectric strength, and low dissipation factor, which make PVDF useful in the fabrication of actuators and sensors [8–11].
The present study aimed to investigate the effect of poly (vinylidene fluoride) on the properties of barium zirconate titanate nanoparticles prepared by the tartrate precursor method to improve electrical and dielectric properties of PVDF nano-composites.

2. Experimental Producers

BZT nanoparticles were synthesized using the tartrate precursor method. Pure grades of Ba(NO$_3$)$_2$, ZrO$_2$, and TiO$_2$, by adding the stoichiometric amount of tartaric acid in a 1:3 molar ratio of metal mixture to tartaric acid, were used as starting materials. On a hot plate magnetic stirrer, 250 mL of distilled water was then added and swirled for 15 min. Once the solution was completely dry, the temperature was increased to 80 °C while stirring continuously. The precipitation was dried for 24 h at 200 °C in a drier. To create homogeneous BZT nanoparticles, the resulting material was manually ground in the air using an agate mortar. [12].

Nanocomposite of PVDF/BZT with chemical formula [x (PVDF)/(1 − x) BZT] (where x = zero, 0.2, 0.4, 0.6, 0.8 and 1) was prepared using the hot pressing method [13]. For electrical studies, disk samples were formed at 120 °C for ten minutes with a pressure of 5 tons [14].

DC electrical resistivity is a useful technique for understanding conductivity mechanisms. The cell used for DC conductivity and dielectric measurements for the investigated samples is illustrated in Figure 1. The temperature was adjusted to be the same at the upper and lower surface of the sample by using the oven, and we increased the temperature gradually using an outer rheostat.

![Figure 1](image-url)

**Figure 1.** The cell used for measuring DC resistivity and dielectric measurements of the nano-composite samples. 1—insulating jacket. 2—thermocouple. 3—liquid nitrogen. 4—vacuum Büchner flask. 5—two electrodes. 6—the sample.
An electrometer type 610 Keithly was used to measure the DC resistivity, and RLC Bridge type 815 B was used to measure the dielectric constant.

The dielectric constant ($\varepsilon'$) was calculated using the formula [15]:

$$\varepsilon' = \frac{Cd}{\varepsilon_0 A}$$

(1)

where $C$ is the capacitance of the sample in (Pico farad), $d$ is the thickness of the sample in (cm), and $A$ the area of the sample in (cm$^2$).

The dielectric hysteresis loops were measured with a modified Sawyer–Tower circuit as shown in Figure 2. A sinusoidal AC applied voltage of 130 V and 50 Hz was applied to the sample during measurements.

3. Result and Discussion

3.1. X-ray Diffraction Characterization

The XRD patterns of the produced nanocomposites are displayed in Figure 3. Without any extraneous secondary phase peaks, the XRD patterns display a typical perovskite structure. With some peaks belonging to the unpolarized ($\alpha$) phase and others to the polarized ($\beta$) phase, the PVDF exhibits a semi-crystalline structure. Up to $x = 0.4$, the ferroelectric phase continues to dominate the crystal characteristics of the composite. Since no more peaks occur in the XRD pattern, the reflected peaks demonstrate the development of a stable solid-state solution composite from BZT and PVDF [16]. The ($\alpha$) phase is converted to the ($\beta$) phase by the addition of BZT, according to the XRD patterns, which show that the ($\alpha$) phase content reduces as the BZT ratio is raised. Due to the ($\beta$) phase’s polar character, which serves as a representation of a piezoelectric phase in the industry, this notification is of utmost importance.

3.2. DC Resistivity

Figure 4a shows that the BZT system has a higher resistivity than the pure PVDF and (BZT-PVDF) composite. The resistivity of the composite sample decreases by increasing the PVDF content. The (ln $\rho$) versus (1000/T) plot shows non-linearity at high temperatures; such features are generally observed for an amorphous polymeric system such as (PVDF) as shown in Figure 4b,c.

The Interaction between the PVDF chain and the BZT results in a structural modification that affects the resistivity due to the increase of the amorphous phase, as given in the XRD diffraction pattern and the improvement of ionic mobility and conductivity.
3. Result and Discussion

3.1. X-ray Diffraction Characterization

The XRD patterns of the produced nanocomposites are displayed in Figure 3. Without any extraneous secondary phase peaks, the XRD patterns display a typical perovskite structure. With some peaks belonging to the unpolarized (α) phase and others to the polarized (β) phase, the PVDF exhibits a semi-crystalline structure. Up to $x = 0.4$, the ferroelectric phase continues to dominate the crystal characteristics of the composite. Since no more peaks occur in the XRD pattern, the reflected peaks demonstrate the development of a stable solid-state solution composite from BZT and PVDF [16]. The (α) phase is converted to the (β) phase by the addition of BZT, according to the XRD patterns, which show that the (α) phase content reduces as the BZT ratio is raised. Due to the (β) phase’s polar character, which serves as a representation of a piezoelectric phase in the industry, this notification is of utmost importance.

Our composite sample has two conduction mechanisms: the ionic conduction belonging to the BZT phase and the PVDF polymeric chain conduction. For pure BZT, the relation shows two regions with breakpoints at nearly (112 °C), which is the Curie temperature of BZT. The same behavior is present for composite samples at higher temperatures with a breakpoint at (120 °C). At low temperature, the resistivity decreases with increasing temperature and reaches a minimum at (8 °C). The low-temperature resistivity region shows a break at the glass transition temperature for the PVDF.

The behavior of the composite sample shows a positive temperature coefficient at low temperature and a negative temperature coefficient at high temperature, with a convergent point (8 °C) at (20% PVDF) and (23 °C) at (60% PVDF) and (25 °C) at (80% PVDF). The convergent point differentiates between the conduction mechanism of BZT and PVDF. At the low-temperature region, the resistivity decreases by increasing PVDF content. The investigated samples’ activation energy was calculated using the relation [17]:

$$\rho = \rho_0 e^{-\frac{E_a}{kT}}$$

where $\rho_0$: is the pre-exponential constant, and $E_a$ is the activation energy in eV, which was calculated from the slope of $\ln \rho$ vs. $(1000/T)$ K$^{-1}$.

As shown in Table 1, the activation energy decreases by increasing the BZT content.

<table>
<thead>
<tr>
<th>Sample</th>
<th>100% PVDF</th>
<th>80% PVDF</th>
<th>60% PVDF</th>
<th>40% PVDF</th>
<th>20% PVDF</th>
<th>0% PVDF</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_a$ (eV)</td>
<td>$3.07 \times 10^{-3}$</td>
<td>$2.48 \times 10^{-3}$</td>
<td>$1.66 \times 10^{-3}$</td>
<td>$1.29 \times 10^{-3}$</td>
<td>$0.97 \times 10^{-3}$</td>
<td>$0.20 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

When the temperature is increased, the mobility of the polymer chain is enhanced, and oxygen vacancies appear, which facilitate the movement of the charge carrier; this is the reason for the decrease of resistivity at low-temperature regions [18–20].
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3.2. DC Resistivity
Figure 4a shows that the BZT system has a positive temperature coefficient at low temperatures, proving that the cooperative segmental motion in the amorphous phase appears in the temperature for all the studied samples' (BZT-PVDF) nano-composites over the temperature range from (215 to 420) K at different frequencies (1 kHz, 10 kHz). It was observed that (a) The DC resistivity as a function of 1000/T of (BZT-PVDF) composite. (b,c) The DC resistivity as a function of 1000/T of (BZT-PVDF) composite at x = 0 and 1.

As shown in Table 1, the activation energy decreases by increasing the BZT content. The presence of BZT in the polymeric matrix makes the polymer chain's segmental motion much easier, increasing the diffusion of charge and reducing the activation energy [21].

3.3. Dielectric Properties
Figures 5a–f and 6a–f show the relation between the dielectric constant (ε) and temperature for all the studied samples' (BZT-PVDF) nano-composites over the temperature range from (215 to 420) K at different frequencies (1 kHz, 10 kHz). It was observed that (c) increases with the amount of BZT. In fact, the composite containing 20% PVDF, 40% PVDF and 60% PVDF had maximum dielectric constant (3000, 1200 and 6000), respectively, at 1 KHZ. At 10 KHZ, the samples 20% PVDF, 40% PVDF, and 60% PVDF had maximum dielectric constants at (800, 4600, and 100), respectively.

The dielectric constant is nearly independent of temperature up to (220 to 280) K and then increases gradually around (T_g), where higher temperature increases sharply. The dielectric constant and dielectric loss decrease by increasing the applied field frequency. At low temperatures, the relaxation related to the glass transition dynamics is present, proving that the cooperative segmental motion in the amorphous phase appears in the composite samples.
Figure 5. (a–f): The effect of temperature on the dielectric constant of (PVDF-BZT) and their composites at 1 KHz.

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At low temperatures, the relaxation related to the glass transition dynamics is present, proving that the cooperative segmental motion in the amorphous phase appears in the composite samples.

Figure 6. (a–f): The effect of temperature on the dielectric constant of (PVDF-BZT) and their composites at 10 kHz.
The dielectric constant increase can be described as the increase of interfacial space charge polarization between (PVDF-BZT) nanoparticles, which increases the ionic mobility of the polymer (BZT/PVDF) composite, leading to a large dielectric constant compared with pure PVDF. The quantity of the accumulated charges for the BZT-PVDF composite is more than the pure PVDF due to the transformation of the (α) phase to the polar (β) phase. This increase of dielectric constant by increasing BZT resulted from the formation of a conducting network for the PVDF polymer, as shown in Figures 4 and 5.

Figures 7a–f and 8a–f show the dependence of the power factor (n) on temperature at (1 KHZ, 10 KHZ).

The real part of electrical resistivity consists of two terms, \( \rho_1(T) \) and \( \rho_2(w, T) \), as given in the following equation [22,23]:

\[
\rho = \rho_1(T) + \rho_2(w, T)
\]

![Figure 7](image-url)
Figure 7. (a–f): The variation of exponent (n) for the composites of (PVDF-BZT) as a function of temperature at 1 KHz.

Figure 8. Cont.
where (\( B \)) has a unit of resistivity and (\( n \)) is the dimensionless power factor parameter.

It is noticed that the variation of (\( n \)) with temperature gives information about the type of conduction mechanism. If (\( n \)) increases with temperature, the conduction obeys a small polaron tunneling mechanism. The exponent (\( n \)) is either temperature-independent or increases with temperature. On the other hand, the correlated barrier-hopping model \([24,25]\) predicts that the exponent (\( n \)) decreases with temperature. The value of (\( n \)) ranged from (0.8) as a minimum value and (2.6) as the maximum value.

The conduction mechanism also depends on the value of (\( n \)), which is either greater or less than unity. In our case, the value of (\( n \)) was higher than one, which means that the polarization was due to free charges, and some were localized \([26–28]\).

### 3.4. Ferroelectricity

Figure 9a–f shows the ferroelectric hysteresis loop of the composite. It is noticed that the increase of BZT content raises the slope of the hysteresis loop and hence the dielectric polarization. The increase of BZT influences the shape and size of the loops as well as the numerical value of polarization. This behavior may be attributed to the dominance of smaller grain size and tetragonality.

The smaller the grain size, the larger the grain boundaries of the lattice and the higher the lattice defect, which enhances the domain wall motion \([29–32]\). This increases the ferroelectric polarization with increasing BZT content. No well-saturated hysteresis loops with regular shapes appeared. The presence of low oxygen vacancies leads to the pinning of the domain wall, making hard saturation to polarization.
Figure 9. (a-f): The dielectric hysteresis loop of the composite samples.

4. Conclusions

BZT show higher resistivity than PVDF and the composite; the resistivity of the composite sample decreased by increasing the PVDF content. The low-temperature resistivity region shows a broken beak at the glass transition temperature for PVDF. At low-temperature regions, the resistivity decreases by increasing PVDF content and by increasing the temperature due to the increase of (β) phase fraction, which is a polar phase. The activation energy decreased by increasing the BZT content. The presence of BZT in the polymeric matrix makes the polymer chain’s segmental motion much easier, increasing the
diffusion of charge and reducing the activation energy. The dielectric constant is nearly independent of temperature and then increases around ($T_g$), where higher temperatures increase sharply. The constant dielectric increase can be described as the increase of interfacial space charge polarization between (PVDF-BZT) nanoparticles, which increases the polymer’s ionic mobility. The increase in BZT content raises the slope of the hysteresis loop and hence the dielectric polarization. This behavior may be attributed to the dominance of smaller grain size and tetragonality.


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**References**


